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[24]The Raman experiments were done on samples containing a small percentage of $J=0$ molecules. Taking this into account will increase the value of Γ by a few percent.

PHOTOEMISSION FROM AMORPHOUS SILICON*

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Measurements of photoelectric yield and energy distributions from amorphous silicon films are presented. The results are consistent with an exponential tail in the density of states extending from the valence band to the Fermi level. Mild heat treatment decreases the amplitude of this tail. Tentative explanations of these observations are given.

Amorphous elemental semiconductors are particularly well suited for studying the influence of long-range order or the lack thereof on the electronic structure of materials. The absence of long-range order in amorphous materials is expected[1-3] to produce exponential tails in the density of states near the band gap were crystals have sharp edges. A puzzling case is presented by germanium, where an exponential tail has been observed by some authors[4,5] by optical absorption measurements, while others[6] report well-defined optical thresholds as in crystals. Additional support for sharp band edges comes from the measurements of photoelectric emission by Donovan and Spicer,[7] who report energy distributions with sharp high-energy cutoffs. Thus the existence of an exponential tail in elemental amorphous semiconductors seems open to question.

We present photoemission data obtained from vapor-quenched amorphous silicon films. Samples were prepared by a sublimation technique described by Thomas and Francombe.[8] The films, several thousand ångstroms thick, were deposited onto etched singls-crystal [111] silicon substrates, held at liquid-nitrogen temperature during deposition and the first experimental runs. The source material was 1-Ω-cm n-type silicon. Transmission electron-diffraction studies of samples similarly prepared in an evaporator showed the broad halos characteristic of the amorphous state.[9] All photoemission samples were prepared in ultrahigh vacuum and measured in situ; ambient pressures were in the 10^{-11} Torr range after bakeout, although this increased to 10^{-7} Torr during sample fabrication. Energy distribution curves were measured by the retarding-field method. A rotatable sample holder supported two amorphous silicon samples and a metallic (W) emitter. Energy distributions from the latter enable measurement of all electron energies with respect to the Fermi level[10]; this is significant in light of the results presented below.

The samples could be heated to temperatures below the crystallization temperature by electron bombardment. Effects of such mild heat treatments have been reported with regard to optical and electronic properties, ESR and conductivity in particular, and have been interpreted as a reduction in number of vacancies[11] or of dangling bonds.[11,12]

Figure 1 presents the yield spectra for three representative amorphous samples, one of which was also heated. The yield is given in electrons emitted per absorbed photon; reflection of incident light was accounted for with the help of the reflectivity measured by Beaglehole and Zavetova.[13] Also shown in Fig. 1 are yields for cleaved[14] and for annealed Si crystals[15] reported by Allen and Gobeli. There are several features to be noted:

(1) The yield of all amorphous samples is higher than for crystals. This is expected since

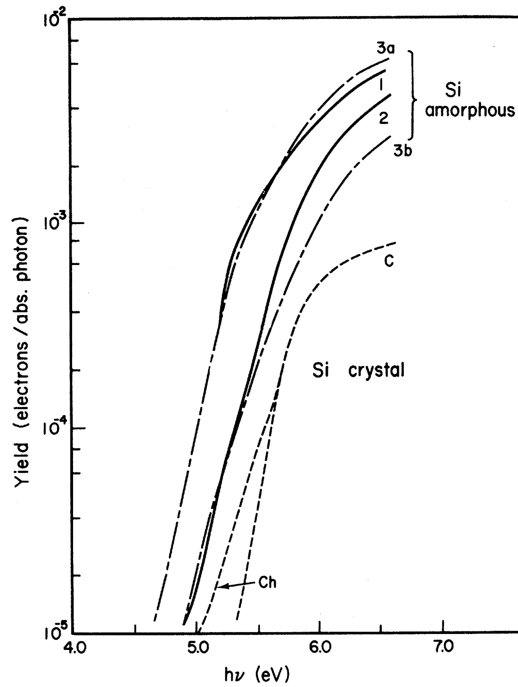

FIG. 1. Photoelectric yield spectra of amorphous and crystalline silicon. C: cleaved Si (Allen and Goveli); Ch: cleaved and heated; 1, 2, 3: amorphous films; $3a$, as deposited; $3b$, after mild heating.

