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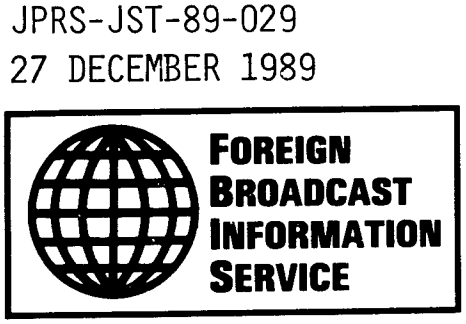
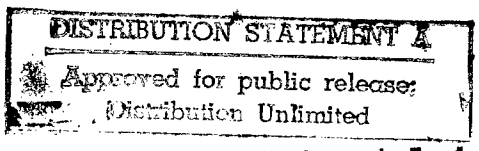


JPRS Report

Science & Technology

Japan

NEW FUNCTIONAL MATERIALS



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SCIENCE & TECHNOLOGY

JAPAN

NEW FUNCTIONAL MATERIALS

[Selected abstracts on the design, production, and properties control for new functional materials; "priority areas of research" sponsored by the Ministry of Education, Science and Culture]

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CONTENTS

Fabrication Process & Control of Functional Materials

Property Control of Compound Semiconductors

Analytical Studies on the Mechanism of Functional Materials and Prospect of Future Development

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1. Introduction

Running parallel with objective oriented studies on semiconductors and biofunctional polymers, theoretical and experimental studies on organic superconductors, conducting polymers, organic magnetic substances, fluoride glasses, intercalated graphites, specific surface-molecular interactions and so on have been carried out. In these studies, the structure-function relationship and structure-synthetic process relations have been elucidated. The comparative discussions between inorganic superconductor - organic superconductors, metallic conductivity - that of synthetic metals and inorganic - organic magnetic substances have been made.

2. Results and Discussion.

To proceed the studies based upon horizontal view covering organic, inorganic and metallic materials, it is most convenient to classify materials into two kinds, the one constructing with the elements and the other with molecular species. The utility of this classification is considered in relation to computer assisted material design. To elaborate the design of synthetic assemblies, features of components, characteristics of assemblies, the dimension of interaction and their interactions are summarized.

Theoretical Studies on Transport Phenomena of Organic Superconductors

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1. Introduction

Following susbjects of various aspects of transport properties are explored; (1) search for the mechanism of superconductivity in oxides and organics, (2) electronic properties in mesoscopic systems, (3) Anderson localization and the size effects on the superconducting transition temperature (4) proximity effect (5) spin-Peierls transition.

2. Results and Discussion

Results of research on some of the subjects listed above are briefly described in the following;

(1) For Cu-oxides, we have derived[1] the effective Hamiltonian based on Cu:$d_{x^2-y^2}$ and O:P_σ orbitals with Coulomb interactions both on-sites and inter-sites. Comparing theoretical results for both cases of electron and hole doping with the experimental discovery of electron-superconductivity by Tokura, Takagi and Uchida,[2] we indicated that the essence of high T_c Cu-oxidees will be described by the t-J model. The phase diagram for this t-J model has already been explored within the mean field approximation.[3]

(2) It has been demonstrated that one can observe fluctuations in transport properties in mesoscopic systems.[4] We have discovered[5] theoretically that such fluctuation effects can be observed in Landau diamagnetism, which is a thermodynamic quantity. This will explain the recent experimental finding by Webb.

(3) It has been established[6] that the superconducting transition temperature in dirty metals is dependent on the size of the systems. This property has become increasingly important in view of the development in technology to fabricate small systems. We have examined this feature in detail for thin films, multi-layers and thin wires.[7]

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Prediction of Limiting Mechanical and Electrical Properties of New Functionality Polymers by Vibrational Spectroscopy

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1. Introduction Evaluation and prediction of physical properties and functionalities of polymers based on molecular-level consideration are of essential importance as the basis of molecular design of new polymeric substances. The aim of the present project is to accumulate the knowledge of molecular-level structures, intra- and intermolecular interactions, molecular motions, and so on by means of vibrational spectroscopy, and to construct a theoretical method for predicting the limiting properties in elasticity, piezoelectricity, and pyroelectricity. Since physical properties of solid polymers are strongly influenced by higher-order structure, our efforts were concentrated to reexamine suitable mechanical model for deriving exact values of elestic moduli of fibers, and to consider the effects of morphology, crystal defects, and molecular motions on the mechanical properties. As for electric properties, phase transitions of ferroelectric liquid crystals were investigated.

2. Results and Discussion 1) Limiting values of elastic moduli of superdrawn fibers of various types were evaluated as functions of applied stress and temperature from the intramolecular force constants obtained by IR and Raman measurement. The calculated moduli E_c^{calc}, which corresponded to the limiting values for the idealized crystals, were compared with the experimental values E_c obtained by X-ray diffraction method. Here, we adopted a parallel-series model instead of the usually used simple series model for taking the role of morphological structure into account. For case of polyoxymethylene, E_c is only a half or less of E_c^{calc} above room temperature. With lowering temperature, E_c increases gradually first, then abruptly around $-100^{\circ}C$, and finally approaches E_c^{calc}. The sharp depression in E_c is caused by onset of a rotational fluctuation of the molecules as has been revealed by NMR, Far-IR, and DSC measurements.

2) Changes in molecular structure occurring on the phase transitions $C \rightarrow S_c^* \rightarrow Ch \rightarrow L$ of a compound having the structure R-O-ϕ-OCO-ϕ-ϕ-$OCH(CH_3)R$ [R: alkyl chain] were investigated by means of IR and Raman spectroscopy. A remarkable hysteresis was found in $S_c^* \rightarrow Ch$ transition.

Theoretical Investigations of Characteristic Electronic Processes in New Functional Materials

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1. Introduction

The purpose of the present study is to analyze the electronic processes and to perform the molecular design of conductive new polymeric materials based on the approach of theoretical chemistry with quantum chemical calculations. In particular, density-functional theory is extended for application to the study of superconducting phase transition , control of high-temperature Cooper-pair condensation.

2. Results and Discussions

(i) The electronic structures of polyiminovinylene (PIV) as well as polyaniline (PAn) are studied theoretically using the one-dimensioanl tight-binding self consistent field-crystal orbital (SCF-CO) method. PIV was employed as a tractable model for PAn to inspect the electronic process when the redox states of PAn are changed. The conduction mechanism caused by partial protonation (oxidation) is discussed and the possibility of the formation of bipolaron in the partially protonated polymer skeleton is examined.

(ii) The importance of the pattern analysis of the frontier orbital is discussed as a guiding principle in the course of theoretical molecular design of polymers intrinsically showing metallic properties. Moreover, actual calculations are performed on polyperimesoanthracene (PPMA) and several kinds of nitrogen-substituted PPMAs (NPPMA) as examples to test the criterion discussed. The result of the actual calculations agrees well with what is predicted from this guiding principle in the molecular design of polymers showing intrinsically metallic properties.

(iii) Vibronic attractive force for Cooper pair of superconducting electrons is calculated for a cluster model CuO_4 of the novel copper-oxide high-Tc superconductors. Vibrational mode-specificity is found for the attractive force, which turns out to be strong enough to overwhelm the Coulombic repulsive force. Dimensionality of the orbital network plays an important role. A model based on the density-functional theory is proposed for a unified description of the superconducting phase transition.

Theoretical Study on the Mechanism of Catalysis occurring at the Transition Metal Surface

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1. Introduction

As the first step to understand the carben-metal complex system, we carried out ab initio calculation on the $CuCH_2$ cluster by MCSCF and CI methods using an extended basis set. Other than this system, we carried out calculations on a cluster taking from $YBa_2Cu_3O_7$ crystal. We focussed our attention to type of 2p hole on O and magnetic interaction between two dimensional CuO_2 surface and CuO chain.

2. Results and Discussion

By the use of the wave function, dipole moment of the $CuCH_2$ was calculated to be 3.90 Debye (Cu^+OC^-). Reflecting the negatively charged carbon side, the structure of CH_2 part is close to that of free CH_2^- rather than the ground state of CH_2. The calculated vibrational frequencies of CH and CuC breathing modes and HCH wagging mode are 2868, 618, and 1408 (cm^{-1}) which agree very well with the experimental frequencies of 2961, 614, and 1345 (cm^{-1}), respectively. The CH bond in $CuCH_2$ is weaker than the ground state of free CH_2.

We carried out SCF and CI calculations on a small cluster taking from $YBa_2Cu_3O_7$ with split valence basis set. Computed ionization energies obtained by CI are in good agreement with photo ionization spectra. The lowest ionization energy is 0.2eV and the state is represented by an ionization of 2p electron of Oxygen which is located at the two dimensional CuO_2 surface. The 2p orbital is laid in the CuO_2 surface and perpendicular to CuO axis, i.e. $2p\pi$. This suggestes that the 2p hole is inclined to occur in O of CuO_2 surface and orbital is $2p\pi$ type. It might be important to take O $2p\pi$ hole into account in discussing the super conducting mechanism. We further carried out CI calculations on the various spin states whose energy levels are separated primarily by interaction between the spins of CuO_2 surface and that of middle layer. The results show that the energy separation between the states of the different spin coupling is $100cm^{-1}$ and $25cm^{-1}$ for two diffeernt hole positions. This suggests that the spin coupling between CuO_2 surface and middle layer easily fluctuates.

Approaches to Organic Magnetic Materials from High-spin Organic Molecules

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1. Introduction

We have succeeded in constructing high-spin polycarbenes m-$Ph\ddot{C}(C_6H_4\ddot{C})_{n-1}Ph$ (n=4,5,6) that have nonet, undecet and tridecet ground states, respectively, and show paramagnetism due to very large magnetic moments. Whereas the extension of the system is expected to generate organic superparamagnets, a number of problems remain to be solved in these molecular systems. It is therefore highly desirable to design new polymer systems that can align $10^2 \sim 10^3$ spins within the polymer molecule.

2. Results and Discussion

2.1. Molecular design of high spin polyacetylenes. According to valence bond theories on the high-spin states of alternant hydrocarbons, poly(phenylacetylenes) and poly(phenyldiacetylenes) consisting of m repeating units and carrying a free radical center at the p-position of each phenyl group are predicted to have spin multiplicities of (m+1). We have confirmed the theory by model dimer radicals.

2.2. Poly(phenylacetylenes). While two catalysts WCl_6/Ph_4Sn and $[Rh(COD)Cl]_2$ are reported to be useful to polymerization of phenylacetylenes, the monomers carrying stable free radical centers on the phenyl group were found to serve as effective catalyst poison. We therefore have had recourse to polymerization leading to precursors followed by chemical modification of the functional groups such as p-bromo, formyl and benzoyl into stable free radicals. These reactions on the polymers have so far proved to be only partly successful; the free radical contents of poly-phenoxyl, verdazyl and nitroxyl were only $10 \sim 25$ % of the theoretical values. Efforts to improve these polymer reactions are in progress.

Determination of Orientational Order in Main-Chain Liquid Crystals Useful As a High-Performance Material

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1. Introduction

The orientational order parameter of the molecular axis is a primarily important structural criterion in characterizing the mesophase. The deuterium NMR technique has been proved to be useful in monitoring the average orientation of anisotropic molecules when they are properly labeled. In this work, we have developed a method to elucidate molecular conformation of main-chain liquid crystals carrying deuterated flexible spacers by utilizing the information provided by the ^{2}H-NMR method.

2. Results and Discussion

Deuterium NMR measurements have been performed for main-chain polymer liquid crystals (PLC) having structures such as

$$[-\phi\text{-}OC(O)\text{-}\phi\text{-}O(CD_2)_nO\text{-}\phi\text{-}C(O)O\text{-}\phi\text{-}O(CH_2)_nO\text{-}]_X$$

with n=9,10. The RIS analysis of the ^{2}H-NMR spectra was performed on the basis of the assignment established for the dimer liquid crystals. The bond conformation probabilities of the flexible spacer in the nematic phase were estimated. The results indicate that the nematic conformation of the flexible segment is amazingly similar between the dimer and polymer with the same n. The difference between these two arises mostly from the orientation of the molecular axis in the liquid crystalline domain. The orientational order parameters of the mesogenic core axis estimated from these analyses were found to be quite consistent with those observed directly by using mesogen-deuterated samples. The molecular scheme described above requires an extension of the polymeric chain with a large persistence length, unless some folds or defects are occasionally involved. Above the NI transition temperature, the conformational restriction imposed by the nematic field should vanish. In the isotropic state, the random-coil conformation becomes most stable. Then, a question arises regarding how sharp is the transition from a highly extended form to a coil. The ^{2}H-NMR method is sensitive only to short-range correlations. To answer the question, a combined use of some other technique such as the small angle X-ray or neutron diffraction is needed.

Fundamental Analysis on the Effect of the Structural Modification on the Electronic Properties of Highly Conductive Polymers

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1. Introduction and Method of Calculation

We have been analyzing the relation between the profile of the density of states of the π-electronic structure of infinitely large periodic benzenoid hydrocarbons and the topological structure of the unit with the HMO and PPP methods. It has already been clarified that (1) main features of the density of states are largely determined by the orbital energies of the hypothetical cyclic dimer, (2) the magnitudes of the HOMO-LUMO gap calculated with HMO and PPP are roughly proportional to each other, and (3) the main features of the partial structure of these systems can well be understood from their typical Kekulé structure. The purpose of the present study is (1) to analyze the effect of the branching to the benzenoid skeleton on the density of states, and (2) to apply the graph-theoretical method to analyze the hitherto obtained relations for the electronic structure of highly conductive polymers.

2. Results and Discussion

(1) From the collection of the calculated results of the density of states of branched linear and zigzag polyacenes it was found that the HOMO-LUMO gap is sensitively dependent on the mode of branching. However, the existence or non-existence of the gap in the HMO scheme can easily be predicted from the typical Kekulé structure. Several model networks of interesting properties were found and discussed.

(2) Poly-p-phenylene, polyanthracene, and polytetracene are known to have non-zero HOMO-LUMO gap, while polynaphthalene and polypentacene have no gap. It was found from the graph-theoretical analysis that these different behaviors can be predicted by seeing if the hypothetical cyclic monomer graph has NBMO's.

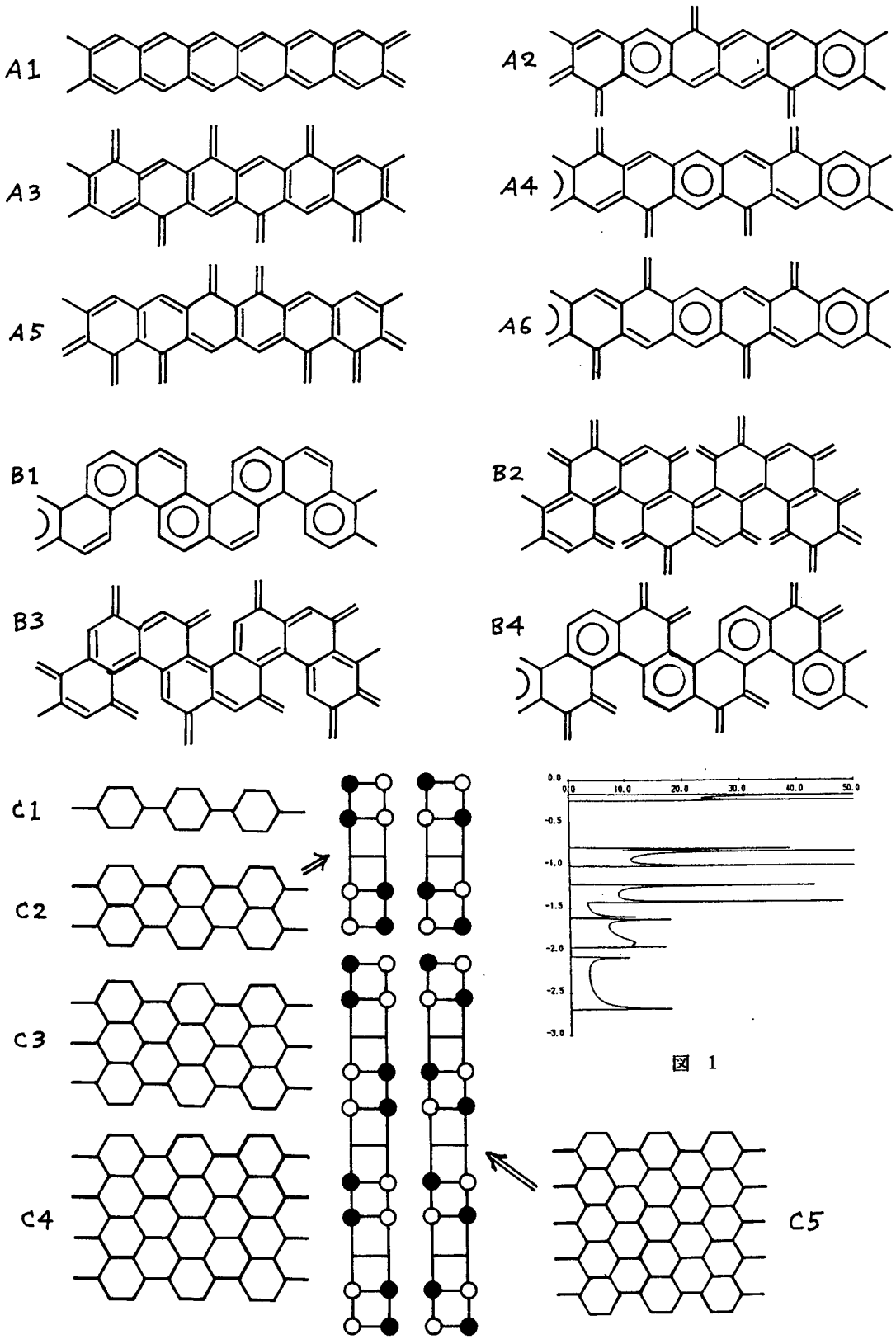
A1
A2
A3
A4
A5
A6
B1
B2
B3
B4
C1
C2
C3
C4
C5
0.0
10.0
20.0
30.0
40.0
50.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0

図 1

Design of High Performance Iron-Base Austenitic Alloys by a New Alloy Concept

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1. Introduction

Iron-base austenitic (fcc) alloys are widely used as heat- or corrosion-resisting high performance materials, and are very important for todays high-technologies. Recently, we have developed a new d-electrons alloy design concept on the basis of the theoretical calculation of electronic structure of alloys. In this design concept two calculated parameters are mainly utilized. The one is the d-orbital energy level (Md) of alloying transition elements, and the another is the bond order (Bo) that is a measure of the covalent bond strength between atoms. The concept was devised at first for austenitic Ni-, Co- and Fe-base alloys and it was proved the phase stability and some physical and chemical properties could be predicted by this approach.

This study aimed to apply this concept to the design of high performance Iron-base austenitic alloys of Fe-Ni-Mn-Cr-C-Ni system.

2. Result and Discussion

The phase stability of various austenitic steels containing Cr, Mn, Ni, C and N was examined experimentally. The results were interpreted using these parameters, and a new "phase stability index diagram" was proposed for the austenitic steels. In this diagram, the $\gamma/\gamma+\alpha_M$ and the $\gamma/\gamma+\alpha(\delta)$ phase boundaries are well represented for solution-treated alloys, and also the $\gamma/\gamma+\sigma$ phase boundary is defined for aged alloys. Here, γ is the fcc matrix phase, and α_M, $\alpha(\delta)$ and σ are the martensite, ferrite and sigma phase, respectively.

Computer-aided design was performed so that the steel could contain the least amount of high activation elements such as Ni and N, and several alloys were selected critically as the materials for fusion reactor.

Novel Graphite Intercalation Compounds with Fluorine, and Fluorides: Synthetic Pathways, Properties and Analyses of Functionality

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1. Introduction

Attempts have been made to prepare a series of fluorine- and fluoride-graphite intercalation compounds(GICs) of which physical and chemical properties are well controlled in a wide range. In addition to the direct fluorination means, a new synthetic pathway to involatile fluoride-GICs has been developed in anhydrous hydrogen fluoride(AHF) solution. The diverse proterties of these materials suggest a number of potential applications such as high electrical conductors, battery and electrode materials, precursors for two-dimentional metal clusters and for magnetic materials.

2. Results and Discussion

Here, we focus our attention on intercalation reactions. Since the impurity amount of HF has a strong influnce on fluorine intercalation, ab initio MO calculations for F_2-HF system have been caried out by Gaussian 82 program with a 6-31 G** basis set. Geometrical optimization and energies calculations were performed by Moller-Presset perturbation method of second order(MP2) and MP4(SDTQ), respectively. The results show that charge transfer does occur from fluorine to HF and that the F_2-HF complex has a considerable stabilization energy(-10.5 KJ/mol). F_2 molecle consequently becomes polarizable " soft Lewis acid ". On the basis of these results and relevant experimental evidences, spontaneous fluorine intercalation reaction is deduced.

The same calculations were extended to the Cl_2-HF system. However the interaction in this system is slightly weaker than that of the F_2-HF, changes in molecular properties and charge distribution occur by Cl_2-HF complex formation. Then the interaction between chlorine and HOPG has been examined under the presence of HF or F_2. Chlorine intercalaiton does occur after 14 days reaction in 2 atm chlorine at 15°C, but fluorine intercalation occurs simultaneously. The pure stage-2 compounds are $C_{11-12}ClF$ with d_I values of 3.06-3.26 A. These materials are very stable even in moist air. The other stage compounds except stage-2 are obtained as admixture. The electrical conductivity of stage-2 compound is 12 times higher than that of pristine HOPG.

An approach to organic ferromagnetic materials through negative spin density

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1. Introduction

Organic magnetic materials, especially ferromagnetically interacting substances, have attracted much attention. One of the possible mechanisms was proposed by McConnell to obtain organic ferromagnets on the basis of negative spin density on the organic molecules. In this study we are to establish an experimental method to ascertain negative spin density and to examine the possibility of McConnell's mechanism.

2. Results and Discussion

The experimental methods to identify the negative spin density were carried out using multiple electron resonance spectroscopy, that is, electron-nuclear double resonance(ENDOR) and triple resonance(TRIPLE). First, we improved on those spectrometers, including resonance cavities and implemented high-sensitivity. Among neutral, anion, and cation radicals, we concentrated our attention to one of the neutral radicals, t-butyl-phenyl nitroxide. The ESR and ENDOR results were found to be compatible and the TRIPLE spectra indicated that the meta-carbon atoms of the benzene ring possess negative spin, whereas the ortho- and para-carbon atoms positive one. This was also assured by the cross-relaxation ENDOR called CRISP. According to the molecular orbital calculations, the negative spin density was rather reduced by steric hindrance between the t-butyl and phenyl groups. In view of the results, only an intermolecular interaction directly between the meta-carbons and N-O group is suggested as a possibility of realizing ferromagnetism in this molecule.

Electronic Structures and Mechanisms in Surface-Molecule Interaction Systems

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1. Introduction

We study in this project the surface-molecule interaction systems, in particular, the solid catalysts, from the theoretical and molecular engineering point of view. Based on the analyses of the electronic processes in these systems, we would like to obtain key ideas for the design of the materials involving surface-molecule interactions.

2. Results cnd Discussion

I. Oxygen chemisorption on silver surface

Silver-oxygen surface interaction system is a very efficient catalyst for partial oxidation of ethylene leading to ethylene oxide, and this reaction is realized in chemical industry. Nevertheless, the catalytic mechanism of this reaction is not yet clarified. Here, we study theoretically chemisorption of a oxygen molecule on a silver surface, an important first step of this catalytic reaction, with the use of the dipped adcluster model (DAM) previously reported [1]. Electron transfer from solid silver to oxygen is essential for the occurrence of the chemisorption. Stable geometry is end-on bent structure. About 0.8 electron is transferred into O_2, 0.6 for the nearer and 0.2 for the distant one. The frontier MO has larger amplitude on the distant atom. The surface structure such as step, terrace, kink, etc., is reflected on chemisorption energy, which is calculated to be 13 - 26 kcal/mol in comparison with the experimental value of 16 - 28 kcal/mol.

II. Chemisorption of alkali metal on a Pt surface

Alkali metal works as a promoter of catalytic reaction. Chemisorption of alkali metal on a metal surface leads to a lowering of the work function, and thereby facilitates electron transfer from a metal surface to an admolecule. We here study chemisorption of Li_2 to a Pt surface with the DAM model. The electron transfer here is from an admolecule to a metal surface, which is reverse to the above Ag-O_2 system. The side-on on-top geometry is studied. The catalytically active state is the excited state of the Pt atom. The ionization potential of $PtLi_2$ is calculated to be 4.82 eV which is lower than the work function of a Pt surface, 5.63 eV. The Fermi level is a mixture of 6s(Pt) and 2s(Li) AO's. We plan to study the electronic processes and mechanisms in the promoted catalytic reaction in more detail.

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A Study on Electrical and Optical Property of Conducting Polymer and Origin of Its Functionality

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1.Introduction

Conducting polymers with highly extended electron system in the main chain have attracted much attention as functional polymers. In this study electrical and optical properties as functions of molecular structure and cnformation are experimentally studied in detail and their mechanisms are discussed.

2.Results and Discussion

Poly(3-alkylthiophene)s with various lengths of alkyl chains were prepared and used as the samples. Following results have been obtained.

