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BAND STRUCTURE AND ELECTRICAL PROPERTIES OF AMORPHOUS SEMICONDUCTORS

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SUMMARY OF MAJOR ACCOMPLISHMENTS

1. Fabrication of Threshold Switches

We developed a procedure for fabricating threshold devices entirely by integrated-circuit photolithographic techniques, using either two Mo electrodes or an arc-deposited carbon lower electrode. These devices exhibited no formation effects, were quite reproducible, and routinely survived 10^7-10^9 switching cycles. The dc stability of the Mo-C devices was found to be much superior to that of Mo-Mo switches.

2. Effects of Contacts on Threshold Switching

Both ohmic and blocking contacts could be obtained. Blocking contacts yielded emission-limited currents until Schottky emission rendered them transparent. Rather than being deleterious to threshold operation, blocking contacts tended to limit the heating at low fields and provided for purely electronic switching.

3. Mechanism for Threshold Switching

Several measurements effectively eliminated thermal runaway as a mechanism for switching. These include the observation of complete independence of the recovery curve to ambient temperature down to below the λ-point of the liquid He bath and to power dissipated in the ON-state. The observation that the holding voltage could be much less than the activation energy for electrical conduction indicated that the ON-state represents a non-equilibrium quasi-metal. This could be induced at a critical carrier concentration by a non-equilibrium Mott or Anderson transition. Heterojunction results imply that double injection is necessary to sustain switching.

4. Electrothermal Calculations

Rather complete three-dimensional steady-state electrothermal calculations were carried out for a realistic geometry for the first time. These were adapted to the case of a purely electronic breakdown mechanism to yield the temperature distribution at several operating points in the ON-state.

5. Origin of the Holding Current

It was proposed and experimentally verified that under ordinary conditions the holding current is an artifact of the internal and stray device capacitance rather than a parameter intrinsic to the device. This observation suggests a technique for reducing the minimum power dissipation in the ON-state and is useful in the analysis of a wide variety of pulse measurements.

6. Characterization of Threshold-Type Amorphous Semiconductors

The electrical, optical, and photoconductive properties of a good threshold-switching chalcogenide glass were studied in detail. The mobility gap, Fermi energy, carrier lifetime, photoconductive decay time, and dielectric relaxation time were evaluated. It was found that these materials are not relaxation semiconductors and that the field activation of conductivity is a carrier-concentration rather than a mobility effect. The internal barriers at Mo-chalcogenide interfaces were characterized by photovoltaic measurements.

7. Fabrication and Properties of Crystalline-Amorphous Heterojunctions

Heterojunctions between a threshold-type chalcogenide glass and p- and n-type crystalline Si were fabricated and characterized. The p-type Si heterojunctions were rectifying at low fields, exhibited reverse

bias breakdown, and eventually assymetric switching for both polarities. There was a large photovoltaic effect. The n-type Si heterojunctions more resembled back-to-back Schottky diodes, and the photovoltaic effect was two orders of magnitude smaller. Simple band models for both types of heterojunctions were constructed which could be used to predict the low and high field behavior. These results suggest a wide range of potential uses for crystalline-amorphous heterojunctions.

SUMMARY OF RESEARCH

1.00 STUDIES OF CHALCOGENIDE-GLASS THRESHOLD SWITCHING

1.01 Fabrication of Threshold Switches

An rf-sputtering facility that permits preparation of a wide variety of films was designed and constructed. The facility consists of two vacuum systems, two stable rf supplies (100 watt, 500 watt), several interchangeable stainless-steel sputtering chambers of 8-inch diameter and 10-inch height; for support of the latter, a console containing gas-flow controls, pressure-sensing electronics, a recycling watercooling system for the targets, and rf matching networks were built. In addition, quartz crystal monitoring of deposit thickness was installed.