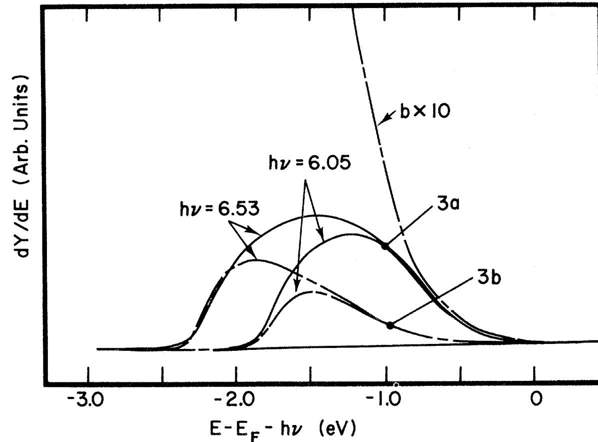

FIG. 2. Energy distributions of amorphous Si film before and after heat treatment at two different photon energies $h\nu$. Curves $3a$: freshly deposited films; curves $3b$, after mild heat treatment. These curves were obtained from the film giving the yield spectra $3a$ and $3b$ in Fig. 1.

the work function of amorphous silicon (4.4 eV from Fig. 2) is lower than that of crystals (4.73 eV).[14]

(2) The yield decreases exponentially towards lower photon energies. (The low-$h\nu$ part of the yield for annealed surfaces has been attributed by Allen and Gobeli to emission from surface states.[15]) It is impossible to fit the amorphous yield data to a power law near threshold as is done for crystals.[14]

(3) The amorphous films do not exhibit the transition to a linear yield at higher photon energies observed with crystals.[14] (This is evidenced by sharper curvature in the log plots C and Ch of Fig. 1.)

(4) Mild annealing decreases the photoelectric yield and displaces the exponential (low $h\nu$) part of the curve.

Figure 2 shows the energy distributions obtained from the amorphous films whose yield spectra are shown in Fig. 1. Note that the plot shows the energy of emitted electrons minus the photon energy $h\nu$; the abscissa thus represents the energy of the initial state of the transition with respect to the Fermi level. These energy distributions from amorphous silicon exhibit a gradual tailing off towards higher energies that extends all the way up to the Fermi level. As expected, the high-energy tails obtained with different photon energies $h\nu$ coincide, an indication of the absence of selection rules based on k-vector conservation.

The dashed lines in Fig. 2 show the effects of mild heat treatment; we observe the following: (1) Heat treatment greatly lowers the number of electrons in the high-energy tail in the distribution. (2) Despite that decrease, a more sensitive scale (×10) shows that the tail still extends to the Fermi level. (3) The low-energy cutoff of the distribution represents a work function of $\varphi = 4.4 \pm 0.1$ eV that is unaffected by mild heat treatment. Therefore the threshold of curves $3a$ and $3b$ of Fig. 1 is the same (4.4 eV); annealing shifts the exponential tail of $3b$ (Fig. 1) in amplitude with respect to $3a$, not in photon energy.

The energy distributions of Fig. 2 are compatible with the existence of an exponential tail in the density of states between the valence band and the Fermi level. The curvature of the distribution $3a$ (Fig. 2) changes sign at $E - E_F - h\nu = -0.6$ eV. In agreement with a mobility edge model,[2,3] this can be interpreted in terms of electrons with $E - E_F - h\nu > -0.6$ eV representing an exponential tail, and those with $E - E_F - h\nu < -0.6$ eV having been excited from the valence band, where the density of states is proportional to $(E_V - E)^{1/2}$. According to this speculation the Fermi level lies approximately in the middle of the band gap ($E_g = 1.2$ eV) of the amorphous silicon films, which is consistent with the fact

that amorphous silicon is intrinsic at room temperature.[16]

Mild heat treatment decreases the emission contributed by the high-energy tail by a factor of 10 (see Fig. 2), indicating a decrease in the density of states in that tail, in agreement with the results of mild annealing on ESR, electrical conductivity, and optical absorption measurements of Brodsky, et al.[12] There is also a marked decrease in the photoemission at energies corresponding to optical excitation from the valence band, i.e., at $E-E_F-h\nu<-0.6$ eV. Although the available data do not allow definite statements, we propose two tentative explanations. One can interpret this change in terms of a decrease in density of states or in density of optical transitions near the band edge. Alternatively, one can consider curve 3*b* (Fig. 2) in terms of an increased splitting between the Fermi level and the valence band; this could occur if the heat treatment causes some of the phosphorus atoms coevaporated with the silicon to become active donors as in crystals or if annealing causes an increase in "band gap."[12]

Figure 2 could be interpreted in terms of band bending near the surface without the above-mentioned tail of localized states. In that case, however, either the bulk or the surface should be at least nearly degenerate *p* type and the temperature dependence of the electrical conductivity of the thin amorphous[17] films should resemble that of strongly doped crystals, which is contrary to experimental results.[12,16] We therefore conclude that band bending (which may very well be present) cannot by itself account for our results, and that the latter are due at least in part to a tail of localized states.