(1) Drastic change of electrical and optical properties of poly(3-alkylthiophene)s upon temperature change can be explained in terms of effect of the change of effective conjugation length.

(2) Anomalous temperature dependence of conductivity of poly(3-alkylthiophene) was observed in the temperature range in which the remarkable spectral change was observed.

(3) Luminescence of poly(3-alkylthiophene) exhibited anomalous temperature dependence. That is, luminescence intensity was enhanced with increasing temperature contrary to the usual inorganic semiconductors.

(4) At the transition from solid to liquid states, the electrical conductivity decreases in stepwise and then in liquid state it again increases with temperature.

(5) Though the absorption peak shifted to shorten wavelength with temperature but the absorption edge was temperature insensitive in the solid state, at the phase transition from the solid to the liquid the absorption edge shifted to higher energy side.

(6) Upon applying hydrostatic pressure, the melting point and the temperature of stepwise decrease of resistivity increases.

(7) Hydrostatic pressure induced the red shift of absorption spectrum.

(8) These novel characteristics can be explained by the change of effective conjugation length upon temperature change induced by the introduction of torsioning of bonds between thiophene rings due to the steric hindrance effect between alkyl chain and sulphur atoms triggered by the conformation change of alkyl chains.

Ab Initio Molecular Orbital Calculations of Effective Exchange Integrals : Design of New Magnetic Polymers

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1. Introduction

The approximately projected UHF Moller-Plesset (APUMP) perturbation method was applied to ab initio calculations of effective exchange integrals (Jab) for clusters of organic radicals, and transition metal oxides and halides. The atomic parameters for the two- and four-band Hubbard models were determined so as to reproduce the calculated Jab-values for transition metal oxides and halides, which were accepted for current interest in relation to the high-Tc superconductivity observed for Cu-O based superconductors. The Hubbard models were solved by the full valence-bond configuration interaction (CI) method.

2. Results and Discussions

The present calculations revealed the following:

(A) Electron correlation effect: The magnitude of Jab-values for clusters of organic radicals was largely dependent on the electron correlation effect, whereas the sign was insensitive to the effect. This supports the results obtained by the PUHF (mean field approximation) method last year.

(B) Spin glass and amorphous ferromagnetism: The signs of Jab-values for organic clusters were largely dependent on the conformation and stacking mode of organic radicals. The spin glass and amorphous ferromagnetism are theoretically concluded for organic solids unless stacking modes are at least controlled by several techniques.

(C) Cooperative mechanism for high-Tc superconductivity. Both the magnetic and charge transfer excitations were contributed to the electronic structures of copper oxides clusters with O2p holes. The extended Hubbard models by the use of realistic parameters supported a mix mechanism of spin and charge fluctuations for the high-Tc superconductivity observed for Cu-O based superconductors. A cooperative model was proposed as an extenstion of the J-model and/or CT model for the high-Tc superconductivity.

(D) Possible organic analogs to copper oxides: The ab inito and extended Hubbard calculations revealed that the CNC unit is isolobal to CuOCu unit. The possible organic analogs to copper oxides were proposed on the basis of this analogy and related experiments.

The further calculations of relatively larger clusters are in progress.

High Conductivity Function and Conduction Mechanism of Fluoride Ion in Fluoride Glasses

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1. Introduction

The main object of this study is to examine the mechanism of fluoride-ion conduction in fluoride glasses in atomic scale and then to present the chemical compositions and the preparation methods for obtaining glasses with faster fluoride-ion conduction. At the same time, however, if conduction due to other ions (e.g. alkaline ions) or electrons is expected in fluoride glasses, examination of such conduction also is one of the object. In other words the final purpose of this research proposal is to elucidate potentialilty of fluoride glasses as a solid-state ionics.

2. Results and Discussion

Last year the design of chemical composition for realizing fast fluoride-ion conduction in fluoride glass systems was investigated by examining the fluoride ion-conduction mechanism in ZrF_4-based glasses using NMR, EXAFS, and ac conductivity techniques. As the result various fluoride systems which can yield glasses with high electrical conductivities were developed. Those are the ZrF_4-, ZnF_2-, FeF_3-, GaF_3-, and InF_3-based systems. Notably the InF_3-based system gave glasses with extremely high conductivities that may be characterized as a super ionic conductor.

This year two researches were performed. The one research is the Zr-EXAFS experiment of ZrF_4-based glasses in Institute for High Energy Physics to obtain more reliable information on the F coordination of Zr. The other is the electrolysis experiment of the FeF_3- and ZrF_4-based glasses. The latter research presented two remarkable findings: mixed fluoride-ion and electron conduction in FeF_3-based glasses, and vitreous state electrolysis in both FeF_3-based and ZrF_4-based glasses. The electronic conduction found in FeF_3-based glasses was proved to be due to the coexistence of Fe^{2+} and Fe^{3+} ions and the electron hopping between these ions. On the other hand, the vitreous state electrolysis was found to result from the fact that glass network-forming fluoride-ions are mobile.

At present a research on the mixed fluoride-ion and alkaline-ion conduction in alkaline fluoride-containing ZrF_4-based glasses is in progress.

Study on the mechanism of the various functions of polymers in terms of the through space/bond interactions

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1. Introduction

The concept of the through space/bond interactions has been known to be useful to relate the ionization potential and the electron affinity of a molecule in question with the molecular structure. Consequently, it is expected that the band structure of a polymer is connected with its molecular structure in terms of the through space/bond interactions. Thus, we are applying the analysis of the through space/bond interactions to polyfluoroacetylene and polyhydroxyacetylene doped with Be atoms.

2. Results and Discussion

Energy band gaps of polyacetylene, polyfluoroacetylene and polyhydroxyacetylene were calculated by ab initio SCF method with STO-3G basis set, and were found to be more than 6 eV, leading to the conclusion that these polymers are insulators. On the other hand, energy band gaps of polyfluoroacetylene and polyhydroxyacetylene were found by calculations to decrease remarkably by doping with Be atoms and are nearly 2 eV. Accordingly, these doping systems are expected to have no band gaps and metallic in nature for the electric conductivity, because it has been well known that the band gap calculated by ab initio SCF method with STO-3G basis set gives too large value in comparison with the experimental data as well as the theoretical value calculated with the electronic correlation effect and the larger basis set.

LUMO energy band includes mainly the contribution of the π orbital on the backbone while HOMO energy band mainly consists of Be 2s orbitals. The reason for the elevating of HOMO energy band and thus for the narrowing of the energy band gap were studied for polyhydroxyacetylene-Be system in terms of through space/bond interactions. It is the coupling terms between the Be-O and the Be-H through space interactions that is responsible for the narrowing of the energy band gap. The effect of these coupling terms are intimately related to the crystal orbital symmtry in accordance with Woodward-Hoffmann rule.

Development of Molecular Conductors with Magnetic Structures

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1. Introduction

Understanding of the relation between magnetic properties and metallic (or superconducting) behavior will give us a new horizon in the chemistry and physics of the molecular conductors (superconductors). A series of highly conducting anion radical salts, $(R_1,R_2\text{-DCNQI})_2Cu$ (DCNQI=N,N'-dicyanoquinonediimine; R_1, R_2 = CH_3, CH_3O, Cl, Br), is a system where the 3d orbitals of Cu interact with the organic $2p\pi$ orbitals through the coordination bond. We have tried to characterize its metallic state with attention to the existence of the Cu^{2+} (d^9) ion.

2. Results and Discussion

We have explained the metallic state of $(R_1,R_2\text{-DCNQI})_2Cu$ with the "mulit-Fermi surface" model based on the mixing of the LUMO of DCNQI and the 3d orbitals of Cu in the mixed-valence state (Cu^+ : Cu^{2+} = 2 : 1). The metal-insulator (M-I) transition at low temperature can be understood as a cooperative structural phase transition induced by the CDW instability of the DCNQI column and the second-order Jahn-Teller distortion around the Cu ion. We have found the novel pressure-induced M-I transition in the case of R_1 = R_2 = CH_3, CH_3O. The static spin susceptibility measurements were performed on the powder samples of $(DMe\text{-DCNQI})_2Cu$ (R_1 = R_2 = CH_3; stable metal down to 0.5 K at ambient pressure) and $(DBr\text{-DCNQI})_2Cu$ (R_1 = R_2 = Br; M-I transition at 160 K). The paramagnetic susceptibility (χ_p) of $(DMe\text{-DCNQI})_2Cu$ is very weakly temperature dependent at $T > 120$ K and $T < 30$ K. The fact that the χ_p value is enhanced at 70 K suggests that the metallic state of $(DMe\text{-DCNQI})_2Cu$ is magnetically classified into two types. The room-temperature χ_p value of $(DBr\text{-DCNQI})_2Cu$ is smaller than that of $(DMe\text{-DCNQI})_2Cu$, which should be related to the fact that the distortion of the coordination tetrahedron of Cu in $(DBr\text{-DCNQI})_2Cu$ is larger than that in $(DMe\text{-DCNQI})_2Cu$. The simple tight-binding band calculation indicates that the increase of the ligand field splitting of 3d orbitals leads to the decrease of the density of state at the Fermi level. We have observed a significant jump of χ_p of $(DBr\text{-DCNQI})_2Cu$ at T_{M-I}.

Non-equilibrium processing and preparation of new magnetic thin films

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1. Introduction

Non-equilibrium metastable phases of the transition metals are expected to display a variety of magnetic behaviors. The interplay between their structural traits such as the interatomic distances and their magnetic properties is especially intriguing and may lead to some vital technological applications. In order to gain some insights into this issue, we are currently attempting to grow various magnetic multilayer systems in the ultra high vacuum (UHV) environments by use of the molecular beam epitaxy (MBE) technique.

2. Results and Discussion

As our first trial, we chose to investigate the magnetic properties of fcc Fe films, which are metastable at room temperature. We have grown a sample of multilayer of Fe(10A thick) and Cu(20A thick) on (100)Cu layers(200A thick) over a $SrTiO_3$ substrate under the following conditions: the UHV at 10^{-8} torr, the substrate temperature at 373K and the layer growth rate at 0.1~0.2 A/sec. Our x-ray diffraction study showed that, contrary to our expectation, our sample had an average period of 14A and contained some bcc Fe phases. By the magnetic measurement, it was also found to be ferromagnetic at room temperature.

We are further pursuing a detailed study of the Fe/Cu multilayers and intend to extend our investigation to other magnetic multilayer systems.

Synthesis of Superconducting Nitrides with High Critical Characteristics

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1. Introduction

Niobium nitride and its relating compounds are expected as stable superconducting materals,especially for radioactive ray. This study aims to synthesize such nitrides in various forms of powders, plates and films by the new processing routes of the combustion synthesis and the non-equilibrium reaction sputtering.

2. Results and Discussion

1) Combustion synthesis of $NbN_{1-x}C_x$ solid solution powders

The experimental results on the combustion synthesis of B1 phase NbN powders were reported last year. In this year,the combustion synthesis of $Nb_{1-x}N_xC_x$ solid solution was tried. The mixed reactants of Nb and C with various compositions were burned in pressurized nitrogen gas at 3 to 10 MPa and the solid solutions of $NbN_{1-x}C_x(0\leq x\leq 0.8)$ with B1 phase were synthesized. The superconducting transition temperature showed a peak value of 18.8 k at around x=0.4, which was 0.9 k higher than the highest reported value for this system.

2) Combustion synthesis of NbN ceramic plate

Ceramic plate of NbN with T_c=16.2 k was formed by the nitrization of Nb metal plate by burning the combustion agent of Nb+NbN mixed powders under pressurized nitrogen atmosphere. This method is available to form various shape components of NbN and other transition metal nitrides such as TiN and TaN.

3) Synthesis of $Mo_{1-x}M_xN$(M=Nb,Zr)thin films

Solid solution films of $Mo_{1-x}M_xN$(M=Nb,Zr, x=0~1) were synthesized by a reaction sputtering. The superconducting transition temperatures were lowered by incorporating Nb and Zr atoms into MoN, which is probably attributed to the electronic states and/or the lattice defects.
The thermal stability of $Mo_{1-x}Nb_xN$ was investigated by annealing test.

Synthesis of Materials and Analysis of The Formation Mechanisms Using Modified and Controlled High Pressure Environments

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1. Introduction

High pressure environments can be utilized for synthesis and development of new materials most effectively, especially when they are characterized precisely or modified with well-controlled other factors. Study on mechanisms of material formation can also be performed advantageously by the use of them.

2. Results and Discussion

(2-1) Graphite/diamond equilibrium pressure

This equilibrium pressure can be calculated using thermochemical properties (specific heat and heat of combastion) of graphite and diamond at the atmospheric pressure, and the molar volumes as functions of pressure, P and temperature, T. In the most believable result of the calculation (Berman, 1979), however, the molar volume of graphite, Vg(P,T), is not a directly measured quantity , but estimated on some assumption. Thus, direct measurement of Vg(P,T) is required for Berman's equilibrium pressure to be reliable. And it is now possible by the use of high pressure-high temperature x-ray diffraction combined with SR (synchrotron radiation). The measurement was performed at Photon Factory of Institute for High Energy Physics, Tsukuba. Compression curves obtained at room temperature and at 600℃ are both in excellent agreement with those used in Berman's calculation. In conclusion Berman's equilibrium pressure is confirmed to be very reliable.

(2-2) Formation of a crystalline solid solution between BN and C.

Amorphous BCN composite was melted by flash heating (heating with a large pulse of electric current) at a pressure of about 2GPa. The obtained material, with an appearance very similar to graphite, showed lattice constants very close to those of gBN (the low pressure phase BN with a graphite-like structure). According to element analysis by AES, the material is composed of B, N and C, where B and N exist in about the same quantity, and C in varied quantity up to about the same as that of B and N. It is very probable that solid solutions with the structure of gBN were realized. Those with the graphite structure (C-rich materials) are in search.

Molecular Design, Synthesis, and Evaluation of High Performance Polymeric Materials for Harsh Environments

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1. Introduction

Recently, we have found that high-strength and high-modulus copolyimide films could be prepared by the introduction of rigid rod poly-p-phenylenepyromellitimide molecule 2 to semi-flexible polyoxydi-p-phenylenepyromellitimide molecule 1 via random and block copolymerizations. The purpose of our present study was to obtain copolyimide films with higher strength and higher modulus. Dynamic mechanical analysis was used as the major tool to evaluate the mechanical properties of the copolyimide films.

2. Results and Discussion

A series of random and block copolyimides consisting of semi-flexible molecule 1 and rigid rod molecule 2 were prepared by the N-trimethylsilyl-substituted diamine method (silylation method), as well as by the conventional diamine method. The plots of dynamic loss modulus E" as a function of temperature showed α-loss peak around 400°C, probably due to glass transition temperature, for both random and block copolyimide films. The dynamic storage modulus E' and the α-loss peak increased with increasing rigid rod segment for all the copolyimide films. It is interesting to note that the E' values of the copolyimide films prepared by the diamine method were higher than those of the films by the silylation method. This may be attributed to the difference in the film microstructures of copolyimides obtained from polyamic acids and polyamic acid trimethylsilyl esters.

Although the E' values of the random copolyimide films annealed at 330°C were almost comparable to those of the films annealed at 280°C, the α-loss peaks of the former films shifted to above 400°C. The uniaxially oriented block copolyimide films were prepared by the cold drawing (50%) of the polyamic acid trimethylsilyl ester films, followed by annealing at 280°C. The E' values and α-loss peaks of the oriented films rose considerably on the basis of those of the unoriented films. The cold drawing also improved markedly the tensile properties of the copolyimide films. The tensile strength and tensile modulus of the oriented films were two to three times higher than those of the unoriented films.

High-pressure synthesis of "periodic compounds" and their optical and electrical properties

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1. Introduction

During the past few years considerable attention has been given to the investigation of the isoelectric semiconductors with carbon. Recently, some of them involved the "periodic compounds" which consisted of elements disposed unsymmetrically with respect to the location of carbon in the periodic table. It would be seemed worth while utilizing the high pressure-temperature conditions to attempt their synthesis. Here we report the high pressure synthesis of new compounds in the boron-sulfur system.

2. Results and Discussion

The mixture of amorphous boron and sulfur powder was charged into a cylindrical gold or hBN capsule, inserted into the high pressure cell assemblage and then subjected to the conditions of 600-1500^{o}C and 1.0-5.5 GPa for 0.5-2.0 hr using a belt-type apparatus. Two phases were recognized in the B/S ratios of 1:1 to 2:1. Most samples were opaque and gray or ivory in color. Chemical analysis of high-temperature phase indicated a B/S ratio 1:1. The phase hence is assigned the formula of BS. The powder x-ray diffraction of BS was very similar to that of GaS, and readily indexed assuming the space group of R3m with hexagonal dimensions of a=3.052 A and c=20.406 A. The absorption edge of BS was estimated to be 3.3-3.7 eV. The electrical property of BS was p-type semiconductive with the activation energy of about 0.14 eV, because its thermoelectric power was in the range of +420-530 μV/K. Its resistivity was about a few kΩ cm at room temperature.

In this system, to clarify the compositional dependence of electrical properties is the subject for a future study.

A Study of the Novel Synthesis Method of Amorphous Alloys by Hydrogen Absorption

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1. Introduction

Recently, it has been demonstrated that amorphous alloys can be prepared without rapid quenching, i.e. by hydrogen absorption. However, the amorphizing alloy systems, the mechanism, the progress and physical properties of hydrogen-induced amorphous alloys are still uncertain. The purposes of the present work are to search amorphizing alloys, to obtain a detailed understanding of the progress, to discuss the mechanism, and to examine the magnetic properties of the resultant amorphous alloys.

2. Results and Discussion

By hydrogenation of the Laves phase RFe_2 and RCo_2 compounds (C15 structure) (where R = Y, Sm, Gd, Tb, Dy, Ho or Er), Ce_3Al($D0_{19}$ structure) and Zr_3In ($L1_2$ structure), we demonstrate that it is possible to produce amorphous alloys containing hydrogen. Hydrogen-induced amorphization in $GdFe_2$ has been studied by means of differential thermal analysis (DTA) in a hydrogen atmosphere in order to know the kinetics and the nature of amorphization. The DTA curve shows four exothermic peaks. The first exothermic peak is due to absorption of hydrogen in the crystalline state, i.e., c-$GdFe_2$ becomes c-$GdFe_2H_{3.8}$. The second one is due to the transformation from c-$GdFe_2H_{3.8}$ to a-$GdFe_2H_{2.8}$. Since the second peak due to amorphization is sharp, we can conclude that hydrogen-induced amorphization is completed in a short time. The present DTA data clearly demonstrate that the hydrogenated crystalline phase is less stable than the corresponding amorphous phase, because the former transforms to latter by an exothermic reaction. The driving force for the hydrogen -induced amorphization is suggested to be the difference in the enthalpy resulting from the different hydrogen occupation sites in both states of alloy. Hydrogen-induced amorphization in RFe_2 (where R = Tb, Dy, Ho and Er) reduced the Curie temperature of the original compounds in the same manner as hydrogen induced amorphization in $GdFe_2$.

Structural Control of Organo-Metal Multiphase Polymer Films by Plasma Processing and the Functions Based on Their Hetero-Interfacial Structure.

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1. Introduction

This research is concerned with the control of preparation, structure, and properties of plasma polymerized thin films from titanium tetraisopropoxide. The objective of this investigation is to obtain thin films consisting of organo-metal multiphase structure and to find out their specific opto-electrical properties based on their hetero-interfacial structure.

2. Results and discussion

Polymeric thin films were prepared from gaseous titanium tetraisopropoxide by low temperature plasma polymerization. The obtained films were n-type semiconductor and showed conductivities of the range between 10^{-8}-10^{2} S/cm and high photoconductivity. The value of photo-current observed was as high as 7.2μA under irradiation of 30mW/cm^2 of visible light. This exceeds nearly 3 orders of magnitude the value of the films obtained by polymerization of copper acetylacetonate (6nA). TEM observation was carried out in detail in order to investigate the texture of the film , particularly the sizes of the metal and organic layers. The percolation structure consisting of metal and organic alternative layers of 20 nm each could be seen.

It was also found that when the film was exposed to fuel gases the conductivity of thin film increased with increase in gas concentration. The extent of the increased conductivity depended on the surface temperature of films. Mechanism of conductivity change of the films in the presence of fuel gases was discussed .

Preparation and Control of New Functional Thin Films by Use of High Dose Ion Implantation.

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Introduction

In recent years, iron nitrides have been investigated to be magnetic materials in expectations of their high corrosion durability and strong hardness. Among them, however, single phase of $Fe_{16}N_2$ has not been synthesized yet, although it might have giant magnetization much higher than that of pure iron. In this study, formation and characterization of $Fe_{16}N_2$ formed by nitrogen implantation into iron thin films is carried out.

Results and Discussion

Nitrogen molecular ions (N_2^+) accelerated to 140 keV were implanted into iron films which were deposited epitaxially onto mirror-polished (100) plane of MgO single crystal. Ion beam current density was kept below 1 ($\mu A/cm^2$) during the implantation to keep the targets from becoming too hot. After the implantation, these films were annealed in vacuum (2.7×10^{-4} Pa) for 2 hr. at 150 °C.

As a result of X-ray diffractometry, it was found that a part of α-iron in target films was transformed into an iron nitride with body-centered tetragonal structure (b.c.t.). Further, the X-ray diffraction line characteristic of $Fe_{16}N_2$ is clearly observed. This shows that the ordered phase of the b.c.t. iron nitride, i.e. $Fe_{16}N_2$, can be formed even at as-implanted state. After the annealing treatment in vacuum, an improvement of nitrogen arrangement led to a slight increase in the characteristic line intensity.

The b.c.t. iron nitride precipitated aligning it's c-axis perpendicular to the film plane. This orientation is regarded to be due to a habit that the stress arising from the tetragonal elongation of the precipitate is released to the direction of thickness.

Preparation and Evaluation of Amorphous Thin Films by Plasma CVD

Ceramics thin films in the B-C-N system were prepared by plasma CVD at 400℃ or below using B_2H_6, CH_4, N_2 and H_2 gases. Amorphous films with BCxNy compositions were easily obtained under the total gas pressure of 267Pa. The flow rate of H_2 gas affected significantly the deposition rate, microhardness(Hv) and structure of the films deposited. The formation of a hexagonal microcrystal, and the maxima of the deposition rate and microhardness were observed at 400 ℃ and the H_2 gas flow rate of 90 cm^3/min. The boron content in the films deposited increased with increasing total gas flow rate and R.F. power. The resistivity of $BC_{0.61}N_{0.70}$ film at room temperature was larger than that of BN or B_4C film similarly to the bulk ceramics.

Studies on Regulation of Microvoid existing in Glassy Polymer Frozen to Unequilibrium State

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Introduction

It is interesting to regulate microvoid by freezing free volume existing in polymer liquid above glass transition temperature (Tg). We developed the regulation of microvoid from the standpoint of gas transport properties for various glassy polymers.

Results and Discussion

The sorption and permeation of CO_2 in and through various quenched polycarbonate [PC] and polyimide [PI] films were investigated. Dual-mode sorption and partial immobilization models were used to analyze their phenomena. The amount of CO_2 sorption in PI and PC films quenched from a certain temperature above Tg increased when compared with that in as received PI and slowly cooled PC films. These changes in the amount of CO_2 sorption can be attributed to a change in the Langmuir sorption capacity term, C_H', owing to quenching from a temperature above Tg, since the other dual-mode sorption parameters, k_D and b, are almost independent of quenching. The two diffusion coefficients, D_D and D_H, for CO_2 also varied remarkably by quenching. The diffusion coefficients of quenched PI and PC films increased when compared with those of as received PI and slowly cooled PC films. The change in diffusion coefficient of the Langmuir mode, D_H, was found to be larger than that of Henry's law mode, D_D. The permselectivity obtained by quenching enhanced when compared with that obtained by raising a temperature in the case of comparison at same permeability coefficients.

PREPARATION OF INORGANIC NON-CRYSTALLINE SOLIDS CONTAINING MIXED ANIONS BY RAPID HEATING AND QUENCHING METHOD

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1. Introduction

Although fluoride glasses are known to have fluoride-ion conduction, the electrical conductivity is still somewhat low to put them to practical use. Recently, it was found that the introduction of both oxygen and fluoride ions in the glass network increased the electrical conductivity. In order to prepare such a kind of oxyfluoride glass having a higher electrical conductivity, the rapid heating and quenching method is tried to employ, since fluoride ions can remain at non-equilibrium state in the glass network without evaporation.

2. Results and Discussion

Thermal image furnace and twin-roller quenching were used to prepare the glass containing both oxygen and fluoride ions in (A)PbF_2-MnF_2-SiO_2, (B)PbF_2-ZnF_2-SiO_2 and (C)PbF_2-BiF_3-SiO_2 systems. The dc electrical conductivities of these glasses were measured as a function of temperature. XPS measurement was also carried out to determine the chemical state of each ion involved in glass. The introduction of both O^{2-} and F^- ions in (A) system markedly increased the electrical conductivity and decreased the activation energy for conduction. This mixed anion effect was explained in terms of the presence of two types of the chemical states for F^- ions such as bridging and non-bridging ions in oxyfluoride glass. However, other systems revealed no mixed anion effect leading to the low electrical conductivity.

