OPTICAL AND ELECTRICAL PROPERTIES OF AMORPHOUS ELEMENTAL SIMICONDUCTORS

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13 ABSTRACT

We report results of electrical and optical measurements on amorphous silicon and germanium. We find that the electrical and optical properties of amorphous silicon can be explained by a model in which internal surfaces or voids have electronic states corresponding to those found on cleaned crystalline surfaces. The results on amorphous germanium deposited at 4°K show an absorption edge of 0.36 eV and parabolic behavior over a large range of energies. This is to be compared with the behavior of films deposited at 300 K which shows a threshold of 0.85 eV and a deviation from parabolic behavior around 1 eV.

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I. Summary

The program for in situ measurements of amorphous materials is in full swing with several new observations on amorphous germanium. When deposited onto 4 K substrates, germanium shows a threshold energy for absorption of 0.36 eV and parabolic behavior over a large range of energies. In contrast films deposited at 300 K show a threshold of 0.85 eV and a deviation from parabolicity around 1 eV. This result is surprising and in some sense opposite to what one might expect.

The program for the study of amorphous silicon was focussed lately on an understanding of the behavior of films deposited at room temperature and mildly annealed. A mechanism which explains this behavior in terms of internal surface states has been proposed.

Recently we have undertaken an investigation of the effect of deposition rates on the ESR signal and conductivity. We find that as the rate decreases, the ESR signal diminishes and the conductivity de-decreases. Our results are only qualitative at this point.

II. Research Program and Plan

Ge films are to be produced at higher substrate temperature (77, 300, 450, 600 K). In situ electrical and optical measurements would be made on these samples. The measurements made on films deposited at high substrate temperatures will be compared with corresponding results obtained on films deposited at low temperatures and subsequently annealed to higher temperatures.

The emphasis in the silicon work will be devoted toward making more definitive measurements of ESR and conductivity in order to obtain a better understanding of the effect of deposition rate.

III. Progress during the Period

1. In Situ Measurements

In situ measurements of reflection and transmission and temperature dependence of conductivity on films deposited at 4.2 K have been continued. The measurements are repeated on in situ annealing the same film to higher temperatures.

As pointed out in earlier reports the absorption coefficient of as-deposited films is much higher as compared to 300 K anneal films. The data of reflection and transmission have been analyzed to obtain the spectral dependence of absorption coefficient. Fig. 1 shows the typical frequency dependence of absorption coefficient measured at 4.2 K of a film deposited at 4.2 K and subsequently annealed to different higher temperature anneal state. As is clear from Fig. 1 the spectral dependence of absorption coefficient is not affected significantly on annealing to 77K. Anneal to higher temperature shifts the curves to higher energy. Replot of the data of Fig. 1 in the form $\sqrt{\alpha h\upsilon} \propto (h\upsilon - E_o)$ is shown in Fig. 2. As-deposited film yields a straight line fit in the studied spectral range of 0.62 - 1.55 eV. The extrapolation to zero enables us to obtain the threshold energy E_o which for as-deposited is found to be 0.36 eV. On the other hand 300 K anneal films yield a straight line fit in the energy range of 1 eV < $h\upsilon$ < 1.55 eV, an energy range relatively smaller than as-deposited film. The corresponding value of the threshold energy for the 300 K annealed film is found to be 0.85 eV. The reduced gap for as-deposited films, 0.36 eV as compared to 0.85 eV for 300 K annealed state is presumably due to enhanced disorder expected in films deposited at low temperature. It is interesting to point out that Keller and Ziman[1] computed the relation between energy gap and degree of disorder in local tetrahedral configuration of tetrahedrally

bonded amorphous semiconductors. They showed that if increasing disorder is introduced in the system by allowing large fluctuations in distances of 2nd nearest neighbors, then the energy gap is considerably reduced. Our observation seems to be consistent with their conclusion.

