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REPORT DOCUMENTATION PAGE			Form Approved GSA No. 0704-0188	
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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE August 31, 1990	3. REPORT TYPE AND DATES COVERED August 1, 1989 - August 31, 1990		
4. TITLE AND SUBTITLE Laser Assisted CVD Growth of AlN and GaN		5. FUNDING NUMBERS F49620-89-C-0108 Proc. Inst. No. F09671-89-01458 2306/ B1 Reg. No.		
6. AUTHOR(S) Dr. Joshua B. Halpern Dr. Joan M. Frye Dr. Gary Harris and Dr. M. Aluko		7. PERFORMING ORGANIZATION REPORT NUMBER AFOSR-TR-89-0000		
8. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry and Materials Science Research Center of Excellence Howard University Washington, DC 20059		9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) USAF/AFSC AirForce Office of Scientific Research Building 410 Bolling AFB, DC 20332-6448		
10. SPONSORING/MONITORING AGENCY REPORT NUMBER 2306 B1		11. SUPPLEMENTARY NOTES		
12a. DISTRIBUTION/AVAILABILITY STATEMENT Unlimited		12b. DISTRIBUTION CODE DTIC ELECTE FEB 15 1991 S B D		
13. ABSTRACT (Maximum 200 words) This is the first annual report of a project for investigating laser assisted CVD growth of AlN and GaN. In the first year three experimental systems have been built. The first is a small, mobile CVD test system for evaluating growth schemes and detection methods for gas and heterogeneous phases. The second is a tunable diode laser spectrometer for monitoring gas phase components in a CVD reactor. The third is a dye laser system for monitoring atoms and small free radicals in the CVD system. First experiments have been done with all three systems. In particular we are investigating the use of 248 nm photolysis of trimethylaluminum near a slightly heated substrate in a mixture of TMAI and hydrazine for growth of AlN.				
DISTRIBUTION STATEMENT A Approved for public release; Distribution Unlimited				
14. SUBJECT TERMS		15. NUMBER OF PAGES		
		16. PRICE CODE		
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT None	

Abstract

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INTRODUCTION

This is the first year progress report of a project to develop photoassisted CVD methods for growth of AlN and GaN. We further proposed to develop diagnostic capabilities for monitoring the concentrations of free radicals and stable species in the growth chamber so as to gain an understanding of growth mechanisms. The results are to be used to obtain and test kinetic (homogeneous/heterogeneous) and fluid mechanic models to aid reactor design and growth optimization. The characterization and use of the grown films in electronic and optical device fabrication will be undertaken.

We have met or are close to meeting all of the goals set forth in the statement of work for the first year. The prototype CVD reactor started working in July 1990, first film growths (Al) were done in July, and the initial series of growths (see below for details) were finished in August 1990. At this point we have identified KrF (248 nm) as being the most promising wavelength for growth and are concentrating our efforts there. There are photochemical and economic reasons for preferring it as we will explain. We have just started analysis of the films. As stated the tunable diode laser and dye laser systems have been set up and calibrated. The first measurements of molecular species and atoms have been made.

PROTOTYPE REACTOR

In the first year we have built a prototype laser photolysis-CVD reactor to be used for proof of concept experiments and for testing of monitoring schemes. The small test cell is a 6" Conflat six-way cross with a moveable heated stage holding the susceptor. The stage for positioning the substrate is a vacuum manipulator with an X-Y-Z mount and tilt and yaw adjustments. At this time only heating current and thermocouple leads are brought to the susceptor. A film thickness gauge will be added soon, although we also intend to test non-contact interferometric methods for which a port is available. Lasers for photolysis or monitoring can be brought into the cell either perpendicular or parallel to the substrate through 50 mm quartz windows. At present the vacuum system is limited to operation above 1 mtorr using a throttled two stage mechanical pump, but a diffusion pump and liquid nitrogen trap are available and can easily be added so that the system could be evacuated to less than 10^{-8} torr to test monitoring schemes for atoms and cluster in MBE systems and to provide an oil-free environment for CVD.

The stainless steel construction of all of the components of the cell and gas handling manifold means that potentially useful devices might be grown in the cell. In our original proposal it was thought that this cell would only be used for testing deposition schemes and would not be useful for growing good films without chemical contamination. The availability of additional support from the Howard University Materials Science Center of Excellence and a substantial donation of equipment from AT&T Bell

Laboratories have enabled us to construct a better system.

Figure 1 is an sketch of the prototype system, which was modelled after an EMCORE reactor delivered to the MSRCE for growth of SiC and other materials. At this time gas flows are regulated by electronic flow controllers via potentiometers. If necessary it will be straightforward to add computer control of the flow and gas selection. The three-way valves are solenoid-switched. In the next year we intend to replace these with pneumatically controlled valves to allow the use of hydrogen as a ballast gas. The susceptor is a resistively-heated piece of graphite with a graphite clip holding the substrate and thermocouple monitoring of the temperatures. The entire heater is held in a glass cup which limits heterogeneous decomposition of the metal alkyl species directly on the heater. We had noticed such a tendency in initial static cell experiments. Since a principal aim of this work is to investigate low temperature methods of AlN and GaN growth it is not necessary to have a high temperature heater.

The manifold and control electronics were built on a 19" plate. The manifold and reactor are supported in a Unistrut frame which is on a set of large wheels so that it may be moved from location to location. This was necessary as we plan to use several different laser systems in the experimental research program and it is safer and more convenient to move the experimental cell then it is to move the lasers or direct the laser beams across the laboratory. It takes about a day to move the system and set it up again.

LASER ASSISTED CVD EXPERIMENTS

GaN and AlN are as fast or faster than GaAs. They have large direct band gaps and high electrical and thermal conductivity. AlN and GaN are physically robust and should be able to withstand high temperatures. AlN and GaN also have electro-optic applications including lasers and LEDs. Both materials have been used as dielectric insulators for integrated capacitors.

