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RESEARCH ON AMORPHOUS MATERIALS

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I. INTRODUCTION

The problems addressed under this contract can most easily be broken down into three groups. The first involves the determination of electronic structure of amorphous materials, e.g., density of states and optical selection rules. Here considerable emphasis was placed on the changes in electronic structure observed in going from the crystalline to amorphous forms of the materials and in comparison of the experimental results with theoretical predictions.

The second part of the work emphasized the structual aspect of amorphous materials and the development and refinement of experimental and theoretical tools by which the structure can be determined.

The third feature of this project was a study aimed at the problem of photoconductivity in the rather complex chalcogenide alloys. Experimentally, the approach was to study the measurement of dark current, photoconductivity, thermoelectric power and field effect. A theoretical model was developed for photoconductivity in these materials which is consistant with the experimental data.

II. STUDIES OF THE ELECTRONIC STRUCTURE OF AMORPHOUS SEMICONDUCTORS

In examining the electronic structure of amorphous materials, it is useful to use the electronic structure of the crystalline material as a starting point and to ask what changes occur when one transforms from the crystalline to amorphous form. Two of the most useful questions which may be asked are: 1) how does the density of states change, and 2) does the propogation vector $\bar{k}$, which is usually a quantum number in crystals, retain importance in the amorphous materials. In all the amorphous materials studied, there is no evidence that conservation of $\bar{k}$ provides an important optical selection rule.[1,2] Thus the answer to the second question seems to be negative. The answer to the first question was found to depend on the material studied. In Ge[1], Si[1], and GeTe[3], the density of states of the amorphous forms was found to differ strongly from that of the crystalline materials. Whereas, in Te[2] only small changes were found between the two forms. It is thought that this is due to the more molecular or localized nature of crystalline Te. Since the electronic states in this crystalline material have a somewhat localized nature, the dependence on long-range order is minimized.

The principal tool used in investigating the electronic structure of these materials was photoemission spectroscopy. Partially as a result of the success in this program, this tool is being used to an increasing extent in studying the electronic structure of solids in general and amorphous materials in particular.[4]

Another important question for the electronic structure of amorphous semiconductors concerns the sharpness of the band edges and the density of localized states.[5] Prior to these studies, it was generally accepted that the destruction of long-range order removed the sharp band edges which characterize crystalline semiconductors and introduce large numbers of localized states into the forbidden gap. Work under this contract has added to the body of material which indicates that the band edges in amorphous materials may approach the sharpness of those in crystalline material.[5] Likewise it appears that the density of localized states may be determined more by local rather than long-range disorder. In all of these studies, it has become increasingly apparent that the properties of amorphous Ge and Si depends on the method of preparation[6] and that sharp absorption edges and low densities ($\lessapprox 10^{18}/\text{cm}^3$) of localized states can be achieved if the samples are prepared with sufficient care.[5]

III. STRUCTURAL STUDIES OF AMORPHOUS SEMICONDUCTORS.

This research has dealt with the atomic arrangements in three types of amorphous semiconductors: germanium-chalcogen alloys, group IV elements and alloys of arsenic triselenide with various metals. The highlights of these three types of studies are discussed below.

At the time this research was initiated, we[7] had already shown that the atomic arrangements in amorphous Ge_xTe_{1-x} alloys are quite different from those in the equilibrium crystalline systems. This result implied that no microcrystalline model is appropriate and appeared to supply structural verification of the Mott[8]-Cohen, Fritzsche and Ovshinsky[9] model for the high resistivity of amorphous chalcogenide alloys. Under the contract, neutron diffraction studies[10] were performed on amorphous $Ge_{.17}Te_{.83}$. The high sensitivity of neutron diffraction to germanium scattering provided increased support for a model in which the germanium is fourfold and the tellurium is twofold coordinated. On the other hand, it was shown in this paper that it is extremely difficult to distinguish such a model from one in which threefold coordinated GeTe is a component of alloys with $x > 0.33$. Various structural models were investigated in detail in this paper. In later papers, it was shown that the structures of amorphous Ge_xS_{1-x}[11] and $Ge_{.42}Se_{.58}$[12] alloys are also quite different from those of crystalline GeS and GeSe. Hence, all the germanium-chalcogen alloys appear to fit a single pattern. It was also shown[13] that it is possible to rationalize threefold coordination for amorphous germanium monochalcogenide compounds. In that paper, a model structure for these compounds was presented. The models presented in reference 7 and 13 have been the subject of considerable study by other workers in the field. At the Fifth International Conference on Amorphous and Liquid Semiconductors considerable evidence was presented for the validity of the model in which the germanium is fourfold and the tellurium is twofold coordinated.