We developed a procedure for producing one-inch diameter disc-shaped sputtering targets by solidification in evacuated quartz ampoules. These solid fused targets were produced in thicknesses of one to four mm and were mounted as-grown onto metal support plates with a thermally conducting silver-loaded epoxy. Such targets proved to be quite homogeneous except for a very thin surface layer, and thus only a small amount of presputtering at low power densities was necessary to produce homogeneous films with hot-pressed fused-glass powder targets.

Chalcogenide films for most of our work were processed by integrated-circuit photolithographic techniques. Prior to deposition of the chalcogenide film, small windows, typically 50 μm in diameter, were etched through a 500 Å-1000 Å SiO_2 film to an underlying molybdenum contact layer. After deposition of the chalcogenide, a Mo film was rf-sputtered to form the top contacts. Electrical isolation of individual devices was accomplished by photolithographic metal etching of this struc-

ture, which resulted in an array of 0.5 mm diameter Mo electrodes contacting the chalcogenide film.

In some devices, arc-deposited carbon was used as the lower electrode. These yielded the highest quality threshold switches, which routinely survived 10^7-10^9 switching cycles with near-constant threshold voltage and greatly improved dc stability.

1.02 Formation in Threshold Switching

Threshold switching is often characterized by either a first-fire effect, after which the threshold voltage is sharply reduced over its virgin value, or a gradual deterioration of threshold voltage over many switching cycles. A photoconductivity study of virgin and formed devices indicated that formation affects both the dark current and the photocurrent in the same manner, thus implying that the conductivity increase which accompanies formation is an increase in average carrier mobility rather than in carrier concentration. Long-time recovery of virgin devices over a period of a few months in formed devices leads to the conclusion that formation is not just a thermodynamically stable phase separation or partial crystallization. Switching studies at low temperatures show that a new formation process must take place after the ambient temperature of a formed device is lowered beyond the minimum at which it was previously switched, also consistent with the above conclusion.

However, the major new result obtained is that we have been able to routinely fabricate devices which exhibit neither a first-fire effect nor a gradual deterioration of threshold voltage with repeated switching. In fact, the most reproducible and longest-lived devices are those which do not exhibit formation. Some of these devices, when switched with a

voltage pulse and a relatively light load, exhibited only a 3% deviation in threshold voltage for over 10^7 cycles. The implication of these results is clearly that formation is not essential to threshold switching.

1.03 Pulse Studies of Threshold Devices

In order to study the I-V characteristics of threshold switching devices in detail, a pulse generator which produces constant-current pulses instead of constant-voltage pulses was designed and constructed. Among other advantages, this has enabled us to investigate the unstable region for which the current is between the threshold and holding values. A major result that has been obtained by this technique is the independence of the recovery curve of threshold switching devices to the operating current over a range of a factor of 100 in operating current. The single time constant (approximately 1 μsec) which characterizes the recovery remains the same, despite an increase in over a factor of 60 in power applied to the device. This result precludes the applicability of a thermal mechanism for switching in these devices at all ordinary operating currents.

Other pulse measurements indicate that the preswitching delay time is largely independent of polarity, but that a sub-threshold prepulse of either polarity reduces the decay. Whereas the current during a sub-threshold pulse quickly saturates, it was found that prior to switching, no such current saturation exists.

1.04 Recovery Studies of Threshold Switches

A study of the recovery of a threshold switch after removal of the holding voltage from a device in the ON-state was carried out. Below 10^{-3} sec after turn-OFF the voltage necessary to reswitch the device ON can be represented approximately by

$$V_t = V_{ho} + (V_{to} - V_{ho})[1 - \exp(t_{off}/t_o)] ,$$

where V_{ho} is the minimum holding voltage, V_{to} is the original threshold voltage, and t_{off} is the time elapsed after turn-OFF. Only V_{to} is temperature dependent; t_o is of the order of 1 μsec, independent of temperature down to 1.6°K. An interesting feature of the last result is that although the device was cooled in a liquid-helium bath, no change in the recovery curve was observed when the helium transformed to its superfluid phase, a transition which increases its thermal conductivity by about a factor of more than 10^5. This is not what would be expected from a thermal switching mechanism.

