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Title: Band Structure and Electrical Properties of Amorphous Semiconductors

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Highlights of Research

1.0 Amorphous Silicon and Germanium

1.1 Tunneling into Amorphous Silicon

Principal Investigator: D. Adler

Tunneling conductance of Al-SiO_2-amorphous Si-Al junctions has been measured as a function of bias, temperature, and frequency. An apparently anomalous temperature dependence has been explained in terms of tunneling into localized states in the amorphous semiconductor. Analysis of the data then yields both the mobility gap and the energy dependence of the density of localized states within the gap. It has been determined that the mobility gap in amorphous Si is 1.6 eV, and that sharp drop-offs in both valence and conduction band tails occur in the vicinity of the Fermi energy. The results also provide very strong evidence in favor of the predominance of phonon-assisted tunneling conductance at least up to 300K in as-deposited films of amorphous Si.

1.2 Irradiation Studies of Amorphous Silicon Films

Principal Investigators: D. Adler, H. K. Bowen

An investigation of the effects of intense thermal-neutron irradiation on the physical properties of amorphous Si films has been carried out. Provided the films had been annealed prior to irradiation, amorphous Si proved to be extremely radiation-resistant. The conductivity and EPR results provided evidence for the predominance of phonon-assisted tunneling conductance in annealed amorphous Si films through at least room temperature. The optical gap of amorphous Si was determined to be 1.5 eV, independent of the radiation.

1.3 Theoretical Models for Amorphous Silicon and Germanium

Principal Investigator: D. Adler

The physical origin of the valence and conduction band tails in amorphous Si and Ge films has been investigated in view of the recent structural studies. The major features of the band tail have been shown to arise from variations in bond length rather than bond angles.

The conduction band tail can be associated with regions in which the local density is anomalously small, while the states deepest in the valence band tail can be associated with high-density regions. Thus the redistribution of carriers that must accompany an overlap of the two bands results in electrons and holes being trapped in spatially separated regions.

2.0 Band Structure of Chalcogenide Glasses

Pricipal Investigator: D. Adler

It has been shown that the experimental results on a large class of chalcogenide glasses can be explained in terms of a model in which the materials are partially compensated semiconductors, without the necessity of either extended band tails or a sharp mobility edge. The effects of electronic correlations have been shown to lead to a sharp optical gap, even if extensive band tails exist.

3.0 Crystalline and Amorphous Silicon Telluride

Principal Investigators: D. Adler, F. O. Arntz

A comparative investigation of the electronic properties of crystalline and amorphous Si_2Te_3 films has indicated that the sharp, temperature-dependent optical edge that characterizes crystalline films becomes an extremely diffuse edge, essentially independent of temperature in the corresponding amorphous material. It has been found that optical absorption and electrical conductivity in amorphous Si_xTe_{1-x} films do not vary strongly with composition.

4.0 Threshold Switching in Thin-Film Devices

4.1 Experimental Studies of Thin-Film Switching

Principal Investigator: F. O. Arntz

Techniques have been developed for the fabrication of amorphous Te-As-XXX threshold switches that sustain over 10^8 switchings without deterioration. Stress measurements on the best material found to date, $Te_{40}As_{3}$ $_{15}Ge_7P_3$, indicate a decrease in threshold voltage of 1.2 V/Kbar. The delay time decreases with stress by 150 nsec/Kbar. Several components of the recovery time were observed, the longest of the order of minutes, strongly indicating the importance of trapping effects.

4.2 Temperature Profile of Threshold Devices

Principal Investigator: D. Adler, F. O. Arntz

It has been shown that no significant heating of the electrodes of thin-film devices occurs, provided the current in the ON-state is within a factor of 10 of the holding value.

4.3 Thermal and Electrothermal Switching Models

Principal Investigator: D. Adler

Solutions to the complete steady-state heat equations have been obtained under the assumption of no significant heating of the electrodes. It was found that pure thermal effects produce neither negative differential resistance regions nor high-current filaments. However, when some electronic effects, such as space charge, narrow Schottky barriers, or field-enhanced conductivity, are explicitly introduced, negative resistance and filamentary conduction result. The solutions then obtained are in general agreement with the available data.

