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Determination of states distribution in hydrogenated amorphous silicon using *MIS* tunnel junctions

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Measurements of *I-V*, *G-V*, and *C-V* characteristics were taken on *MIS* tunnel junctions where *M* is a metal, *I* is silicon oxide, and *S* is hydrogenated amorphous silicon, *a*-Si:H. The results indicate a peak in the density of states which lies 0.45 eV below the conduction-band edge. The states distribution concluded from the present study is in good agreement with the conclusions based on field-effect measurements.

I. INTRODUCTION

The usefulness of tunneling studies to reveal the electronic structure of semiconductor bulks and surfaces was first recognized by Gray[1] in 1965. Later, his ideas were discussed in a more quantitative manner[2,3] and were made a tool for the study of surface states.[4-6] On the other hand, no quantitiative theory and no significant experimental work were presented concerning tunneling into impurity bands. Ten years ago it was hoped that tunneling would be a useful tool to study the electronic structure of the band gap in amorphous semiconductors, since no wave-vector conservation is required for tunneling between a metal and localized, non-Bloch state. The experimental studies were carried out on amorphous silicon (*a*-Si),[7,8] amorphous germanium (*a*-Ge),[9-12] some other amorphous semiconductors,[12-14] and chalcogenide alloys.[15] All the results obtained in the measurements had the same features. The current voltage, *I-V*, and the conductance voltage, *G-V*, characteristics were found to be symmetric, structureless, and the same for all materials. This is in contrast to the typical characteristics found in tunnel junctions of crystalline semiconductors and, in particular, in crystalline silicon (*c*-Si).[1-6] Moreover, a monotonic distribution of states was expected for the chalcogenide glasses, and a nonmonotonic (Mott-Davis) distribution was expected[16] for *a*-Si and *a*-Ge. The tunneling characteristics, however, could have been associated, in all cases, only with either a uniform[11] or monotonically increasing[16,17] distribution of states. It was suggested then that surface states[10,16] and the bulk conduction mechanism[11,17] are largely responsible for the observed characteristics, and any attempt to interpret the results should consider these effects. No such attempt has been made thus far.

In the present work we would like to show that tunneling can be an effective tool for the study of states distributions in amorphous semiconductors, and that results obtained on hydrogenated amorphous silicon, *a*-Si:H, can not only yield information concerning this material, but can also shed light on the tunneling studies mentioned above. This is possible now, since by changing the preparation conditions of *a*-Si:H the tunneling characteristics of this material can be changed continuously from the ones similar to those found for *c*-Si to the ones similar to those found for *a*-Si. As pointed out above, tunneling into *c*-Si is well understood qualitatively, but quantitative interpretation of experimental results is possible now only for the determination of surface state distributions.[3] We shall use this understanding and interpretation to discuss our results on *a*-Si:H. For this purpose we review the principles of tunneling between a metal and a crystalline semiconductor. Later, we describe the samples prepared for this study and present our experimental results on *a*-Si:H and their interpretation. Finally, we discuss the information deduced from this study concerning *a*-Si:H and *a*-Si.

II. TUNNELING IN *MIS* STRUCTURE

The principle of tunneling between a metal and a semiconductor via an insulating thin layer is illustrated by the band diagram given in Fig. 1. Suppose that a voltage is applied to the tunneling junction and that the Fermi level of an *n*-type semiconductor E_{F_s} is pinned so that the entire applied voltage V drops across the insulating oxide. Tunneling is possible when an allowed energy level of the metal E is facing an allowed energy level of the semiconductor, and only one of them is occupied. If V is negative (metal negative with respect to the semiconductor) the most effective tunneling process will be from the metal to the semiconductor. This process will be set in when $|V|$ will be large enough so that $E_{F_m} \geqslant E_c$. Here, E_{F_m} is the Fermi level of the metal and E_c is the conduction-band edge. Similarly, for positive V, the most effective tunneling process is from the semiconductor to the metal. This process will set in when $E_{Fm} \leqslant E_v$, where E_v is the valence-band edge. Correspondingly, the current I, through the junction, will rise sharply when $V = V_c$, where $qV_c = E_c - E_{Fs}$, and when $V = V_v$, where $qV_v = E_v - E_{Fs}$. Here, q is the (negative) electronic charge. Similar qualitative behavior is expected for the dc differential conductance of the junction $G = dI/dV$. In this idealized picture we have neglected other tunneling and nontunneling processes which tend to smooth the behavior shown.[2] These contributions are marked by the dashed curves in Fig. 1. We note then that measurements of the I-V or the G-V characteristics yield the values V_c and V_v, from which one may deduce the forbidden gap E_g $[E_g = (V_c - V_v)/q]$ and the relative position of the Fermi level in the gap. This position can be characterized by the parameters $\alpha \equiv (E_v - E_{Fs})/qV_v$ and $\beta \equiv (E_c - E_{Fs})/qV_c$. In the simple case described above $\alpha = \beta = 1$.