The fact that switching and recovery proceeds normally down to 1.6°K indicates that the ON-state cannot be frozen in even at the lowest temperatures. If the ON-state is maintained by Schottky barriers due to trapped charge in the interface regions, it is difficult to understand why recovery of the OFF-state is characterized by the same time constants at 1.6°K and 300°K, since the trapping times should be enormously longer at the former temperature, especially in view of the fact that the observed conductance is more than a factor of 10^5 larger at 300°K than at 4°K.

An important result which emerged from the recovery studies is that the minimum holding voltage V_{ho} was found to be considerably below the activation energy for electrical conductivity of the bulk glasses. This observation strongly implies that localized states within the mobility gap of the amorphous semiconductor are rendered more mobile in the ON-state of the device.

1.05 Delay-Time Studies of Threshold Devices

The delay time before switching occurs, t_D, was found to obey an inverse square law of the form

$$t_D = K/(V-V_t)^2 ,$$

where K is a constant independent of voltage up to $2V_t$ and of temperature from 4°K to 300°K. Thus, the entire effect on the delay time of varying the temperature is the increase of V_t with decreasing temperature in the 250-300°K regime. A subthreshold pre-pulse of either polarity was found to decrease the delay time. Polarity reversal prior to switching was found to slightly increase the total delay time.

At still higher values of overvoltage, the delay time gradually deviates from an inverse square dependence and approaches an exponential dependence of the form

$$t_D = t_o \exp(-V/V_o)$$

where t_o and V_o are independent of voltage.

1.06 Low-Temperature Studies of Threshold Switching

Pre-switching behavior and switching parameters were studied over a temperature range from 1.6°K to 300°K. At all temperatures, in the preswitching regime, a region exists in which the conductance can be written

$$G(V,T) = T_o(T) \exp[V/V_o(T)] .$$

The evidence is strong, at least near room temperature, that this is bulk behavior and represents a field-assisted freeing of trapped carriers. Near room-temperature, $G_o(T)$ varies with temperature as

$$G_o(T) = G_{oo} \exp(-\Delta/kT) .$$

However, below about 250°C, the behavior can be better expressed as

$$G_o(T) = G_M \exp[-T_o/T)^{1/4}] ,$$

the temperature variation expected when phonon-assisted-tunneling conduction predominates. A typical value for T_o was 2×10^6 K. Since this conduction mechanism represents bulk behavior and since $G_o(T)$ is the observed value for the conductance at near-zero applied voltage, these results imply that phonon-assisted tunneling of trapped carriers near the Fermi energy is the predominant low-field conduction mechanism below 250°K.

Low-temperature studies of switching showed that the threshold voltage increases with decreasing temperature down to the vicinity of 250°K, below which a saturation occurs and the threshold voltage remains relatively constant. However, the threshold current decreases monotonically with decreasing temperature and appears to vanish as T approaches zero. Given the saturation of threshold voltage and the observed pre-switching conductance, the fact that the threshold current goes to zero at very low temperatures is then just a consequence of the vanishing of the conductance at T = 0.

1.07 Composition Dependence of Switching Parameters

The effects on the switching parameters of substituting Se for Te in some memory-type chalcogenide glasses were systematically investigated. In particular, the system $As_4Ge_{16}(Te_{1-x}Se_x)_{80}$ was studied in detail. Except for the regions near x = 0.5, no difficulty in producing homogeneous bulk glasses was encountered. However, good memory switching was obtained only near x = 0. The region $0.1 < x < 0.3$ provided threshold

switching with an increasing threshold voltage and relatively poor dc stability. The material could be thermally crystallized by annealing, but was then quite inhomogeneous and possessed a resistivity two orders of magnitude higher than that of the $x = 0$ conducting state. For $x > 0.6$, the threshold field had increased sufficiently that no electrical switching was obtained up to 400 V. These results are consistent with the hypothesis that doped, crystalline Te is primarily responsible for the high-conductivity state. Since Se is a wide-gap semiconductor and has a much higher crystallization temperature than Te, substitution of Se for Te should indeed have deleterious effects on the switching process.