Self-Organization of Polymer Alloys at Phase Transitions and Control of Patterns under Nonequilibrium State

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1. Introduction

Objectives of this series of studies are to explore mechanism and dynamics of pattern formation of polymer alloys (polymer mixtures and block and graft copolymers) at phase transitions. Fundamental studies along this line are hoped to give impacts for developments of new and industrially useful polymeric materials as well as for advances of nonequilibrium statistical physics in general, especially in polymers.

2. Results and Discussion

Number of outputs were obtained, as summarized in publication lists, on dynamics and mechanisms of self-organization of various polymer mixtures at phase transitions, as well as on the equilibrium aspects of order-disorder transition in block copolymers. Typical polymer mixtures studied are isotactic-polypropylene (i-PP)/ethylene-propylene random copolymer (EPR) (1, 4, 7), polybutadiene (PB)/styrene-butadiene random copolymer (SBR) (1-3, 6, 7), polystyrene (PS)/PB/dioctylphthalate (DOP) (6, 7, 11-13), poly(ethylene terephthalate) (PET)/thermotropic liquid-crystalline polymer (X-7G) (5, 15), polystyrene-polybutadiene (SB) and polystyrene-polyisoprene (SI) block copolymers and their blends with PS and/or PB (PI) (8-10, 14). Here the number in the parentheses denote the number in the publication list.

The studies in polymer mixtures involve investigations of the ordering processes in the later stage spinodal decomposition (SD), especially scaling analyses on the structure factor and wavenumber of the dominant mode of the fluctuations. The universality and unique features of polymer behaviors were explored in comparison with the behaviors found in small molecular systems. The studies in block polymers involve experimental and theoretical investigations of the order-disorder transition and formation of the microdomains of about 100A with a long range spatial order at thermal equilibrium. Thermodynamic stability limits of the mixtures containing block copolymers were theoretically analyzed, and the results elucidated coexistence of two types of liquid-liquid phase transitions, i.e., "macrophase" and "microphase" transitions. Those informations obtained here will be important as a key to control the patterns.

Formation of Non-Equilibrium Phases by High-Energy Electron Irradiation

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The general rules of solid amorphization was already established by the authors. In the present work, the following two items have been examined: 1)Correlation between the general rules and the phase diagrams of various alloys; 2)electron irradiation induced foreign atoms implantation from their compounds.

Various Al-base alloys such as Al-Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zr, Mo, W, Au alloys have been used for item 1). In their phase diagrams, Al-Zr and Al-Ni alloys are especially interested. Ten intermetallic compounds are formed side by side in Al-Zr alloys, and eight of them cause crystalline-amorphous transition. Furthermore, there are no deep eutectic point near any of these eight compounds in the phase diagram. In Al-Ni alloys, very fine particles of Al_3Ni_2 are newly formed when an intermetallic compound Al_3Ni is electron-irradiated, and an Al_3Ni crystal itself changes to an amorphous solid inside which the formers are involved. The facts mentioned above give new concepts on the solid amorphization of materials. In item 2), a new type of relaxation mechanism of the lattice distortion induced by implantation of oversize-foreign atoms has been verified.

Control of Electrical Properties of Zinc Oxide - Niobium Oxide Ceramics by Nonequilibrium Microstructual Treatment

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1. Introduction

Nonlinear current-voltage characteristic of zinc oxide ceramics is well-known to be based on properties of grain boundary of the ceramics and strongly influenced by their microstructures. To obtain fundamental information on relations between microstructure and electrical properties of the ceramics, which are the bases of microstructual control of their electrical properties, effects of silica addition on the electrical properties and microstructure of ceramics consisting of ZnO, Nb_2O_5, and MnO were examined.

2. Results and Discussion

Bodies of 98.0ZnO -1.0Nb_2O_5 -0.5MnO -0.5SiO_2 and 98.5ZnO -1.0Nb_2O_5 -0.5MnO(mol%) were prepared from the purest grade chemicals, and formed small specimens by isostatic compression of 1000Kgf/cm^2. The compacts were fired at 1305℃ for 0 to 2h. Electrical properties and microstructure of the fired specimens were examined.

Plots of the electrical current against applied voltage of the all specimens showed apparent nonlinear relation. Addition of the silica lowered temperature of eutecticmelt formation, promoted penetration of the melt among zinc oxide grain boundaries,and also suppressed growth of the zinc oxide grains, and consequently increased homogeneity of microstructure of the fired bodies. As a results of these effects, the addition of silica make increase the nonlinear V-I behaviour and regularity of these properties of the fired ceramics.

Characterization of the polymers obtained by the photopolymerization of unsaturated compounds

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1. Introduction

It is well known that on photoirradiation several conjugated diolefin crystals afford highly crystalline linear polymers. The polymerization behavior and the structure of resulting polymers are strictly controlled by the crystal strucutres of starting diolefinic monomers. The polymers having new functional behaviors can be designed, based on the crystal engineering of these monomers, followed by the topochemical photopolymerization.

2. Results and Discussion

Several new linear high polymers were successfully prepared by means of the photopolymerization of unsymmetric diolefin crystals. In addition to the expected photo-depolymerization behavior of these polymers in solution, all the polymers having a pyrazine moiety in their repeating structure, on the irradiation in the presence of oxygen, gave a considerable amount of nitrile derivatives, such as 2,4-diphenylcyclobutane-1,3-dicarbonitrile.

Alkyl α-cyano-4-[2-(2-pyridyl)ethenyl]cinnamate crystals gave the polymers having an alternating zigzag and linear main chain structures with the alternating opposite chiralities. This result is the first example of the topochemical photopolymerization affording the polymer configuration not of that predicted from the molecular arrangement in the starting crystal, and that the induction of a non-random, alternating arrangement of both enantiomers was confirmed to occur during the reaction of the prochiral molecules in the achiral crystal.

Design of Synthetic Reactions for Developing Organic Materials with Electrical Conducting Function

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1. Introduction

Our attention has so far been directed toward electrical conducting properties of charge-transfer (CT) complex and radical cation salts based on electron-donating [3]-, [4]-, and [5]-radialenes substituted with 1,3-dithiole and thioxanthene groups. For this second year in addition to this research another research on the preparation of molecular organic ferromagnets by using electron-donating odd-numbered [n] radialenes was started.

2. Results and Discussion

The electron-donating odd-numbered [n] radialenes have a pair of degenerate HOMOs of comparatively high energy, assuming that the molecular symmetry is C_n or higher. In consequence of several attempts such two radialenes, tris(thioxanthen-9-ylidene)cyclopropane (1) and pentakis(1,3-benzodithiol-2-ylidene)cyclopentane (2), were so far synthesized. Unfortunately, 1 did not form a CT complex with any of the usual acceptors. On the other hand, 2 formed CT complexes with comparatively strong acceptors such as DDQ. In contrast to the 1:1 ionic CT pair expected theoretically for the CT ferromagnets, the 1:2 CT complex of 2 with DDQ was obtained, and the magnetic properties were investigated. The temperature change of the paramagnetic susceptibility of the $2\cdot(DDQ)_2$ solid followed a Curie-Weiss law, and the Weiss constant was ca. -2K. In the EPR spectrum at 298K the half-field resonance signal also appeared. The temperature change of the signal intensity in the range of 298 to 4.5K, followed a Curie law, indicating involvement of a ground-state triplet in the solid. Both these results lead to the conclusion that 2^{2+} is a ground-state triplet which undergoes a weak antiferromagnetic interaction with $DDQ^{-\cdot}$ radical ions in the CT solid.

Molecular Design of Functional Polymer Materials by Living & Immortal Polymerizations with Metalloporphyrin

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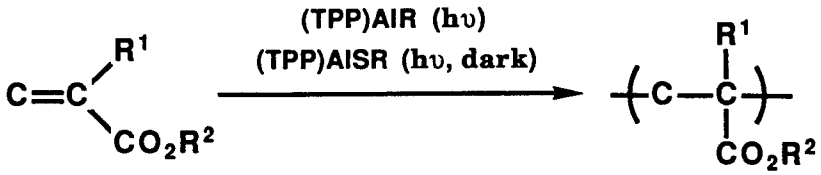
1. Introduction

The present research is to develop a novel method for molecular design of polymer materials of elaborate functions based on the *living* and *immortal* polymerizations with *metalloporphyrins* as initiators.

2. Results & Discussion

An alkylaluminum porphyrin (**(TPP)AlR**) such as methylaluminum porphyrin (**(TPP)AlMe**) has been found to bring about the living polymerization of alkyl methacrylates under visible light irradiation. On the contrary, aluminum porphyrin carrying alkylthio group (**(TPP)AlSR**) can initiate the living polymerization of alkyl methacrylates even in the dark.



Polymerization of alkyl acrylates also proceeds with living nature by using **(TPP)AlSR** as initiator. Furthermore, the sequential polymerizations of alkyl methacrylates and alkyl acrylates by aluminum porphyrin give the corresponding block copolymers of controlled molecular weight with narrow molecular weight distribution.

The addition polymerization of alkyl -methacrylates or -acrylates by aluminum porphyrin, followed by the ring-opening polymerization of heterocyclic monomers such as epoxides or lactones, gives novel polyvinyl - polyether or - polyester block copolymers of uniform, controlled block lengths.

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Design and Synthesis of New Polymer Materials by the Oxidation-Reduction Copolymerization

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1. Introduction

Novel copolymers having phosphorus, tin, or germanium atom in the main chain have been synthesized according to the concept of oxidation-reduction copolymerization.

2. Results and Discussion

Oxidation-Reduction Copolymerization Using Phosphorus (III) Compounds

New 1:1 alternating copolymers have been prepared by the reaction of vinylphosphonic acid mono-ester as new Mox monomers with three Mred monomers of five, six, and seven-membered cyclic phosphonites. The apparent copolymerization parameters were determined according to the Mayo-Lewis integral method. The difference of the reactivity of three cyclic phosphonites was also investigated.

Oxidation-Reduction Copolymerizations Using Stannylene

Various p-benzoquinone derivatives (Mox) have been copolymerized with bis [bis(trimethylsilyl)amido]tin (II) (Mred) to give the corresponding 1:1 alternating copolymers having p-hydroquinone unit and tin (IV) unit.

Oxidation-Reduction Copolymerizations Using Germylene

The oxidation-reduction copolymerizations between p-benzoquinone derivatives (Mox) and bis[bis(trimethylsilyl)amido]germanium (II) (Mred) took place under mild reaction conditions to afford 1:1 alternating copolymers of high molecular weight. The resulting copolymers are soluble in hexane, diethyl ether, and chloroform, and can be purified by reprecipitation from acetone.

Further investigations for the synthesis of new copolymers from silylene derivatives (Mred) and p-benzoquinone derivatives (Mox) are now in progress.

Production, Structural Analysis, Evaluation and Alloy Design of High Performance Intermetallic Compounds

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1. Introduction

Intermetallic compounds are regarded as being single phase materials of unique practical applicability. Recently, attempts to use as high temperature structural materials, electronic devices, magnetic materials and so forth have been made for the intermetallic compounds. However, the brittleness and no workability has prevented it from being used as engineering materials. The present study aims to develop the ductile intermetallic compounds with useful functional properties. Furthermore, the correlation between functionality, atomic (and electronic) structure and properties in these compounds was analyzed.

2. Results and Discussion

(1) Based on the ductilization model for the $L1_2$ ordered alloys proposed by the present authors, ductile $Ni_3(Si,Ti)$ compounds were newly found. Obtained mechanical properties were excellent. Also, using the single crystals of this alloy, test temperature, orientation, strain rate and compositional dependences on the flow stress, and the operative slip system were investigated.

(2) Plastic flow properties of the B2-type CoTi compounds were investigated in terms of test temperature, strain rate, orientation and composition. Positive temperature dependence of the strength was observed and also deformation was proceeded by the (110) slip.

(3) Simultaneous addition of the boron and the substitutional elements of Fe and W was done in order to improve the mechanical properties of Co_3Ti compounds. Also, the creep deformation and creep rupture were investigated to understand the deformation at elevated temperatures.

(4) To develop new types of high temperature structural compound with low density, the phase diagram, crystals structure and mechanical properties of the pseudo-binary alloy system between Zr_3Al and Ti_3Al were investigated. Among these alloy systems, $L1_2$-type $(Zr,Ti)_3Al$ alloys showed strong positive temperature dependence without the loss of the ductility.

(5) Environmental effect attributed to hydrogen atoms was investigated in polycrystals and single crystals of Co_3Ti alloys and their ternary alloys. Atomistic observation by transmission electron microscope was done for the samples deformed in H_2 gas, air and vacuum, respectively, and the mechanism associated with this phenomenon was proposed.

Synthesis and Characterization of Organic Superconductor Donors Containing Germanium

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Introduction

Donors for organic superconductors generally contain C=C bond as the central pi-electron donor moiety as a result of simple derivation or modification of tetrathiafulvalene (TTF). We propose incorporation of Ge=Ge bond into TTF like skeleton. In the first year of the project, research was devoted mainly to the design and synthesis of the chalcogen units to be incorporated into the TTF-like skeleton. Since Ge=Ge are not usually very stable, we first synthesized and characterized 2,2'-diselenocyanato-1,1'-binaphthyl (1) (Compound numbers refer to those described in the preceding abstract) by X-ray structure analysis.

Results and Discussion

In the present fiscal year, synthesis of a few other chalcogen units such as 2 and 4 and application of these chalcogen units (including 1) were performed to prepare the target compounds together with a brief study of electronic properties of 1. The most promising results were obtained when 2 was allowed to react with diiodogermylene: a yellow crystalline material was obtained. The structure of this compound was suspected to be 4 based on the spectral data (NMR, MS) and elemental analysis. Although the structure of 4 is not a desired one, the compound may present an interesting class of conducting material. The two pairs of sulfur atoms in two dithiane units are perpendicular with each other thereby allowing multi-dimensional column structure in the crystal lattice. Crystallization and X-ray analysis of this compound and synthesis of analogues of 4 are the tasks in the following year.

Synthesis of Microporous Membrane from Microphase Separated Block Copolymer Having Functional Domain

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1. Introduction

A new attempt here investigated to make microporous membranes from the film of a block copolymer with well-defined chain structure which is prepared by anionic living polymerization. This method involves casting a block copolymer film with microphase separated lamellar structure, fixation of one microdomain by cross-linking between the polymer chains, oxidative decomposition of the other microdomain and leaching out the degraded low molecular weight compounds from the inside of micropores formed by oxidation.

2. Results and Discussion

Four block copolymers of isoprene and (4-vinylphenyl)dimethyl-2-propoxysilane with different block lengths were prepared by anionic living polymerization technique. The TEM observation of thin films of the obtained block copolymers reveals that the domain sizes of the lamellar structure correspond to the block lengths. After etching the polyisoprene domain by treating with ozone, the surface and cross section of the obtained porous membranes were observed by SEM. It was found that the shape and size of the micropores were almost the same as those of microdomains of the original polymers. The pore size was controlled from 20 to 30 nm by the polyisoprene block length($\overline{DP}$) from 340 to 550. Furthermore, the surface areas of the membranes were measured by BET method. Very large surface areas, 70 - 90 m^2/g, were obtained, which suggested that the micropores were open and continued through the membrane from one side to the other. The permeability of nitrogen gas was also measured, 0.2 - 12 x 10^6 $cm^2/sec \cdot cmHg$, corresponding to the pore size of the membrane.

From the IR measurement, elemental analysis, BET measurement, and SEM observation, the obtained membranes were characterized, the microstructures of which were found to be controlled by the primary structures of the block copolymers.

Synthesis and Polymerization of Novel Spirocyclic Monomers and Evaluation of Their Functions

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1. Introduction

Shaping function is one of the important functions required for precision molding such as elastomeric sealants, precision coatings, adhesives, etc. However, common monomers generally polymerize with large shrinkage in volume, and thereby it is a big problem in the field of material science. The authors have been studied so far on the synthesis of materials that show no shrinkage on polymerization or curing. In this project, synthesis and function of spirocyclic monomers which expand on polymerization, as the most promising candidates for the above-mentioned materials, have been investigated.

2. Results and Discussion

New Spirocyclic Monomers and Cationic Polymerization

Behavior of cationic polymerization and volume change on it were examined for spiroorthocarbonates (SOC1) containing nitro group which are easily derived from the corresponding 1,3-diols with nitro group. About 10% expansion in volume was observed on polymerization which afforded polyether-carbonate.

Seven-membered SOCs were synthesized and benzo type SOC (SOC2) offered the first example of monomer undergoing cationic polymerization without any elimination of tetrahydrofuran derivative to yield polyether-carbonate which has been obtained only with six-membered SOCs so far.

Tetrathioorthocarbonate (STOC), sulfur analogue of SOC, was synthesized and polymerized to afford ring-opening product consisting of three different segment structures, only when seven-membered STOC was used. Benzo derivative of the seven-membered STOC also polymerized and behaved similarly to the corresponding SOC to give polythioether-trithiocarbonate in high efficiency.

Control of Volume Change on Polymerization of Epoxides

In order to control volume shrinkage on polymerization of epoxides by addition of SOC, degree of volume change on cationic polymerization of the mixture of phenyl glycidyl ether (PGE) or bisphenol A diglycidyl ether (BGE) and SOC was studied and is found to be proportional to composition or feed ratio of SOC to the epoxides.

Development of Efficient Photochromic Materials Using Electrocyclic Reaction

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1. Introduction

Fulgide is considered to be the most promising candidate to be applied to the erasable-and-rewritable photomemory. Since we have succeeded to enlarge the quantum yield of the coloration of (E)-2-(1-(2,5-dimethyl-3-furyl)ethylidene)-3-isopropylidenesuccinic anhydride by modifying its substituent, we next tried to solve three other important problems: (1)enlarge the quantum yield of decoloration; (2)lengthen the maximum absorption wave length of the colored form; (3)clarify the effect of the reaction media.

2. Results and Discussion

On the hypothesis that the steric bulkiness of the alkylidene group may cause the decoloration reaction fast, we synthesized furyl fulgides with 7-norbornylidene group and with adamantylidene group. A fulgide of the latter with isopropyl group on the furylalkylidene moiety showed the properties as we had hoped: It recorded 0.42 and 0.24 for coloration and decoloration quantum yields, respectively.

In order to lengthen the absorption maximum of the colored form, we synthesized a simple indolylfulgide. Unfortunately, it has the absorption maximum at only 585nm. This observation indicated that the ability of electron donation of the indolyl group was not sufficient. Introduction of a methoxyl group to the 6 position of the indole lengthened the absorption maximum to 622nm, and this compound has the molar absorptivity at 780nm, the wave length of the diode laser.

We examined the photoreaction of a furyl fulgide in various solvents and polymer films in order to clarify the effect of the reaction media. Both in solvents and films, the decoloration quantum yield decreased with the increase of the dielectric constant of the reaction media. In polymer films, the quantum yields of coloration and olefinic isomerization were smaller than that in solvents, whereas that of decoloration was larger.

Preparation of New Functional Materials from Layered Compounds by Redox Reaction

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1. Introduction

By topochemical reactions using layered compounds, it is possible to prepare new compounds which can not be obtained by usual calcination method. Then, the charge density of layer is necessary to be controlled to fit the size of ions and desirable interionic distances in the interlayer spaces. Charge densities on the layer indicated by areas per an univalent cation in the interlayer spaces are 25Å^2 for $Sn_xH_yWOP_2O_7 \cdot nH_2O$ ($2x+y=0.7$) and 11Å^2 for $HTaWO_6 \cdot nH_2O$. Their intercalation of n-alkylamines and n-alkyldiamines and ion exchange properties will be reported here.

2. Results and Discussion

Small alkaline ions ($Li^+$and Na^+)showed high degrees of ion exchange >90% for protons in $HTaWO_6 \cdot nH_2O$, while the degrees for large alkaline ions were <30%. Replacement of adjacent layers is caused to reduce interionic repulsion and accommodate the large ions.

Intercalation of organic molecules showed clearly the effect of charge density on the arrangement of alkyl chains in the interlayer spaces. Basal spacings of the intercalation compounds from $Sn_xH_yWOP_2O_7 \cdot nH_2O$ depended on the number of carbon atoms linearly and the odd-even alternative relation for the ordered paraffin type structure was observed. On the other hand, the intercalation compounds of $HTaWO_6 \cdot nH_2O$ are divided into three groups by dependence of their basal spacings on length of amines and diamines. The dependence denotes that existences of gauche or (and) kink blocks must be taken into accounts.

Preparation of Piezoelectric $LiNbO_3$ Film by Controlled Wet-Epitaxy Reaction of Organometallic Compounds

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1. Introduction

$LiNbO_3$ is one of the most attractive materials for the application to electro-optic devices and surface acoustic devices. Single crystals of $LiNbO_3$, which are grown from melts of lithium-defficient harmonic composition, have been used for the devices. The crystal with homogeneous and well-controlled composition has been required, since the physical properties of $LiNbO_3$ vary remarkably with Li_2O content. A dip-coating method using metal alkoxide solutions is a promising chemical processing of preparing thin films of electric ceramic materials. This work was carried out to study about the processing of the stoichiometric $LiNbO_3$ thin films with preferred orientation from metal alkoxides solution.

2. Results and Discussion

Homogeneous, crystalline $LiNbO_3$ films with the stoichiometric composition could be prepared on substrates from a double alkoxide solution. Thickness of the film changed linearly with the concentration of the solution. The relationship between the thickness(t) and the speed of withdrawing substrates(U) agreed to $t \propto U^{1/2}$. The crystal system and the orientation of the substrates affected the crystallinity of the films on them. $LiNbO_3$ films crystallized on Si(100) and Si(111) substrates showed the same crystallinity as $LiNbO_3$ powders prepared from the alkoxide solution, while films crystallized on sapphire substrates showed preferred orientation such as (012), (110) and (001). Refractive indices of films crystallized at 400°C on Si substrates were about 2.0. Films crystallized at the same temperature on sapphire were higher than 2.3 due to the crystallinity of the films. The index of the film on sapphire (001) was the highest, since the films compressed by the substrates along the a axis.

Synthesis of fluorine doped silica by sol-gel process and its characterization

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1. Introduction

In connection with fabrication of light guide fiber, a fluorine doped silica glass has been noted as a cladding material. In this study some properties of F-doped silica gels were investigated inconnection with heat trearment of changing to vitreous state. The sol-gel process by using partially fluorinated silicon alcoxides was also investigated.

2. Results and Discussion

2-1. Some physical properties of F-doped silica gels:The measurements of density by means of a pycnometer and of specific surface area by the BET method and the observation of micro structure by a scanning electron microscope were carried out to clarify the feature of the gels made by hydrolysis of SiF_4. The results revealed that the gels were in state of agglomeration of thin films having many "closed pore" which gave extremely low density. The bahavior of defluorination reaction and sintering of the gels in the course of heat treatment were explainable by taking into account these features.

2-2. Hydrothermal treatment of the gels: In order to make F-doped silica glass the hydrothermal treatment of the gels were testified. Samples in Au capsules were heated 2h at 500℃ or 700℃ under the pressure of 50, 200 and 1000 atm, respectivelly. All of sample treated under the pressure more than 200 atm showed vitreous structure. In the case of 50 atm treatment, however, small quartz or cristobalite crystals with no fluorine were found in a F-containing vitreous matrix. This fact suggests that the equilibrium release pressure of SiF_4 for the F-doped gels at 500℃ was in the range of 50-200 atm and the existence of fluorine in a silica glass inhibited the transition to the crystals from the vitreous state.

2-3. F-doped silica from silicone alcoxides: In contrast with hydrolysis of SiF_4 the sol-gel process of silicone alcoxides with H_2SiF_6 solution or of partially fluorinated silicone alcoxides is considered to be feasible to control the developement of silica network in the course of the reaction. With partially fluorinated silicon tetraetoxide F-doped silica glass fiber having relative reflective index $\Delta n = -0.3$ was fabricated. However, more detailed study is needed to understand the reaction mechanism and to apply to fabrication of F-doped silica glass.

Molecular Design of Functionalized Photochromic Materials with High Efficiency by Modification of Spiropyrans

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1.Introduction Pyran derivatives, e.g., spiropyrans, undergo ring-cleavage upon UV-irradiation to give the corresponding dienone derivatives, which are usually colored and reproduce the starting compounds either upon visible-light irradiation and/or by heating. The reactions are potentially attractive for designing photochromic materials.

2.Results amd Discussion The photochromic properties of spiro [indoline-2,2'-2'H-1'-benzopyrans](SP) were found to be greatly changed in going from a homogeneous to a micellar system. Thus, 3-methyl derivative of SP showed very weak color upon irradiation in most organic solvents and the colored species faded very rapidly in the dark. In a marked contrast, it showed very intense color of the corresponding merocyanine (MC) upon irradiation in cetyltrimethylammonium bromide (CTAB)-H_2O micelles and, moreover, the thermal stability of MC was dramatically increased. The water-soluble SP also showed an interesting behavior in a reversed micelle. Thus, 6-sulfonate derivative of SP showed intense yellow color of MC in the dark, but MC faded upon irradiation to produce SP, which again reproduced MC color in the dark. The thermal coloration rate was greatly reduced in CTAB-H_2O-$CHCl_3$ reversed micelle. These results are interpreted as indicating that not only the microscopic polarity but also the viscosity of the micelle plays an important role in determining the rate of the molecular motion accompanying the photochromism.

Naphthopyrans also showed the photochromism. Naphthopyrans having two pyran rings were prepared systematically from the corresponding dihydroxynaphthalenes and their photochromic properties were investigated. Absorption maximum as well as stability of the colored species were interestingly changed depending on the substitution patterns.