Pyrolysis and lamp photolysis maintain Boltzmann distributions of radicals and atoms in the growth cell. However, only unstable species that are near the substrate take part in growth. Radicals more than a few mean free paths from the surface react before they reach the substrate. Pulsed laser photolysis can form concentrations of radicals orders of magnitude higher than pyrolysis within several mean free paths of the substrate without significant additional heating. While such a distribution disappears rapidly the growth rate may be significantly enhanced. Initial laser assisted experiments have been done in our prototype system starting in July 1990. The first experiments are simple, but have great potential. Work in our laboratory on another project has shown that at 248 nm, trimethyl aluminum (TMA) has a higher absorption coefficient at 100°C than at 20°C (Figure 2). This is somewhat surprising as the TMA exists as a dimer at the lower temperature and a monomer at the higher (Figure 3). Usually the dimer absorption is red shifted with respect to monomer absorption. However, what this means is that for KrF light, the TMA absorption will be higher at the hot susceptor than at the cold

window. Thus, for 248 nm light, one should have no problem with Al coating of the "cold" windows of the CVD reactor. Figure 4 shows our proposed "process design". The TMA will only absorb 248 nm light near the heated susceptor. The amount and depth of absorption can be controlled by controlling the temperature of the substrate and the concentration of TMA in the cell. Thus, the energy of the laser, and the concentration of dissociation fragments can be kept within a small distance of the substrate. With some practice it should be possible to tailor the concentration profile and the growth rate.

There are three possible sources of nitrogen atoms. The first, and probably the simplest would be hydrazine. Hydrazine absorbs 248 nm light as is shown in Figure 5a, while ammonia does not, as shown in Figure 5b. Secondly, one could use some amine, such as trimethylamine. A possible problem with the amines and ammonia is that they would form strong complexes with the TMA. The Al atom would accept the free electron pair donated by the nitrogen atoms in the ammonia or amine. Not only would the complexes probably absorb light along the entire path, they would decrease the concentration of monomeric TMA near the heated substrate. On the other hand hydrazine would not form such a complex. Moreover, heterogeneous decomposition of hydrazine would not result in surface carbon deposition.

In order to test the feasibility of this scheme an initial set of experiments has been done, depositing a simple Al film from 248 nm photo CVD of TMA as a function of susceptor temperature. The

TMA is diluted in He and flowed slowly over the susceptor. There is no deposition in the absence of the laser. As shown in Figure 6, the experiments clearly show that the rate of deposition is much higher if the substrate is at 125 °C than if it is at 25 °C. At present the films are uneven on a gross level because the laser beam has hot spots. In this regard it is much easier to remove such hot spots from a KrF beam than from the lower gain ArF and KrCl beams.

We may continue the direct deposition work with Al as there appears to be some interest in these methods for metallization [1] and for projection patterning of metal films [2]. Photoassisted growth of such films with TMA as a feed gas at 193 nm appears to form rough films. Better results are obtained if the laser is used to form nucleation sites followed by pyrolytic growth. KrF 248 nm growth directly from TMA may prove superior.

Experiments with a mixture of TMA, hydrazine and Ar or He are underway starting in the last week of August. Films will be characterized by electron microscopy, Auger spectroscopy and X-ray analysis.

LASER DIAGNOSTIC EXPERIMENTS

Dye laser and tunable diode laser systems have complementary diagnostic capabilities. CH, CH₂ (triplet a state), NH and NH₂ concentrations can be measured sensitively by dye laser induced fluorescence (LIF). Metal atom detection is straightforward. Tunable infrared diode laser absorption spectroscopy is not as sensitive but can be used to detect species that do not emit.

Specifically, the concentrations of reactive species in the chamber, such as the methyl or ethyl radical can be measured as well as the feed gases TMG, TMA, hydrazine, ammonia, ethane or recombination products such as ethane. The sub-Doppler resolution of the spectrometer will allow routine observation of rotational structure, and from the intensity distribution we can calculate the in-situ temperature.

It was proposed to use two different type of laser probes. Tunable diode laser spectroscopy is used to monitor stable species in pyrolytic and laser assisted CVD systems and free radicals in laser assisted CVD. Dye lasers are used to monitor atom and radical populations.

Figure 7 shows a laser induced fluorescence signal from Ga atoms in a small oven. The density of Ga is less than 10^{-6} torr under the conditions of measurement. We are setting up to measure Ga atoms following photolysis of trimethylgallium.

Low resolution spectroscopy of both monomeric and dimeric TMA has previously been reported (3): matrix-isolation infrared studies indicate the presence of several strong bands for the monomer and gas phase infrared studies show bands at slightly shifted frequencies for the dimer. The diode laser spectrometer has been assembled and calibrated, and initial searches for the dimer and monomer in the 700 cm^{-1} region have recently been undertaken in this laboratory.

NUMERICAL SIMULATION EFFORT

Theoretical computer-aided modeling of the thermodynamics, fluid dynamics and heat and mass transfer characteristics for Aluminium Nitride (AlN) crystal LICVD growth are currently being initiated. This is primarily in order to predict reactor performance measures such as film deposition rate as a function of substrate temperature, reactor pressure, inlet gas composition, laser beam intensity and beam configuration (i.e. parallel or normal) relative to the substrate.

Preliminary work has involved the establishment of a database of thermodynamic properties (heats of formation, standard entropies and heat capacities) of over 48 (forty-eight) gaseous compounds, radicals and solids which can conceivably be present in the LICVD chamber. Several sources are currently being employed [4-8]. A NASA-Lewis computer program, CHEMKIN/EQUIL, with which the heterogeneous equilibrium (via Gibbs free energy minimization) can be calculated, already exists (on our VAX 11/780 computer) and has been used successfully in the evaluation of our silicon carbide systems.

As the first stage of our full modeling effort, two- dimensional fluid mechanics calculations are also being initiated primarily to predict the hydrodynamics in the reaction chamber. This involves the use of FLUENT, a finite-volume code for solution of the Navier-Stokes equations. This well-tested code is currently in use in our center for similar purposes with regard to three silicon carbide reactors (vertical CVD, horizontal CVD and sublimation furnace reactors).