Usually, E_{Fs} is not pinned and the applied voltage V is distributed between the insulating oxide and the space-charge region of the semiconductor. Hence α and β will always be smaller than 1. The quantitative theory for the unpinned case has been worked out,[2] and the values of α and β may be deduced from the theory. These values and the measured V_c and V_v can yield then the quantities E_g and $E_c - E_{Fs}$ in the nonpinned case. It was shown[2] that the values of α and β will depend on the thickness of the oxide, t, the dielectric constants of the oxide, and the semiconductor ϵ_t and ϵ_s, respectively. The values also depend on the shallow donor concentration N_D, on the energy level of the surface states E_t, on the concentration of these states N_{St}, and on the surface potential V_{s0}, at $V = 0$. For example, in the case to be discussed later with $t = 24$ Å, $\epsilon_t = 4\epsilon_0$, $\epsilon_s = 11\epsilon_0$, $N_D = 10^{15} - 10^{17}$ cm^{-3}, $N_{St} < 10^{-12}$ cm^{-2}, and $V_{s0} = 0$, one finds (using the theory in Ref. 2) that $\alpha \approx \frac{2}{3}$ and that $\beta \approx \frac{1}{8}$. The voltage distribution thus makes the "conductance well" width $(V_v - V_c)$ larger and more symmetric than expected in the simple case of a pinned Fermi level.

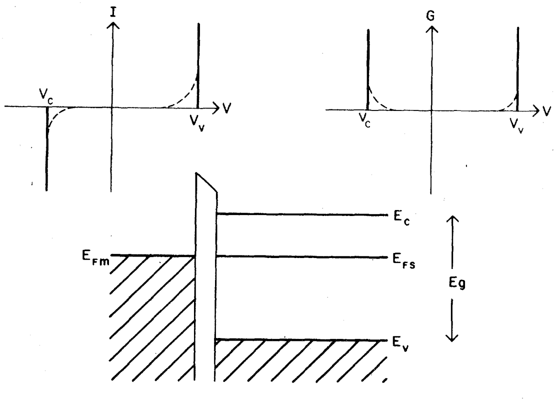

FIG. 1. An energy-band diagram of a metal-insulator-semiconductor (*MIS*) tunnel junction and the I-V and G-V characteristics predicted for such a junction.

Thus far we have considered tunneling between the allowed bands in the semiconductor and the metal. Let us now discuss tunneling processes associated with states in the forbidden gap. In particular, an impurity band is an additional conductance channel.[1] As before, let us consider first a pinned E_{Fs}. In the band diagram shown in Fig. 2(a) the impurity band is represented by its mid-energy level E_x. The expected contribution of the tunneling current into the impurity band is shown in Fig. 2(b). When E_{Fm} is raised by the voltage $V_x = (E_x - E_{Fs})/q$, electrons tunnel from the metal into the impurity band in which conduction takes place by hopping. It is apparent that the impurity-band contribution to the conductance is larger, the larger the impurity concentration, and that there is a lower limit to the concentration ($\approx 10^{18}$ cm^{-3}) under which no hopping is possible and, consequently, no conductance channel exists.[1] This channel, when present, manifests itself by a step in the I-V characteristic at $V = V_x$. We must note, however, that this tunneling process yields a small contribution compared to the metal-semiconductor bands tunneling and nontunneling processes (dashed curve in Fig. 1), and thus experimentally the "current steps" may be unrevealed due to the more dominant processes.[1]

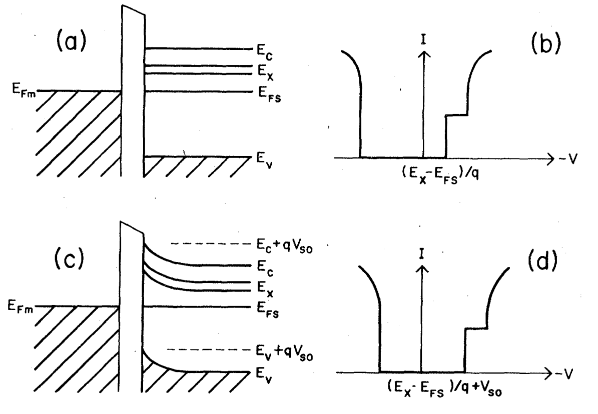

FIG. 2. An energy-band diagram of an *MIS* tunnel junction (a) and the corresponding I-V characteristic (b) in the presence of an impurity band centered at the energy E_x. The same junction with a zero-bias band bending qV_{s0} (c) and the corresponding I-V characteristic (d) are also shown. Here I represents the absolute value of the current, $|I|$.

All the above discussion applies also when the bands are bent by the surface potential V_{s0}. The energy scale of all the I-V features will be shifted then by V_{s0}. The corresponding band diagram and I-V characteristics are given in Fig. 2(c) and Fig. 2(d), respectively. If E_{Fs} is not pinned, one has to make the same considerations that were made above regarding the quantities α and β. In this case the corresponding value of E_x will be given by $qV_x\beta = E_x - E_{Fs}$.

Let us now examine the role of a surface-state level E_t when it lies under E_{Fs}. Tunneling into a localized surface state cannot yield a contribution to the conductance unless a conducting channel through the semiconductor bulk is present. Such a channel is provided by the recombination of carriers in the surface states. This process and the tunneling yield the current continuity. The entire process is known as recombination-controlled tunneling.[3] If E_{Fs} is pinned, tunneling will only be possible from E_t to the metal, and a "step" in the current will be found for $V = (E_t - E_{Fs})/q > 0$. If E_{Fs} is not pinned, the semiconductor bands will bend due to the application of voltage, and tunneling from the metal to E_t will be possible for $V < 0$ (when $E_{Fm} > E_t > E_{Fs}$). It is important to note that unlike the tunneling into an impurity band, the magnitude of the current step in the recombination-controlled tunneling will be proportional to the free carriers concentration.[3] The expected I-V characteristic for the unpinned E_{Fs} case is shown by the solid curve in Fig. 3.