Synthesis of Novel Functional Polymers Derived from 2-Oxazolines.

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Introduction

During the course of our studies on the ring-opening polymerization of 2-methyl-2-oxazoline, we have found that the resulting poly(N-acetylethylenimine) (PAEI) has high hydrophilicity and well compatibility with organic commodity polymers. Recently, we reported the preparation of novel non-ionic hydrogel based on PAEI by two methods; (i) cross-linking reaction of partially hydrolyzed PAEI (PAEI-PEI random copolymer)[1] and (ii) copolymerization between 2-methyl-2-oxazoline and bis-oxazoline.[2]

Results and Discussion

(1) Synthesis of Polyoxazoline Hydrogel by Photo-Dimerization

Partially hydrolyzed PAEI was treated with acid chloride of (7-coumaryloxy)acetic acid in the presence of triethylamine. This coumaryl-PAEI was cast upon a slide glass and irradiated for 3 h (450W High-Pressure Hg Lump) to form a gel, which showed a quite high swelling property in water as a hydrogel. From the results of UV spectroscopy, the gelation was caused by photo-dimerization of coumarin moieties in PAEI. The swelling degree of the obtained gel can be controlled by the coumarin content or by the irradiation time.

(2) Synthesis of Polyoxazoline Hydrogel by Diels-Alder Reaction

Furan or maleimide group was introduced to PAEI as a diene and a dienophile moiety, respectively. Intermolecular Diels-Alder reaction between these two groups caused the gelation at r.t. The obtained gel absorbed water to form a non-ionic hydrogel.

(3) Polyoxazoline Hydrogel Having S-S Bonds

The gel having S-S bonds at the cross-linking points was prepared. The S-S bonds were cleaved reductively to form -SH groups. This means that the gel was transformed to the soluble polymer after the reductive treatment. This reversible conversion by redox system has a potential to new functional materials.

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Design and Synthesis of Substituted Polyacetylenes as New Functionality Materials

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1. Introduction

Since substituted polyacetylenes $[-\{CR=CR'\}_{\overline{n}}]$ possess unique structure and properties, they are expected to exert new functions and high performances. Hence, their design, synthesis and appliciation are urgent problems. In 1988 we studied the following subjects: i) Synthesis of substituted polyacetylenes with controlled MWD; ii) Pervaporation of liquid mixtures through substituted polyacetylenes.

2. Results and Discussion

i) Synthesis of Substituted Polyacetylenes with Controlled MWD.[1)]

Using 1-(trimethylsilyl)-1-propyne (TMSP) as monomer, the synthesis of a polymer having narrow molecular weight distribution (MWD) was investigated. The polymerization by $NbCl_5$ in cyclohexane solution proved to produce a polymer with narrow MWD. In this polymerization, the number-average molecular weight ($\bar{M}_n$) of the polymer increased in direct proportion to conversion, while the MWD remained narrow ($\bar{M}_w/\bar{M}_n \sim 1.2$) irrespective of conversion. Poly(TMSP)s having narrow MWD and $\bar{M}_n$ in the range 1×10^4 - 20×10^4 could be obtained by changing the monomer-to-catalyst ratio. Thus, the present polymerization involves a long-lived propagating species, and provides a useful method for synthesizing poly(TMSP) with a narrow MWD.

ii) Pervaporation of Liquid Mixtures through Substituted Polyacetylenes.[2)]

Pervaporation was examined as an application of substituted polyacetylenes to membrane separation. In the $EtOH/H_2O$ pervaporation through poly(TMSP) membrane, the separation factor, $\alpha(EtOH/H_2O)$ reached 17 at 10% ethanol in the feed. This is similar to that for poly(dimethylsiloxane), a well-known ethanol-permselective membrane. In general, aliphatic polyacetylenes showed ethanol permselectivity, while aromatic polyacetylenes were rather water-permselective. In the pervaporation of $MeCN/H_2O$ and acetone/H_2O mixtures through poly(TMSP), the α(org. liq./H_2O) values were as high as ca. 100.

3. References

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2) T. Masuda, M. Takatsuka, B.-Z. Tang, and T. Higashimura, J. Membrane Sci., submitted.

Plasticity and Hot-Forming of Ceramics

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1. Introduction

In order to examine the possibility of the hot-forming of ceramics by utilizing their plastic property and to elucidate the mechanism of the process, a hot-extrusion processing was applied to polycrystalline Ba-ferrite ($BaO\ 6Fe_2O_3$). The effects of the stem speed and area contraction ratio on the microstructure and mechanical properties of extruded Ba-ferrite were studied.

1. Results and Discussion

Sintered Ba-ferrite samples were capsulated into stainless steel (SUS 304) to prevent the fracture of the ceramic, and heated from 1100°C to 1390°C. The heated capsule was immediately transferred into the container and then extruded at a stem speed of 3.5mm/sec to 17.5mm/sec with varying area contraction ratios from 48% to 84%. The extruded Ba-ferrite ceramic was found to exhibit finer and denser microstructure than the non-extruded. These effects were accelerated with larger deformations and lower stem speeds. The Vickers hardness (H_V) and fracture toughness (K_C) of the extruded Ba-ferrite were remarkably increased and their values were comparable to those observed for hot-pressed body. As for K_C, anisotropy was observed: K_C perpendicular to the extruding direction was higher than that of the parallel direction. In the case of extrusion of the billet at large contraction ratios, smooth extrusion of the ceramic could not be realized due to the difference in deformation resistance between the capusule and Ba-ferrite.

Molecular Design of Polycationic Functional Elastomers

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1. Introduction

As ionic thermoplastic elastomers have high polar groups and reactive species, they are interested in functional polymeric precursors for obtaining conducting, non-thrombogenic, hydrophilic and other functional elastomeric materials. Although polybutadiene ionene seems to be particularly interesting, as they may be useful as a novel elastomer carring cationic charges, the poor mechanical properties (i.e., 1.73 MPa in tensile strength at break (T_B)), which have been reported on polybutadiene ionene (1970), seems to arrest the development of elastomeric ionenes.

Thus, we have reported that the polybutadiene ionene (PBI) prepared by the reaction of isocyanate-terminated liquid polybutadiene (IT-PB), 2-dimethylaminoethanol (DMAE) and 1,4-dibromobutane attains 19.2 MPa in T_B (1981). To obtain more high performance polycationic elastomers, we tried to synthesize two sorts of novel ionic polymers and clarified their mechanical properties.

2. Results and Discussion

(a) Polyester-blocked polybutadiene urethane ionene (PCLI) : Dimethylamino-terminated polyester (AT-PCL) and polybutadiene (AT-PB) were obtained by the reactions of isocyanate-terminated polyester (IT-PCL) and polybutadiene (IT-PB) with DMAE respectively. The mixtures of AT-PCL and AT-PB were allowed to react with α, α'-dichloro-p-xylene (DCX) to give PCLIs having different molar ratios of AT-PB to AT-PCL. Best tensile strength at break (T_B) of the cast film has attained 38.5 MPa, and the modulus at 100 % elongation (M_{100}) and the elongation at break (E_B) reached 35.2 MPa and 148 %, respectively, at r = 25/75.

(b) Polymeric ionene of poly(butadiene-co-acrylonitrile) (NBPI): Dimethylamino-terminated oligo(butadiene-co-acrylonitrile) (AT-PB) obtained from the reaction of DMAE and carboxy-terminated liquid nitrile rubber, was allowed to react with 4, 4'-dipyridine to produce NBPI. The NBPI cast film thus obtained was found to attain 45 MPa in T_B, 4.2 MPa in M_{100} and 410 % in E_B.

From these results various capabilities of controlling physical properties will be one of the possibilities of developing high performance as well as high functional characteristics on elastomers.

Synthesis of Conducting Organic Materials and Their Physical Properties

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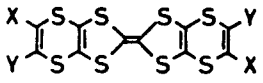
1. Introduction

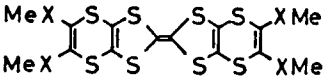
Conducting organic materials have attracted much attention. Synthesis of new materials has played a crucial role in the development of this field. We have studied syntheses of both low-molecular conducting organic materials and conducting polymers, and the correlation between their structures and electrical properties.

2. Results and Discussion

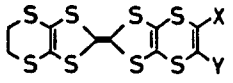
Several new TTF derivatives possessing eight or twelve chalcogen atoms (VT, DMVT, TMVT, TMSVT, EVT) were synthesized. Crystal structures of TMTVT and EVT were also studied. Most of the complexes formed by electrocrystallization of these materials showed metallic behavior in electrical conduction. Among them, VT_2PF_6 was found to retain the metallic behavior down to 0.5 K under a pressure of 14 kbar.



VT : X=Y=H
DMVT : X=H,Y=Me
TMVT : X=Y=Me

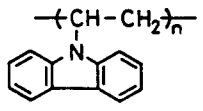


TMTVT : X = S
TMSVT : X = Se

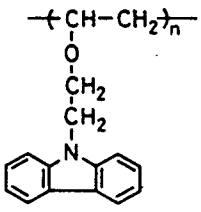


EVT : X=Y=H
EMVT : X=H,Y=Me

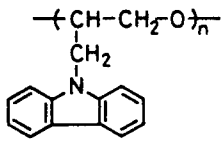
Insulating polymers containing the carbazolyl moiety were transformed into semiconducting polymers with room-temperature conductivities from 10^{-7} to 10^{-4} S cm^{-1} by electrochemical doping. They are radical-cation salts and their structures are partially cross-linked at the 3-position of the carbazole ring. The correlation between the structures of the starting polymers and electrical conductivities of doped polymers were studied. An electrically conducting polymer containing a pendant coronene moiety was also prepared by the electrolytic polymerization of vinylcoronene.



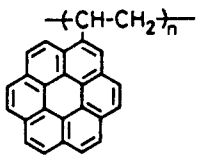
PVCz



PCEVE



PGCz



PVCo

Molecular Design, Synthesis and Characterization of Organometallic Liquid Crystals

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1. Introduction

One of the current interests in material science lies in the research of liquid crystals which comprise a number of intermediary states of matter that occur between the isotropic liquid and the organized solid state. The majority of liquid crystalline materials consist of C, O, N, and H atoms. Though a few examples containing metal atoms are known, they are of special interest in terms of the unique properties based on metal atoms. Previously we reported transition metal-poly(yne) polymers as the first examples of lyotropic liquid crystalline materials containing organotransition metal species, and also reported new thermotropic liquid crystalline materials incorporating boron atoms(II).

2. Results and Discussion

2-1 Organometallic Polymers: Lyotropic Liquid Crystalline Materials

Now we have synthesized a variety of cationic polymers(III), $\{Pd^{+}(PR_3)_2\text{-}NC_5H_4\text{-}Z\text{-}C_5H_4N\text{-}Pd^{+}(PR_3)_2\text{-}Y\}_n \cdot 2nPF_6^{-}$, where Y= -C≡C-, -C≡C-C≡C-, -C≡C-C_6H_4-C≡C- etc.; Z= -CH_2CH_2-, -CH=CH-, -C≡C-. They may be prepared by the reaction of bimetallic acetylides with bidentate nitrogen donor ligands. They were characterized by spectral methods such as IR and ^{31}P-NMR spectroscopies. The cationic poly-nuclear complexes are soluble in common organic solvents such as tetrahydrofuran and chloroform in spite of containing transition metals. Some of them form nematic liquid crystals in concentrated dichloromethane solutions which exhibit responce toword a magnetic field. They provide the first lyotropic liquid crystalline materials containing ionic organotransisition metal species.

2-2 1,3-Dioxaborinane Derivatives: Thermotropic Liquid Crystalline Materials

We previously showed the dioxaborinane derivatives, $RC_6H_4\text{-}BO_2C_3H_5\text{-}C_6H_4R'$ (II), form thermotropic liquid crystals. Now we have prepared a new series of the type, R-O-C_6H_4-$BO_2C_3H_5$-R' (IV), having a chiral alkyl group R, where R= $C_2H_5(CH_3)CH(CH_2)_n$ and R'= C_nH_{2n+1}, and found that some of them form a chiral smectic C phase. It shoud be noted that the two-ring system (IV) among dioxaborinane derivatives shows enantiotropic phase transition to S_C^*.

Synthesis of New Organosilicon Polymers and Their Functionalities

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Introduction

As a part of an investigation concerning the design of new organosilicon materials we have synthesized silicon polymers in which the alternate arrangement of a disilanylene unit and a π-electron system such as an ethylene or butenyne group is found regulary in the polymer backbone. We also carried out doping experiments using the film of these polymers and antimony pentafluoride as a dopant, in the hope of obtaining a new class of silicon polymers with high conductivity.

Results and Discussion

trans-Poly[(1,2-dimethyldiphenyldisilanylene)ethylene] (1) was prepared by the condensation of trans-1,2-bis(chloromethylphenylsilyl)-ethene with sodium dispersion by irradiating with ultrasound at room temperature. The polymer 1 thus obtained melts at 64-71°C without decomposition. The molecular weight of 1 was determined to be $\bar{M}w$=40,000 by GPC. Poly[(1,2-dimethyldiphenyldisilanylene)butenyne] (2) whose molecular weight was determined to be $\bar{M}w$=17,000 was synthesized by the reaction of 1,2-diethynyl-1,2-dimethyldiphenyldisilane with a catalytic amount of $RhCl(PPh_3)_3$ at room temperature.

Polymers 1 and 2 can be cast into films. Characteristic of these polymers is strong absorption in the ultraviolet region. The polymer 1 exhibits absorption at 237 nm and 2 at 294 nm. As expected, these polymers are photoactive. Irradiation of the polymers at frequencies of 254 nm leads to cleavage of silicon-silicon bonds in the polymer chain.

We have succeeded in making conducting films of polymers 1 and 2 upon contact with a strong electron acceptor. Thus, the reaction of the new polymers 1 and 2 in the form of film with antimony pentafluoride as a dopant produced colored materials with a conductivity of 0.47 S/cm for 1, and 0.23 S/cm for 2 at room temperature.

Material designs of organic-inorganic composite films and their perfomances

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1. Introduction

Recently, various thin films formed by dry processes have been interested in the region of material science. Metal-containing organic thin films have been intensively studied for the properties such as conductivity, catalytic activity or modification of electrodes.

2. Results and Discussion

The thin film of metallocene, such as dichlorobis(cyclopentadienyl)titanium (Cp_2TiCl_2), was prepared by the radiofrequency ion plating (RFIP) with 13.56 MHz discharge. The thin film formed by ion plating had some of crosslinking structure, but the crystal structure of Cp_2TiCl_2 monomer remained in the thin film. Cp_2TiCl_2 thin films showed approximately similar IR spectra to that of Cp_2TiCl_2 monomer, but each peak was broadened with the increase of rf power. From the analysis of XPS spectra of Cp_2TiCl_2 thin film, Ti/C ratio in the thin film formed by ion plating was similar to that of Cp_2TiCl_2 monomer, but the peak of Cl atom decreased with the increase of the rf power. It was found that the electrical resistivity of Cp_2TiCl_2 thin film formed by ion plating varied uniformly according to the humidity with the high sensitivity.

Fabrication Process and Functional Design of Molecularly-Organized Aggregates

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1. Introduction

To improve functional properties of ultra-thin films, such as monolayer and LB films, it is important to investigate the molecular aggregation mechanisms of organic thin films.

2. Results and Discussion

(1) The characteristic areal modulus ($LogK_{S(max)}$) - temperature behaviors for monolayers of fatty acids in both the crystalline and amorphous states, were investigated in addition to morphological and structural studies. The temperature dependence of $logK_{S(max)}$ is strongly related to the phase transitions of monolayers or thermal molecular motion of amphiphilic molecules. It becomes apparent that the melting temperature of monolayer on the water surface is much lower than that of bulk material.

(2) The morphological observation and electron diffraction study indicate that formation of crystalline or amorphous monolayer of fatty acid is strongly dependent on the melting temperature of monolayer and the temperature of water subphase.

(3) An elctron diffraction of crystallized monolayer prepared by cooling an amorphous monolayer showed the sharper hexagonal spot than that of the crystalline monolayer in which two-dimensional small crystallites were aggregated by compression process at 283K. Further, the dark field image of the crystallized monolayer was almost homogenious. These results indicate that the crystallized monolayer from an amorphous state by cooling has larger crystalline size and lower amount of crystalline defects than the aggregated crystalline monolayer.

(4) The LB films with high regularity normal to the layer plane could be actually obtained under the following conditions; 1)by using amphiphiles of which intermolecular aggregation force is larger 2)at the surface pressure at which an apparently homogeneous monolayer is observed 3)by a slower compression speed 4)by a faster transfer speed onto a substrate and also, 5)by transfering monolayer up to the number of monolayer that roughness of the substrate surface does not affect the surface state of the monolayer.

(5) The crystalline disorder, g along parallel to the layer plane (lateral direction) in the LB films were evaluated on the basis of a single line technique of X-ray measurement. The magnitude of g increased with increasing the surface pressure. This may be due to local collapse of the monolayer on the water surface owing to an excessive compression.

Synthesis and Design of Rigid Vinyl Polymers with Molecular Orientation

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To synthesize and characterize new rigid vinyl polymers, the radical polymerizations of dialkyl fumarates (1), dialkyl maleates (2), N-substituted maleimides (3), vinylene carbonate (4) and dialkyl itaconates (5) were investigated. These monomers were found to homopolymerize in the presence of a radical initiator to give polymers consisting of a rigid structure. The highest polymerization reactivities were observed for maleimides, and the resulting polymers showed the highest thermal stability (>350°C). It was also found that dialkyl itaconates underwent radical homopolymerization easily, and the polymers with molecular weight of 2-10 x 10^4, were obtained although their rigidities were somewhat lower than those of the respective fumarates.

Design of Functionality of Membranes with Supramolecular Structures

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For the objective of construction of a reaction-transport coupling system, some fundamental researches were carried out on the albumin-facilitated transport of long-chain fatty acids across an aqueous membrane. In order to simulate albumin systems with some artificial membrane system, the transport of fatty acids with amphiphilic substance has been experimentally studied and the transport functionality of molecular associates with supramolecular structure as a carrier is elucidated.

The transport behavior of some fatty acids across an aqueous membrane containing hexadecyltrimethylammonium bromide (HTAB) is summarized in Table 1. The transport rate decreases with an increase in carbon number of fatty acid.

Table 1. Transport rate of fatty acids

Fatty acid	Rate(mol s cm^{-2})x10^{11}	Conc.in aq.phase(mmol l^{-1})
Capric acid	3.1	-
Lauric acid	1.3	0.54
Myristic acid	0.4	0.39
Palmitic acid	0.2	0.04
Stearic acid	0.0	0.01

27°C, HTAB 10 mmol

The transport rate increases abruptly at the concentration of HTAB of cmc, and this result demonstrates clearly that fatty acids transport in solubilized states in micelles of HTAB. The transport rate grows up in the cmc region and reaches a saturated value with a further increase, although the concentration of fatty acids in the aqueous phase increases monotonously above cmc. The transport system is analysed kinetically and the rate constants of up-take from heptane phase to aqueous phase and of release from aqueous phase to heptane phase were estimated. With an increase of concentration of HTAB, the up-take rate decreases and the release rate increase, and the rate-determining step changes from the up-take step to the release step. This transport mechanism provides a reasonable basis for interpretation of the present experimental results.

Layer Formation and Functionality Control in Carbon Materials in relation to Molecular Orientation in Polymer Precursors

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1. Introduction

Functionality of carbon materials, which are widely used in various industries, strongly depends upon the preferred orientation of anisotropic hexagonal carbon layers. The purposes of the present series of work are; 1) to relate the orientation of carbon layers in carbons to the molecular orinetation of polymer precursors, and 2) to extend the functionality of graphite by intercalation.

In this year, behaviours of carbonization and graphitization of a polyimide "Upilex" are studied and compared with those of "Kapton".

2. Results and Discussion

Two step carbonization was found on the polyimide film Upilex, as observed on another polyimide Kapton; large weightloss up to about 22 % and linear shrinkage to 20 % at a narrow temperature range from 500 to 650°C, and small additional weightloss and shrinkage in a wide range of 700 - 1000°C. Yield of carbonization agreed roughly with the one calculated by assuming release of impurity atoms as simple species of CO, O_2 and N_2.

Remarkable difference in graphitization was found between two Upilex films with 25 and 50 μm thickness. The former showed layered structure under SEM, high magnetoresistance value as 74 %, and sharp 002 peak at d-spacing of 0.336 nm after heat treatment at 3000°C. However, the latter showed only low magnetoresistance as 4 % and very broad 002 peak.

The degree of graphitization of carbon film from Upilex was much lower than that from Kapton which gave high magnetoresistance as 500 % and sharp 002 peak at exactly the same d-spacing of 0.3354 nm as graphite. These experimental results suggest the following conditions for getting carbon films with high graphitizability; 1) flatness of original organic molecules, 2) high degree of their orientation, 3) simple release of impurity atoms during carbonization.

Synthesis and Design of Functionality of Organic Molecular Assemblies

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1. Introduction: Preparations, crystal structures and physical properties of single-component organic conductors, organic metals and superconductors of charge-transfer type including LB films have been investigated. A series of tetrakis(alkylchalcogeno) tetrathiafulvalenes TYCn-TTF(Y=sulfur, selenium, tellurium) was synthesized and their crystal structures and physical properties such as the electrical conductivities, thermal properties were investigated to elucidate the crucial role of the chalcogene atoms in the molecular stacking and packing in the crystals and their functionality. A variety of physical measurements has been done on the organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ to understand the superconductivity of this compound. Since there are not enough space, some results on this compound will be described as follows.

2. Results and Discussion: Distorted-hexagon-shaped crystals of the Cu(NCS)$_2$ salt were prepared by the electrochemical oxidation of BEDT-TTF. The crystal structure analyses indicate that both dextro- and levorotatory optical isomers are present and the absolute crystal structures of both isomers were determined. The specific rotatory power is about 230° at 25°C and 632.8nm. Tc of the BEDT-TTF-h_8 salt is 10.2-10.4K by four-probe dc resistivity measurements. An inverse isotope effect was observed in our samples so far measured (more than seven each samples). By four-probe method Tc of the deuterated samples was observed at 10.8-11.0K. The inverse isotope effect was confirmed by the RF penetration depth measurements. The estimated anisotropy in the GL coherence length from the critical field near Tc is $\xi bc(0)$: $\xi a^*(0)$ =182A:9.6A=19:1. The Shubnikov-de Haas signal with the period of 0.0015T^{-1} was observed below 1K and above 8T. The period corresponds to the area of extremal orbit of 18% of the first Brillouin zone. The anisotropic nature of the thermoelectric power of the crystal in the 2D plane can be explained on the basis of the complicated Fermi surface. No EPR signal ascribed to Cu^{2+} was observed. The linewidth of the EPR signal of BEDT-TTF$^+$ increased monotonically with decreasing temperature in contrast to the predictions of the Elliot formula for the spin relaxation in metals. A Korringa relation was observed in ^{1}H NMR measurements between 77K and 10K. Below 10K a big enhancement of the relaxation rate was observed with a peak at considerably lower temperature than Tc. Anisotropic superconducting gaps were detected by tunneling spectroscopic work.

Photocontrol of Polypeptide Conformation in Ordered Molecular Assemblies

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1. Introduction

Photosensitive systems are ubiquitous in nature. In rhodopsin system, cis-trans photoisomerization of retinal followed by a conformational change of opsin is a trigger for subsequent biological events. The purpose of this study is to construct similar photo-switchable systems with designed polypeptide systems. As an analogous system of rhodopsin, where the protein (opsin) is embeded in lipid bilayer membrane, copolymers of n-octadecyl-L-aspartate and (p-phenylazo)benzyl-L-aspartate (pO copolymers), in which azobenzene groups are surrounded by flexible long alkyl chains, were prepared. The study in this year deals with conformational versatility influenced by trifluoroacetic acid (TFA) and temperature.

2. Results and Discussion

The pO copolymers exist in solution at 25 ℃ as right-handed (RH) and left-handed (LH) α-helices depending on the copolymer composition, a reversal of helix sense from RH to LH occurring with increasing azobenzene content between 47 and 68%. The copolymers are very sensitive to TFA, and their conformations are converted into random coil below 2% of TFA content. Among the copolymers, the copolymer with 47% azobenzene groups is unique since it exhibits a TFA-induced conformational change from RH α-helix to random coil via LH α-helix. The LH α-helices of the copolymers containing 68 and 69% azobenzene groups are changed to RH α-helices when irradiated in solution at 25 ℃. The copolymer with 47% azobenzene groups and the copolymers with more azobenzene groups changed their helix senses when temperature is raised for the former and lowered for the latter. On this basis, the copolymer with 47% azobenzene groups was made photosensitive at high temperatures (50-60 ℃). A new series of copolymers (pM copolymers), which have methyl group in place of octadecyl one, were also prepared for comparative studies. All copolymers of this series exist in solution as LH α-helices, and their conformational changes occurring upon irradiation were negligible or slight. This result suggests that octadecyl group is very effective to make copolymers photoreactive.