Results of all the above modeling work will be fully described in later reports and peer-reviewed publications.

STATEMENT OF WORK (SECOND YEAR)

In the second year we will optimize the photo-CVD process for growth of AlN and start experiments on growth of GaN. Species maps will be made of feed gases, atoms, radicals and products in our prototype system. Detection limits will be determined. Attempts will be made to use optical methods such as surface-mediated frequency doubling and resonant surface Raman scattering as in-situ probes of the solid phase. The stress layer induced by the mis-match between the nitride and the base crystal would greatly enhance these processes. The measured data would be used to optimize computer models of the laser induced CVD reactor.

FACILITIES AND EQUIPMENT - ADDITIONAL COST SHARING

This year Howard University has provided \$45,000 for the purchase of an excimer laser to be shared by Dr. Frye for the diode laser probe experiments and another Assistant Professor, Dr. Prabakhar Misra who is working on other research projects. This money was provided as part of an internal program to support the research of new faculty. In addition, the Graduate School of Arts and Sciences has established a Collaborative Core Unit to encourage the sharing of equipment and facilities. The Laser Laboratory is a member of this program. The principal benefit is the availability of funds for repair of laser equipment on a cost-matching basis. The benefit to this research program was approximately \$5,000 last year including the purchase of a slit

nozzle for the diode laser work.

The Materials Science Center of Excellence is the interdisciplinary unit under which this research is being done. Last year part of the NSF umbrella grant supporting this work was used to purchase additional equipment used in this project. This includes a complete power train for the Questek excimer laser used in this work (\$10,000) and a low frequency detector for the diode laser spectrometer (\$3,000).

This is substantial additional cost sharing.

RESEARCH FACILITIES

The work is being performed in the Howard University Laser Laboratory. This is a free-standing building of approximately 5,200 square feet, which was renovated by the University in 1983. The Photochemistry Laboratory occupies about two thirds of this space, and its facilities are shared by Dr. Frye, Dr. Halpern and Dr. Hideo Okabe.

Among the major pieces of instrumentation available for this project are a tunable diode laser, two Nd-YAG pumped dye laser systems, three excimer lasers, two nitrogen-laser pumped dye lasers and a flashlamp pumped dye laser. One of the Nd-YAG pumped dye laser systems is new (Quanta-Ray DCR-11/PDL-2), and the other is about eight years old, but is working well (Molelectron). The tunable diode laser gives us the capability of measuring absolute concentration profiles of polyatomic radicals and stable species. For excimer laser photolysis we will use either a Questek Model

2000 excimer laser (50Hz, 200 mJ/pulse on XeCl) or an older EMG 101 system that has been refurbished (20Hz, 200 mJ/pulse). This will allow us to devote one laser to fluorine exciplexes (ArF 193 nm, KrF 248 nm and XeF 351 nm) and the other to chlorine (KrCl 222 nm and XeCl 306 nm). Changing from one gas to another in the same laser requires extensive and time consuming depassivation and repassivation.

There is a sufficiency of experimental cells, gas handling manifolds, and vacuum and electronic instrumentation. We have built a small experimental CVD system to test growth concepts for nitrides. A larger resistively heated high temperature/laser CVD system has been delivered by EMCORE to the MSRCE and is operational. A third RF heated system is being refurbished in the MSRCE. For data acquisition we use IBM-PC/XT based modules that were designed in our laboratory. The diode laser absorption spectrometer and dye laser systems will enable us to measure all significant gas phase components involved in thin film growth. For film and device characterization we have scanning Auger microprobe, transmission electron microscopy, deep level transient spectroscopy and a photoluminescence. We are currently working with a CVD development group at AT&T Bell Laboratories on a different project for characterization of gases used in the CVD process. At this time we are discussing with them the possibility of their doing additional analysis work on films that we grow.

MATERIALS SCIENCE CENTER OF EXCELLENCE

This work will be part of the program of the Materials Science Research Center of Excellence (MSRCE). The MSRCE was founded in October of 1988 with principal support from the National Science Foundation. The research focus of the center is the growth, characterization and fabrication of novel electronic and electro-optic materials and devices for high frequency and high temperature applications. The MSRCE is a multidisciplinary center with student and faculty participation from the departments of electrical, mechanical and chemical engineering, and physics, chemistry and mathematics. Center members are working to define and solve complex technical problems which will impact the next generation of electronic components and systems.

We are also responding to the demands of industry, government and universities for highly trained personnel to enable our country and citizens to compete in the global economy. Our educational focus is increasing the number of minorities with Bachelors, Masters and Ph.D. degrees in engineering and the physical sciences. This is in direct response to the National Academy of Sciences' call for programs to improve the quality, distribution and effectiveness of the Nation's human resource base.

Howard University has always been a leading and effective force in this endeavor. The Department of Chemistry has produced more black American Ph.D chemists than any other institution. Our first Ph.D. graduated in 1959. Even today we grant between ten and twenty percent of the Ph.D.s awarded to black Americans. Howard

University's School of Engineering annually graduates the largest number of black engineers - more than any other single university in the country. The MSRCE is building on this legacy.

The MSRCE by itself is making a significant contribution to the pool of minority scientists. Currently the center has over 20 graduate student, a majority of whom are black Americans. They are all involved in materials science research projects. Our graduates are finding jobs in leading companies and government laboratories including AT&T Bell Laboratories, IBM, Texas Instruments, Lawrence Livermore, etc.

Our investigations focus on understanding and optimizing the growth of artificially structured materials and wide-bandgap semiconductors. Improvements in the growth of these materials will allow the fabrication of devices which promise to extend the performance of microwave and optical devices at higher frequencies and power levels.

The MSRCE seeks linkages with industry and government laboratories to support and enhance its research effort. We have collaborations with the University of Illinois, Cornell University, Martin Marietta Laboratories and the Naval Research Laboratory. An industrial affiliates program has been set up. The initial affiliate is the Digital Equipment Corporation. Other agreements are being negotiated. In addition, the 3M Corporation is supporting a project for the development of a non-linear optical converters.