A systematic study of the effects of varying phosphorus concentration on a threshold-type chalcogenide alloy, $Te_{40}As_{35}Si_{15}Ge_7P_x$ was also carried out. The glasses are metastable only for $x < 5$, and the switching properties vary significantly with small changes in the phosphorus concentration. Optimal behavior occurred for $x \simeq 1$.

1.08 Strain Dependence of Threshold Switching Parameters

The influence of static strain on switching was investigated by depositing films on PZT-4 ceramic piezoelectric transducers. Decrease of more than 25% were obtained when contraction in the plane of the substrate was 100 ppm (linear measure). However, the devices tolerated few deformation cycles before irreversible loss of the resistive state occurred. Measurements were than carried out on improved devices formed on passive silicon substrates and subject to more homogeneous strain provided by either hydrostatic pressure or modest biaxial deformation via substrate bending. These measurements failed to confirm the existence of large strain effects, the earlier observations being due to inhomogeneities in

the applied strain arising from the granular nature of the substrate. Careful measurements indicated that the actual decrease of threshold voltage with stress for a 17 V device is 1.2 V/Kbar. The delay time also decreases 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.

1.09 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 can be a good approximation.

1.10 Noise Measurements on Threshold-Switching Devices

The fluctuations in voltage across several thin-film devices of varying cross-sectional areas and thicknesses both in the absence and the presence of applied bias has been measured and frequency analyzed up to 100 kHz. The equivalent noise voltage without a dc bias exhibits a 1/f frequency dependence. However, in the presence of dc bias, a $1/f^{2.2}$ dependence was observed. The magnitude of the rms noise exceeded 10 mV at 50% of the threshold current. The observations were interpreted as burst noise, and is the effect most likely to cause the statistical fluctuations in delay time in the region just above threshold.

1.11 Non-Ohmic Effects in the Pre-Threshold Region

For a wide class of threshold devices, the ohmic region lasts only out to approximately 25 mV. It is followed by a small V^2 region, characteristic of space-charge limited currents. At still greater values of the field, a quasi-ohmic region exists, in which I is again proportional to V; however, this has been identified as emission-limited current. For such films, in the 1-10 V regime, the current increases proportional to $\exp (V/V_o)^{1/2}$, characteristic of Schottky emission from the electrodes. Finally, from about 10 V to threshold (60-70 V in these devices), the current is proportional to $\exp (V/V_o)$, and can be associated with a bulk effect such as Poole-Frenkel emission of trapped carriers.

However, in more carefully prepared devices, the ohmic region can be made to persist out to much higher fields, smoothly joining the Poole-Frenkel regime. In such devices, the threshold voltage is considerably smaller, approximately 10-20 V. Sub-threshold pulse measurements on these devices indicate that the current may saturate at a value larger than that attained after the decay of the displacement-current spike.

1.12 Optical Absorption, Photoconductivity, and Field-Dependent Conductivity in Threshold-Type Chalcogenide Films

A comprehensive study of optical and photoconductive properties of a sputtered chalcogenide film of composition $Te_{40}As_{35}Si_{15}Ge_7P_3$ was carried out. Optical absorption results yield a linear dependence of $(\alpha\hbar\omega)^{1/2}$ on photon energy, indicating an optical gap of 1.1 eV. Ten major conclusions follow from a detailed investigation of the field and polarity dependence of the photocurrent: (1) the predominant carriers are holes rather than electrons; (2) accumulation layers exist at molybdenum-chalcogenide interfaces; (3) these barriers sensitively depend on preparation

techniques; (4) the field activation of the conductivity is a carrier-concentration effect; (5) the carrier mobility and lifetime are essentially independent of applied field; (6) these materials are not relaxation semiconductors; (7) the carrier lifetime at room temperature is of the order of 10^{-9} sec; (8) the photoconductivity decay time is of the order of 10-15 μsec at room temperature; (9) the drift mobility is trap-controlled, and of the order of 3×10^{-5} sec; and (10) switching could not be induced by application of light of intensity up to 10 mW/cm^2.

