Tunneling in Hydrogenated Amorphous Silicon

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(Received 23 February 1979)

For the first time, structure has been found in the electron tunneling characteristics of a metal-oxide-semiconductor tunnel junction of an *amorphous* semiconductor. In the present study the amorphous semiconductor is phosphorus-doped hydrogenated amorphous silicon. The results have been analyzed to determine the *surface density of states* over part of the forbidden gap. The basic features of the density-of-states distribution are in agreement with the results of field-effect measurements reported for this material.

Fifteen years ago Gray[1] demonstrated that information concerning the electronic states of a semiconductor can be deduced from the conductance-voltage (G-V) and capacitance-voltage (C-V) characteristics of a MOS (metal-oxide-semiconductor) tunnel junction. His ideas were extended[2,3] and were made a tool for the determination of the density, the energetic location, and the recombination time of semiconductor surface states.[4,5] The intensive study of amorphous semiconductors in the last decade prompted many researchers to try to apply this tool with the hope that the G-V characteristics could be analyzed to yield information about the density of localized states in these materials.[6] The results of all these studies were rather disappointing since these characteristics were found to exhibit a universal symmetry and to lack any structure even for elemental amorphous semiconductors, where a structure in the density-of-states distribution might be expected.[6,7] Thus it appeared "that tunneling studies do not yield an easy answer to the question of localized-state distribution but instead they pose new and interesting problems."[7] This universality of the G-V tunneling characteristics must be attributed to the two typical qualities of amorphous semiconductors, viz. the high density of states in the gap and the hopping-conduction mechanism in the bulk. These two qualities were removed to a large extent in the dopable amorphous silicon-hydrogen alloy, a-Si:H, first investigated by Chittick, Alexander, and Sterling.[8] More recently Spear and LeComber[9] have shown that doping with phosphorous makes the dominant conduction take place in the conduction band and that the density of states, $g(E)$ (determined by field-effect measurement), is relatively low. Since they found a distinct structure in the density of states, it seemed reasonable to investigate this amorphous material as a test case for determining whether tunneling in such materials can be as useful a tool as it is for crystalline semiconductors. In this Letter we intend to show that

indeed this is the case.

The junctions prepared for this study were made by first depositing ~1100 Å of a-Si:H on a stainless-steel substrate. The material was prepared by decomposition of SiH_4 with 0.1% PH_3 in a dc proximity[10] glow-discharge system[11] with a substrate temperature, T_S, of 350°C. Films made under these conditions were found to have a resistivity of about 500 Ω cm, in agreement with the resistivities obtained by Spear and LeComber[9] for the same gaseous impurity ratio. The films were oxidized for a few days in air at temperatures up to 150°C. The thickness of the oxide of the tunnel junction reported here was 24 Å. The oxide thickness was obtained by ellipsometry where we used the SiO_2 refractive index for the oxide (1.45) and the recently determined[12] optical constants of a-Si:H ($n = 4.5$ and $\kappa = 0.34$). While it is likely that the oxide contains a significant amount of hydroxyl groups, we have found that its physical and chemical properties are similar to those of SiO_2. In particular, if we assume a dielectric constant of 4.0 for this oxide, the thicknesses obtained from capacitance and ellipsometry were always in agreement with each other to within 20%. The top electrodes of the junctions were made by evaporating Cr dots, with an area A of 1 mm^2 and a thickness of 1500 Å. In the measurements we have employed, the standard techniques of measuring the dc current versus voltage (I-V) characteristics[1,6] and of measuring the differential conductance (G-V) and capacitance (C-V) characteristics.[4] The latter quantities were determined by the in-phase and out-of-phase components of the current induced by a small (1 mV) ac test signal, and detected by a PAR model 124 locl-in amplifier. The voltage across the junction was gradually increased using a ramp generator (5 mV/sec).

The I-V characteristics of junctions for which the oxide thickness, d, was between 20 and 30 Å were found to be asymmetric and a structure could be recognized between -0.1 and -1.0 V.

This structure becomes more apparent if one takes the derivative of the I-V characteristic by numerical or electronic differentiation. The latter, obtained from the low-frequency G-V characteristic of the junction, is shown by the dashed curve in Fig. 1. As the frequency of the test signal is increased, a clear peak in the G-V characteristic is revealed. This is shown by the solid curve in Fig. 1. Beyond the voltages $V_c = -1.50$ and $V_v = 2.25$ V the characteristics become independent of frequency. As is apparent from Fig. 1 the resistance of the junction is 10^6 Ω at $V = 0$. Comparing this with the corresponding metal-semiconductor-metal structure resistance which is about 1 Ω, indicates clearly that the problem of the voltage drop across the bulk of the amorphous semiconductor[6] does not exist. The C-V characteristics, to be discussed elsewhere, have also shown a peak at -0.3 V. This peak was found regardless of the thickness of the oxide (as expected for the surface-state differential capacitance of an MOS structure) while the structure in the I-V and G-V characteristics disappeared for very thin oxides (< 15 Å). The latter observation is due to the fact that in the thin-oxide case the tunneling into the conducting bands masks the tunneling into interface states.[3] All these observations are consistent with the tunneling-controlled mechanism[3] where the surface-state recombination time is much shorter than the tunneling time
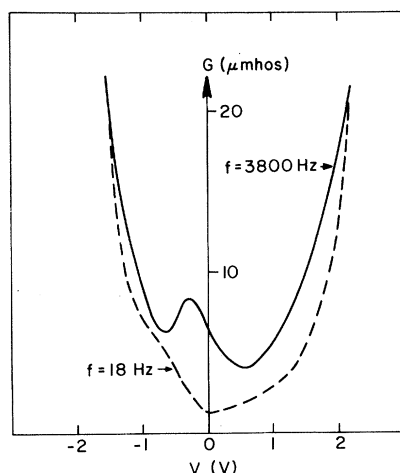