PERSONNEL

In March of this year Dr. Kanekazu Seki began work as a post-doctoral research associate for this project. His resume is attached as an appendix. At this time one graduate student is working with him.

FOOTNOTES

1. G.S. Higashi, Appl. Surf. Sci. 43 (1989) 6.
2. G.S. Higashi, Chemtronics, 4 (1989) 123.
3. S. Kvisle and E. Rytter, Spectrochim. Acts 40A (1984) 939.
4. Barin, O. Knacke and O. Kubachewski. Thermochemical Properties of Inorganic Substances (Springer Berlin, 1977)
5. H.H. Landolt and R. Bornstein, Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik, Technik, Vol II, No. 4 (Springer Berlin 1961)
6. D.R. Stull and G.C. Sinke, Thermodynamic Properties of Elements (Am. Chem. Soc., Washington, DC 1965)
7. JANAF Thermochemical Tables (3rd Ed.), Eds: M.W. Chase et al, (Am.Chem Soc.), 1985.
8. M. Tirtowidjojo and R. Pollard, Equilibrium Gas Species for MOCVD of $\text{Al}_x\text{Ga}_{1-x}\text{As}$. J Cryst. Growth, 77 (1986) 200-209.

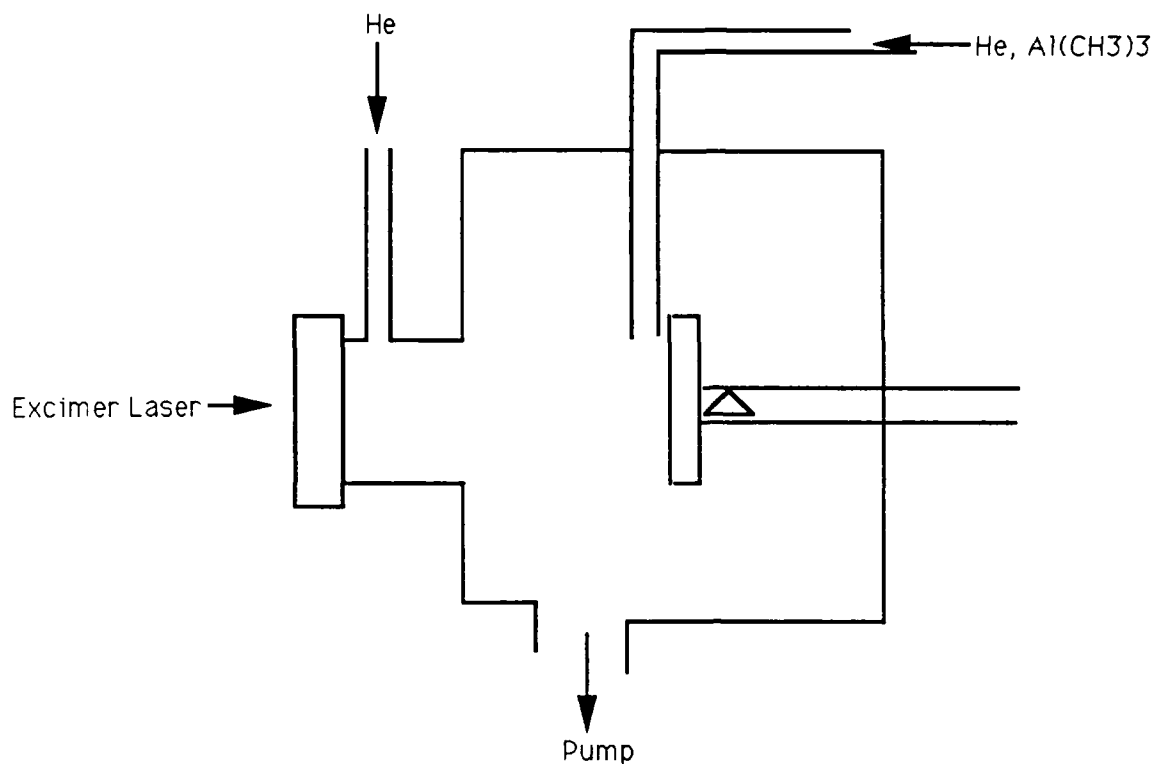


Figure 1.

Helium flow rate is 5ml/sec. Chamber pressure is approximately 10torr.

Substrate: glass; 20x10mm²

Laser: energy per pulse is 100-230mJ. Beam spot size: roughly 15x30mm².
wavelength: 248nm