1.13 Electron-Beam-Induced Conductivity in Threshold-Type Chalcogenide Films

Electron-beam-induced conductivity (EBIC) resulting from bombardment by 5-20 KeV electrons has also been studied as a function of applied voltage on these films. A threshold energy of about 7 KeV for appearance of the EBIC signal indicates a schubweg of much less than 1 μm. The EBIC gain was of the order of 100, resulting in carrier lifetimes of the order of 10^{-9} sec, in agreement with photoconductivity results. The calculated schubweg is approximately 1500 Å. The EBIC decay time of 50 μsec is also consistent with the photoconductivity experiments.

1.14 Origin of the Holding Current in Threshold Switches

It has been shown that the minimum holding current which characterizes threshold switching is just a consequence of the time rate of recovery of the threshold voltage after turn-OFF of the switch taken together with the total device capacitance. The lower-current regime of the transient ON-characteristics is made unstable by the noise intrinsic to the ON-state. These ideas have been verified experimentally by altering the external circuit capacitance. Using the associated analysis, we have been able to successfully analyze the results of recent double pulse experiments.

1.15 Electrothermal Mechanisms for Threshold Switching

Electrothermal switching models were theoretically analyzed as a mechanism for threshold switching in chalcogenide films. Numerical techniques were developed for simultaneously solving the set of steady-state electric and heat current flow equations, the energy-conservation equation, and Maxwell's equation in three dimensions. Solutions of these equations were obtained for a material whose electrical conductivity is either temperature-activated and field-independent or both temperature and field activated. In the former case, no differential negative resistance is obtained unless there is significant heating of the electrodes or Schottky emission or space-charge effects occur. The latter case always gives current-controlled differential negative resistance and high-temperature filamenting conduction paths between the electrodes. Comparison between theory and experiments shows that only the latter model can be applicable to amorphous switches. These solutions represent the only fully three-dimensional electrothermal analysis presently available, and they can be used to predict the I-V characteristics of a wide variety of materials and geometries. When pure electronic breakdown is the actual switching mechanism, these calculations can be used to evaluate the temperature distribution in the ON-state.

1.16 Electronic Mechanisms for Threshold Switching

The results of many of the experimental studies of threshold devices were found to be inconsistent with a thermally initiated origin for the switching process. Although several electronic mechanisms remain possibilities, the results are difficult to reconcile with avalanche or Zener breakdown processes. Because the minimum holding voltage was observed to be smaller than the activation energy for electrical conduc-

tion, the ON-state now appears to be most likely that of a non-equilibrium quasi-metal. Such a state can be brought about by a critical carrier concentration, which yields sufficient screening to induce either a Mott transition or an Anderson transition. Such a model is consistent with all the presently available data.

2.00 STUDIES OF MEMORY-TYPE CHALCOGENIDE ALLOYS

2.01 Nuclear Magnetic Resonance in Bulk Memory-Type Material

The NMR signals in both the conducting and non-conducting states of a chalcogenide alloy, $Te_{81}Ge_{15}As_4$, were measured. It was found that the nuclear magnetic resonance line of the Te^{125} nucleus undergoes a 0.1% shift between the conducting and non-conducting states. The Te^{125} resonance in the conductive state was observed to be at precisely the same frequency as in pure crystalline Te, but the spin-lattice relaxation time, T_1, was considerably reduced in the alloy. We concluded that the conducting state of the alloy contains polycrystalline regions of As-doped Te, the ionized As^- ions being the paramagnetic impurities responsible for the decrease in T_1. The 0.1% shift in the non-conducting state then represents a chemical shift due to a change in environment of the Te atoms in the glass, necessary if all of the valence requirements of each atom are locally satisfied in the latter, in accordance with the random covalent model for the structure of chalcogenide glasses.