The above discussion was concerned with the I-V and G-V characteristics under the application of a dc voltage. G is usually obtained by numerical or electronic differentiation of the I-V characteristics. The latter differentiation is carried out using a small ac test signal which is applied under constant voltage conditions,[6,18] and thus the measured in-phase ac current is proportional to the conductance G. However, in so doing other tunneling and nontunneling processes may contribute to the measured conductance. These processes are easily recognized by their dependence on the test-signal frequency. Here, in this particular case of interest, we notice the recombination process has a characteristic time τ which is inversely proportional to the free carriers concentration.[3,19] In the absence of tunneling (thick oxide) the ac conductance ΔG, associated with the oscillation of E_{Fs} through E_t will be peaked around $\omega\tau = 1$, where ω is the angular frequency of the test signal. This peak in ΔG is simply associated with the communication of E_t with the semiconductor bands.[19-21] If the oxide is thin, additional ac conductance contributions with the same frequency dependence will be provided by the recombination-controlled tunneling process.[3] These contributions set in when E_{Fs} oscillates through E_t ($V < 0$) and when E_{Fm} oscillates through E_t ($V > 0$). The corresponding two peaks are shown by the dashed curves in Fig. 3. However, since the first peak also represents the above nontunneling contribution it is shown to be larger. In fact, this contribution is much larger than that of the recombination-controlled tunneling.[2,3]

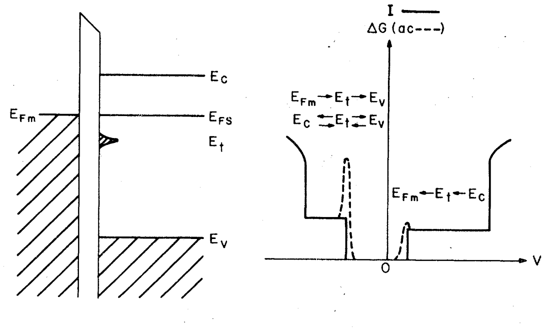

FIG. 3. An energy-band diagram of an *MIS* tunnel junction in the presence of surface states at the energy level E_t and the expected effects of recombination-controlled tunneling on the dc I-V and on the ac (dashed) ΔG-V characteristics. The larger peak in the ΔG-V characteristic marks the dominance of the nontunneling ac current flow between the semiconductor's bulk and the semiconductor's surface. Here I represents $|I|$.

The surface states are localized charge sites which may be looked upon as forming one plate of a capacitor, the other plate of which is the metal surface. The differential capacitance $C = dQ/dV$ associated with the surface states decreases at high frequencies[1,19] for which the surface states are unable to communicate with the corresponding bands. At low frequencies, C probes the charge sites available. As E_{Fs} sweeps across the forbidden gap at the surface, C monitors the surface-state density (if we neglect the oxide capacitance and the space-charge region capacitance). Hence a peak in both C and G at the same applied voltage indicates a peak in the surface-states density.[19-23]

To summarize, let us recall the characteristic features of the tunneling I-V and G-V characteristics as predicted and observed in crystalline-silicon tunnel junctions. The characteristics have "wells" and "steps" within the wells.[1,3,24] The steps are associated with tunneling either into impurity bands[1] or into surface states.[25] The latter two mechanisms can usually be distinguished by their ac conductance and capacitance. A frequency-dependent peak in both ΔG-V and C-V characteristics is expected to be found only in the case of surface states.[5,19,26]

III. JUNCTIONS PREPARATION AND MEASUREMENTS

The junctions used in this study were prepared either in the configuration shown in Fig. 4 or in the configuration shown in the insert on Fig. 5. In the first configuration, molybdenum electrodes 1000 Å thick were beam evaporated onto a quartz substrate. Then, using a proper mask, a strip of amorphous silicon film was deposited. The top of the film was oxidized in air at temperatures between 25 and 150 °C, until the desired oxide thickness was achieved. In the present study the oxide layers were 20–40 Å thick. Their thickness was determined by ellipsometry using the optical constants[27,28] of a-Si, a-Si:H, and SiO_2. The use of the optical constants of SiO_2 is justified by our findings that the ellipsometry, the oxide capacitance, the contact angle of water,[29] and the oxide dielectric strength were all found to yield the same oxide thicknesses as one would have found for SiO_2 on crystalline silicon. On top of the oxide, a 1000-Å thick layer of chromium was evaporated to form the upper (gate) electrodes. In this structure the area of the junction was always 3×10^{-3} cm^{-2}. We used molybdenum as a back electrode since it yields the best "Ohmic" contact to a-Si:H, while we used Cr as the upper electrode since it yields a low Schottky barrier in the nonoxidized films and its deposition does not damage the surface onto which it is evaporated. In contrast to these junctions, the structure shown in Fig. 5 was a two-terminal device in which the back electrode was stainless steel and the upper electrode was a 1-mm^2 chromium dot.

The investigated amorphous films were deposited in four different systems. One was a sputtering system for the preparation of nonhydrogenated a-Si films and the other were glow-discharge systems. Most of the films were prepared in a glow-discharge ac (60-Hz) proximity system with a gap voltage of 1.5 kV, a pressure of 0.6 Torr, a gas flow rate of 15 sccm (standard cm^3 per minute), and a substrate temperature T_s of 300 °C. The gases used for the glow-discharge decomposition were SiH_4 or premixed gases of SiH_4 with 2000 ppm PH_3, or with 500 ppm B_2H_6. In another system a dc proximity glow discharge was used under the same conditions except that $T_s = 350$°C and the PH_3 (1000 ppm) gas was introduced by a H_2 carrier gas. The third system was an rf (13.56-MHz) magnetron-diode glow-discharge system. In this system SiH_4 was decomposed under a pressure of 10^{-2} Torr, a flow rate of 40 sccm, a power of 2 W/cm^2, and $T_s = 300$°C. The SiH_4 used in this system was of a very high purity, and no traces of other elements (other than Si and H) have been detected by secondary-ion mass spectroscopy (SIMS) analysis. In order to compare these films with nonhydrogenated a-Si films, we have used an rf sputtering system in which the argon pressure was 10 μm and the rf power was 250 W. A high-purity (99.999%) undoped silicon target was used and T_s was room temperature. The junctions made in the dc-proximity system had the structure shown in Fig. 5. All other junctions had the structure shown in Fig. 4.