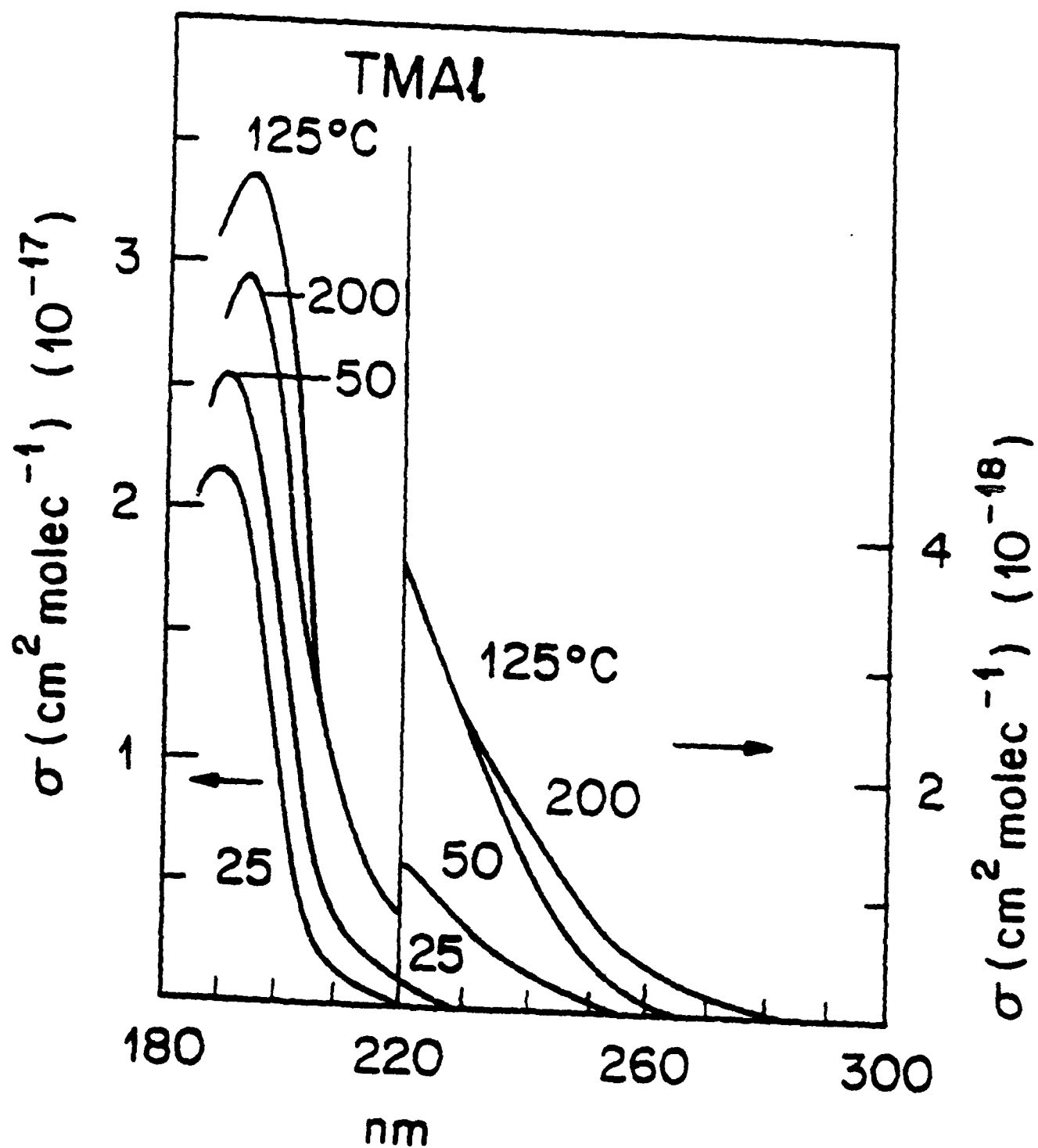


Figure 2

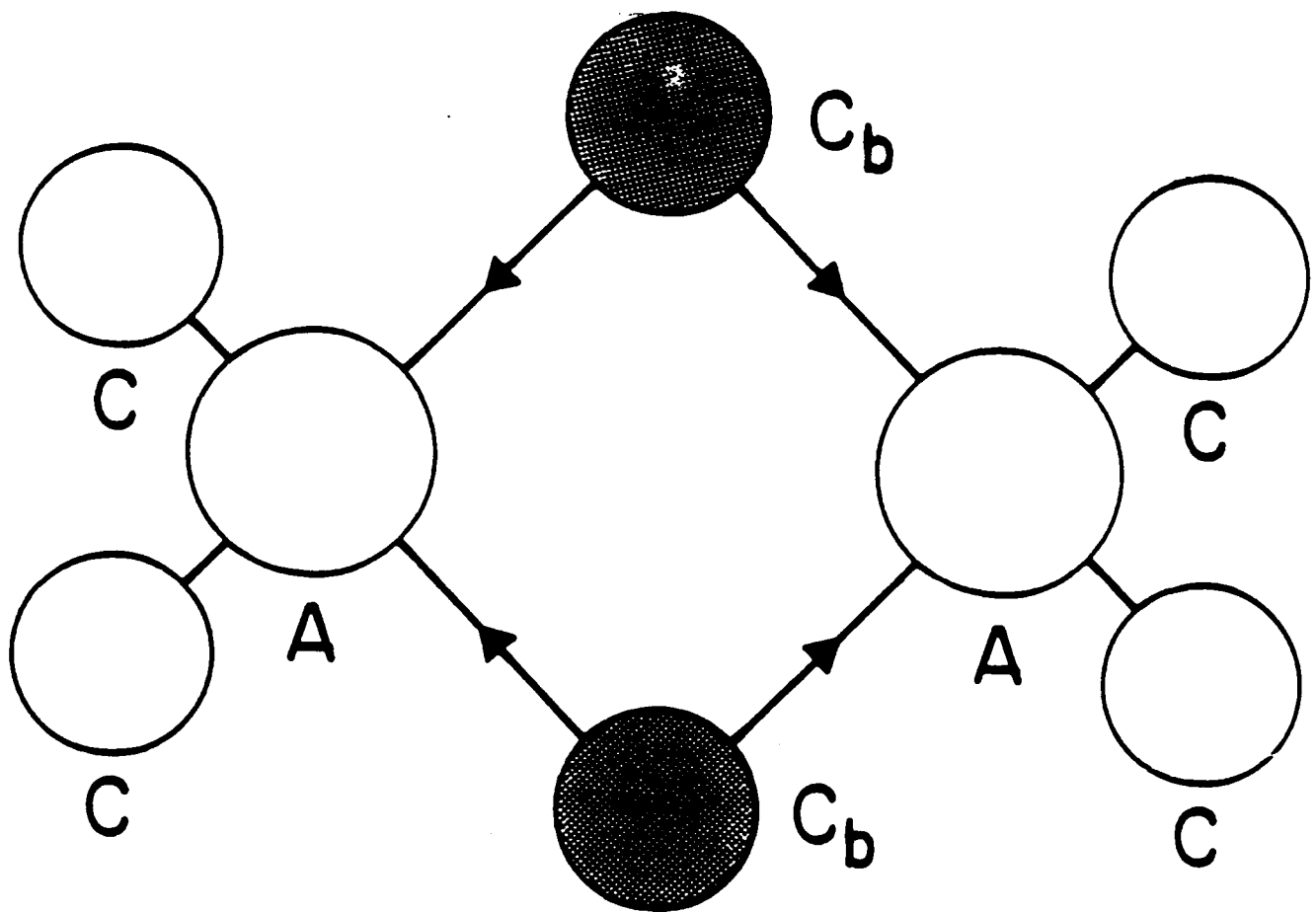


Figure 3

AlN Process Design

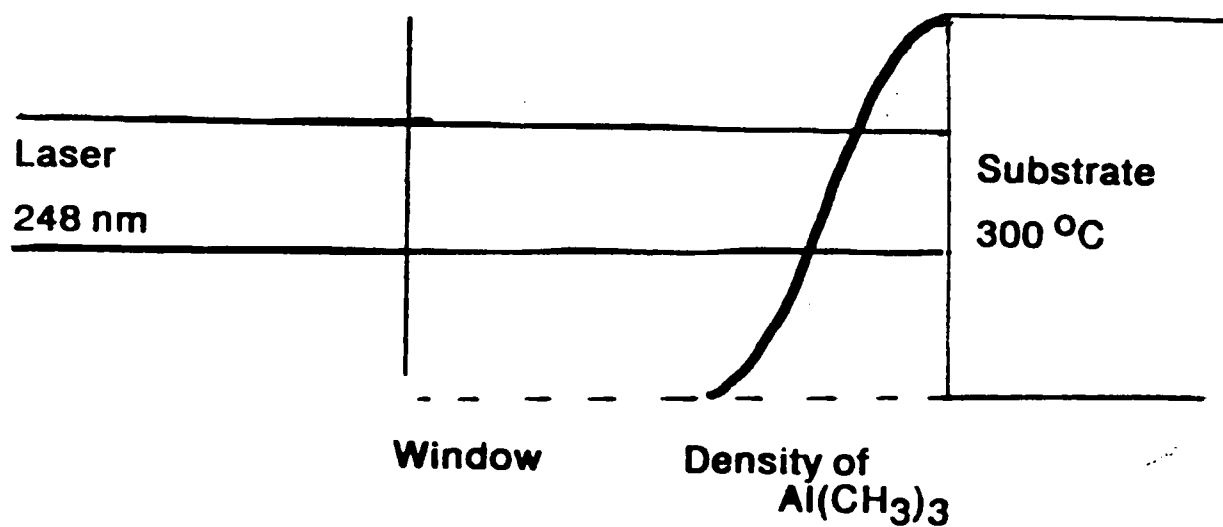