Studies on Design and Controll of Functionality in Ultrathin Films of Ferroelectric Polymers

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1) Introduction

Copolymer of vinylidene fluoride(VDF) and trifluoroethylene(TrFE) exhibits conspicuous ferroelectricity even in a film as thin as 500A. In such a ferroelectric films a strong internal electric field due to inhomogeneous polarization is expected in crystallites or interlamellar regions. Utilizing such an internal electric field, the photogeneration efficiency of electron or holes from photoreceptors doped in ferroelectric films may increase considerably. The purpose of this study is (1) to construct asymmetrical films to assist transport electric carriers in the films, (2) to search for photoreceptors to generate electrons and holoes with high efficiency, and (3) to clarify the effect of internal electric field on photogeneration of electrons or holes to transpot across the films.

2) Results and Discussion

Charge transfer complex of polyvinylcarbazole(PVK) and trinitrofluorenone (TNF) has been known as an organic photoconductor. We have found that transfer of electrons from PVK and trapped on TNF occurs on irradiation of light with energy higher than 1.7 eV at low temperatures below 150K to give elctron TNF^- and hole (PVK^+) pairs with considerable high quantum yield (0.01-0.1 depending on the ratio TNF/PVK). Among other various charge transfer complexes examined, we found a considerablly high quantum efficiency of electron-hole pair generation in the complexes PVK-chloranil, and PVK-tetracyanoethylene. However, the efficiency is not higher than that in PVK-TNF. A chlorophyll-a and phylloquinone system embeded in the X-type LB film of stearic acid was also found to give a ESR signal on light irradiation at low temperatures.

We have found interesting phenomena suggestive of the effects of internal electric field to enhance the photogeneration of electron-hole pairs in the charge transfer complexes embeded in the ferroelectric films: the quntum efficiency measured by ESR at 77K in the P(VDF-TrFE) film doped with 1:1 complex of vinylcarbazole (VK) and TNF (2 mol% per monomer unit of the ferroelectric polymer) are very small, but it becomes quite high after the film experienced annealing at 140°C. Since ferroelectric lamellar crystals in P(VDF-TrFE) films grows only when it is annealed above its Curie temperature (130°C), these enhanced quntum yield is attributable to the electric fields developed, possibly, in the interlamellar regions. Further studies are now in progress.

Physical and Chemical Properties of Functional Groups Organized in High-Quality LB Films.

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1. INTRODUCTION

Applying the monolayer assemblying techniques for amphiphiles with chromophores we can obtain organic thin films with a well-defined orientation and packing of the functional groups. In this work, using a long-chain merocyanine (MC), long-chain derivatives of α-L-naphthylalanine and oligothiophenes, molecular organizations with a specific J-aggregate, a photobiological system and a conducting molecular element, respectively, have been constructed and examined by some spectroscopies.

2. RESULTS AND DISCUSSION

The dye MC forms J-aggregates in the mixed monolayers with various matrix agents and charactristic visible absorption and fluorescence which is radiative annihilation from the free exciton state were obserbed. From the fluorescence decay of the J-aggregate LB films, two components of the lifetimes were estimated to be about 40 and 230 ps. In its time-resolved fluorescence spectra, the fluorescence band at 610 nm disappeared at about 600 ps, whereas another band at 570 nm was grown up.

The monolayer of a long-chain lysine derivative of α-L-naphthylalanine exhibited a phase transition from the expanded to condensed states. From circular dichroism of the LB films deposited at various surface pressures, different packings of the naphthalene groups were observed.

Regarding with oligothiophenes mixed with Cd arachidate in the LB films, quinquethiophene molecules were found to be well organized with nearly vertical orientation from angle-resolved photoemission and polarized electronic spectra.

Development of New Charge-Transfer Complexes Exhibiting Bistable Switching Phenomenon

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1. Introduction

Charge-transfer salts exhibit a wide array of electrical properties ranging from insulators to semiconductors, and moreover to superconductors. TCNQ and its derivatives form anion radical salts which display bistable switching phenomena. Thus charge-transfer salt is a rich source of new functional matrerials. The purpose of our project is to explore new donor and acceptor species for charge-transfer complexes which show new electrical properties and functions. In particular, superconductivitiy and switching phenomenon have been pursued.

2. Results and Discussion

[1] Unsymmetrical donor, DMET Dimethylethylenedithio(dithiadiselenafulvalene) (DMET) has been prepared. This unsymmetrical donor was found to give various kinds of superconducting radical salts. The $(DMET)_2AuBr_2$ crystals exhibited superconducting at ambient pressure below 1.9 K, which is the highest transition temperature among the superconducting DMET salts.

[2] Thiophene-fused TCNQ An isomeric series of thiophene-fused TCNQ have been prepared. Among four isomers which condense two thiophene rings, the isomer of benzo[1,2-b:4,5-b']dithiophene skeleton was the best acceptor and formed the charge-transfer complex with TTF. The crystal of this complex is composed of the -DD-AA-DD-AA- sequence of a mixed stack.

[3] Thieno-acene Tetrathienoacene and pentathienoacene, which have an isoelectronic structure with chrysene and picene, respectively, have been synthesized. The ionization potentials of these new donor species were very low, being comparable to those of TTF and TMTSF, and formed the charge-transfer complex with TCNQ.

Magnetic Interaction in Organic Crystals

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1. Introduction

We have been studying the intermolecular magnetic interactions in organic crystals. In this year, we have studied the magnetic interactions of several phenoxy radicals, which are expected to have enhanced spin polarization and extended pai-conjugation.

2. Results and Discussion

Galvinoxyl(I): The paramagnetic susceptibility follows the Curie-Weiss law with θ =+19 K in the range of 85 - 300 K. The positive Weiss constant means that there exists a ferromagnetic intermolecular interaction. This has prompted us to the study of the following compounds.

2,4,6-tri-t-butylphenoxy radical(II): This compound has been reported to have a positive Weiss constant. However, our re-examination shows that the susceptibility follows the Curie-Weiss law with θ =-3.2 K in the range of 2-300 K. The weak antiferromagnetic interaction may be understood by the existence of a bulky group at the 4-position.

2,6-di-t-butyl-4-phenylphenoxy radical(III): The crystal of this compound shows the susceptibility well described by the singlet-triplet dimer model above 15 K. The curve fitting yields the antiferromagnetic coupling constant of 2J/k = -90 K. The planar phenyl group seems to have promoted the pai-electron overlap between the radicals in comparison with II.

2,6-di-t-butyl-4-xenylphenoxy radical(IV): As far as the frontier orbitals are concerned, this compound has an electronic structure most similar to I, among the compounds studied here, in a spin unristricted INDO MO calculation. Thus we expected a ferromagnetic interaction. However, the susceptibility is found to be of Curie-Weiss type with θ =-0.2 K, indicating no apparent magnetic interaction. A possible explanation for this is, though seems to be rather farfetched, that the expected ferromagnetic interaction is cancelled out by the antiferromagnetic interaction similar to that found in III.

Photo-Induced Effect of Electron-Lattice Systems of Organic Solids

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1. Introduction

Organic solids with very anisotropic π-electonic structures, such as conjugated polymers and charge-transfer(CT) complexes, exhibit in general the strong electron-"lattice" interaction , which includes the interaction with polymer backbones, molecular stacks, hydrogen-bonds etc. The purpose of this research is to experimentally investigate transient and/or permanent change of optical properties induced by photo-excitation arising from such a strong π-electron-lattice interaction.

2. Results and Discussion

We have investigated two kinds of photo-induced phenomena; the photo-induced bond-structure phase transition in polydiacetylenes (PDAs) and the photo-doping effects of charge- and spin-carriers (solitons) in ionic CT crystals. Some of PDAs show the transformation form the blue-form to the red-form, when photo-excited above the energy necessary for carrier-generation. To our knowledge, this is the only known esample of photo-induced cooperative phase change of organic polymers triggered purely by photon-mode. Its transient response was investigated here for the first time, whcih has revealed the very fast process in the bond structural change (less than laser pulse-width, 10ns) as well as the rather slow process associated with the re-arrangement of side-groups.

On the other hand, the strong photo-induced absorption or reflectance change was observed in some prototypical ionic CT crystals with Peierls-type stack dimerization. Measurements of dynamics and temperature-dependence of the photo-induced signals indicate that the oberved large signal can be interpreted in terms of the photo-injections of domain-wall-type excitations in dimerized molecular stacks. Further, in some of ionic DA mixed-stack CT crystals such a photo-injected domain-wall is mobile as a spin-or spinless-soliton with fracttional charge in the ferroelectrically ordered one-dimentional stack.

We are seeking possibility to apply these unique photo-induced effects in low-dimensional organic solids to possible molecular photonics.

Preparation of Organic Thin Films for Ultra-fast Photo-electric Conversion by LB and OMBE Methods

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The energy conversion from scalar light into vectorial electricity could be successfully attained at molecular levels by utilizing a general tendency of amphiphilic compounds to be oriented unidirectionally at a phase boundary. It seems quite reasonable from experimental evidence to assume that the amphiphilic folded triad molecules (Fig. 1a) synthesized for a molecular photodiode oriented unidirectionally as we would expect. Namely, the triads were spread first at an air-water interface with a polar electron-acceptor group (A) of the triad molecule located at one end toward water, a nonpolar electron-donor group (D) at the other end toword air, and a nonpolar light-absorbing, i.e. sensitizer, moiety (S) in between them in a closely packed mixed monolayer of the triad and fatty acid. Then, the mixed monolayer was transferred onto a vapor-deposited gold film electrode (Au OTE) by the Langmuir-Blodgett (LB) method.

In this work, we investigated the following factors which would affect the efficiency of these photo-electric devices; 1) the surface pressure applied for monolayer deposition, 2) the applied electrode potentials, 3) the wavelength of the incident photons, 4) the distances between A and S and between S and D, and 5) the role of the D moiety.

The kinetic parameters of intramolecular electron transfer processes in picosecond region was estimated by using a mode-locked Nd:glass laser and streak camera system for S-D and A-S molecules (Fig. 1b and c).

The photo-electric conversion properties were also examined for the linear triad (Fig. 1d) and their mixture with antenna molecules (Fig. 1e).

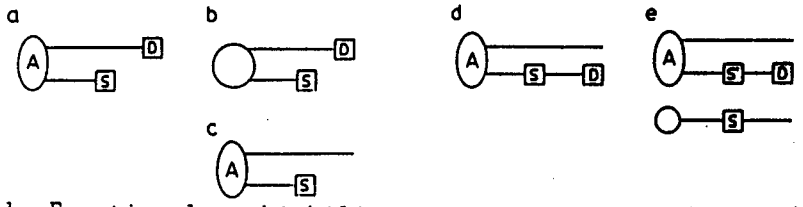

Fig. 1. Functional amphiphilic compounds used in this work.

Characterization of Langmuir-Blodgett Films by Piezoelectric Quartz Plates

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1. Introduction

Interest in Langmuir-Blodgett (LB) films is widespread and formation of ordered thin films by transferring lipid monolayers from a water surface is well known. The characterization of LB multilayer films has been widely studied in the dry state by various methods such as FT-IR spectroscopy, X-ray diffraction, ellipsometry, and photoelectron spectroscopy. However, the *in situ* evaluation of LB films during the dipping process has not been fully explored. In this paper, we report that water is incorporated when LB films are deposited, which can be directly observed by using a piezoelectric crystal plate as a dipping substrate, and that the molecular orientation in the monolayers influences both the amount of water incorporated and its evaporation rate from the layers.

2. Results and Discussion

Typical time courses of the frequency change of the crystal (9 MHz, AT cut) in air are shown in Figure 1. The crystal was lowered at point A and lifted out of the stearyl cadmium monolayer-covered subphase (surface pressure 20 mN m^{-1}) at point B four times. The frequency of the crystal gradually increased with time and reached a constant value after 15 min in air. The increased mass on the crystal with each cycle (w_1) was calculated, from the decrease of the frequency of 183 ± 3 Hz from points A to C, to be (2.32 ± 0.03) x 10^{-7} g. This value was consistent with the theoretical mass of four dry monolayers of cadmium stearate (2.25 x 10^{-7} g). The increase of the frequency between points B and C (the decrease of mass) can be explained by evaporation of water from interlayers of the LB films. The amount of incorporated water (w_2) and its evaporation speed (v) were calculated from the frequency change and the initial slope of the curves between points B and C, respectively.

When monolayers were deposited on the crystal at a low surface pressure (5 or 10 mN m^{-1}), both the amount of lifted water and its evaporation speed were increased, but the mass of deposited LB film was less than that lifted at the high surface pressure. Thus, a relatively large amount of water is lifted with disordered monolayers and this incorporated water evaporates easily through the disordered monolayers.

In conclusion, we can evaluate *in situ* the molecular orientation of monolayers using this technique.

Design of Functions of Graft Copolymers for Separation by the Control of Their Orientation at Interfaces.

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INTRODUCTION

In order to establish the principle to precisely control gas permeability and permselectivity, by designing the structure of polymers in the solid state and at interfaces, three approaches were attempted.

Gas permeation channnel could be prepared by taking advantage of micro-phase separation of hydrophilic and hydrophobic graft copolymers prepared from well-defined macromers. Co-complexes were introduced by reacting with bromomethyl groups in polymer side chain to enhance the selectivity in permeation. It was also found that surface accumulation of polydimethylsiloxane based graft copolymers could effectvely enhance both permeability and permselectivity of oxygen gas over nitrogen gas. This principle was applied to enhance the permeability and permselectivity of oxygen permeation through the commercialized polydimethylsiloxane-b-polycarbonate oxygen separation film.

Meanwhile, factors controlling the permeation of gases through polymer films were investigated. It was elucidated, by invesitigating the glass transition temperature, diffusion coefficient and relaxation phenomena in the permeation, that mobility of side chains of polymer is playing essential roles in permeation. The mobility of side chains can be precisely controlled by introducing siloxane spacers between polymer main chain andside chains. The number and the type of siloxane linkage have big effect on the property of the polymers. For instance, one siloxane linkage reduce the glass transition temperature by 100_{o} and permeability coefficient was increased by 30 times. According to this principle, it could be shown that polynorbornenes with oligodimethylsiloxane side chains were quite good materials for oxygen selectively permeable membrane materials.

KEY WORDS
Polydimethylsiloxane/ Graft Copolymer/ Gas Permeation/ Spin-spin Relaxation/ Glass Transition/ Diffusion/ Molecular Design

Preparation of Polymer Thin Films by Photopolymerization and Photofunctional Properties of Oriented Polymer Films

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1. The purpose of this project is (1) to explore several preparation techniques of polymer thin films, (2) to explore techniques to align dopants molecularly in polymer films, and (3) to investigate photofunctional properties of polymer films thus prepared.

2. This year we focused our investigation on the following two subjects.

(i) Preparation of polymer Langmuir-Blodgett (LB) films with photofunctional chromophores and development of photofunctional LB layered films: The polymer samples with different concentrations of pyrenyl groups were synthesized by the reaction of poly(vinyl alcohol) with octylaldehyde and pyrenecarbaldehyde. The polymers were deposited on a quartz plate as Y-type layers with a deposition ratio nearly unity. The fluorescence spectra consist of pyrene monomer band and a very weak excimer band, depending on the concentration of pyrenyl group. Analysis of the monomer fluorescence decay for LB layered films showed that pyrenyl groups are uniformly distributed without isolated site. Dependence of the excimer emission intensity on the number of layers was observed, and the relation between the decay curve behavior and the number of LB layers shows that energy migration occurs between pyrenyl groups of different layers. Then, it is concluded that such polymers are appropriate to prevent the chromophores from forming various kinds of aggregates, and to attain uniform distribution of chromophores in the monolayers, and that efficient energy transfer between inter-layers is attained for such a polymer LB films.

(ii) Control of molecular orientation under electric field and evaluation of the molecular orientation: In order to develop electro-optical devices, we studied an alignment process of a polar dye by electric field poling. Evaluation of the molecular orientation was made by absorption and fluorescence polarization method. Polystyrene (PS) films (thickness $\simeq$ 50 μm) containing 4-dimethylamino-4'-nitrostilbene was used. Poling was carried out under 100 kV/cm near T_g (110 ^{o}C) and the film was quenched to room temperature immediately after the poling. A few tens of minutes were sufficient for the electric poling. The order parameter $f = 0.5$ was obtained by such a procedure, where $f = (3 \cos^2\omega - 1)/2$. Orientation relaxation of the ordered structure was considerably slow and its relaxation time was of the order of several months.

Synthetic Studies on Electric Conducting Organic Compounds Containing Chalcogen Atoms

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1. Introduction

New organic electron donors and acceptors containing chalcogen atoms were designed and synthesized to obtain highly electric conducting organic compounds from them.

2. Results and Discussion

Amoung the electron donors synthesized, peri-ditelluroacenaphthene and 2,3,6,7-tetramethyl-1,4,5,8-tetrachalcogenonaphthalenes show strong electron donating properties and afford highly conducting molecular complexes and radical cation salts, respectively. Selenium analogues of TPDT ((2-thiopyran-4-ylidene)-1,3-dithiole) are also good donors and form TCNQ complexes having a metallic conductivity.

Among the electron acceptors synthesized, linearly conjugated and condensed type heteroquinonoid analogues of TCNQ are generally weak donors but show a remarkable characteristic to have very small on-site Coulomb repulsions. Introduction of electron attracting substituents, e.g. halogens, much improves their electron accepting properties and bring them up superior acceptors bearing both good electron affinities and small on-site Coulomb repulsions. They formed many highly conducting molecular complexes, whose conductivities sometimes reach to 170 Scm^{-1} in spite of compressed powder pellets. The pyridine and pyrazine analogues of TCNQ are strong electron acceptors than TCNQ. Although they could not be isolated as neutral molecules, they also afford highly conducting TTF complexes.

Molecular design of asymmetrical Langmuir-Blodgett films for conversion of optical signals

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1. Introduction

Using the Langmuir-Blodgett (LB) technique, last year, we could construct an asymmetrical films with hetero Y-type structure. Then we have pursued the study of the molecular design for constructing stable asymmetrical LB films with the aim of developing pyroelectric and second order non-linear optical films.

2. Results and Discussion

Two homologous azobenzene derivatives, 1 and 2, were synthesized ($C_{18}H_{37}O$-ϕ-N=N-ϕ-X, 1:X=NO_2, 2:X=$COOC_2H_5$, ϕ:phenyl). A polar amphiphile 1 posseses a strong electron-withdrawing nitro group as a hydrophilic head. In its monolayer, the polar molecules did not orient vertically to the monolayer plane. A less polar amphiphile 2 gave a monolayer with well-defined H-aggregated structure. We found that the complete mixing of 1 into 2 was attained in the molecular level and was favorable to accomplish the vertical orientation of the polar amphiphiles 1 to the monolayer plane. On the contrary, the mixed monolayer of 1 to a conventioanl fatty acid (arachidic acid) gave similar absorption spectrum caused by azobenzene chromophore to that of the single monolayer 1.

We obtained the LB film with hetero Y-type structure of the mixed monolayer (1+2), when the mixed monolayer and a monolayer of cadmium arachidate were deposited alternately on quartz substrates. The spectrum of the alternating multiplayer well corresponded with that of the mixed monolayer (1+2) at the air-water interface. The aggregation structure at the air-water interface was preserved in the alternating multilayer film.

We measured the linear Stark effect (electroabsorption) for quantitative evaluation of the asymmetrical orientation of amphiphiles in LB films. A strong Stark signal was observed from the alternating multilayer film composed of the mixed monolayer (1+2) and cadmium arachidate. The order parameter $\langle \cos\theta \rangle$ in this film was determined to be 0.47. A strong pyroelectric response was obtained for the alternating multilayer and the pyroelectric coefficient was determined to $10^{-10}Ccm^{-2}K^{-1}$. By irradiation of pulsed Nd-YAG laser, we could observe a pronounced second harmonic generation (SHG) signal from the alternating multilayer.

Effect of Light-Irradiation and Electric Field for the Preparation of Highly Oriented Organic Molecular Thin Films

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1. Introduction

It is crucially important to develop new substances or materials for a substantial progress in basic sciences. The purpose of this research project is to establish the preparation of organic ultra-thin multi-layered films with the use of a Molecular Beam Epitaxy (MBE) technique, and especially to improve the orientation of organic molecules in a film with the help of light-irradiation and electric field in the course of evaporation.

2. Results and Discussion

We have tried to prepare a homogeneous and oriented film and make it as thin as possible without using light or electric field as an initial step. Aluminum phthalocyanine polymer (bridged by F), AlPc(F), was evaporated onto several kinds of substrates in an MBE system to check the effects of substrate materials and temperature.

The structures of films evaporated on a silicon or quartz are rather irregular in the image of SEM and polycrystalline in the electron diffraction pattern. The TEM image shows that Pc molecular planes are perpendicular to the substrate and polymer axies are paralled to it.

On the contrary, the TEM image of the film grown on a KCl (100) cleaved crystal plane shows clear square lattices (12.6 Å) and the Pc molecular planes are paralled to the plane. There are two preferential orientations in the 2-D growth direction of which mutual angle is 37°. These orientations are just corresponding to two possible configurations of ca. 14 Å square lattices on the KCl (100) crystal surface, and Al and N atoms of AlPc are well accommodated on K and Cl ions, respectively.

In the case of KBr substrate, the TEM image is of uni-directed square lattices, and this orientation is just derived from the unique orientation of ca. 14 Å square lattices on KBr crystal surface.

These 2-D orientations give a clear evidence for the epitaxial growth of AlPc(F) on the surface of potassium halide crystals. Moreover, the optical absorption spectra of these films show extra peaks near the principal Q-band of Pc, and their origin could be the strained lattice structure (14 Å to 12.6 Å lattice) of the interface between organics and substrate.

Photo-Processing for the Preparation of Inorganic Thin Films

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1.Introduction

Species, sometimes in the ionic form, formed by the photoexcitation may be usable in the CVD growth of a thin layer on a suitable substrate. It is deeply desirable to elucidate a role of the irradiated light in the layer growth. In this report growth of SiC and GaN thin layers with ArF excimer laser light was studied: in the former the irradiation onto the substrate was significant while in the latter excitation of the source gases was effective.

2. Results and Discussion

Epitaxial SiC films

Epitaxial 3C-type SiC films grew under the ArF excimer laser irradiation. The reaction was performed in a CVD chamber at a very low reaction gas pressure of about 10^{-2}Pa, in order to avoid the collision between the gas molecules so as to make the reaction simple. The light irradiation of the substrate was necessary to grow adherent and epitaxial SiC films. The improvement of adhesion and epitaxy means that the irradiation has significant effects on the interface formation between Al_2O_3 and SiC. In fact, the irradiation only at the initial stage of film growth was enough to prepare adhesive and epitaxial films. The initial stage of the growth was observed with a high resolution SEM. The irradiation increased the nucleation concentration and made the deposits cover the Al_2O_3 surface. The irradiation effects depended on the wavelength. It revealed that the chemical species concerning the effects were not the reaction gases nor the substrate. The irradiation may cause the photo-chemical reaction of absorbed species on the Al_2O_3, resulting in having desired effects on adhesive and epitaxial growth. For the Si substrate, the light irradiation enhanced the atomic diffusion through the SiC film and increased the film growth rate in the carbidization reaction.

Epitaxial GaN films

A GaN thin layer was grown on Al_2O_3 (001) using $Ga(CH_3)_3$ and NH_3 as a source gas in the molar ratio of 50-100 and under the total pressure of 0.1-0.5 Torr. At 500-800 C products were oriented preferably parallel to (001) and (101). With decreasing temperature crystals with the (001) orientation grew more dominated. Thus the present method has opened a new way towards the growth of GaN at temperatures lower by 400 C compared with the previous thermal CVD.

CONTROL OF INTERFACES OF GELS IN THE SOL-GEL SYNTHESIS OF MATERIALS

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1. Introduction

Reactions of alkoxysilanes in the starting solutions for the sol-gel synthesis of silica and silicates have been studied to have a basic information for designing the structure of sol-gel products. Secondly, the stability of the dried silica gel monolith with micropores of 160 A in diameter and its heated products to exposure to solvents has been studied, in order to have a basic knowledge required for applying the silica monoliths as functional porous material.

2. Results and Discussion

2.1 Reactions of Alkoxysilanes in the Solutions

It has been found that partial or full replacement of the ethoxyl groups by trimethylsiloxyl groups gives $RSi(OEt)_n(OSiMe_3)_{3-n}$ (n = 0, 1, 2), when alkyltriethoxysilane is treated with Amberlyst 15, a cation exchange resin, in the presence of hexamethyldisiloxane. Also it has been shown that transesterification reaction is seen between tetraethoxysilanes and butyl alcohols in the presence of Amberlyst 15. It has been observed that when tetraalkoxysilanes are mixed in (2-hydroxyethyl)trimethylammonium hydroxide aqueous solution, (2-hydroxyethyl)trimethylammonium silicate with cubic octamer structure is rapidly precipitated as solid.

2.1 Stability of Gel Monolith to Solvents

The dried silica gel monolith with micropores of about 160 A in the average diameter, prepared by the sol-gel method, has been tested for the crack formation by exposing it to the vapor of various solvents. It has been found that cracks are formewd when the surface tension of the solvent is higher than 47.5 dyne/cm. The same gel monolith was heated at various temperatures up to 1030 ^{o}C and then tested for the crack formation on immersion in water. It has been shown that the heating temperatures of 850 ^{o}C and 900 ^{o}C give gel monoliths which are not cracked. The occurrence of cracks may be explained by the changes of pore diameter, strength of gel skeletons and character of pore surfaces.