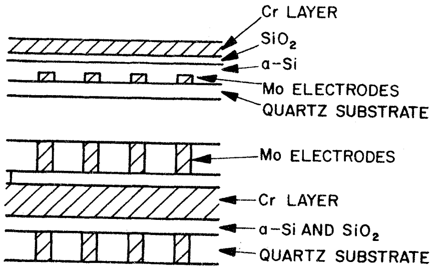

FIG. 4. A side view (a) and a top view (b) of the *MIS* structures used in the present study. The junctions area was 3×10^{-3} cm^2 and the oxide thicknesses were 20–40 Å.

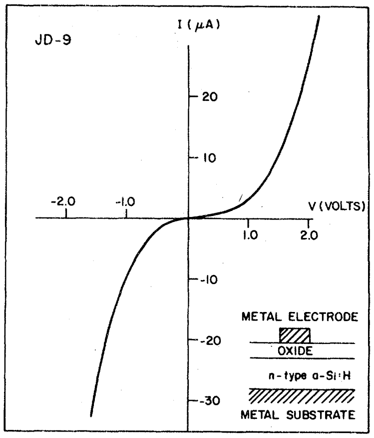

FIG. 5. Typical I-V characteristic of an n-type a-Si : H tunnel junction. Junction JD-9 was prepared by the dc-proximity glow-discharge method using 10^3 ppm PH_3 in SiH_4 and $T_s = 350$ °C. The thickness of the film was 1100 Å and the thickness of the oxide was 24 Å. The junction's structure is also shown in the figure.

In the measurements of the junction characteristics the voltage was applied using a variable-speed ramp generator which was operated, usually, with a rate of 5 mV/sec. The current through the junction was either measured using a small series resistor (e.g., for the results shown in Fig. 5) or by a logarithmic picoammeter. Both the conductance and the capacitance were measured using a 1-mV test signal having a frequency f of 15–150 000

Hz. The detection of the in-phase current (proportional to G) and the out-of-phase current (proportional to ωC) was done by a lock-in amplifier.[6] All the measurements to be discussed here were carried out at room temperature.

IV. EXPERIMENTAL RESULTS

In Fig. 5 we show typical I-V characteristics of an *MIS* tunnel junction where the semiconductor is n-type hydrogenated amorphous silicon. The current is found to increase almost linearly for small applied voltages ($V \lesssim 0.1$ V) and then much faster. This behavior is common to tunneling between a metal and a semiconductor.[2,26] In contrast to similar characteristics in amorphous semiconductors[7,14] (with one exception[15]), the characteristic is not symmetrical with respect to $V=0$ and the current rises faster for $V<0$. This is the predicted behavior (see Fig. 1) for an n-type semiconductor, since $E_{Fs}-E_v > E_c - E_{Fs}$. In fact, for the resistivity of the material used, 500 Ω cm, one expects[30] that $E_c - E_{Fs} \approx 0.2$ eV, while $E_g \approx 1.7$ eV. There is some structure in the characteristic around −0.3 V which may be associated with recombination-controlled tunneling. This becomes more apparent by examining the corresponding low-frequency (18 Hz) G-V characteristic reported previously.[31]

Comparison of the I-V characteristics of nonhydrogenated and hydrogenated amorphous silicon is made in Fig. 6. In this figure we show, on a logarithmic scale, the dependence of the absolute value of the current on the applied voltage. This is done in order to demonstrate the features of the "current wells" and their association with the electronic properties of the studied material. The results shown in this figure were all taken on the four-terminal devices (Fig. 4), and the a-Si:H films were all made under identical conditions in an ac-proximity glow-discharge system. The characteristic of sputtered a-Si, shown in Fig. 6(a), is typical of this (nonhydrogenated) material[7,8] and other amorphous semiconductors.[8,14] No structure is observed and the symmetry around $V=0$ is apparent. We have found that the temperatue dependence of the I-V and the G-V characteristics was also in agreement with previous results on this material.[12,17] In Fig. 6(b) we show a typical I-V characteristic of undoped a-Si:H. The characteristic is slightly asymmetric, indicating (see Fig. 1) an n-type semiconductor. This was confirmed by thermopower measurements that were carried out on all materials studied here.[32] The measured resistivity of the a-Si:H as deposited was 10^6 Ω cm. However, as noted before,[33] this value can be regarded only as the lower limit of the actual resistivity of the undoped material. Comparison of Figs. 6(a) and 6(b) reveals the most basic differences between the I-V characteristics of a-Si and a-Si:H tunnel junctions. In the latter case a current well is always found at the current levels shown. This difference reflects the fact that in a-Si conduction takes place in the forbidding gap,[17] while in a-Si:H considerable conduction may take place only in the allowed (or extended-states) bands.[30] We should note, however, that the measured width of the current well cannot be determined by an arbitrary current level, since the observed current depends on many factors such as the oxide thickness t, the conduction mechanisms of the carriers, bulk and surface recombination effects, and the bias-induced band bending.[2] The characteristics obtained for a-Si:H are very similar to those obtained[24,26] for c-Si. The junctions studied in this work yield, for the arbitrary choice of $10^{-8} \geqslant I \geqslant 10^{-9}$ A, current wells which have the same width as the conductance wells. The common width is in good agreement with theory[2] and expectations (see below).