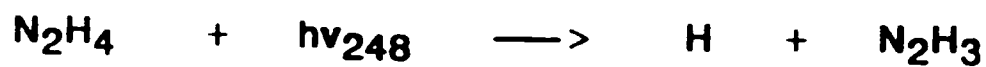
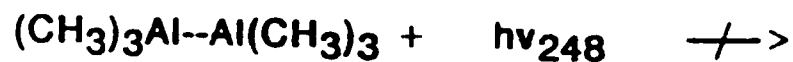
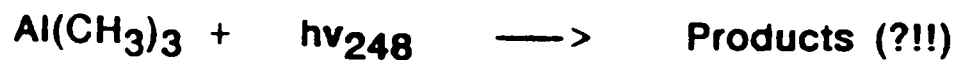
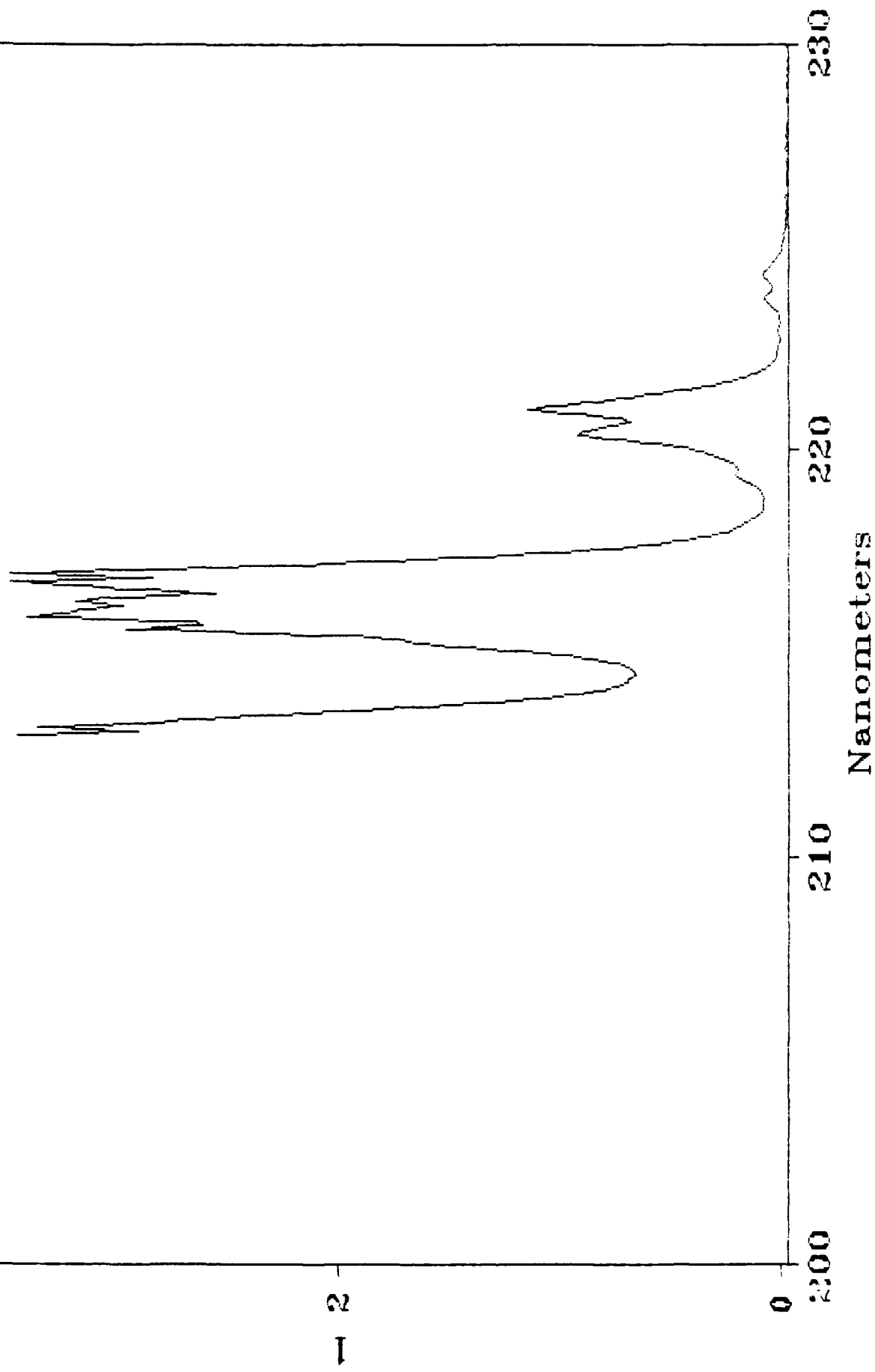