METAL-CERAMIC BONDED INTERFACE, ITS DESIGN, OBSERVATION OF THE BEHAVIOR AND ASSESSMENT

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1. Introduction

Metal-ceramic joining is considered indispensable in using ceramics to structural components, because enhancement of the toughness is achieved by this way. Nature of the bonding, however, differs so extensively understanding the structure and the behavior of the interface and the control is considered urgent. This study intends to design the interface through understanding the interface by high resolution electron microscopy. Niobium/alumina system was chosen as the suitable system to do the study.

2. Results and Discussion

Cross-sectional high resolution electron microscopic observations were made with various bicrystalline bonded specimens. For example a Nb/Al_2O_3 bicrystal was produced by joining face to face the sapphire $(11\bar{2}0)$ and niobium (110) at 1873K in vacuum under a load of 12MPa. sliced, thinned and observed from two directions, alumina[0001]//niobium[$1\bar{1}1$] and alumina[$1\bar{1}00$]// niobium[$1\bar{1}\bar{2}$]. Atomic ledges are shown parallel to alumina[0001]// niobium[$1\bar{1}1$] refelcting smallness of the lattice mismatch of alumina$(11\bar{2}0)$ and niobium(110).

Syntheses of New Functional Materials by Using Interlayer Surfaces of Layered Crystals and Their Characterization

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1. Introduction

The interlayer spaces in layered crystals can be regarded as two-dimensional interfaces in between adjacent crystalline layers. The main objectives of this study are to fablicate low dimensional materials in the interlayer spaces through intercalation processes and to tailor new types of functional materials by the hybridization of the crystalline layers as a building compornent at molecular levels.

2. Results and Discussion

(1) Intelayering of $Cu(OH)_2$ in montmorillonite

Na-montmorillonite was dispersed in copper(II) perchlorate solutions and titrated with NaOH very slowly. The montmorillonite was converted into a Cu-chlorite like phase having $Cu(OH)_2$ interlayers without forming basic copper salt. It is noteworth that the $Cu(OH)_2$ precipitated in the interlayer spaces has the brucite type layer structure although only the γ-FeOOH type structure is known for the bulk crystal of $Cu(OH)_2$. This may be considered to be a special interface effect of the interlayer spaces of montmorillonite.

(2) Lithium intercalation in layered perovskite

Lithim intercalation in layer structured niobate perovskites has been studied. A double and a triple layer structured perovskites, $KLaNb_2O_7$ and $KCa_2Nb_3O_{10}$, respectively, were prepared and the pressed powder was subjected to reaction with n-butyllithium solution in hexane. The pellet was simultaneously colored dark blue on immersion, indicating that the intercalation accompanied by charge transfer occurred. The crystal changed from insulator into semimetal, increasing the electrical conductivity by a factor of $\sim 10^{12}$.

(3) Intercalation of hydrogen in β-ZrNCl

β-ZrNCl has a unique layer structure with two kinds of interlayers (Cl-Cl and N-N) in one layer structure. When the crystal was treated with H_2 or NH_4Cl at elevated temperatures, hydrogen was taken up into the N-N interlayer spaces of β-ZrNCl. The hydrogenated crystal was an n-type semiconductor with very shallow impurity donor levels.

Preparation of Composite Particles Comprised of Organic-inorganic Compounds and Ordering in Fine Particle Suspension

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a), Effects of an electrolyte(K_2SO_4) and water-soluble polymer(Hydroxylpropl Cellulose ; HPC) on the formation of composite particles comprised of organic (amphoteric latices ; particle diameter,2a = 250 nm) and inorganic(spherical silica ; 2a = 240 - 1590 nm) compounds have been investigated as a function of concentration of the electrolyte and the polymer in the medium of the basis of hetero coagulation theory. It is apparent that the addition of the electrolyte increases the adsorption densities of latices on silica and eventually approaches θ(fraction coverage of adsorption) = 1 at 1.46×10^{-2}M K_2SO_4 for the largest silica used. On the other hand, the addition of the water-soluble polymer in the medium weakens the affinity of latex adsorption. This effect was influenced dramatically by the concentration of polymer and its molecular weight. Furthermore, it is realized that these additives are useful to control the composition of organic and inorganic compounds in the composite particles prepared by the hetero coagulation technique.

b), It is generally accepted that nonadsorbing polymers also can affect the stability of colloidal systems when the other interparticle forces are relatively weak. The physical reason is that nonadsorbing polymer will try to avoid the surface region because of a lower conformational entropy close to the surface. The resulting effect has been named depletion effect because the reason of the effect is the depletion of polymer near a wall. In this study, the depletion effect has been studied by the two different approaches. The first is from a view point of rheology. The curves of relative viscosity of the latex + free polymer(HPC) systems under a lower shear rate have a peak about a concentration of free HPC, which depends on the molecular weight of HPC.

The second approache has been based on the ordering behaviour of the latex suspension. It is apparent that the depletion effect from free polyelectrolyte molecule decreases the interparticle spacing in the ordered layers and sometimes brings about destruction or phase separation of the uniform ordered layers.

Fabrication of Epitaxial Thin Films of Conducting Materials by MO-CVD Method

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1. Introduction

Since the discovery of cuprate oxide superconductor, La-Ba-Cu-O, fabrication of thin films has been a subject of intensive works. These cover sputtering, evaporation, screen printing, dip coating and so on. In this study, we report the synthesis of Ba-Y-Cu-O and Bi-Sr-Ca-Cu-O thin films by a mist pyrolysis technique. In addition, construction of small size STM, which can be incorporated in the reaction chamber of mist pyrolysis apparatus, and its application to the tunneling spectroscopy at low temperature will be described.

2. Results and Discussion

Fine mist of Y, Ba, Cu or Bi, Sr, Ca, Cu mixed solution created by an ultrasonic nebulizer was introduced into the reaction chamber along with a nitrogen or oxygen gas flow. The thin films of oxide superconductors were deposited on a YSZ substrates set on a carbon or Pt holder, which were heated inductively through an rf coil. From the compositional analysis of thin films, it turned out that Cu tended to be enriched compared to other elements. However, the enrichment of Cu was substantially improved by utilizing oxygen as the carrier gas and the Pt holder. Furthermore, the resistivity measurement of obtained films indicated the significance of post-annealing process. The best specimens of Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O showed the zero resistivity temperatures of 35 and 63 K, respectively.

The small size STM (23mmϕx80mm) was applied to the tunneling measurement of Bi-Sr-Ca-Cu-O single crystal at 4.2 K. From the dI/dV-V curve, superconducting gap was estimated to be 17 meV, which was fairly in good agreement with the predicted value by BCS.

Studies on Synthetic Processes of Transparent Conducting Polymer Thin Film Obtained by Controlling the Solid-Air Interface Reaction

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Introduction

Conductive polypyrrole can be synthesized by electro- chemical as well as chemical method. The latter method generally yield low conductive material. However we recently found that polypyrrole obtained by chemical polymerization can exhibit very high electrical conductivity when suitable solvent is selected and the oxidation potential of the oxidant media is controlled.

Results and Discussion

In this work polypyrrole has been prepared by chemical polymerization in $FeCl_3$ solutions with various solvents. When 2.5M $FeCl_3$ in methanol was used as an oxidant solution, for 20 minutes polymerization time and 0 °C polymerization temperature, the polypyrrole obtained shows an electrical conductivity as high as 190 S/cm. It is found that the oxidation potential of the solution strongly effects the polymerization process and hence the conductivity, this oxidation potential depends on the concentration ratio of $FeCl_3$ and $FeCl_2$. The optimum value of oxidation potential (vs. SCE) to produce a high conductive polypyrrole is approximately 500 mV. It is clear that the $FeCl_2$ produced during the reaction will reduce the potential and thus results in low conductive material. When the oxidation potential of $FeCl_3$ in methanol solution was controlled to the optimum value by adding small suitable amount of $FeCl_2$ before the reaction, along with proper polymerization condition the conductivity of the synthesized polypyrrole can be increased up to 220 S/cm; comparable to values obtained by electrochemical polymerization.

Photoinduced Surface Reactions for Thin Film Deposition

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1. Introduction

Photoinduced chemical vapor deposition (photo-CVD) is a useful technique for thin film deposition, and currently it is under intense investigation. We are in particular interested in surface photolysis of adsorbed source molecules on substrates, which plays an important role in photoinduced metalorganic chemical vapor deposition. Also, the surface reaction can be utilized to achieve area-relative deposition with such applications as direct writing and pattern transfer.

2. Results and Discussion

We deposited aluminum thin films on silicon, using a metalorganic source gas, dimethylaluminum hydride (DMAlH). For the light source, a deuterium lamp and an ArF excimer laser were used to photolyze DMAlH. Deposition occurred at substrate temperatures lower than required by thermal decomposition of DMAlH (about 250 °C). The deposition rate increased with both substrate temperature and vapor pressure. For light intensity the rate became independent above a certain level. Also the rate for laser irradiation, defined as the thickness increase per pulse, decreased with its repetition frequency.

The observed irradiation effects were induced by surface photolysis as evidenced by the following reasons: (1) With low vapor pressures (typically, 6.7×10^{-3} Pa) used throughout this experiment, light can not be used effectively in gas phase. (2) Area selectivity: Radicals generated in gas phase should diffuse over a wide area, and deposition would occur even outside the irradiated area, in contradiction with the observed fact. (3) In gas phase, the amount of radicals generated by each pulse should be independent of the repetition rate, again in contradiction with the experiment. (4) We set up a rate equation for the number of adsorbed DMAlH molecules, including the impingement, thermal and photoinduced desorption and photoinduced dissociation. Using this equation, we can explain all the experimental facts.

Preparation and Characterization of Magnetic Oxide Single Crystal Films

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1. Introduction

Preparation of magnetic oxide films has recently attracted much attention because of the potential utility of their magnetic and magneto-optic properties. In the present laboratory a reactive evaporation method has long been applied to preparation of various transition metal oxide films on various types of substrates. Reported here is the growth of Fe_3O_4 on the (0001) surface of α-Al_2O_3.

2. Results and Discussion

Deposition conditions, such as the substrate temperature, oxygen partial pressure, deposition rate etc., appropriate to the growth of well-crystallized Fe_3O_4 were determined, and epitaxially grown films were characterized by XRD, resistivity measurements, and conversion electron Mossbauer spectroscopy (CEMS).

Film-thickness dependence of the XRD (hhh) peaks indicated that the structural coherence remained below 500Å. This fact and the columnar growth of particles having a typical diameter of ~500Å has been considered to result from a large lattice mismatch of ~8% between Fe_3O_4 and α-Al_2O_3.

CEMS spectra indicated good stoichiometry for films thicker than ~100Å, while remarkable tendency toward oxidation and superparamagnetism was found for thinner films. Restivity measurements indicated the occurrence of the well-known electronic and structural transition called Verwey transition.

Preliminary studies using the (100) surface of MgO as substrate have suggested that the improvement in lattice matching allows the growth of Fe_3O_4 of a much higher crystalline quality.

Preparation of Ionically Conductive Amorphous Films under Controlled Atmosphere

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1. Introduction

Ion-conductive amorphous films have potential for the applications to the electrochemical devices such as thin film batteries, displays, and sensors. In the present study, the ion-conductive amorphous films have been prepared under controlled atmosphere by the various methods (rapid quenching, sol-gel method, and thermal decomposition), and characterized, with the purpose to develop the stable, highly ion-conductive amorphous films.

2. Results and discussion

The following results have been obtained through the present study:

(1) The silica gel films containing up to 42 wt% molybdophosphoric acid (MPA) have been obtained by the sol-gel method. The proton-conductivity of these films varies almost reversibly with the relative humidity in a range of 20 to 95%, indicating their applicability to humidity-sensors.

(2) The ion-conductivity of cation- and anion-mixed halide glasses have been studied systematically and a hypothesis has been proposed to explain the "mixed-ion effect" on the conductivity observed in these glass films.

(3) The amorphous transition-metal oxides and sulphides have been prepared by the rapid quenching and the thermal decomposition, respectively. These materials have shown the cathode behavior superior to the corresponding crystalline ones in lithium cells.

(4) The structure of the newly-prepared amorphous films has been analyzed by the IR, Raman spectroscopy, the x-ray diffraction, and the molecular dynamics. The importance of the structure of the melts, rather than the corresponding crystalline phases, has been demonstrated to understand the structure of the glasses obtained.

Growth of Aluminum Nitride Thin Film

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1. Introduction.

Aluminum nitride (AlN) is a III-V compound with a direct band gap of 6.2eV. AlN thin films have potential use in surface acoustic wave (SAW) devices, blue light emitting devices, passivation and packaging materials, etc., because of its high SAW velocity, high thermal conductivity, and thermal expansion coefficient which is equal to that of GaAs and Si. We have investigated the growth of epitaxial AlN films on α-Al_2O_3 and Si substrates, and developed zero-temperature coefficient SAW devices.[1)]

In this research project, AlN thin film growth technologies are investigated under the following three subjects.

(1) Relaxation of the large lattice mismatch between AlN epitaxial film and α-Al_2O_3 substrate (about 13%),
(2) Low temperature growth, and
(3) Higher purification of CVD environment and source materials.

In this year, we optimized an epitaxial growth of AlN with an initial nitriding layer, in order to relax the large lattice mismatch. We deposited high purity epitaxial layer using TMA with low oxgen content.

2. Results and Discussion

AlN films were grown on $(01\bar{1}2)\alpha$-Al_2O_3 substrates using MO-CVD which involves a chemical reaction between trimethylaluminum(TMA) and ammonia(NH_3). We have developed an epitaxial growth technology with an initial nitriding layer.[1)] In this year, we have optimized the initial nitriding conditions of nitriding pressure, nitriding temperature, and nitriding duration. The half width of the X-ray rocking curves of AlN epitaxial films with initial nitriding layer under 5torr of NH_3 was smaller than AlN films with initial nitriding under atmospheric pressure. We found the optimum initial nitriding condition was 5torr of NH_3, 1200°C, and 5min.

The conventional TMA contains about 50-100ppm oxgen, which degraded the crystal quality. We found that AlN epitaxial films using the high purity TMA with low oxgen content of 2ppm exhibited the higher crystal quality than that using the conventional TMA. High purity TMA should be used in order to obtain a high purity and high quality AlN films.

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Crystal Growth and Optical Properties of Wide Band-Gap Semiconductors

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1. Introduction

GaN, $Al_xGa_{1-x}N$ and ZnS_ySe_{1-y} are promising for photonic devices in the spectral region of blue through ultraviolet. It has been fairly difficult, however, to grow high quality crystal as well as to control their optical and electrical properties. The hetero-epitaxial growth and optical and electrical properties of these wide band-gap semiconductors are studied.

2. Results and Discussion

High-quality GaN film with a smooth surface free from cracks can be grown successfully on sapphire C and A substrates by MOVPE using a thin AlN buffer layer. The most essential role of the buffer layer is found to be (i) the supply of the nucleation sites with the same crystal orientation as the sapphire and (ii) the promotion of the lateral growth oh GaN due to the decrease in an interfacial free energy between the sapphire and the GaN film.

The FWHM of X-ray diffraction profile for the GaN film is much reduced and the optical and electrical properties can be remarkably improved by this process.

From the measured strain and the shift of PL peak energy, the deformation potential of GaN is found to be 12eV for the first time.

For the efficient formation of blue EL centers, it is found that, GaN film doped with Zn must be grown on sapphire A substrate at temperatures lower than 950℃.

$Al_xGa_{1-x}N(0\leq x\leq 0.4)$ films grown on sapphire C substrate are found to be composed of many mosaic crystallites with various orientations. This fluctuation of orientation can be considerably reduced and the surface morphology of the film can be remarkably improved by the AlN buffer layer in MOVPE.

The hetero-interface of $ZnS_ySe_{1-y}(0.45\leq x\leq 1.0)$ grown on GaP by VPE is studied by Raman Spectroscopy. The hole prasmon-LO phonon coupled mode is observed near the hetero-interface in samples with smooth surface morphology. The holes of such a high density are probably due to Zn atoms, which are introduced during the growth.

Impurity doping effects on the growth behavior of II-VI compound semiconductor epitaxial layers

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1. Introduction

Although II-VI compound semiconductors are promising materials for optoelectronic devices, the growth mechanism of these epitaxial layers is not fully understood. This research is intended to investigate the impurity doping effects on the growth rate and the crystallinity of ZnS and ZnSe epigrown layers in order to make clear the principal factors controlling the growth mechanism of these layers.

2. Results and Discussion

ZnS and ZnSe layers were grown on GaP and GaAs substrates by using a hydrogen-transport vapor phase method. The effects of iodine-doping on the hetero-epitaxial growth of ZnSe on (100) and (111)B GaAs substrates were investigated. In case of the low values of iodine transport rate, a remarkable increase in growth rate on both the substrate planes was found. These phenomena will be attributed to the generation of more volatile reactive materials including zinc iodide. At the same time, the change in the limiting factor of the ZnSe growth mechanism from surface reaction process to the thermodynamical equilibrium one will be suggested. Similar iodine-doping effects on ZnS epilayers on GaP were also obtained.

The influences of the substrate materials upon the growth rate of the ZnS layers were also studied. The growth rates of the layers on GaP and GaAs were found to be strongly influenced by the Ga auto-doping. These phenomena were ascertained by the experimental fact that the growth rate on (111)A decreased and that on (111)B increased by the addition of Ga atoms to the reactant vapor. These Ga-doping effects showed nearly the same behaviors with those of In-doping for the growth of ZnS.

MBE growth of II-VI Semiconductor Mixed Crystals

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1. Introduction

ZnS_xSe_{1-x}, which is a promising material for blue light emitting devices, can be lattice-matched with a GaAs substrate but has large mismatch in thermal expansion coefficient. Therefore the lattice-matching compositions were 0.06 at room temperature (x_{rt}) and 0.08 at growth temperature (340°C)(x_{gt}). In this study, MBE-ZnS_xSe_{1-x} (x=0~0.13) on GaAs(100) subsrates were evaluated in order to determine the optimum lattice-matching composition. Also, the photon energies which were effective in the photo-assisted MBE growth were investigated.

2. Results and Discussion

The observation of the surface morphology by Nomarski microscope revealed that the extremely smooth surface was obtained at the lattice-matching composition x_{gt}. The half width (FWHM) of X-ray rocking curve took a minimum at the composition x_{gt} in spite of the thermal strain (two dimensional tensile strain).

The fluorescence microscopic study on the (110) cleavage plane of the epilayers were performed at room temperature. The epilayers with the composition from x_{rt} to x_{gt} had the uniform violet luminescence over the thickness, while the epilayers with other compositions had orange emissions just at the epilayer-substrate interface. The origins of these orange emissions were tentatively ascribed to the SA centers assosiated with diffused Ga from the GaAs substrates. The Ga diffusion is considered to be enhanced by the lattice mismatch.

Considering the above results, the epilayers with the lattice-matching composition at growth temperature have the highest crystallinity despite the thermal strain due to the large difference of thermal expansion coefficient.

In the photo-assisted MBE growth, a Hg-Xe lamp was used as an irradiation source and the photon energies were selected by low-pass filters.

The increase in the free exciton emission intensities in photoluminescence was observed and the surface morphologies roughened slightly when the irradiated photon energies were larger than the band gap of the epilayers. It is considered that the photon absorption or electron-hole pair generation in the growing surface play an important role in the MBE growth of ZnSSe.

HETEROEPITAXIAL GROWTH OF WIDE GAP COPPER CHALCOPYRITES AND ZINC SULFIDE

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1. Introduction

The heterojunction formation using $CuGaAlS_2$ and ZnS offers an interesting approach for obtaining optoelectronic devices in the short wavelength region of the visible spectrum. This research concerns with vapor phase epitaxy (VPE) of $CuGaS_2$ using metal chlorides and H_2S, and with conductivity control of VPE ZnS.

2. Results and Discussion

The vapors of metal chlorides controlled by respective source temperatures were transported together by carrier gas Ar to the reaction zone in a furnace, and then mixed with the gas stream of H_2S+Ar. X-ray diffraction studies showed that the epitaxial growth of single crystals with chalcopyrite c-axis normal to the substrate GaAs(100) face can occur in spite of a large difference in the layer and substrate lattice constants. In the case of ZnS/GaAs substrates, the growth with c-axis parallel to the substrate (100) face was dominant. Studies on X-ray diffractions, Raman scattering, photoluminescence and atomic composition by EPMA indicated the necessity of further efforts for improvements in layer uniformity which is possibly related to local off-stoichiometry.

The low resistivity p-type conduction has been observed for the first time in VPE ZnS layers on GaAs grown from a ZnS powder source using an open tube system under simultaneously NH_3 and Zn added condition. The p-type behavior of the layer has revealed either by the sign of Seebeck voltage, a Hall-effect measurement, or I-V characteristic between the layer and substrate. Crystallographic and optical studies provided the confirmation that the p-layer grown is really composed of nearly stoichiometric ZnS.

STUDY on EPITAXIAL GROWTH of NARROW GAP II-VI SEMICONDUCTORS

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1. Introduction

MBE and MOCVD epitaxial growth techniques have been studied for Cadmium Mercury Telluride (CMT : $Cd_xHg_{1-x}Te$) films, for the purpose of applying them to high-speed electronics.

2. Results and Discussion

(1)MOCVD of HgTe

Based on the atmospheric pressure MOCVD technique,using novel metal-organic gas, DTBT, we have set up a low-pressure MOCVD system. The system has a small loading mechanism. Air-operated valves controlled by personal computer are connected for the purpose of quick change of source gases. Sufficient amount of mercury gas has successfully introduced into the chamber by heating its specially designed gas controlling system to about 300°C. Epitaxial growth experiment has been started recently.

(2)Preliminary Experiment of MBE growth of HgTe

Conventional MBE growth of HgTe needs more than 100g of metallic mercury for each run. This causes results in inferior film quality. We have thus carried out, this year, a preliminary experiment to reduce the mercury gas flow rate by activating metallic mercury.

Specially designed ion source having hot tungsten cathode and coaxial magnets is attached to the simple evacuation chamber. The discharging current as high as several hundreds mA at voltage less than 100V has been obtained at pressure of about 10^{-4} Torr. HgTe films have been deposited by evaporating Te atoms near the substrate. It was found that activation of Hg by plasma is very effective for introducing Hg atoms in the film.

(3)CdTe/InSb Hetero MIS Transistor

Good interface properties of MBE grown CdTe/InSb structure had been evaluated by C-V method last year. The detailed process technology has been studied, this year, for fabricating MIS-type field-effect transistor having CdTe/InSb structure operating at liquid nitrogen temperature. The device structure has been fabricated, but the device shows only a small drain current change. Origin of the unexpected results is now under investigation.

GROWTH OF ZnSe CRYSTAL AT LOW TEMPERATURE UNDER CONTROL OF ATOMIC HYDROGEN

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1.Introduction

The control of the non-equilibrium processes are required for the crystal growth from the gas-phase on the substrate kept at low temperature as far as possible. Primary aim of this study is to develop a novel preparation technique for the II-VI compound thin films, e.g., ZnSe or ZnTe, on GaAs(100) with the ability to make their thin films on the substrate at low temperature from organometallic compounds such as diethyl zinc (DEZn), diethyl selenium(DESe) and diethyl tellurium(DETe), under the control of the reactive plasma and the flow of atomic hydrogens.

2. Results and Discussion

High quality ZnSe thin film was epitaxially grown on the GaAs(100) substrate at about 200 °C with this novel technique using atomic hydrogens which are effective for either the decomposition of DEZn and DETe or for cleaning the surface. Resulting from the kinetic analysis, we proposed a mechanism based on the quasi-chemical equilibrium consisting of two processes, e.g., the equilibrium between adsorption and desorption and the reaction for production of compound (ZnSe, or ZnTe) on the substrate. The negative activation energy found in the deposition of both ZnSe and ZnTe gives a support to this idea. A coherent growth was observed on GaAs(100) substrate of over 1 μm thick for ZnSe and not for ZnTe depending on the amount of the lattice miss-match by virture of the lower substrate temperature. The blue emission attributed to the recombination of the free excitons was observed in the ZnSe. Doping feasibility was successfully established for n-type film by mixing triethyl aluminum, namely, the mobility of160 cm^2/Vs and carrier concentration of $1.3x10^{18}$ cm^{-3}.

Homoepitaxial Growth of ZnTe by MOCVD Method and Analysis of Growth Mechanism

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1. Introduction

This report describes the in-situ gas analyses using the quadrupole mass spectrometer and ultraviolet spectrometer during the ZnTe epitaxial growth by low-pressure MOCVD method. Here the pyrolysis properties of source materials (DETe and DMZn) are investigated as a function of stage temperature or pressure in the chamber when He or H_2 was used as a carrier gas.

2. Results and Discussion

The gas sampling and anlysis using the mass spectrometer was carried out. The results are surmmerized as follows;

(1) The pyrolyses in DMZn and DETe begin around 350℃ and around 400℃ for H_2 carrier gas, respectively. On the other hand, for He carrier gas the temperature at which the pyrolyses in these materials begin is higher by about 50℃ than that for H_2 carrier gas. Hence, it is considered that DETe is more stable than DMZn, and H_2 plays an important role in the pyrolysis.