Thermal cycling of the material between the two states indicated only two distinct states exist, the NMR lines having the same frequencies to five significant figures, the same peak heights, and the same line widths, independent of thermal history. This result is the most sensitive experiment to date indicating the inherent reversibility of memory switching.

2.02 Transport Studies of Memory-Type Chalcogenide Alloys

The dc conductivity from 4°K to 300°K, the ac conductivity at 300°K up to 150 KHz, the ac Hall effect from 77°K to 300°K, and the magnetoresistance at 1.6°K up to 140 kG of the conducting state of $Te_{81}Ge_{15}As_4$ were measured. The dc-conductivity measurements showed no carrier freeze-out down to 4°K, evidence for the semimetallic nature of the state. The Hall experiments showed a temperature-independent carrier concentration, in agreement with this interpretation, and a room temperature mobility of 85 cm^2/V-sec. The ac-conductivity results were typical of band-like conduction in an inhomogeneous material, and the magnetoresistance indicated a two-band model is applicable. All of these results are consistent with thermally activated memory switching being caused by a nucleation and growth of As-doped Te crystallites, with turn-off representing simply the revitrification of these crystallites.

2.03 Effective Charge of Ions in Chalcogenide Glasses

The Te^{125} NMR experiments discussed above were compared with similar measurements of PbTe and SnTe in order to obtain an estimate of the effective charge on the Te ions in the amorphous chalcogenides. It was concluded that the effective charge of a Te atom with two Te nearest neighbors is very small, that of a Te atom with two neighboring Ge atoms is -0.18 e, and that of a Te atom with two neighboring Ge atoms is -0.35 e. These relatively small values for effective charge in the chalcogenide glasses make it unlikely that a field-induced ferroelectric-type displacement accounts for the observed switching properties.

2.04 Optical-Memory Switching

A model was proposed to account for the surprising result that several chalcogenide alloys can be transformed from the amorphous to a crystallized phase and back again by applying identical laser pulses of the same intensity and duration. A combination of the effects of photocrystallization and the differences in absorption of laser radiation between the two phases can explain the experimental results in a simple manner.

3.00 PROPERTIES OF BULK CHALCOGENIDE GLASSES

3.01 Electronic and Structural Properties of the Amorphous Silicon-Tellurium System

Thin-film and bulk samples of silicon telluride glasses, Si_xTe_{1-x} with $0.02 \leq x \leq 0.25$, were prepared and studied by means of optical absorption, photoconductivity, infrared transmission, electrical conductivity, Hall effect, DTA, EPR, and x-ray measurements. The resistivity, optical energy gap, and glass transition temperature all increase with increasing silicon concentration throughout the glass-forming region, thus suggesting that the system does not phase separate. No EPR signal was detected in the bulk glasses down to 4°K, in sharp contrast to the Si_2Te_3 crystals. A p-type Hall effect was obtained; the Hall mobility is about 1 cm^2/V-sec and essentially independent of temperature, implying that small-polaron hopping conduction does not predominate in this system. All the results are consistent with a structural model for the amorphous system in which each silicon atom is four-fold coordinated and each tellurium atom is two-fold coordinated.

3.02 Transport Properties of $(As_2Se_3) \cdot (Sb_2Se_3)$ Glasses

Electrical conductivity and thermoelectric power were measured on several glasses in the pseudo-binary $(As_2Se_3)_{1-x}(Sb_2Se_3)_x$ system over the temperature range 300-470°K. The activation energies obtained from both conductivity and thermopower are equal within experimental accuracy for $0.0 \leq x \leq 0.2$. For larger values of x, the activation energies also appear to be the same, although the possibility of partial devitrification during the experiment precludes a more definitive conclusion at this time. The thermoelectric power was found to be p-type for all samples investigated. The activation energy drops essentially linearly from 0.94 eV for x = 0.0 to 0.76 eV for x = 0.4.