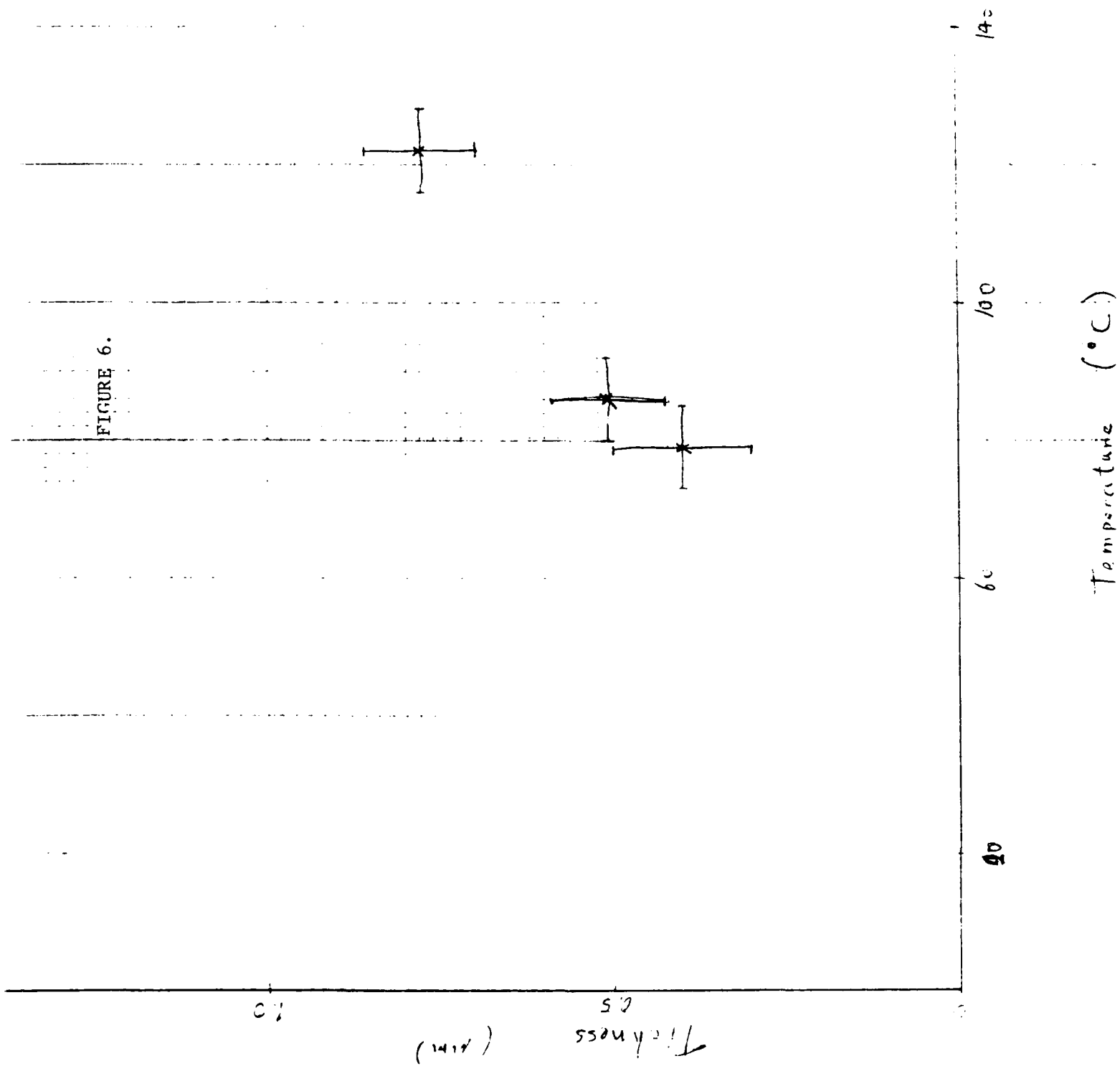
FIGURE 4



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nh3,100torr,sbw=0.3

FIGURE 5.

FIGURE 6.