The question whether the unannealed or/and annealed films show exponential dependence of absorption coefficient (α) has been reported by others[2] is not obvious from our measurements. A relation of the form $\alpha \propto \exp \frac{h\upsilon}{\Delta}$ is taken as an evidence of the exponential tailing of density of states with Δ describing the characteristic energy of such distribution. As is clear in Fig. 1, although in a limited energy range, we can describe our curves by the exponential relation but not over the whole energy range. A better fit over the studied energy range for as-deposited films is the relation $\alpha\, h\upsilon \propto (h\upsilon - E_o)^2$ relation (Fig. 2). This relation suggests non-direct transition between parabolic filled (bonding) to empty (antibonding) bands. In contrast to as-deposited films the 300 K anneal state shows a deviation from this parabolic relation $\sim$ 1 eV. The parabolic fit over extended energy range for as-deposited films as compared to 300 K films is surprising. One would have intuitively expected that films deposited at low temperature would have given rise to larger numbers of dangling bonds as compared to room temperature deposited films. The presence of dangling bonds would severely affect the parabolicity of the bonds. Although one should treat such a parabolic fit with caution, we have observed this behavior in 15 films studied so far. This gives us enough confidence to trust the fit. The origin of dangling bonds in room temperature deposited films has been reported to be due to the presence of voids or/and microcracks.[3] The presence of voids[2] has been suggested as affecting the parabolicity. On annealing to 300 K it is shown that at higher energy it is possible to describe the absorption curve by the parabolic relation. We can argue that

for low temperature deposited films atomic mobility is negligible for formation of voids and/or microcracks. Therefore we get homogeneous highly disordered amorphous Ge films. On annealing to higher temperatures > 300 K, the system relaxes due to increased atomic mobility. This relaxation process may cause voids in the film affecting the parabolicity of the bands at lower energy.

Electrical measurements show the following features:

a) The electrical conductivity of low-temperature deposited films when measured at 77 K is about 5 orders of magnitude higher as compared to 300 K anneal films.

b) For conductivity values at low temperatures we have found a relatively good fit of the Mott relation for hopping conduction:[4]

$$\sigma = \sigma_o \exp -\left(\frac{T_o}{T}\right)^{1/4} \tag{1}$$

$$T_o \sim \frac{18\,\alpha^3}{k\,N(E)} \tag{2}$$

$$\sigma_o = \left(\frac{N(E)}{\alpha\,kT}\right)^{1/2} \left(\frac{3e^2\,\nu\,\phi_o}{2}\right) (2\pi)^{-1/2} \tag{3}$$

where α is the inverse fall-off length of the wave function of a localized state near the Fermi level, N is the volume and energy density of such states, k is the Boltzmann constant, e is the electronic charge, ν is the typical phonon frequency, and ϕ_o is an overlap integral and is a constant of order unity.

We find that on annealing films to higher states of anneal (at annealing temperatures of 32, 77, 120 and 300 K), T_o increases systematically

from values of 10^7 to 10^8 K. If we try to qualitatively interpret this result from Eq. (2) this would suggest the density of localized states N(E) decreases on annealing. This is a result one would expect, since one expects relaxation of the lattice on annealing.

Since the prefactor also contains the term of the density of states, we tried to calculate N(E) by knowing from our data both σ_o and T_o. We found that $\sigma_o\sqrt{T}$ increased from 10^6 to 3×10^8 $\Omega^{-1}cm^{-1}K^{1/2}$ on annealing from 32 to 300 K. On calculating N(E) simultaneously from Eqs. (2) and (3) we found that for films annealed up to 32 K we got $N(E) \sim 10^{18}$-$10^{19}cm^{-3}eV^{-1}$, a very reasonable number. But for anneals to higher temperatures we got $N(E) \sim 10^{25}cm^{-3}eV^{-1}$ and it was increasing with annealing temperature due to dominance of increased values of σ_o. We believe that at low anneal states when the conductivity is high, we can measure temperature dependence of conductivity at low temperatures where hopping is expected to be the dominant mode of conduction. On anneals to higher temperatures, conductivity shows an irreversible decrease by a large magnitude as pointed out before. Because of large resistance we cannot measure resistance at low enough temperatures where hopping conduction is only expected. For this reason, for higher temperature anneal states we may be probing that temperature region where in addition to hopping conduction we may have contribution from extrinsic conduction. So relation (1) may not be applicable.

2. Electrical and Optical Properties of Amorphous Silicon

This project has largely constituted the thesis of Adam Lewis and has now been completed. Portions of this work describing the anneal stable state were published as a Physical Review Letter.[5] Since the last report the electrical properties of as-deposited and mildly annealed

amorphous silicon have been investigated. It appears that the electrical and optical properties for such conditions can be accounted for by internal surface states which correspond to surface states of cleaved crystalline silicon. The basic idea is that films produced at room temperature presumably have internal voids which form an interconnected network. These voids are believed to produce a large ESR signal and large d.c. conductivity. As the material is annealed, the ESR signal and conductivity diminish corresponding to the decrease of the total void volume. The identification of internal surface states in the void structure with surface states at a cleaved surface is made by identifying the activation energies found in these measurements with the known energies of the cleaved surface. Support for this is obtained also from optical data of other investigators.