(2) The reaction products are identified and it is found that these gas densities decrease in the following order: $CH_4 \geq C_2H_6 >> C_3H_8, C_4H_{10}$ in the case of H_2 and $CH_4, C_3H_8 >> C_4H_{10}$ in the case of He.

Next, the measurement of DETe absorbance was carried out and its pyrolysis property was analyzed using the simple model.

(3) The activation energy can be estimated around 33 kcal/mol. This value is near the activation energy estimated from the relation between the growth rate and substrate temperature.

(4) The model used here explains well the experimental results such as the pressure dependences of absorbance and growth rate.

An Investigation of Crystal Growth by Molecular Beam Epitaxy of II-VI Compound Semiconductors and Its Mechanism

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1. Introduction

Zinc selenide (ZnSe), one of the II-VI compound semiconductors, is a promising material for blue-light emitting devices. Crystal growth of ZnSe by the molecular beam epitaxy (MBE) method was performed using (100) GaAs substrates. The evaluation of epitaxial layers with different thicknesses has been made by the double-crystal X-ray diffraction technique.

2. Results and Discussion

After substrates were heat-treated at 600°C for 20 minutes under ultra-high vacuum, epitaxial ZnSe layers with different thicknesses were grown at 330°C. The layer thickness was varied by changing molecular beam flux and deposition time. The crystalline quality of these layers was evaluated by measuring rocking curves, layer curvatures and lattice spacing.

The full width at the half maximum (FWHM) of the (400) Bragg peak was about 90" for very thick ($\sim 6.4\,\mu$m) layers. This is a fact indicative of a high crystalline quality. The FWHM increases with decreasing the thickness and becomes a maximum at a thickness of 1-1.5 μm. The maximum value was about 270". As the thickness decreases further, the FWHM decreases again and amounts to less than 100" at a thickness not more than 0.2 μm. The FWHM depends also, to a great degree, on the curvature of epitaxial layers, that is, layers with lower FWHM values are convexly bent to the growth direction remarkably, but those with larger values only a little. It is suggested that the high crystalline quality has been obtained by the lattice match due to the layer bending. The difference of the (400) Bragg angle between GaAs and ZnSe increases abruptly at a thickness less than 0.2 μm, indicating that the lattice spacing of ZnSe along the growth direction is extended, but the spacing in the interface plane matches that of GaAs. This result is consistent with the results for the FWHM and curvature.

The high crystalline quality of thin ZnSe layers was confirmed also with the observation of photoluminescence spectra.

Crystal Growth and Defect Control of $AgGaS_2$

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1. Introduction

A ternary chalcopyrite-type compound semiconductor $AgGaS_2$ is expected as one of the new candidate materials for blue emitting diode and non-linear optics. The purpose of the present study is to grow high-quality large single crystals and to evaluate the lattice defects of the crystal for future applications.

2. Results and Discussion

The single crystals have been grown from the melt by the Bridgman method and from the vapor by the iodine chemical transport method. By researching the detailed growth conditions, transparent yellow single crystals of $10\times5\times3\times10^{-9}$ m^3 and $6\times5\times2\times10^{-9}$ m^3 were obtained, respectively as the biggest size with good quality.

From photoluminescence(PL) spectra at 4.2K of the crystals grown by the Bridgman method and heat-treated under various sulfur vapor pressures (P_{S_2}), the emissions increasing or decreasing their intensities with increasing P_{S_2}, were found and the native lattice defect responsible for each emission was discussed. Clear band edge-emissions, not reported so far, were observed only for the crystals heat-treated under low P_{S_2}(=0.01 Pa) and excitonic emissions, so called I_1, I_2 and E_x lines, were assigned. In the spectra, three weak emission lines(2.708, 2.715, 2.720eV), probably due to the excited state(n=2) of free and bound excitonic emissions,were found newly in the energy region higher than the energy of free excitonic line(E_x=2.699eV). Emission intensities as a function of the temperature were also measured and blue emission was observed even at room temperature. Same PL behaviors were found for the crystals grown by chemical transport using iodine less than $2\times10^{-3}g/m^3$.

It was found that the dark conductivities for the above two kinds of crystals are extremely low of the order of $10^{-9}\sim10^{-10}(\Omega\cdot cm)^{-1}$ and the dominant shallow levels(0.10eV), probably related with intrinsic defects, are highly compensated with the deep levels(0.7$\sim$0.8eV).

Microscopic characterization of defects in II-VI semiconductors with laser Raman spectroscopy

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1. Introduction

It is very important to make clear various characteristics of II-VI compound semiconductors in order to control them for various electronic and optoelectronic devices. Especially micro-defects in crystal and effects of stress in hetero-structures are needed to be made clear. We are studying characterization of some properties of II-VI materials relating to stoichiometric composition and stress with laser Raman spectroscopy.

2. Results and Discussion

At first we studied the relation between TO phonon intensity and VI/II ratio for ZnSe grown by MOVPE. TO phonon is a forbidden mode for (100) ZnSe and a measure of incompleteness of crystal structure. TO phonon intensity increased with decrease in VI/II ratio when VI/II ratio was smaller than 10. It means that completeness in crystal structure is low when VI/II ratio is small.

The relation between LO phonon frequency of ZnSe-like mode and composition x in ZnS_xSe_{1-x} was studied in order to make clear the effects of stress. The results were similar to those reported before.

Local modes due to carbon in ZnSe were also studied. At first frequencies of the local modes were calculated based on a simple linear chain model. The frequency due to C in Se sites was about 404 cm^{-1} and that due to C in Zn sites was about 401 cm^{-1}. Some peaks were observed in Raman spectra from ZnSe in a region 320-480cm^{-1}. However it is possible that some other modes are included in the region. Therefore it is necessary to study Raman spectra from ZnSe doped with carbon at different concentrations.

Evaluation of defects in the heteroepitaxial films and at the interface of ZnS and ZnSe using transmission electron microscope and optical methods

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1. Introduction

During the last few years, a number of attempts have been made to incorporate shallow donors and acceptors in ZnSe and ZnS to achieve p-n junction. Therefore, the indentification of defects associated with excitonic lines and edge-emission bands, as well as those observed in other II-VI compounds, is a very important subject in the characterization of ZnSe and ZnS epitaxial films. However, there has been very little information available on the principal bound-exciton (BE) lines and edge-emission bands in ZnS by which extrinsic shallow impurities and native defects can be characterized, in comparison with those of ZnSe.

In order to understand basic optical properties of acceptor Na impurity, we describe photoluminescence (PL) properties of Na doped ZnSe and ZnS films grown on (100) GaAs substrates by a low-pressure MOCVD method.

2. Results and Discussion

A doublet structure observed in the neutral-Na-acceptor bound-exciton (I_1^{Na}) emission line has been investigated by the temperature-dependence of photoluminescence spectra. Two-hole transitions appeared under the below-bandgap excitation; the ionization energy of the 1s Na acceptor is estimated to be 102 meV using acceptor central-cell corrections. Dependence of spectral feature of the I_1^{Na} line and of related donor-acceptor pair bands on thermal diffusion conditions was found. It is cofirmed from the presence of a strong I_1^{Na} line that Na was incorporated into a ZnSe layer grown on GaAs substrate at 300 ℃ by low-pressure metalorganic chemical-vapour-deposition (MOCVD).

Electrical and photoluminescence studies were performed for ZnS hetero-epitaxial films doped with I donor and Na acceptor impurities using MOCVD method at about 300 ℃. The ZnS:I film obtained on a (100) GaAs substrate exhibits typically n-type conduction and has extremely low-resistivity of $2\times10^{-3}\Omega$cm at room temperature. The 4.2 K PL spectrum of the n-type layers is mainly dominated by a strong donor-acceptor pair band at about 3.5 eV. On the other hand, a neutral-acceptor Na bound-exciton line at 3.781 eV and Na-related free-to-bound acceptor transition (Kz band) at about 3.68 eV appear in the intentionally-Na-doped films. It has been shown that Na was incorporated in ZnS layers as it can offer the shallow acceptor whose ionization energy is estimated to be about 160 meV.

Characterization of Interface Stress and Defects at II-VI/III-V Compound Semiconductor Heterostructure

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1. Introduction

It is well known that optical spectroscopic techniques are useful for characterization of defects involved in semiconductor materials. We have performed the characterization of compound semicondcutors by using such techniques, in particular luminescence spectroscopy in the recent few years. In this work we have studied the interface stress and defects at OMVPE-grown ZnS_xSe_{1-x}/GaAs heterostructures using the Cr-related luminescence at GaAs substrate and also using the near-band-edge luminescence of the ZnS_xSe_{1-x} epitaxial layers.

2. Results and Discussion

We have systematically investigated the interface stress at ZnS_xSe_{1-x}/GaAs heterostructures in the S composition of 0 - 0.14 %, which were grown on GaAs substrate by organometallic vapor phase epitaxy. As a result of the interface stress characterization by Cr-related luminescence measurements on GaAs at 4.2 K, we have found that the interface stress at these ZnS_xSe_{1-x}/GaAs heterostructures is biaxial compressive stress to GaAs substrate in all S composition range, in spite of the fact that the interface stress changes tensile to compressive at the S composition of 0.06 % for lattice matching between ZnS_xSe_{1-x} and GaAs. This anomalous behavior has been explained by a model that such biaxial stress is due to thermal stress introduced during cooling down from the growth temperature (773 K) which is caused by the difference of the thermal expansion coefficients between ZnS_xSe_{1-x} and GaAs. We have also examined substrate orientation effects on the interface stress, and found that the interface stress is strongly relaxed at (111) heterostructure than (100) heterostructure. This is interpreted in terms of the difference in the stress relaxation by the introduction of misfit dislocations at the interface, and this model has been confirmed by the results of luminescence measurements at the near-band-edge of the ZnS_xSe_{1-x} epitaxial layers which showed the low luminescence intensity in the case of (111) ZnS_xSe_{1-x}/GaAs heterostructures. This result is also in agreement with the observation of the surface morphology on the ZnS_xSe_{1-x} epitaxial layers.

Electronic Structure of 3d Transition Atom Impurities in II-VI Compound Semiconductors

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1. Introduction

II-VI compound semiconductors posses potential importance in application to opto-electronic devices because of their wide variety of fundamental energy gap. Deep impurity levels induced by transition atom impurities are promising candidates to realize, e.g., a blue-color light-emitting-diode. From the theoretical point of view, the lack of reliable electronic structure calculations impedes proper interpretation and prediction of the optical spectra. Thus, first principles reliable calculations are required to predict the variety of physical phenomena inherent in impurities in II-VI semiconductors.

2. Results and Discussion

(1). A unified picture of the electronic structure of Cr impurities in ZnS is presented on the basis of the first-principles spin-polarized Green's function calculations. We found that Cr(+), Cr(++), and Cr(+++) are stable near the substitutional Zn-site with Jahn-Teller lattice distortion. The obtained results on physical properties (donor and acceptor ionization energy, hyperfine coupling constant, g-values and Jahn-Teller distortion) are in good agreement with the available experimental data.

(2). We proposed new calculation method using a norm-conserving pseudopotential and super-cell method within the local spin-density functional formalism. We applied this method to solve the mechanism of the hydrogen passivation in p-type silicon, and gave the unified physical picture to the mechanism of hydrogen passivation.

Thin-film growth and defect control of alkaline-earth sulfides

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1. Introduction

Rare-earth doped alkaline-earth sulfides (II_A-VI_B compounds) are promising materials for full-color thin-film electroluminescent (TFEL) devices. They, however, tend to decompose thermally quite easily, and hence, lattice defects due to sulfur vacancy are generated during thin-film growth. The purpose of this study is to establish thin-film growth method and control lattice defects of the alkaline-earth sulfide thin films. We investigated the growth behaviour of CaS and SrS thin films and proposed the growth mechanism of CaS and SrS thin films. We also investigated EL excitation mechanism of rare-earth doped CaS and SrS TFEL devices.

2. Results and Discussion

2-1. Growth behaviour of evaporated CaS and SrS thin films

The crystalinity of CaS and SrS thin films is improved with substrate temperatures higher than 300°C and sulfur coevaporation. In order to investigate effects of the substrate temperature (T_{sub}) upon the crystalinity of CaS thin films, we measured XPS spectra of S_{2p} core electrons in the evaporated CaS thin films. The experimental results indicate that S atoms in the free state decrease and those in form of CaS increase with increasing T_{sub}. We can, therefore, control sulfur defects by increasing the substrate temperature.

2-2. Growth mechanism of evaporated CaS and SrS thin films

The grown films show specific plane orientations and they change remarkably with increasing substrate temperature. To explain these characteristics, we investigated the thin-film growth mechanism by using a theoretical model of nucleation of CaS and SrS thin films. The theoretical considerations give us the following; (1)The plane with the lowest surface energy tends to grow. (2)Owing to re-evaporation of adsorbed atoms, the planes with lower surface energy become unstable with increasing T_{sub}.

2-3. EL excitation mechanism of CaS:Eu and SrS:Ce,K TFEL devices

We investigated the EL excitation mechanism experimentally and also developed a theoretical model.

Study on the Controls of Lattice Defects in I-III-VI_2 Semiconducting Compounds

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1. Introduction

The I-III-VI_2 semiconducting compounds have recently received considerable attention because of its potential uses. However, these materials are backward in research and development compared with the II-VI compounds, especially in the area of the lattice defects. This work is a fundamental study on the lattice defects in ternary semiconductors centering around the I-III-VI_2 (I:Cu,Ag; III;In,Ga,Al; VI;S,Se,Te)compounds.

2. Results and Discussion

We have made a comparison of the carrier concentration dependence of Hall mobility between several $CuInSe_2$ samples doping with various impurities, i.e. In, Cd, Zn for n-type and Se for p-type. It was found that the effect of doping on the lowering of mobility is large in order of In, Se, Cd, Zn, the tendency of which is consistent with the effect on the energy gap.

We tried to grow the epitaxial films of $CuGaS_2$ and $CuGa_{1-x}Al_xS_2$ on GaAs substrate by the methods of vapor phase deposition and solution growth. The photoluminescence(P.L.) spectra of the films obtained showed emission bands at 2.4 eV and 2.8 eV at liquid nitrogen temperature and 2.3 eV at room temperature, though the grown films were likely Ga_2S_3.

We have studied on the phase diagram, optical absorption and P.L. spectra and electrical properties of $CuGa(S_{1-x}Se_x)_2$ system for $x \geq 0.1$. It was found that both the P.L.intensity and the electrical resistivity increase by an annealing in vacuum and decrease by the succeeding annealing in S or Se vapor. The following annealing in vacuum again increases the P.L. intensity and the resistivity for the S-treated samples but not for the Se-treated samples.

The Hall mobility of the $CuGa(S_{1-x}Se_x)_2$ system shows a maximum at x=0.5 in the compositional dependence, in contrast to the tendency expected from the alloy scatterng theory.

We have studied on the optical properties of Cd_xInGaS_{3+x} system and found materials exhibiting blue, green, orange and red P.L., depending on the composition x and the method of preparation.

Optical Properties in I-III-VI_2 Semiconductors Controlled by Doping of Transition Elements

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1. Introduction

There is a growing interest in chalcopyrite type I-III-VI_2 semiconductors as materials for optoelectronic devices with new functionality. However, number of problems are to be solved to provide them for practical use: e.g impurities and defects.

Transition atom impurities have been known to introduce serious effects on the optical properties of the ternary system. The present investigation aims at a systematic research from both experimental and theoretical view points on optical properties of transition atoms in the ternary semiconductors in order to get some perspective to control optical properties by using transition atoms.

Single crystals of undoped $CuGaS_2$ and $CuAlS_2$ were grown by the chemical vapor transport technique. Chemical analysis of these crystals revealed that trace iron impurities amount to the order of 100 ppm in these crystals, which result in coloration in green($CuGaS_2$) and blue($CuAlS_2$) due to the existence of strong photoionization transitions associated with iron impurities. These crystals show sharp photoluminescence line in the infrared region, i.e. 0.61 eV in $CuGaS_2$ and 0.72 eV in $CuAlS_2$. These PL lines (hereafter referred to as IRPL) have been assigned to the ligand-field transition in the $3d^5$ manifold of Fe^{3+} ion. To get further information on the PL characteristics we measured excitation spectra, decay characteristics, and alloying effect of IRPL.

2. Results and Discussions

(1)Excitation Spectra of IRPL

The excitation spectra of the IRPL in both crystals showed well-defined threshold at the same energy position as the threshold of photoionization absorption bands in Fe-doped crystals. However, the shapes of the excitation spectra were much different from that of absorption spectra. Absorption spectra show two distinct peaks at 1.2 and 1.8 eV in $CuGaS_2$ with 1.2 eV peak dominating, while the PL excitation occurs much more efficiently at 1.2 eV than at 1.8 eV. The similar situation is also observed in $CuAlS_2$. It is concluded from these experiments that the lower energy peak in the photoionization absorption spectrum is associated with the deep level of 3d nature and the higher one of the dangling-bond hybrid nature.

(2)Decay Characteristics of IRPL

Time-decay characteristic of the IRPL was measured at 20 K using a pulsed xenon lamp and a boxcar integrator. The decay time was 1 ms and 0.63 ms for $CuGaS_2$ and $CuAlS_2$, respectively. This fact suggests a possibility of application of $CuGaS_2$:Fe to a solid state laser material.

(3)IRPL in $CuAl_xGa_{1-x}S_2$ Alloy

Since the infrared PL is associated with a localized Fe center it should show influence of local atomic arrangement surrounding the Fe ion. We, therefore, measured PL spectra in $CuAl_xGa_{1-x}S_2$ alloy. PL spectrum of the alloy is not a sharp line as in the extreme composition but a broad band with fine structures. The spectrum was decomposed into five lines, each of which is associated with either of five possible atomic arangements, assuming that the iron impurity subsitutes the Al or Ga site. On the other hand, if the iron impurity substituted the Cu-site the PL structure would have nine peaks instead of the five peaks. It is thus determined Fe substitutes group III site in $CuAl_xGa_{1-x}S_2$ alloys.

Electronic Properties and Luminescence Processes in II_A-VI_B Compound Semiconductors

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1. Introduction

The II_A-VI_B semiconductors are compound crystals formed between alkaline-earth metals (Mg, Ca, Sr, Ba) and chalcogenes (O, S, Se, Te). These crystals have been known as useful phosphors and thermionic semiconductors, and more recently as high efficiency color CRT phosphors and multicolor EL films. The aim of this research plan is to provide fundamental knowledge on electronic properties and luminescence processes in typical II_A-VI_B binary compound semiconductors. The emphasis of the study in this year was placed upon the following subjects; (1) preparation of well qualified single crystals of CaS, SrS, and related compounds, either undoped or doped with specific impurities, by means of a floating-melt-zone method developed before by this group, (2) systematic measurements of optical spectra, such as absorption, luminescence, and photoconductivity, on these crystals.

2. Results and Discussions

The major results obtained in the period from April 1988 till now are summarized as follows.

[1] The nominally pure crystals of CaS and SrS are transparent in the visible region, but are colored after a heat treatment in the vapor of component metals, such as Ca for CaS or Sr for SrS, at about 1800K. From the absorption and luminescence spectra, it has been concluded that the coloration is due to the formation of color centers, that is, cation vacancies which trap either two electrons (the F center) or one electron (the F' center). The visible absorption bands are predominantly due to the F center, where as the luminescence bands at about 1.5 eV in both CaS and SrS are due to the transitions in the F' center. A mechanical deformation of crystal gives rise to a conversion of the F centers to the F' centers.

[2] The characteristic broad luminescence bands are induced by doping of isoelectronic impurities, such as Se or Ba, in CaS and SrS. It has been suggested that photo-generated excitons are effectively localized at these impurities by the combined effect of exciton-lattice interaction and the short-range impurity potential, although these excitons are free from the localization in the pure crystals.

CRYSTAL GROWTH AND MAGNETO-OPTICAL STUDY OF SEMIMAGNETIC SEMICONDUCTORS

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1. Introduction

The objective of present research is the growth of bulk and thin-film semimagnetic semiconductors and their characterization for new magneto-opto-electronic applications. Semimagnetic semiconductor is a mixed II-VI compound semiconductor containing Mn or Fe ions in cation sites, which shows remarkably enhanced magneto-optical properties.

We develop "hot wall epitaxy (HWE)" method for the growth of thin films and superlattices of $Cd_{1-x}Mn_xTe$. HWE is expected to realize high quality epitaxial films of semimagnetic semiconductors. Obtained specimens are investigated by picosecond luminescence spectroscopy and Raman scattering. Study is made on both basic properties and application of these semimagnetic semiconductors.

2. Results and Discussion

1) Time characteristics of the exciton luminescence has been investigated by picosecond time resolved spectroscopy. Extremely fast time variation is observed in the early stage of the exciton luminescence of $Cd_{1-x}Mn_xTe$ with $x=0.1-0.3$, which is found as an evidence of the magnetic polaron formation due to the exchange interaction of the excitons with the Mn ions.

2) A Faraday rotator operating in red light region at room temperature has been fabricated using $Cd_{1-x}Mn_xTe$ of $x=0.38$. By varying the Mn concentration, it is possible to produce the Faraday rotator or the optical isolator in wide visible light region, which will be useful in coming optics communication and high-density optical recording by visible laser diodes.

3) HWE has been developed using the newly designed HWE furnace. Thin films of CdTe have been successfully grown, which exhibit high yield exciton luminescence. Epitaxial growth of $Cd_{1-x}Mn_xTe$ is under progress.

Study on Luminescent Properties of II-VI Compound Semiconductors

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1. Introduction

Systematic studies on the growth of high-quality crystals and their luminescent properties are indispensable for the development of opto-electronic devices using II-VI compounds. In this respect we purpose

1) photo-assisted MBE growth of ZnSe to control native defects inherent in II-VI compounds and to obtain high-quality crystals, and

2) pico- and femtosecond spectroscopy to study nonlinear relaxation processes of electron-hole system in II-VI's.

2. Results and Discussion

1) ZnSe thin films were grown under the irradiation of UV light from a He-Cd laser at 325nm (3.81eV). RHEED pattern during the growth, surface morphology after the growth, and photoluminescence properties at 4K lead to the facts that the UV light irradiation enhances the migration of atoms and/or molecules on the epilayer surface, resulting in the increase of the growth rate. This result can be ascribed to either or both of the following two mechanisms; dissociation of selenium molecules caused by the UV light results in the increase of the effective density of selenium atoms in the vicinity of the epilayer surface. And also the interaction of impinging atoms (molecules) with the surface atoms on the epilayer which are in the excited state should differ from what occurs during conventional growth. Further experiments in which these two mechanisms affect separately to the growth are necessary to clarify the photo-irradiation effects in detail.

2) The occurrence of higher-order Fourier components in an originally sinusoidal free-carrier index grating produced in CdS by interference of two picosecond light pulses is demonstrated by monitoring simultaneously the temporal behavior of the first- and second-order diffraction intensity of transparent probe pulses for the temperature range from 10K up to 140K.

Nonlinear processes which take part in the decay of photoexcited carriers result in a deformation of the shape of the grating, which leads to the occurrence of higher-order Fourier components in the diffraction grating. Theoretical analysis of the experimental results yields the following processes; bimolecular recombination of electrons and holes for degenerate plasma, free carrier-to-exciton Mott transition for nondegenerate plasma at low temperatures, and nonlinear relation between exciton density and free carrier density at high temperatures.

"Wide Gap Semiconductors at Extreme Conditions"

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1. Introduction

In the view of seeking a possibility to apply the experimental knowledge to the field of optoelectronics especially in short wavelength region, we have been studying the basic properties of wide gap semiconductors, the I-VII, II-VI compounds materials such as AgCl, AgBr, $AgCl_xBr_{1-x}$, CdS, CdSe, $Cd_xMn_{1-x}Te$, Cu_2O at extreme conditionsas at low temperatures, intense magnetic and electric fields and even at high density excitations.

2. Results and Discussion (Preliminary stages)

We have performed the following experiments;

1) Optical studies such as absorption and luminescence due to polarons and excitons in AgCl, AgBr, $AgCl_xBr_{1-x}$ particularly from the viewpoint of evaluation of degrees of purity and imperfection,

2) Time-resolved luminescence studies of AgBr and $AgCl_xBr_{1-x}$ in the nanosecond region to clarify the relaxation mechanisms of polarons, excitons and also excitonic molecules down to 500 mK, and

3) Nonlinear transport phenomena and population inversions of carriers in AgCl AgBr, $AgCl_xBr_{1-x}$ and CdS by studying transient photoconductivity at intense crossed electric and magnetic fields. Similar studies also on the II-VI compounds have been found to be of considerable interests.

As an extension stage of this project, we have refined to further develop our area to cover the one for the II-VI compounds especially also a new study started on Cu_2O.

Anderson Localization and Gigantic Optical Nonlinearity of Excitons in Compound Semiconductor

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1. Introduction

Exciton is an elementary excitation which is made of coherent superposition of atomic excitations in solids. Large nonlinear response to the coherent laser light may be naturally expected to come from coherent excitations of these excitons. The exciton in an ideal crystal has a macroscopic transition dipolemoment, but it is an ideal harmonic oscillator so that it cannot show any nonlinearity in itself. On the other hand, the bound exciton localized at impurities has mesoscopic transition dipole moment and can show large optical nonlinearity. Therefore we try to search for the optimum condition to get the large and quick nonlinear optical response.