Ga atom detection by LIF in a 800° C cell

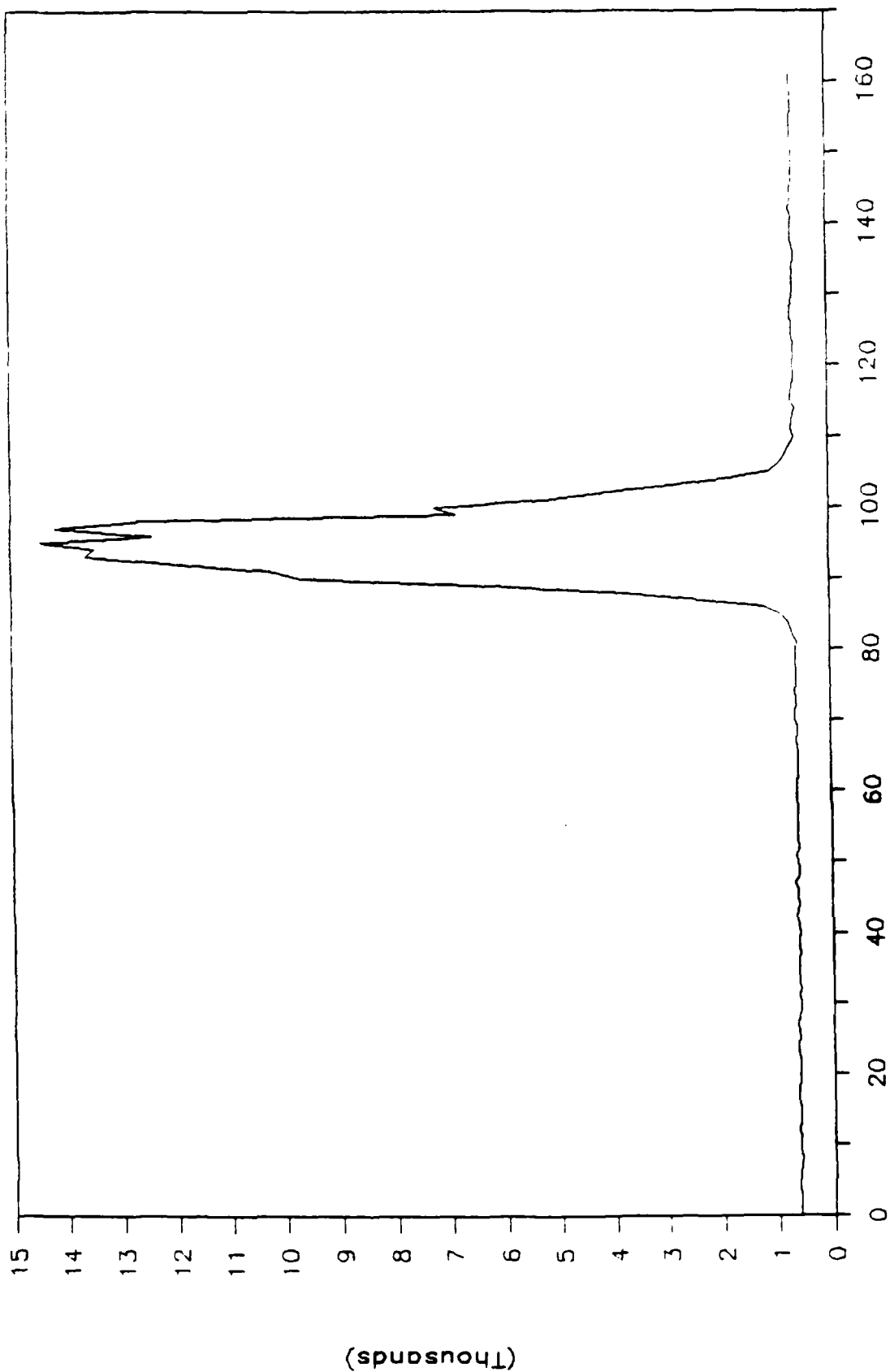


FIGURE 7.

Kanekazu Seki

Curriculum Vitae

1. Personal: Address: Advanced Research Laboratory,
Research and Development Center, Toshiba
Corporation, 1-Komukai-Toshiba-cho,
Saiwaiku, Kawasaki, Kanagawa 210, Japan

Born: August 8, 1957 (Age 31)

Married: October, 1989 (appointed)
2. Education: B.A.: Yokohama National University, 1981

Rigaku Hakushi (Doctor of Science):
The University of Tokyo, 1986
3. Employment: Toshiba Corporation, Researcher (1986-)

Kanekazu Seki

Background of Research

He got his B.A. degree at Yokohama National University where his research advisor was Professor Jiro Higuchi, and he had studied in the field the excited triplet state using the technique of ESR. Then as a graduate student, he continued his research at the Institute for Solid State Physics of the University of Tokyo, under the direction of Professor Minoru Kinoshita. The title of his Master thesis at Kinoshita's Laboratory was "Studies of excited triplet state for aromatic molecules by Optical Detect Magnetic Resonance" and one of Doctor thesis was "Photochemical processes of simple unsaturated molecules". Main part of the studies of doctor degree was done at Institute for Molecular Science at Professor Nishi's Laboratory.

At Toshiba Corporation, he is deeply involved with the fundamental research of organic thin films using Surface enhancement Raman scattering and time-resolved n-second laser photolysis.

Kanekazu Seki

List of publication

- 1) "Infrared absorption spectroscopy of phosphorescing molecules Naphthalene-d₀",
K.Nishikida, Y.Kamura, K. Seki, N.Iwasaki and M.Kinoshita,
Mol.Phys., 49(1983)1505.
- 2) "Photofragmentation of mono- and dichloroethylenes: Translational energy measurements of recoiling Cl and HCl fragments",
M.Umemoto, K.Seki, H.Shinohara, U.Nagashima, N.Nishi, M.Kinoshita, and R.Shimoda, J.Chem.Phys., 83(1985)1657.
- 3) "Photochemistry of Acetylene at 193 nm: Two pathways for Diacetylene formation",
K.Seki, N.Nakashima, N.Nishi and M.Kinoshita, J.Chem.Phys., 85(1986)274.
- 4) "Infrared diode laser kinetic spectroscopy of CCH radical ν_3 bond",
H.Kanamori, K.Seki and E.Hirota, J.Chem.Phys., 87(1987)73.
- 5) "Surface-enhanced resonance Raman scattering of Langmuir-Blodgett monolayer of Azo-containing amphiphile",
K.Seki and H.Nakanishi, Chem.Phys.Lett., submitted.
- 6) "Dependence of polarized surface enhanced resonance Raman spectrum of Langmuir-Blodgett monolayer film on the incident light angle",
K.Seki and H.Nakanishi, Thin Solid Film, in press.
- 7) "Evidence for laser induced cis-trans isomerization of Langmuir-Blodgett monolayer using of SERRS",
K.Seki, C.Ohyama and H.Nakanishi, in preparation.