Summary of Research

1.0 Amorphous Silicon Germanium

Personnel: D. Adler (in cooperation with Professor H.K. Bowen and Dr. C.J. Mogab)

Sponsorship: Advanced Research Projects Agency, U.S. Army Research Office-Durham

1.1 Tunneling into Amorphous Silicon

The tunneling conductance of Al-SiO_2-amorphous Si-Al junctions has been measured as a function of bias, temperature and frequency. The SiO_2 layers were 20-40Å thick, thermally grown on the amorphous Si. Despite the facts that the impedance of the amorphous Si was negligible compared to the tunneling impedance of similarly thick layers of SiO_2 between metallic electrodes at all temperatures investigated and that such tunneling is essentially temperature independent, a large temperature dependence was observed in the Al-SiO_2-amorphous Si-Al junctions at low biases. Thus the simple model of such tunneling junctions as two series impedances fails in this case. This problem has been resolved by postulating that the low-bias conductance represents tunneling into localized states in the amorphous Si. Consequently the tunneling carriers must not only traverse the SiO_2 but also some distance into the Si. The temperature dependence arises because the electrons must tunnel farther into the amorphous Si at low temperatures than at high temperatures. A variational calculation shows that if the localized states are sufficiently far apart, phonon-assisted tunneling must dominate below a critical temperature. In such a case the low-bias differential tunneling conductance should vary with temperature as

$$G = G_o e^{-[\lambda/g(E_F + V)\ kT]^{1/4}}$$

where $g(E)$ is the density of localized states, V is the applied bias, and λ is a constant determined by the barrier characteristics of the amorphous Si. Just such a temperature dependence is observed at low biases throughout the 77-300K range investigated. The tunneling conductance thus provides a means for determining the density of localized states in amorphous semiconductors. It has been found that large densities of such states exist well into the mobility gap in as-deposited films of amorphous Si. Sharp drop-offs in both valence and conduction band tails occur in the vicinity of the Fermi energy, but the density of states at the Fermi energy remains significant. The temperature dependence of the tunneling conductance essentially vanishes for biases greater than $\pm$ 0.8 eV. From this result, the mobility gap of amorphous Si can be estimated as 1.6 eV. AC measurements indicate the predominance of phonon-assisted tunneling conduction in both the tunneling junctions and plain amorphous Si films throughout the temperature range investigated.

1.2 Irradiation Studies of Amorphous Si Films

An investigation of the effects of intense thermal neutron irradiation on the physical properties of amorphous Si films has been carried out. Thermal-neutron fluxes up to 8.3 x 10^{18} n/cm^2 were used. Large fluctuations in electrical and optical properties of the as-deposited films were observed. However, if the films were annealed at 300°C prior to the irradiation, only very small changes in the physical properties were observed. Thus, most of the effects on the as-deposited films could be identified as thermal in origin, and annealed amorphous Si appears to be quite radiation-resistant. The facts that a 25% increase in the free-spin density and a factor of four decrease in resistivity were observed at the highest thermal-neutron flux employed provide strong evidence in favor of the predominance of phonon-assisted tunneling conductance in annealed amorphous Si films at room temperature. The optical gap of amorphous Si was found to be approximately 1.5 eV, independent of irradiation, in agreement with the previously described tunneling results.

1.3 Theoretical Models for Amorphous Silicon and Germanium

The physical origin of the valence and conduction band tails in amorphous Si and Ge films has been investigated in view of the recent structural studies. In ideal amorphous Si and Ge, Polk's model indicates a constant bond length but strained bond angles up to $\pm$ 20°. These can be shown to lead to only slight valence and conduction band tailing. Furthermore, the bands tail in the same regions of space. On the other hand, non-ideal films possess variations in bond length, which can produce extensive tailing, particularly of the valence band. Local decreases in bond lengths have been shown to shift both valence and conduction band states sharply up in energy; thus local compressions contribute only to the valence band tail. Since such increased band lengths can be expected on the internal surfaces of voids, extensive band tails should exist in as-deposited films. Furthermore, since valence band states occur in regions of anomalously high density and the lowest conduction band states occur in low-density regions, the redistribution of carriers that accompanies a CFO-type overlap of the two bands leads to electrons and holes being trapped in different regions of space. This is in agreement with a recent analysis of electrical and optical properties of amorphous semiconductors carried out by Fritzsche.

2.0 Band Structure of Chalcogenide Glasses

Personnel: D. Adler

Sponsorship: Advanced Research Projects Agency, Office of Naval Research

A complete review of the observed properties of many of the chalcogenide glasses, in particular the binary and pseudobinary systems, has indicated that the experimental results can be most easily explained in terms of a model in which the materials are partially compensated semiconductors, with large densities of both donor and acceptor levels in the mobility gap. This provides a density of states at the Fermi energy, which accounts for the radiation hardness, the lack of field effect, the transient photoconductivity, and the photoluminescence in a simple manner, without coming into conflict with the optical absorption results.

The effects of electron-electron and electron-phonon interactions on the band structure within the mobility gap have been investigated qualitatively. It can be shown that correlations lead to a rather sharp optical gap, even if extensive band tails exist.