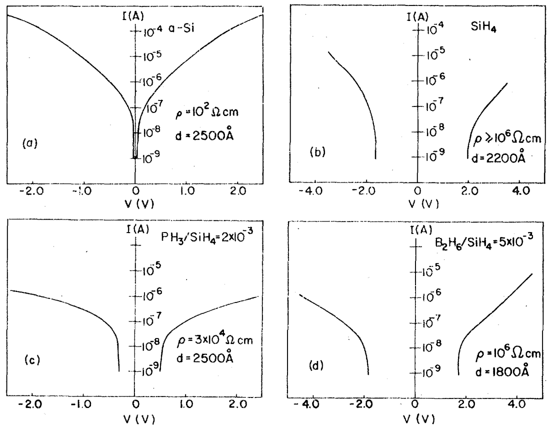

FIG. 6. I–V characteristics of sputtered amorphous silicon (a), undoped hydrogenated amorphous silicon ($T_s = 320\,^\circ$C) (b), n-type a-Si : H ($T_s = 220\,^\circ$C) (c), and p-type a-Si : H ($T_s = 320\,^\circ$C) (d). The oxide's thickness of all samples was 40 Å and the a-Si : H materials have all been prepared by the ac-proximity glow-discharge method.

The effect of doping is demonstrated in Fig. 6(c). As is clear, the ratio $|V_c/V_v|$ is smaller than in Fig. 6(b), indicating, as expected, that the doping makes the a-Si:H a better n-type material. On the other hand, since T_s was lower than the T_s used for the undoped material, we observe, as one would expect,[30,34] more states in the gap and a reduction in the width of the well. Doping SiH$_4$ by B$_2$H$_6$ is known to yield a p-type a-Si:H, and this is also confirmed by the I-V characteristics for the corresponding material. Figure 6(d) shows this in the corresponding characteristic $|V_v/V_c| < 1$, as expected (see Fig. 1) for a p-type material. In view of all the characteristics shown in Fig. 6, it is apparent that tunneling studies confirm the known facts about a-Si and a-Si:H: (1) the latter has a lower density of gap states; (2) the latter can be doped, and (3) the substrate temperature T_s is an important parameter in controlling the above two properties. As far as the usefulness of tunneling studies is concerned, it is clear that they provide a tool for the determination of the doping efficiency which can be deduced from the measured $|V_c/V_v|$ ratios.

As was discussed in Sec. II, the presence of surface states at the level E_t, or an impurity band around E_x, will be revealed by a peak in the G-V characteristic. Such a peak is found in the G-V characteristic of undoped a-Si:H, as can be seen in Fig. 7. However, due to the background (see Sec. II) one should describe the observed structure as a step which appears at about $V_x = -0.6$ V. This step was found to be independent of frequency, and the characteristic shown is essentially a dc characteristic. As explained in connection with Figs. 2 and 3, this is quite a clear indication that the step is associated with tunneling into an impurity band of a semiconductor rather than with tunneling into a surface state which requires communication between the surface states and the conducting bands. Since the material used for this junction was made of "top grade" SiH_4 ("resistivity > 1000 $\Omega\,cm^2$"), and since SIMS analysis did not indicate any impurity in the material, we may assume that the observed impurity band is a peak in the density of states of the studied material. This conclusion is also justified by the following analysis. From the asymmetry of the G-V well, $|V_c/V_v| < 1$, it appears that the material is n type. Measurement of the activation energy[32] of this sample yielded a value of $E_c - E_{Fs} = 0.63$ eV, in agreement with similar results on undoped a-Si:H prepared by rf glow-discharge.[30] As is apparent from Fig. 7, $V_c/V_x \approx 4$, which means that the peak in the density of states, $N(E)$, lies about 0.45 eV below E_c. This result is in excellent agreement with the position of the density-of-states peak found by field-effect measurements.[30] Hence, our findings are at least consistent with the results deduced from these measurements. Comparison of the magnitude of the conductance step, 5×10^{-2} μmho, with the high-voltage ($V > \pm 4$ V) conductance values, 5×10^2 μmho, indicates that the density of states above E_c or below E_v is three to four order of magnitude larger than at the observed peak of the density of states. If we interpret the step as due to tunneling into an impurity (or rather an intrinsic) band, the above comparison yields $N(E_x) \approx 10^8 - 10^{19}$ $cm^{-3}\,eV^{-1}$, in good agreement with both the results obtained by field-effect measurements[30] and the density of states needed for impurity-band conduction.[1]

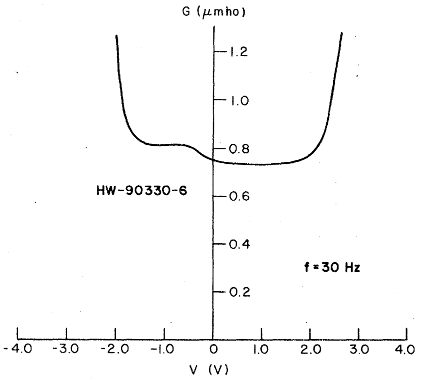

FIG. 7. A G-V characteristic of undoped a-Si : H prepared in an rf-magnetron-diode glow-discharge system. The film thickness was 1900 Å, and the measured resistivity of the material was 3×10^7 Ωcm.