2. Results and Discussion

As the first step toward the study of the Anderson localization of the exciton, we study the effects of its precursor on the nonlinear optical response. Polaritons are formed by diagonalization of the strongest exciton-photon interaction. One of these polaritons suffers from multiple elastic scatterings by impurities. Here this process and its time reversal process interfere constructively, resulting in a weak localization of the polariton. This is the precursor to the Anderson localization. On the other hand, phase-conjugated wave is time-reversal propagation of the probe light under optical pumping of two colliding pump waves. We have just shown that the generation of the phase-conjugated wave is very much enhanced by the weak localization of the polariton as long as the inelastic life time of the polariton is much longer than the scattering time[1,2]. This result looks reasonable because two concepts come from the same time-reversal symmetry of the system. We have also discussed how to observe this enhancement.

As the next step in the future, we will show how this weak localization of the polariton proceeds to the Anderson localization and how this localization enhances the optical nonlinear response.

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Investigation of the effect on energy transfer and local crystal field to the electroluminescence center

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1. Introduction

In the field of photoluminescence, energy transfer process from the excited-center to the emission center and the effect on the local crystal field to the luminescenct center are well investigated in oder to increase efficiency of the luminescence. However, as these foundamental phenomena of the electro-lminescence were not yet well understood, the mechanism of electroluminescence will be made more clear through the investigations on the energy trasfer and the local crystal structure of the luminescent center in this research.

2. Results and Discussion

The ZnS:Tb,F films were prepared by rf-sputtering in a mixture of 60%-Ar and 40%-He. The crystallinity and luminescent property were studied as a function of the gas pressure during film growth. The experimental results have shown that the gas pressure has the strong effects on the cystallinity and luminescent property.

We have some other results about the luminescence of Tb,for examples,energy transfer from ZnS to Tb in ZnS : Tb phosphor,large improvement of brightness at high temperature in La PO_4 : Ce,Tb,and ECR plasma MOCVD method is taking to make more efficient films.

We have also been made red-emintting CaS:Eu thin films by sputtering . The utilization of sputtering techonolgy as a film growth method is mainly due to the low temperature processing. In fact the films fabricated at the substrate temperature less than 300℃ have luminance exceeding 300 cd/m^2 at 1 kHz drive, the value of which is hinger than that in those prepared by vacuum evaporation.

We are proceeding to make several rare earth doped ZnS,CaS and SrS thin film by rf-sputtering, ECR plasma MOCVD, and EB methods, to investigate the relations between photoluminescence and crystal quality including local imperfections using time resolved and fine spectroscopy,and to compaer the photoluminescent results with electroluminescence phenomena.

Optical Properties of Compound Semiconductors at High pressure and Low Temperature

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1.Introduction

Lattice and electronic properties of compound semiconductors (ZnSeS, CdMnTe, AlGaN and Chalcopyrite) have been studied by measurements of X-ray diffraction, Raman scattering, optical absorption, photoluminescence, PAS, DLTS and ICTS as a function of pressure, temperature and alloy composition.

2. Results and Discussions

2-1 MOCVD growth and characterization of ZnSe, ZnS, and ZnSeS, compound semiconductors of ZnSe, ZnS and ZnSeS were prepared onto GaAs substrate heated at 350 C by MOCVD method. The lattice and electronic properties were studies by X-ray diffraction patterns, Raman spectra, optical specter, PAS, DLTS and ICTS. It is shown by measurements of ICTS emission signals in Schottky diodes (Au/n-ZnSe=In/i-GaAs)as a function of pressure that the emission rate (en) decreases by a factor of 103 with increasing pressure to 1.5GPa and the deep level concentration (NT) decrease by a factor of 10, The activation energy decrease from 0.75eV to 0.65eV. The capture cross section a increases by a factor of 10.

2-2 The luminescence lines observed in single crystal $Cd_{1-x}Mn_xTe$ are assigned as (A^0,X) line and D-A pair emission by the dependence of excitation intensities and the analogy with the results in CdTe.

2-3 The Raman spectra in GaN of single crystal and thin films on sapphire substrate are observed. In single crystal grown under high pressures of N_2 there is no LO line but in thin film it is observed. It is considered that this LO line is enhanced by the interface of GaN and sapphire substrate. In mixed compound AlGaN the width of TO line increases with increasing Al concentration by the mixing of different bonds. But there is no shift in energy (persistence type).

Crystal Growth and Conductivity Control of II-VI Compounds from Solution

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1. Introduction

Zinc sulfide and zinc selenide are promising materials for solid state blue light emitting devices because of their wide band gap. To produce high efficient LED's it is necessary to get n and p type of high conductivity. However self-compensation and/or residual impurities makes it difficult to control its electric conductivity type by impurity doping. The object of this work is to grow II-VI compound crystals from solution in quasi-thermal equibrium to control conductivity by preventing generation of intrinsic defects or using high purity source materials. When the element of solvent is different from the chemical composition of the crystal, the atom will be mixed into the crystal to the solubility limit as impurity. In this work chalcogenide is selected as solvent, such as Sb_2Te_3 or Sb_2Se_3. It has lower vapor pressure at growth temperature and higher solubility of ZnS or ZnSe than chalcogens, such as Te or Se. Moreover, if an atom of Vth group of element substitute the atom of VIth group of element in the II-VI crystal, it will work as an acceptor impurity.

2. Results and Discussions

ZnSe is grown from Sb_2Te_3 , Sb_2Se_3 and $(Sb_2Te_3)_{0.82}$-$(Sb_2Se_3)_{0.12}$. ZnSe grown from Sb_2Te_3 took in atoms of solvent as impurities at higher concentration than the other solvents. The lattice constant of ZnSe grown from Sb_2Te_3 is larger than the source powder ZnSe. The color of the ZnSe grown from Sb_2Te_3 is orange and XMA shows the existense of Sb and Te as impurities in the crystal. In photoluminescence spectrum at 4.2K of grown Sb_2Te_3, there is a green emission band peaking at 530nm which originates in the cluster of Te substituted S.

ZnS grown from Sb_2Te_3 has larger lattice constant than ZnS grown from Te solvent. However, it shows the same photoluminescence spectrum at 4.2k as ZnS from Te. There are no signals from Sb or Te in the crystal grown from Sb_2Te_3, so the concentration fo Sb or Te is less than 0.1mol% at the highest. ZnS grown from Sb_2Te_3 shows n type photoconductivities, however, no p type conductivity yet.

The behavior of ZnS or ZnSe grown from Sb_2Te_3 sugest that if acceptor impurity is added into Sb_2Te_3, it will be incorporated with grown crystal at higher density than now.

Control of Electrical Conductivity of Wide-Gap II-VI and I-III-VI_2 Compound Semiconductors

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1. Introduction

The purpose of this project is to attain the control of electrical conductivity of ZnSe over a wide range without any cost of degradation of the optical properties. This report describes (a) the doping of In as a donor impurity, (b) the doping of N as an acceptor impurity and (c) the characteristics of ZnSe/GaAs heterostructure.

2. Results and Discussion

In-doped ZnSe layers were grown by supplying In vapor during the low pressure VPE of ZnSe. The growth pressure was 1×10^{-4} Torr and grown layer thickness was $3 \sim 5$ μm. The carrier concentration increased with increasing In cell temperature and was controlled in the range of $5 \times 10^{15} \sim 2 \times 10^{18}$ cm^{-3}. When the In cell temperature was higher than 500°C, ZnSe layers were of high resistivities and deep level emissions appeared in PL spectra. A sample with a carrier concentration of 5×10^{15} cm^{-3} had a low temperature mobility as high as 8000 $cm^2/V \cdot s$.

N-doped ZnSe layers showed residual donor bound exciton emission (I_x) in addition to N acceptor bound exciton emission (I_1^N). The intensities of the two lines were investigated as a function of the VI/II ratio during the epitaxial growth, and the following results were obtained. The origins of residual donors responsible for the I_x line were lattice defects at the Se site (group VII impurities and/or Se vacancies) for low VI/II ratios and lattice defects at the Zn site (group III impurities) for high VI/II ratios.

Misfit strain in ZnSe layers grown on GaAs(100) substrates were measured in the temperature range of $80 \sim 800$ K for layer thicknesses of $0.2 \sim 4.0$ μm by X-ray diffraction. Layers as thin as 0.2 μm grow coherently on the substrate and the coherency held even at low temperatures. Strain free layers at room temperature including the two-dimensional expansive strain of 0.03 % at 80 K, and layers including the two-dimensional compressive strain of 0.03 % at room temperature became strain free at 80 K. The X-ray analysis was consistent with low-temperature optical reflection spectra.

The ZnSe/GaAs heterointerface was investigated by C-V and DLTS technique. The carrier accumulation and depletion regions were observed at the heterointerface. New electron emissions with activation energy of $0.6 \sim 0.9$ eV were detected near the heterointerface.

Material Control of Widegap II-VI Semiconducting Compounds by MOCVD

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1. Introduction

Widegap II-VI semiconducting compounds, such as ZnSe, are promising candidates for high efficiency blue light-emitting-devices. However, self-compensations due to the effects of intrinsic defects and/or residual impurities make it difficult to control their material properties. The objective of this work is to investigate the way to control the properties of widegap II-VI compounds, especially ZnSe, by MOCVD. In this work, nitrogen- and iodine-doped ZnSe films have been grown by atmospheric-pressure (AP) and low-pressure (LP) MOCVD, respectively, and the films have been characterized.

2. Results and Discussion

AP-MOCVD growth of nitrogen-doped ZnSe

Nitrogen-doped ZnSe films have been grown by AP-MOCVD using a new dopant source, dimethyl hydrazine (DMHz), and the films have been characterized by photoluminescence at 18 K. It has been found that DMHz can be much easily decomposed compared with ammonia. That is, when using DMHz, a lot of nitrogen atoms can be incorporated into ZnSe as shallow acceptors at much lower temperatures and lower dopant flow rates than the case of ammonia. It has been shown that DMHz can be a useful acceptor dopant source for ZnSe alternative to ammonia.

LP-MOCVD growth of iodine-doped ZnSe

Iodine-doped ZnSe films have been grown by LP-MOCVD using diluted ethyl iodide as a dopant source. It has been shown that the carrier concentration in the films can be widely controlled from 10^{15} to 10^{19} cm^{-3}. In the films with carrier concentrations below 10^{18} cm^{-3}, it has been found that the room temperature photoluminescence is dominated by a strong blue near-band edge emission with suppressed deep level emission. It has been concluded that iodine is a superior donor dopant for ZnSe from a standpoint of the controllability and reproducibility of electrical and photoluminescence properties of n-type ZnSe films over a wide range.

Study on Controlling the Conductive Type of ZnSe Using High Purity Single Crystals

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1. Introduction

Zinc selenide, a wide gap semiconducting compound of direct transition type, is one of promising materials for a blue light emitting diode. In spite of many experimental works, a low resistivity p-type single crystal has not grown with good reproducibility. In order to prepare a low resistivity p-type crystal, acceptor type impurities should be incorporated into the high purity single crystals. In this work, we have studied the doping effects of Group I_a elements on the photo-luminescence(PL) spectra and the electrical properties.

2. Results and discussion

We have tried the doping of Li,Na and K into ZnSe single crystals by dipping the crystal in the molten I_a-Se alloys. In the case of Li and K doping, especially Li, strong D-A pair emission was observed in PL spectra and this suggests the incorporation of the alkaline metals into interstitial site which acts as a donor. For the case of Na doping, the I_1^{Na} line was observed clearly and D-A pair line became extremely small. This suggests that Na atoms replace mainly the Zn sub-lattice and it was confirmed that the crystals were p-type, though the resistivity is 10^5 (Ω·cm) and still high. Through the results, it was concluded that Na doping is most suitable in obtaining p-type conduction,and it is necessary to investigate the detailed doping conditions and the after heat-treatments in future.

Exact acceptor levels of Na and K in ZnSe crystals were estimated from selective excitation spectra.

Vapor Phase Epitaxial Growth of p-ZnSe under a Controlled Partial Pressure

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1. Introduction

It is desirable to make highly conductive pn junctions to fabricate an efficient blue LED of ZnSe. It is considered that acceptor impurities can be highly doped under the controlled partial pressures. The vapor phase growth of ZnSe had been investigated to fabricate the blue-LED. This year, we have studied the phosphorus doping effect in an open tube method and the pressure dependence of atmosphere in a closed tube method.

2. Results and Discussion

Open Tube Method The p-type ZnSe had been reported in a previous annual report by a conventional VPE with phosphorus doping. However, it was revealed that p-type ZnSe films were obtained with phosphorus-and-lithium doubly doping. A concentration of Li was unknown. ZnSe films with either P or Li showed high resistivity. When P was transported at various tempertures($T_P = 150 \sim 330$℃), two types of PL were observed. When $T_P \geqq 230$℃, strong SA emission was observed. When $T_P \leqq 210$℃, the edge emission was the main one. RHEED patterns showed the epitaxy when $T_P \leqq 240$℃. It was difficult to obtain the transport rate of phosphorus at low T_P. However, it is clear that the films were doped with P at all T_P since all films showed high resistivity.

Closed Tube Method When ZnSe single crystal is grown with a sublimation method, argon gas is enclosed with the source ZnSe to control the transport rate. The pressure dependence of atmosphere with Ar or H_2 was investigated. T_{source}'s and ΔT's were (1068℃, 940℃) and (21℃, 20℃), respectively. Transport rate decreased with the enclosed gas pressure above 1 Torr. The decrease with use of H_2 was faster than that with Ar. When $T_{source} = 1068$℃, $\Delta T = 6$℃ and ($p_{H_2} = 3$ Torr or $P_{Ar} = 30$ Torr), a single crystal of $5 \times 5 \times 15$ mm in size was grown in 4 days and showed.

Strained-Layer Superlattices for High-Quality Heterointerfaces and Heteroepilayers

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1.Introduction

Heteroepitaxial growth of Zn(S,Se) on GaAs substrates involves serious problems which degrade epilayer qualities, e.g., thermal stress, diffusion of constituent atoms in substrate into epilayers, or defects generation due to lattice mismatch. The objective of this study is to obtain high-quality epilayers by the introduction of strained-layer superlattice (SLS) buffers by which gettering effects against impurity diffusion and barrier effects against dislocation propagation from the underlying layer. Folowing to the results in 1987 that SLS buffers successfully improved the epilayer quality, our research in this year was directed towards obtaining optimum structure of the SLS buffers and fabricating well-defined SLSs with very thin epilayers.

2.Results and Discussion

(1) We fabricated ZnSe(0.6μm)/$(ZnSe\text{-}ZnS_xSe_{1-x})_n$ SLS/ZnSe buffer(1.2μm)/GaAs structure by organometallic vapor-phase epitaxy (MOVPE). With the increase of either x or n, photoluminescence intensity of impurity-related peaks (I and SA) weakened, but that of defect-related peak (Y) became stronger when they exceeds certain values. However for n=2, these defects were not distinctly generated even for higher x. The optimum SLS structure revealed so far was n=18% and x=2, under which both impury- and defect-related peaks appeared fairly weak.

(2) Alternative introduction of Zn and Se beams in organometallic molecular beam epitaxy (MOMBE) results in different pattern in in-situ RHHED, which corresponds to the reconstruction structure of one monolayer of Zn or Se on the growing surface. Layer-by-layer growth became possible by controling the sequence of the source gas flow according to the change in the RHEED pattern during the growth. This technique can be extended for atomic-layer controlled epitaxy of SLSs.

(3) Our research will be continued for new functionality in SLSs and for higher-quality heteroepilayers.

Material properties control of II-VI compound semiconductors using strained-layer superlattices

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1.Introduction

ZnSe, ZnS and ZnTe are semiconducting materials ideally suited for the fabrication of short-wavelength optoelectronic devices. In this study, a new material named strained-layer superlattice(SLS), made up of thin alternating lattice-mismatched layers has been grown and characterized to control optical and electrical properties of wide band-gap II-VI compound semiconductors.

2.Results and Discussion

ZnSe-ZnTe strained-layer superlattices (SLSs) were grown by atomic layer epitaxy (ALE) using molecular beam epitaxy (MBE). In ALE, constituent elements are alternatively deposited on the substrate. It was found that the layer thickness per one cycle of opening and closing the shutters of the constituent elements corresponds precisely to one monolayer growth. We achieved a drastic improvement in the interface abruptness and optical properties compared with SLSs grown by the conventional MBE.

We prepared ZnSe(1-4 monolayers)-ZnTe(1-4 monolayers) SLSs with periods of 200-1000 on InP substrates by ALE at a growth temperature of 260^{o}C which is about 60^{o}C lower than that in conventional MBE. It is interesting to note that the PL intensity of the SLS grown by the ALE is more than ten times greater than that of the SLS grown by the conventional MBE method. The FWHM value of a PL peak for ALE $(ZnSe)_4$-$(ZnTe)_2$ SLSs (70meV) is smaller than that of MBE SLS with an equivalent structure (95meV). Modulation doped n-type SLSs showed the carrier concentration of 3.8×10^{16} cm^{-3}. Furthermore, we prepared $(ZnSe)_1$-$(ZnTe)_1$ monolayer superlattices. The PL intensity from $(ZnSe)_1$-$(ZnTe)_1$ superlattice is much stronger than that from mixed crystal (alloy) with the same composition ($ZnSe_{0.5}Te_{0.5}$). We could observe the strong green-yellow emission even at the room temperature. These results indicate that the monolayer superlattice is superior in optical quality and could be used in optical device applications.

Study of CdZnSSeTe semiconductor superlattices prepared by hot wall epitaxy

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1. Introduction

The wide gap CdZnSSeTe II-VI compounds have large ionicities, and this makes it difficult to form covalent bonding, introducing defect levels in the wide gaps. Strained layer superlattices(SLSL's) are considered to be one of hopeful materials which will break through barriers stood in our way. In the SLSL's each layers are uniaxially strained, and thus the bond angles must be largely changed. This suggests that the covalent bonding component is enhanced, which will make it possible to get shallow impurities in such cases as Ge or Si. On the other hand, the type I SL's of large band offsets, which become usually SLSL's, will be hopeful as the active layers for double insulating layer electrroluminescent devices. The large band offsets confine carriers into the wells. This not only increases the probability of the direct recombination but also decreases the probabilities of those through defect states near the SL interfaces.

1. Results and Discussions

(ZnSe-ZnS SL); The SL structure was improved by using ZnSe and ZnS compound sources, which was ascertained by X-ray diffraction and photoluminescence(PL) measrements.
(ZnTe-ZnSe SL); High quality of the SL made by using ZnTe or ZnSe buffer layer was ascertained by the observations of resolved X-ray diffraction patterns due to Cu $K\alpha_1, \alpha_2$ and of high angle spectra of narrower width and folded acoustic phonon modes in Raman scattering measurement. The valence band offset of the SL is found to be 0.52 eV through the analysis of the PL spectra associated with the band gap of the SL.
(CdS-ZnS SL); Glass/ITO/SiO_2/Si_3N_4/CdS-ZnS SL/Si_3N_4/Al_2O_3/Al electroluminescent device was made and the quantum effects depending on the SL structure were ascertained by optical transmission, PL and electroluminescent measurements at room temperature. The device will not only be hopeful for the electroluminescent device which can be easily designed for desired spectrum characteristics but also it is useful for studying electroluminescent mechanisms including determination of impurity levels such as Mn and TbF.

Laser Spectroscopy of II-VI Semiconductor Thin Films

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1. Introduction

Wide gap semiconductor superlattices, such as ZnSe-ZnS strained layer superlattices, have the potential application to the optoelectronic devices. In this work, we have studied the nonlinear absorption and the picosecond time-resolved luminescence of excitons in ZnSe-ZnS strained layer superlattices. We have also studied the ultrafast relaxation processes of photoexcited carriers in the thin film of CdSe by means of femtosecond pump-and-probe spectrometer developed by us.

2. Results and Discussions

We have observed the absorption saturation of excitons in a ZnSe-ZnS strained layer superlattice, consisting of 2.5 nm ZnSe layers and 5 nm ZnS layers. The measurement was performed by using a dye laser (7 ns) pumped by a nitrogen laser. The saturation density observed is 19.0 mJ/cm^2 at 4.2 K or 24.5 mJ/cm^2 at 77 K. These values are extremely large compared with the value 2.6 $\mu J/cm^2$ reported for ZnSe-ZnMnSe. We have also measured the lifetime of excitons in ZnSe-ZnS strained layer superlattices. The observed lifetime is 50 ps for the 7 nm well smaple, while 200 ps for the 2.5 nm well sample at 10 K.

Broadening and blue shift of the exciton absorption spectrum have been observed in the thin film of CdSe by the femtosecond pump-and-probe spectroscopy. New and interesting phenomena observed will be analyzed by the future study.

Lattice Strain and Effects of Strain on Electron-Phonon System in II-VI Compound Semiconductor Superlattices

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1. Introduction

Recent advance of thin-film growth techniques has enabled us to fabricate new materials such as superlattices. The strained layer superlattices consisting of ZnSe, ZnTe, and ZnS have been interested from the applications as efficient blue light emitting diodes and semiconductor lasers. To get a good quality sample, it is important to control strain in each layer as well as to probe the effect of strain on electronic states and lattice vibrational properties in these materials. We have two purposes in the present theoretical research program. One of them is to explore the features of strain in the near vicinity of interface by considering the chemical bond distortions. This may provide a clue of understanding the origin of misfit dislocations which appear above some critical thickness of layers. Another is to examine the effect of strain on excitons, electrons, and phonons in a quantum well. Optical gap energy obtained from photoluminescence and absorption measurements in these superlattices are discussed in detail.

2. Results and Discussion

Distortions of both bond length and bond angle for a tetrahedral unit in a superlattice such as ZnSe-ZnTe have been estimated by minimizing the total bond distortion energy in a valence force field model. Further, effects of long range Coulomb interaction among ions on distortions are discussed. The results are adopted to explain appearance of small atomic displacements near hetero-interface of GaAs/AlAs.

We present also a theoretical study of excitons in ZnSe-ZnS strained layer superlattice within an effective mass approximation. We demonstrate the exciton effects on the optical gap of ZnSe-ZnS superlattices by a variational method. The calculated optical gap exhibits inverse square dependence on the well width in consisting with recent experimental data.

Investigation on Layer- and Interface-Strain and Interdiffusion in II-VI Superlattices

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1. Introduction

Superlattices of II-VI semiconductors are expected to be useful for opto-electronic devices in the visible region. For making good superlattices, it is necessary to know natures of elastic strains, dislocations, interdiffusion, and impurities in the layers or on the interfaces. In this study, Raman and photoluminescence experiments are utilized for the understanding of strains in the ZnSe-ZnS strained superlattices made by metal-organic vapor phase epitaxy, and metal-organic molecular beam epitaxy methods.

2. Results and Discussion

Strained superlattices ZnSe-ZnS on GaAs substrate with equal layer thicknesses from 25 to 100 Å are prepared for Raman and photoluminescence measurement. In the Raman spectra, two LO-phonon lines are observed, which originate from ZnSe layers (about 250 cm^{-1}) and from ZnS layers (about 330 cm^{-1}). Their positions, especially LO_{ZnS} positions, are noticeably shifted from the bulk LO-phonon frequencies owing to the strains induced by the lattice mismatch. From the degree of shift, strains could be estimated to be about 0.1% for ZnSe, and 2.5% for ZnS. Lattice constant of GaAs substrate (5.65 Å) is near to that of ZnSe (5.67 Å), as compared with that of ZnS (5.41 Å), and therefore, ZnS layers in the ZnS-ZnSe superlattices are stressed strongly.

Raman intensity is enhanced by a resonance effect with increasing excitation photon energy. In the samples with thinner layer thicknesses, the enhancement occurs at higher photon energies. This observation is consistent with the result of photoluminescence experiments, in which the near-band-edge luminescence shifts to the high energy side in the thinner-layer samples. Such shifts are due to the quantum-size effect in the superlattice layers.

Superlattice effects and optical characteristic of excitons and bound electrons

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1. Introduction

Superlattice systems with the use of II - VI and III - V compounds have a large possibilty to be applied to new optical devices. The purpose of the present research is to perform the quantitave and comprehensive study, which charifies the optical characteristic of excitons and bound electrons in superlattice systems by taking into account of the many variety of the constitution of the systems. The obtained results will be very useful to develop new optical devices and to control material properties.

2. Results and Discussion

(1) General properties of excitons in type II quantum well systems are studied. It has been found that (a) excitonic properties depend very much on the electron-hole mass ratio and the well widths, (b) the characteristic dimensional character of an exciton appears in some limits of physical parameters of the system, (c) the dielectric mismatch effects affect excitonic properties of the system very much, and that (d) oscillator strengths become large in accordance with the degree of the spreading of the subband wave function in to the barrier part.

(2) Excitons in type II quantum well system in an electric field have been studied. In an electric field exciton splits in two states, whose optical behaviours are different each other for the increace of the electric field strength. These features are very different from those of excitons in type I quantum well systems. This difference will be very useful to identity the type (I or II) of the quantum well systems.

(3) Exciton states in double quantum well systems are calculated. It has been found that the middle barrier part affect excitonic properties very much and the size of the quantum well affects the extension of the subband wave function and yields the minima for the binding energy of excitons when the width of the middle barrier part increases.

(4) The localization of an electron interacting with acoustic phonons in multi-dimensional quantum well systems is studied . The dimensionality of the well has been found to be the important factor for the degree of the localization.

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