FIG. 1. Conductance-voltage characteristics of a tunnel junction of phosphorus-doped hydrogenated amorphous silicon. The oxide thickness was 24 Å and the resistivity of the amorphous semiconductor was 500 Ω cm. Note that negative V means that the Cr upper electrode is negative and that the metal's Fermi level is above the semiconductor's Fermi level.

constant.

Since the features of the data shown in Fig. 1 are similar to those expected[2,3] and observed[1-5] in crystalline MOS structures, and since the density of surface states N_S, expected for the present material [i.e., $g(E)^{2/3}$ using the data of Ref. 9], yields an N_S distribution of similar magnitude and energy dependence as observed in crystalline MOS structures,[5] we shall interpret our results according to the procedures[3,4] used for these structures.

To set the energy scale we must determine the applied voltages that correspond to tunneling into the conduction and valence bands. A good criterion is the frequency independence of such a tunneling process.[2-4] Using the theory of Ref. 2 with the dielectric constants of Si and SiO$_2$ for a-Si:H and the present oxide, respectively, we found that for positive voltages approximately $\frac{1}{3}$ of the voltage drops across the accumulation layer, while for negative voltages approximately $\frac{5}{6}$ of the voltage drops across the depletion layer (using $d = 24$ Å, $V_c = -1.5$ V, $V_v = 2.25$ V, and a carrier concentration, n_b, of 5×10^{15} cm^{-3}). We have assumed in this calculation (in accord with Ref. 9) a value of 5 cm^2/V sec for the extended states mobility (to deduce n_b), and a zero surface potential[9] at $V = 0$. Away from the band edges the theory[2] is not sensitive to variation of carrier concentrations in the range $10^{17} \geq n_b \geq 10^{15}$ cm^{-3}, to N_S smaller than 10^{12} cm^{-2} eV and to the assumption of zero surface potential. Since the ac conductance method, to be described below, is also not applicable close to the band edges,[5] E_c and E_v, our energy scale becomes less reliable as these edges are approached. However, using the theory of Ref. 2, we get $E_c - E_F = 0.27$ eV and $E_c - E_v = 1.72$ eV in good agreement with the values obtained in Ref. 9 for samples of comparable resistivity. Here E_F is the semiconductor's Fermi level.

The structure in the ac G-V characteristics is well known to represent the recombination-generation kinetics via surface states.[1-5] As the magnitude of the applied negative voltage increases, E_F sweeps across the band-gap region $E_F \geq E \geq E_v$ while for positive voltages E_F sweeps across the region between $E_F \leq E \leq E_c$. Since it is easier and more common[2-5] to interpret these characteristics rather than the dc characteristics,[3] we will use the former procedure to deduce $N_S(E)$. The relation between the surface density of states N_S at a given energy E (or the corresponding applied voltage V) and the ac conductance associated with

it, $\Delta G(V)$, is given by[3-5]

$$N_S(V) = 2[\Delta G(V)/\omega]_m/qA, \tag{1}$$

where q is the electronic charge and $[\Delta G(V)/\omega]_m$ is the $\Delta G(V)$ to angular frequency ratio at the applied frequency $(f = \omega/2\pi)$ for which this ratio has its maximum. We could identify such maximas for voltages in the range $0.9 \geqslant V \geqslant -0.6$ V. Outside this range but within the interval $V_v > V > V_c$ a rather universal monotonic increase of G with ω was observed. Typical results for the two voltage regimes discussed are shown in Figs. 2(a) and 2(b). $\Delta G(V)$ was determined by subtracting the monotonic frequency-dependent background [shown in Fig. 2(a)] from the measured conductance. As can be seen in Fig. 2(a), this was a small correction in the frequency range where maxima were found, $1000 \geqslant f \geqslant 40$ Hz. From results such as those shown in Fig. 2(b) we were able to map out N_S as a function of the energy $E - E_F$ in the region $E_F + 0.1 \geqslant E \geqslant E_F - 0.5$ eV.