In principle, the observed step in the dc conductance could have been attributed to recombination-controlled tunneling via surface states, since this process has also a small dc contribution[3] (see Fig. 3). This is the most likely explanation for the structure found in the low-frequency characteristics of the low-resistivity material,[31] since this structure is at the same energy as the peak in the ac conductance. We believe, however, that for the present high-resistivity material there are three arguments to favor the interpretation of impurity-band tunneling to that of recombination-controlled tunneling. First, as shown in Fig. 3 and as expected from results on the P-doped n-type material used in a previous study,[31] the conductance step due to the latter mechanism should be detectable at a positive rather than a negative voltage. This conclusion is based on the fact that in the doped material, where $E_{Fs} > E_t$, the structure in the low-frequency G-V characteristics was found[31] for $V < 0$ and thus (see Fig. 3) the corresponding structure for the undoped material, where $E_{Fs} < E_t$ is to be expected for $V > 0$. In a forthcoming paper we will show that indeed, for p-type materials where $E_{Fs} < E_t$, the peak in the ac conductance is found for $V > 0$. Second, in the previous study[31] the maximum magnitude of the low-frequency conductance step that may be associated with the dc contribution of the recombination-controlled tunneling had a magnitude of about 1 μmho. Considering the five orders-of-magnitude ratio between the resistivities of the doped and undoped materials and the fact that the recombination conductance is proportional to the number of carriers,[3] the step in the undoped material should have been 10^{-5} μmho, while the observed step is 5×10^{-2} μmho. Third, as pointed out above, the magnitude of the peak in the density of states that can be deduced from the assumption of tunneling into an impurity band is $10^{18}-10^{19}$ $\text{cm}^{-3}\,\text{eV}^{-1}$. This result and the fact that the peak lies 0.45 eV below E_c are in good agreement with previously reported results.[30,31,34]

Since no quantitative theory has been worked out for the tunneling into impurity bands, we cannot analyze the above data in more detail. However, as mentioned already, the conductance associated with surface states may be analyzed quantitatively. In view of this, we have studied a low-resistivity n-type a-Si:H, where the number of carriers is high enough to yield an observable effect of the surface recombination on the G-V characteristics. This effect, as explained in connection with Fig. 3, should yield frequency-dependent peaks both in the ΔG-V and C-V characteristics. The expected[3,20] behavior was indeed observed as shown in Fig. 8. It is seen that the material is n type $|V_c/V_v|<1$ and that both G and C have peaks at $V=-0.3$ V. $\Delta G/f$ was found[31] to have a peak as a function of frequency at $f=120$ Hz, while C was found to decrease monotonically for higher frequencies. The latter behavior, shown in Fig. 9, is well understood. At very high frequencies the states cannot be charged and one measures the "crystalline-like" depletion-region capacitance. In the present case the depletion region can be wider than the film's thickness. As states in the depletion region or on the surface charge up, i.e., at low frequencies, the depletion-region width decreases and the capacitance increases. The fact that only one peak is observed indicates that the dominant recombination mechanism is due to the communication between E_t and the semiconductor bands, as in common nontunnelable metal-oxide-semiconductor (MOS) devices.[21-23] Since both the voltage dependence[1,18] and frequency dependence are very similar to those observed in c-Si tunnel junctions,[1,6] we have analyzed the present data in the manner used for the crystalline material.

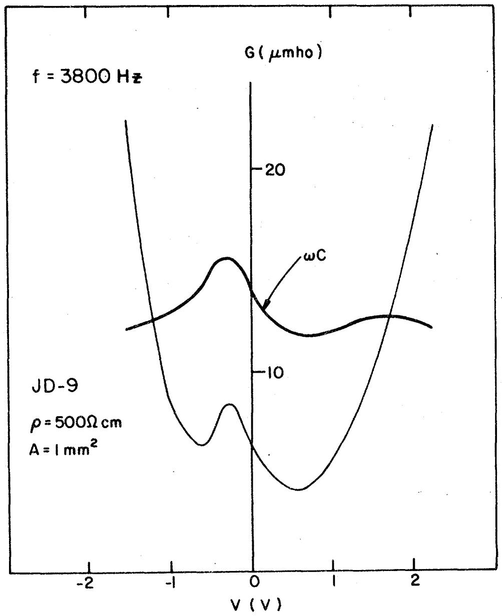

FIG. 8. G-V and C-V characteristics of the junction JD-9.

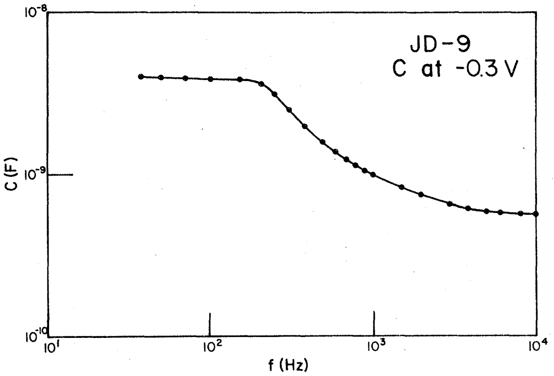

FIG. 9. The frequency dependence of the tunnel junction capacitance at $V=-0.3$ V.

At low frequencies the surface states are simply charge sites so that the differential capacitance $C_S=\Delta Q/\Delta V$ associated with them can be given by $C_S=qN_SA$, where N_S is the surface-states density and A is the junction's area.[21] If one assumes[5,22] that the oxide capacitance is small compared with C_S and that the space-charge region capacitance is small compared with C_S, then the measured capacitance is expected to be C_S. The associated ac conductance can be worked out by simply analyzing the equivalent circuit.[3,20] Such analysis[35] shows that the maximum value of $\Delta G(V)/\omega$ is just $\frac{1}{2}C_s(V)$.