Consistent with the random covalent model for the germanium-chalcogen alloys, Moss and Graczyk[14] had shown that a random covalent model is consistent with their diffraction studies of amorphous silicon, but that no microcrystalline model appears appropriate. The validity of the second conclusion had been widely questioned, however, because Moss and Graczyk neglected the possible effects of inter-particle interference in their calculations of the scattering from microcrystallites. We[15] obtained a general equation for the calculation of the inter-crystalline interference contribution to the scattering of x-rays by arrays of small crystallites under the assumption that there is no correlation between the orientations of neighboring cyrstallites. Numerical calculations for the case of amorphous silicon were performed. It was shown that these inter-crystalline interference terms are significantly smaller than the intra-crystalline terms in all but the small-angle region. Hence, the conclusions reached by Moss and Graczyk concerning the lack of validity of the microcrystalline model for amorphous silicon were strongly supported.

Of the studies[16] of alloys of various metals with arsenic triselenide, the most interesting involves the addition of copper. Glasses with up to 30 at.% copper have been obtained in this system. These glasses are extremely interesting because the conductivity increases and the band gap decreases markedly with increasing copper concentration. X-ray diffraction radial distribution studies[17] show that the average coordination number per atom increases from 2.4 in the arsenic triselenide glass to nearly 4 in the glass with the highest copper concentration. Hence, the average coordination would appear to be going towards tetrahedral. Further support for the tetrahedral coordination is obtained from combined DTA and x-ray diffraction studies which show that the first crystallization product obtained by heating these glasses is $CuAsSe_2$. This compound is one in which all the atoms are tetrahedrally coordinated. We have prepared glassy $CuAsSe_2$ and have shown, through radial distribution studies,[18] that its structure is very close to that of amorphous germanium and, therefore, that the fourfold coordination is retained in the amorphous compound. ESCA valence band studies[17,18] on these materials indicate that the copper d-band electrons are not likely to account for the high conductivity and the small band gap. Instead, both are attributed to the formation of tetrahedral coordination in a system where such coordination is not a consequence of the 8-N rule. Hence, one would anticipate smaller band gaps with the structural change.

IV. PHOTOCONDUCTIVITY AND RECOMBINATION KINETICS IN AMORPHOUS CHALCOGENIDE SEMICONDUCTORS[19]

A model for photoconductivity in amorphous chalcogenides has been developed[20,21] by starting with traditional semiconductor recombination statistics[22] and a generalized distribution of localized states within the mobility gap of an amorphous semiconductor.[23-34]

Photoconductivity in a wide variety of amorphous chalcogenide semiconductors displays a maximum in the temperature dependence, varies exponentially with reciprocal temperature on either side of the maximum, and asymptotically approaches a constant value at low temperatures.[35-59] The photoconductivity is linearly dependent on light intensity under all conditions except high intensities at temperatures just below the maximum where it varies as the square-root of intensity.

Consistency with these experimental phenomena requires the inclusion in this model not only of the traditional nonlocalized-to-localized state recombination transitions, but also of two types of localized-to-localized state recombination transitions: (1) from nearer than a critical energy to the conduction band edge, to similar states nearer than a critical energy to the valence band edge; (2) from states near the mobility edges to states near the thermal equilibrium Fermi level. Such a model provides a way of estimating the characteristic parameters of localized states in these materials.

This model was applied to severl complex chalcogenide alloys[20,21] and to a pseudobinary arsenic triselenide-arsenic tritelluride alloy.[60] It was found that the density of recombination centers near the band edges is about 10^{19} per cubic centimeter per electron-volt within one-to two-tenths of an electron volt from the mobility edge.

Various electronic and optical properties of the bulk and thin film amorphous forms of the arsenic triselenide-arsenic tritelluride alloy were compared. It was found that the surface and the volume of the bulk material have essentially identical properties, and that the thin film properties are essentially the same as the bulk properties.

In addition to the steady-state photoconductivity in this material, dark conductivity, optical absorption, photoconductivity spectral response, photoconductivity decay, thermoelectric power, field effect, and electroabsorption dataare reported.

Conductivity and optical absorption measurements indicate that the bandgap in this material is about one electron-volt. The thermoelectric power shows the conductivity to be p-type and suggests that the carrier mobility is thermally activated. The fied effect and photoconductivity decay measurements suggest that near the Fermi level the density of states is about 10^{19} states per cubic centimeter per electron-volt. Extrinsic electroabsorption modulation spectroscopy at liquid nitrogen temperature shows a number of closely spaced absorption peaks, which can be interpreted in a way consistent with the photoconductivity behavior.[61]

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