Although the results obtained by the procedure described above are strictly associated with the surface states, we present them in terms of $N_S^{3/2}$ vs $E - E_F$ in Fig. 3. This is done in order to make a comparison with the results reported in Ref. 9 [that were claimed to be associated with the bulk density of states $g(E)$]. In addition, we show our $N_S^{3/2}$ vs $(E - E_F)$ results as obtained from the low-frequency capacitance measurements with the use of the well known $N_S(V) = C_S(V)/qA$ relation.[5] In the latter measurements we were able to cover a somewhat wider energy range. The agreement between our two sets of results is quite good and the difference between them is probably indicative of the error in estimating N_S. Since the capacitance and the conductance measurements are expected to yield the same information we do not elaborate on the capacitance measurements here. The above agreement indicates that our interpretation of the data in terms of surface-states distribution is justified. We should note, however, that because of the high density of surface states the energy range that the semiconductor's Fermi level is able to cover is probably smaller than indicated in Fig. 3. Hence the scale around $E - E_F = 0$ should be "compressed." This is in the direction of improving further the agreement between the present results and the field-effect results (given by the dashed curve).

From other field-effect measurements[13] and optical absorption measurements,[12] it appears that
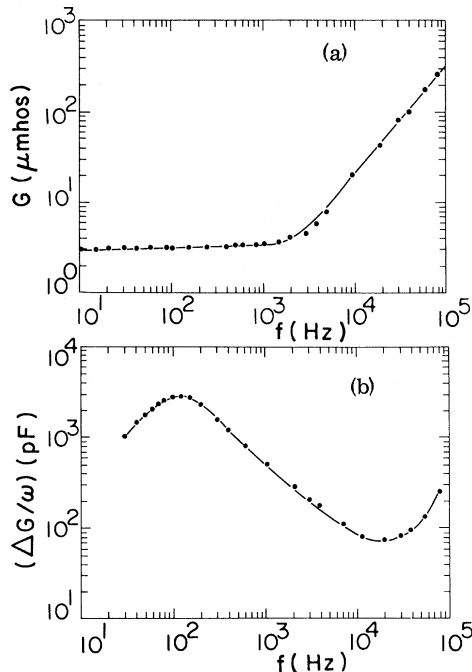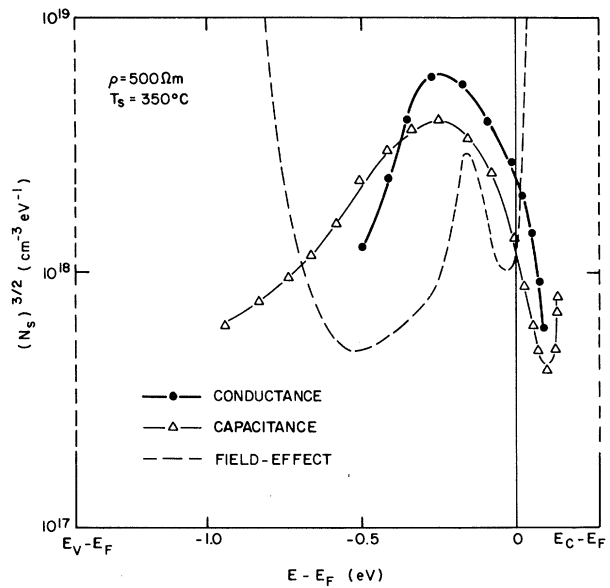
FIG. 2. (a) The frequency dependence of the tunnel-junction conductance at $V = 1.0$ V and (b) the frequency dependence of the ratio of the additional conductance (above the background) to the applied frequency at $V = -0.3$ V.

FIG. 3. The energy dependence of $(N_S)^{3/2}$, where N_S is the surface state density as determined from the G-V and the C-V characteristics of the tunnel junction. Also shown (dashed curve) the bulk density of states as deduced in Ref. 9 from field-effect measurements. E_c and E_v are the conduction- and valence-band (mobility) edges defined in Ref. 9.

increasing the amount of phosphorous[12] or arsenic[13] doping enhances the peak in $g(E)$. Since it is known[14] that in crystalline silicon the vacancy-phosphorous complex yields an energy level at $E = E_c - 0.4$ eV this may not be surprising. We therefore believe that one may miss[15, 16] the peak in $N_S(E - E_F)$ if the samples are undoped or very lightly doped.

The comparison of our results with those of the field-effect technique leads to quite significant conclusions regarding the states distributions in amorphous semiconductors. If one concludes from the present comparison that the field-effect measurements do also reflect the surface rather than just the bulk distribution of states, then one realizes that until now the distribution of the states in the forbidden gap in the bulk is unknown. If, on the other hand, one accepts the claim[17] of the authors of Ref. 9 that in their material the density of surface states is very low, then one has to assume that their field-effect measurements do yield the bulk density of states. Our study does indicate then that in amorphous semiconductors unlike crystalline semiconductors the distribution of surface states is a reflection of the distrubition of bulk states.

In summary, we have found, for the first time, structure in the G-V tunneling characteristic of an amorphous semiconductor. We have analyzed the ac conductance data and found the density of surface states across part of the forbidden gap. The present study indicates that the surface density of states obtained here is in agreement with expectations based on the results obtained from field-effect measurements.

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