Setting the energy scale is somewhat problematic since the observed capacitance is C_S rather than the crystalline space-charge region capacitance which is used[5,6] to determine the dependence of E_c-E_{FS} at the surface on V. One can assume, however, that E_{FS} is not pinned at the surface, since C_S varies with V and since the measured capacitance is small compared with the oxide capacitance. Another justification for a nonpinned E_{FS} comes from the following argument. If E_{FS} is assumed to be pinned, then $|V_c/V_v|=(E_c-E_{FS})/(E_{FS}-E_v)\approx\frac{2}{3}$. Since $E_g\approx1.7$ eV, this implies E_c-

$E_{FS} = -0.7$ eV. The latter value is very different from the value of $E_c - E_{FS} = 0.2$ eV found[30] for n-type a-Si:H having the same resistivity as our samples. On the other hand, if we assume a nonpinned E_{FS} and use the parameters given in connection with Fig. 1, which yielded $\alpha = \frac{2}{3}$ and $\beta = \frac{1}{6}$, we will obtain,[31] from the observed V_c and V_v values, $E_c - E_{FS} = 0.27$ eV and $E_c - E_v = 1.72$ eV. This indicates that a nonpinned E_{FS} is a better description of the situation in the present n-type material. Using this description we get for the observed peak in the conductance at $V_t = -0.3$ V a peak in the density of states which is located at E_t, where $E_c - E_t = 0.47$ eV. Considering the assumptions made, this value is in excellent agreement with both the location of the impurity band found above at $E_c - E_x = 0.45$ eV and the field-effect peak at $E_c - E_x = 0.4$ eV. We may conclude then that all the observed structures result from the same peak in the density of states.

In view of the close relationship between the surface states and the impurity band, and the lack of a quantitative theory for the latter, one may use the density of surface states $N_S(E)$ to estimate the density of bulk states $N(E)$ by the simple relation $N = N_S^{3/2}$. Of course, due to the difference between the bulk and the surface, such a relation does not necessarily exist. However, comparison with $N(E)$ derived by other methods may indicate whether this simple relation holds, i.e., whether the surface states are representative of the bulk states. To do this we have plotted, in Fig. 10, $N_S^{3/2}$ vs $E - E_{FS}$. N_s was found by using the above relations to determine N_S from C_S and $\Delta G/\omega$. Comparison with the field-effect data[30] indicates quite good agreement. The difference in the energy scale was not unexpected since, probably, E_{FS} does not sweep the surface as freely as assumed. Hence the peak shown should be narrower (compressed around $E - E_{FS} = 0$), improving the agreement with the field-effect result. The differences in the magnitude of $N_S^{3/2}$ and $N(E)$, as derived by field effect, may be due to the different material used here (phosphorous-doped film made in a dc discharge) as compared to those used in the field-effect measurements (undoped or lightly doped films made in an rf discharge). We do know that doping a-Si:H with arsine[34] does increase the density of gap states, and this is expected[31] to be the case for doping with phosphorus. The expectation is also confirmed by the increased optical absorption of P-doped a-Si:H compared with undoped[27] a-Si:H. This is shown in Fig. 11, where the dependences of the optical-absorption coefficients on the light wavelength are shown for doped a-Si:H, undoped a-Si:H, and c-Si. It is clearly seen that for the long wavelengths the absorption coefficient is large by a factor of 5–10 for doped a-Si:H than for the undoped material.[36]

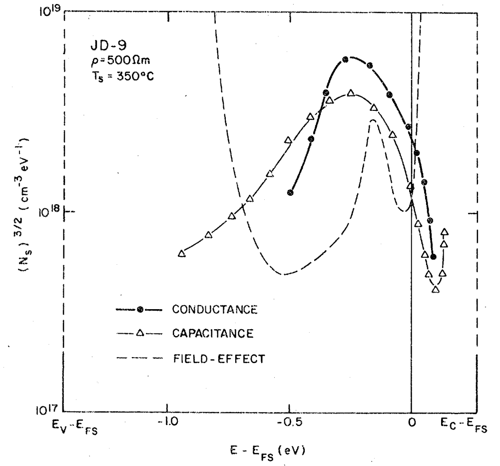

FIG. 10. The energy dependence of $N_S^{3/2}$, where N_S is the surface-states density as determined from the ΔG-V and C-V characteristics. The dashed curve shows the bulk density of states as deduced in Ref. 29 from field-effect measurements. The energy scale was determined by using the theory of crystalline *MIS* junctions.

V. DISCUSSION

As pointed out previously, no quantitative theory is available for tunneling into impurity bands, and thus only estimates could be made for the bulk density of states derived from tunneling measurements. Except for Gray's pioneering work[1] not much work was devoted to the study of tunneling into impurity bands. There were two reasons for this: (a) in the technologically more interesting

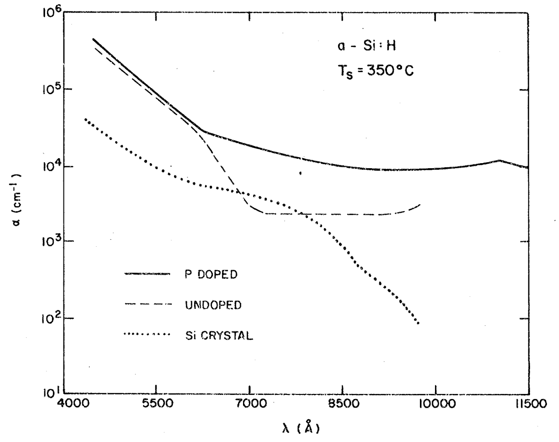

FIG. 11. The light-wavelength dependence of the optical absorption coefficient of c-Si, undoped a-Si : H, and P-doped a-Si : H.