4.00 STUDIES OF AMORPHOUS SILICON AND GERMANIUM

4.01 Properties of Amorphous Silicon and Germanium Films

A critical review of the available transport and optical properties of amorphous silicon and germanium films suggest that at least two sharply distinct types of films exist. Type I films are deposited in ultra-high vacuum at low deposition rates; they show little or no effects upon annealing and have small optical gaps with relatively sharp abosrption edges. Type II films are deposited in lower vacuum, exhibit optical gaps about twice those of the type I films and are extremely sensitive to annealing. A consistent, although by no means unique, explanation of the available results is that there is considerable oxygen contamination of the type II films. Irradiation studies of type II amorphous silicon films carried out here indicate that both the optical gap and the observed band tail is essentially independent of radiation-induced defects, in agreement with the previous suggestion.

4.02 Heat of Crystallization of Amorphous Germanium and Silicon

The heat of crystallization of amorphous germanium and silicon has been evaluated in terms of bond bending and stretching energies, assuming the continuous random network model for the structure could be represented as a distortion of the diamond cubic crystalline structures. For the case of amorphous Ge, the distortion energy was found to be 17 meV/electron using force constants derived from the phonon dispersion curves of the crystal. The experimental enthalpy of crystallization is about 35 meV/electron, suggesting the calculation underestimates the distortion energy. The most likely explanation of the discrepancy is that the observed heat of crystallization contains large contributions from defects, such as internal voids and deposition-induced strains, not intrinsic to the ideal random network.

4.03 Irradiation Studies of Amorphous Silicon Films

An investigation of the effects of intense thermal-neutron irradiation on the physical properties of amorphous Si films was carried out. Thermal-neutron fluxes up to 8.3×10^{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 tunnelling 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 tunnelling results described in the previous paragraph.

4.04 Tunnelling into Amorphous Silicon

The tunnelling conductance of Al-SiO_2-amorphous Si-Al junctions was measured as a function of bias, temperature and frequency. The SiO_2 layers were 20-40 Å thick, thermally grown on the amorphous Si. Despite the facts that the impedance of the amorphous Si was negligible compared to the tunnelling impedance of similarly thick layers of SiO_2 between metallic electrodes at all temperatures investigated and that such tunnelling 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 tunnelling junctions as two series impedances fails in this case, This problem has been resolved by postulating that the low-bias conductance represents tunnelling into localized states in the amorphous Si. Consequently the tunnelling carriers must not only traverse the SiO_2 but also some distance into the Si. The temperature dependence then 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 tunnelling must dominate below a critical temperature. In such a case the low-bias differential tunnelling 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 77-300°K range investigated. The tunnelling 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 tunnelling conductance essentially vanishes for biases greater than $\pm$ 0.8 eV. From this result, the mobility gap of these evaporated films of amorphous Si can be estimated as 1.6 eV in agreement with optical measurements. AC measurements indicate the predominance of phonon-assisted tunnelling conducting in both the tunnelling junctions and plain amorphous Si films throughout the temperature range investigated.