Also, emission from surface states, in the rare cases where it has been observed,[15] gives energy distributions that are qualitatively different from those in Fig. 2.

Two of the ten films studied gave a different result, although all samples were prepared in the same manner.[18] The energy distributions of these samples were very similar to those obtained from metals, although the respective yield data were similar to those of Fig. 1 and the work functions were about 4.4 eV as for the other samples. These metal-like distributions were also consistent with the lack of optical selection rules expected for amorphous materials, as evidenced by the observation that the high-energy end superimposed for an $E-h\nu$ plot. Further work including structure studies and in situ Auger spectroscopy will be carried out to elucidate differences in thermal history or chemical makeup of the two kinds of samples, which would account for the differences in electron energy distributions.

The data presented above are in contrast to those obtained from germanium by Donovan and Spicer[7] who report the absence of an expontial tail. Thus the lack of long-range order has different effects on the two elements. It is also possible that the difference in method of preparation is responsible for the varying results; Donovan and Spicer deposited their germanium onto substrates at room temperature while our films were deposited onto substrates cooled with liquid nitrogen. It is evident that thermal history of the films also affects the photoemissive properties in addition to the reported dependence of conductivity and ESR on thermal history.[12]

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MEASUREMENT OF n-TYPE GERMANIUM MICROWAVE CONDUCTIVITY DURING IMPACT IONIZATION OF IMPURITIES AT 4.2°K

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We have measured the microwave conductivity of n-type germanium with $N_D-N_A \sim 10^{14}$ cm^{-3} during impact ionization at 4.2°K, by means of a cavity perturbation method which requires no knowledge of the electronic spatial distribution. Values of the electronic temperature derived from the microwave conductivity are compared with theoretical predictions and Hall mobility data at higher temperatures.

We present a measurement of the complex microwave conductivity of n-type germanium at 4.2°K during impact ionization of neutral impurities (arsenic, N_D in the range 10^{14} cm^{-3}), using a dielectric cavity perturbation method. The cavity, containing dielectric of relative permittivity $K \sim 9$, is rectangular and operates at a central frequency $F_0 = 4065$ MHz in the TE_{011} mode. The germanium rod is introduced as shown in Fig. 1. The measurements can be performed either with stable dc current across the sample, with the dc electric field parallel to the rf electric field, or with short pulses to check whether or not heating occurs. rf measurements are made at a very low power level to avoid nonlinear effects. The apparatus is immersed in liquid helium and is protected from light. Variations of the resonant frequency F_0 and the quality

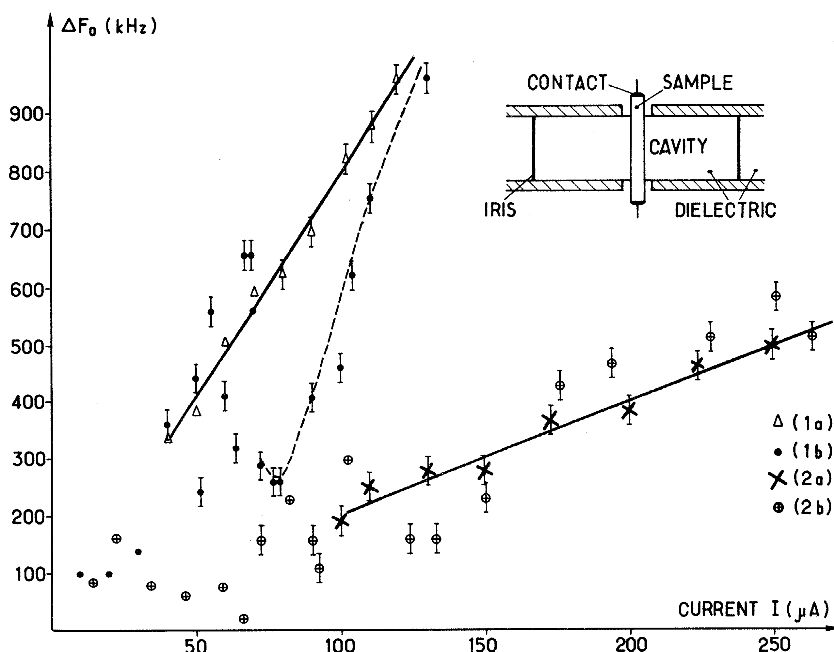

FIG. 1. Resonance-frequency shifts versus the current in the samples, and schematic drawing of the apparatus.