3.0 Crystalline and Amorphous Silicon Telluride

Personnel: D. Adler, F.O. Arntz, V. Birkholz, K.E. Petersen

Sponsorship: Advanced Research Projects Agency, U.S. Army Research Office-Durham

The physical properties of crystalline Si_2Te_3 and amorphous films in the Si-Te system are being investigated. Single crystals 50 - 1000 μm thick have been prepared by vacuum sublimation in a temperature gradient near 750°C. Optical absorption results indicate a 2.0 eV gap, which blue shifts with decreasing temperature by about 1 meV/K. A broad photoluminescence peak appears near 1.3 eV. Thin films, 200Å - 2 μm thick, of both crystalline and amorphous Si_2Te_3 have also been prepared, as well as amorphous films of other compositions in the Si-Te system.

The amorphous films, as opposed to the crystals, do not exhibit a sharp optical edge, at least down to 0.7 eV. Furthermore, no temperature shift of optical absorption was observed in the amorphous films in the 77 - 300K range studied. Optical absorption and conductivity do not vary strongly with composition.

4.0 Threshold Switching in Thin Film Devices

Personnel: D. Adler, F.O. Arntz, M.A. Barman, K.B. Kanarek, T. Kaplan, B.P. Mathur, D.K. Reinhard, E.J. Sokolowski

Sponsorship: U.S. Army Research Office-Durham, Advanced Research Projects Agency, Office of Naval Research

4.1 Experimental Studies of Thin-Film Switching

A technique has been developed, employing a blend of integrated-circuit technology and rf-sputtering methods, for fabricating threshold devices based on chalcogenide glasses capable of withstanding over 10^8 switchings. The best composition obtained to date is $Te_{40}As_{35}Si_{15}Ge_7P_3$. Stress measurements indicate a decrease in threshold voltage of 1.2 V/Kbar. The delay time decreased with applied stress by 150 nsec/Kbar. Several components of the recovery time were observed, the longest being of the order of minutes, strongly indicating the importance of carrier trapping effects.

4.2 Temperature Profile of Threshold Devices

A study of the outer temperature of the top electrode of a thin film device was carried out using a thermocouple and a 1 μm probe. Just above the holding current, only a 0.01°C maximum increase in temperature above ambient was observed over the 10^{-12} m^2 area of the probe. This maximum temperature increases with increasing current through the device, although the observed increase becomes significant only when the current is a factor of 50 greater than the holding value. The results indicate that the assumption of infinite heat sinking of the electrodes in a sandwich-structure threshold switch is a good approximation.

4.3 Thermal and Electrothermal Switching Models

Solutions to the complete steady-state heat equations have been obtained under the assumption of no significant heating of the electrodes. It was found that pure thermal effects can lead to neither negative differential resistance regions nor high-current filaments. It can be shown that the discrepancy between this result and much of the published literature arises because of poor approximations in the latter calculations. Alternatively, when some electronic effects, such as space charge, narrow Schottky barriers, or field-enhanced conductivity, are explicitly introduced, negative differential resistance regions and filamentary conduction exist in agreement with the experimental results. Current-voltage characteristics, temperature distributions, and current density distributions have been derived as functions of thickness.

Approximate solutions to the time-dependent heat equations have also been obtained as functions of thickness and ambient temperature. The delay time and filament radii have been calculated and approximate analytic expressions for these functions have been determined.

Future Research Directions

Tunneling studies into chalcogenide glasses are planned, in order to determine the density of localized states in these materials. Low-temperature (4-77K) switching will be investigated in order to determine whether or not trap-filling is a significant feature of the ON-state. The photovoltaic properties of metal-chalcogenide glass junctions will be studied. The effects of thermal-neutron irradiation on the physical properties of chalcogenide glasses will be investigated in detail. An intensive study of the EPR spectra of memory-type material in both the conducting and non-conducting states is planned. We shall proceed with the comparative investigation of crystalline and amorphous Si_2Te_3.

The influence of strain, temperature, and electron bombardment on the properties of threshold switches are the three foci of the experimental work on thin-film devices planned for the coming year. Electron-beam-induced transitions in both threshold and memory material will be studied.

Publications

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6. D. Adler, "Metal-Insulator Phase Transitions: Science and Technology", Intern. J. Magnetism, in press.
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2. "Temperature Characteristics of an Amorphous Semiconductor Threshold Switch", Edward J. Sokolowski, Jr., S.B., M.I.T., June 1971.
3. "An Experimental Investigation of Physical Properties of Threshold-Type Amorphous-Semiconductor Devices", Marc A. Barman, S.B., M.I.T., June 1971.