5.00 THEORETICAL STUDIES OF AMORPHOUS SEMICONDUCTORS

5.01 Electrical Conductivity in Disordered Systems

The semiclassical theory of electrical conductivity of disordered systems was analyzed by means of a Monte Carlo technique. Both analog and digital solutions of the two- and three-dimensional conductivity of a heterogeneous lattice have been obtained and found to be in agreement. As opposed to the percolation probability, which indicates sharp behavior, the electrical conductivity exhibits only a gradual rise with the fraction of conducting sites. For the three-dimensional problem, the bulk conductivity obeys the relation

$$\sigma(p) = A(p - p_c)^2 ,$$

where p is the fraction of conducting sites, p_c is the critical value for percolation (0.30 for a simple cubic lattice), and A is a constant. If the disorder is Gaussian, as is the case for many systems of physical interest, the temperature dependence of the electrical conductivity can be evaluated. For relatively symmetric valence and conduction bands and band tails of the order of tenths of an electron volt, plots of the logarithm of the calculated conductivity as a function of $T^{-1/4}$ were essentially linear from 77°K through 300°K, in agreement with a great deal of experimental data. In this case, however, such behavior does not indicate the predominance of hopping in the vicinity of the Fermi energy, but rather band-like conduction in the absence of a sharp mobility edge.

5.02 Band Structure of Amorphous Semiconductors

A qualitative procedure for taking into account the effects of electronic correlations and electron-phonon interactions in the band tails of amorphous semiconductors was proposed. The resulting quasi-particle spectrum has many of the same features as appear in the simple one-electron approximation, but two important modifications must be introduced. Electronic correlations split the localized states in the valence-band tail into two quasiparticle bands, the splitting being of the order of tenths of an eV. On the other hand, localized states in the conduction-band tail are also pushed up in energy relative to the valence-band mobility edge, so that if the one-electron band tails overlap, the quasi-particle bands do also. Thus, a density of states at the Fermi energy and the presence of equal numbers of positively and negatively charged traps persist in the presence of strong electron-electron interactions.

The effects of electron-phonon interactions partially compensate for correlation effects, since ionic distortions around localized electrons reduce the energies of the localized states relative to those of the extended states.

5.03 Optical Absorption in Amorphous Semiconductors

The physical origin of the valence and conduction band tails in amorphous Si and Ge films was investigated in view of the recent structural studies. In ideal amorphous Si and Ge, the experimental evidence 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.

6.00 NON-OHMIC AND SWITCHING EFFECTS IN CHALCOGENIDE-SILICON HETEROJUNCTIONS

A study of the characteristics of heterojunctions between amorphous chalcogenide films and p- and n-type crystalline silicon has been

carried out. Very different results were obtained, depending on the nature of the silicon. Heterojunctions between the amorphous chalcogenide and p-type Si exhibit a rapid rise in current with voltage in forward bias, once an offset voltage of two volts has been exceeded. In reverse bias, an offset voltage of about one volt is also found, but for greater biases, a saturation current in quickly obtained. On the other hand, for n-type Si heterojunctions, the low-field I-V characteristics resemble those of back-to-back Schottky diodes.

Photoconductivity of these heterojunctions also was investigated. For the p-type heterojunctions, the reverse saturation current increases with increasing light intensity, yielding photo-diode behavior. A white-light intensity of 10 mW/cm^2 is sufficient to increase the reverse current by a factor of 40. The forward current is only slightly affected by the incident photons. With the n-type heterojunctions, both the forward and reverse currents are increased by the incident light. In the reverse direction, the saturation portion of the I-V characteristic is increased, similar to the p-type results. With a positive bias, the forward current is increased by photon bombardment, resulting in a forward characteristic similar to the high-conductivity portion of the reverse characteristic.

At sufficiently high fields, both types of heterojunctions exhibit ordinary switching behavior in forward bias. In the n-type heterojunctions, this switching can be induced by applied light. Switching in reverse bias was suppressed in the n-type heterojunctions, but was evident in the p-type heterojunctions after junction breakdown was obtained.

Simple band models for both types of heterojunctions were inferred from zero-bias photocurrent results. These models successfully predict the observed I-V characteristics. It can be concluded that in the p-type heterojunctions, the chalcogenide bands bend down and the silicon bands bend up at the interface. However, for n-type heterojunctions, both the silicon and the chalcogenide bands bend up, implying a net negative charge at the interface.

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