The results were recently discussed at the New York American Physical Society meeting[6] and also have been submitted for publication. A preprint is attached.

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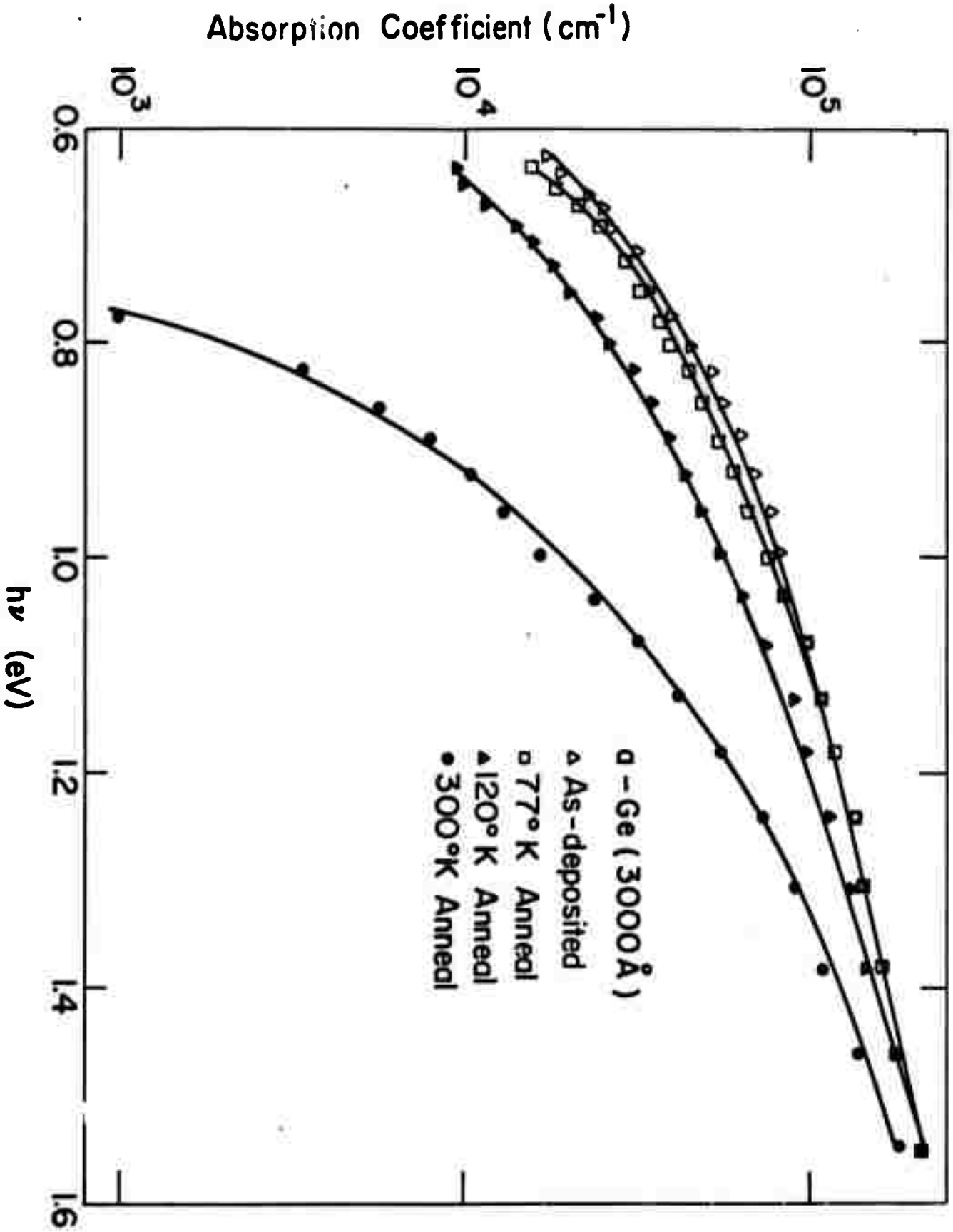
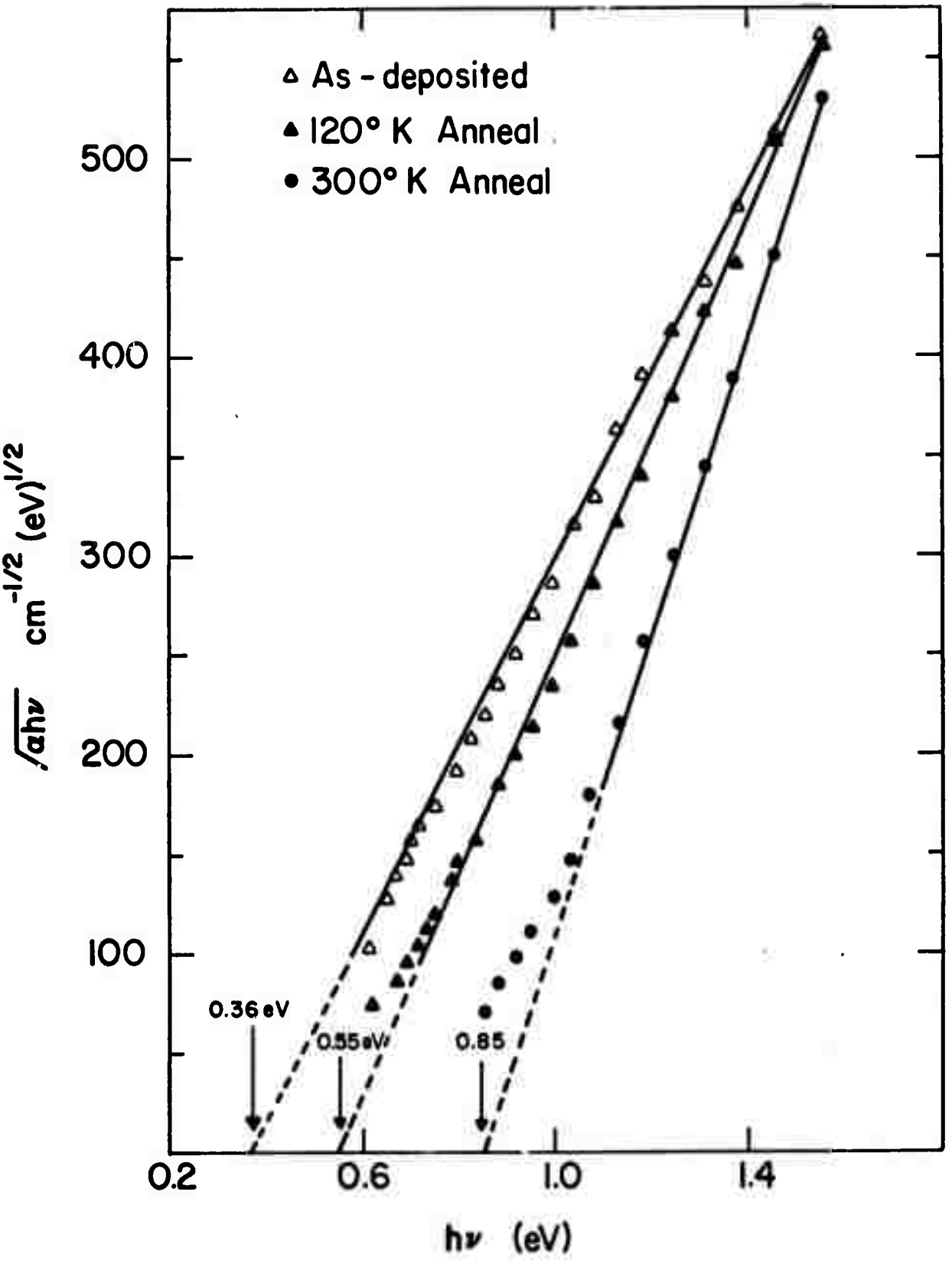

Absorption Coefficient (cm^{-1})
10^3
10^4
10^5
0.6
0.8
1.0
1.2
1.4
1.6
hν (eV)
a-Ge (3000Å)
As-deposited
77°K Anneal
120°K Anneal
300°K Anneal


△ As - deposited
▲ 120° K Anneal
● 300° K Anneal
500
400
300
200
100
$\sqrt{\alpha h\nu}$ $cm^{-1/2}(eV)^{1/2}$
0.36 eV
0.55 eV
0.85
0.2
0.6
1.0
1.4
$h\nu$ (eV)