materials (lightly doped crystals) the density of impurities was too low (less than 10^{18} cm^{-3}) to yield a channel of hopping conduction throughout the bulk,[37] and thus the corresponding states were not detectable by tunneling. (b) In order to determine the dopant concentration, much more accurate methods (e.g., MOS or Schottky barrier capacitance[21,38]) were used. Here, because of failure of other methods to determine unambiguously structure in the density of states, we studied tunneling characteristics. The object of the study was to check qualitatively the existence of a nonmonotonic distribution of states in the bulk of a-Si:H, and then to estimate the density of states within an order of magnitude. While such an estimate may be too crude for crystalline semiconductors, it seems to be good enough for amorphous semiconductors (at least in the present stage of their study). The procedure used for the interpretation of the results is supported by the order-of-magnitude agreement between the results obtained from the present tunneling study and other available data, as explained in Sec. IV.

The similarity of the tunneling characteristics of a-Si:H and those found in crystalline Si, on the one hand, and the differences between these characteristics and the observations here and in the literature,[7-17] on a-Si and a-Ge, on the other hand, deserve some detailed discussion. In particular, in the latter materials one expects[37] a nonmonotonic states distribution in the gap, due to the various defect states (see below). As was shown in Figs. 7 and 8, the same measurements which yielded monotonic and symmetric I-V and G-V characteristics for a-Si have yielded nonmonotonic and nonsymmetric I-V and G-V characteristics for a-Si:H. Since there is no way to interpret the present raw data on a-Si:H other than to associate the structure in the characteristics with a nonmonotonic density of states, one would expect structure in the characteristics of a-Si and a-Ge. As was pointed out in Sec. I, this contradiction between expectations and observations is still a puzzle.[16] We believe that some light can be shed on this problem from the crystalline-like behavior of a-Si:H.

The well-known difference between a-Si and a-Si:H is their density of states in the "mobility gap." In a-Si (and in particular in the nonannealed a-Si used here) the density of states in the midgap is at least 10^{19} cm^{-3} eV^{-1}, and it increases to the order of 10^{21} cm^{-3}eV^{-1} at the band edges.[16,17] On the other hand, from the various data on a-Si:H we know[39] that in this material the corresponding density of states increases from about 10^{17} cm^{-3} eV^{-1} to about 3×10^{21} cm^{-3}eV^{-1}. Disregarding for a moment the additional nonmonotonic structure in the states distribution, one finds that the density of states which is required in order to maintain hopping conduction[37,40] throughout the bulk, N_h ($\approx 5\times10^{18}$ cm^{-3} eV^{-1}), is available in a-Si for all energy levels in the gap, while for a-Si:H it is available only close to the band edge ($E \gtrsim E_c - 0.2$ eV). Hence conduction through the bulk (following the tunneling through the oxide) is possible for a-Si throughout the entire gap,[17,41] while for a-Si:H it is possible only close to the band edges. The close-to-the-band-edges tunneling conduction is making tunneling into a-Si:H similar to tunneling into crystalline Si. This explanation is consistent with the observations exhibited in Fig. 6, which shows that the current through the a-Si tunnel junction is larger, at a given bias, than the current through the a-Si:H tunnel junction. In regard to these observations, we may further note that there are different voltage distributions between the various materials and their oxides (for a-Si all the voltage drops across the oxide,[17] for undoped a-Si:H about $\frac{1}{3}$ of the voltage drops across the oxide, and for doped a-Si:H see Sec. IV). This distribution determines the relation between the applied voltage and the energy level in the gap. The comparison of the various characteristics shown in Fig. 6 shows then that for states in the gap the tunnel current is larger for a-Si than for a-Si:H, while for the extended states the currents are much the same. Considering the high sensitivity of the tunnel current to the oxide thickness, this observation indicates that our ellipsometry determination of the oxide thickness is also representative of the small-area tunnel junctions and that below and above the mobility gap both a-Si and a-Si:H exhibit similar transport properties.

Returning to nonmonotonic states distributions, we expect additional structure in the tunneling characteristics if there are impurity bands in the crystalline material[1] or if there are peaks in the density of states in the amorphous material. The density at the peak has to be larger than N_h in order to yield a hopping channel throughout the bulk. Indeed, hopping between the states associated with the peak detected here, E_x, has been discussed previously.[42] From the present results this peak appears to exist in a-Si:H (Fig. 7) at about 0.45 eV below E_c. We note that field-effect measurements[39] indicate a second peak in the density of states at about $E_v + 0.4$ eV. This peak is not observed here. In a forthcoming paper we shall show that this feature has to do with states which are sensitive to material preparation, and it thus appears that while they were present in the materials used in the field-effect measurements they are not detectable in the materials studied here.

The above discussion does not resolve the puzzle concerning the structureless and symmetric tunneling characteristics of *a*-Si and *a*-Ge. The simplest possibility of a monotonic and symmetric distribution of states will explain these characteristics but will be contrary to the expectations based on the various defect states[37] (see below). We should note, however, that the existence of many different levels may yield the smearout of the characteristics which would have been obtained if fewer levels would have been present. In particular, one expects a smearout of features associated with levels which lie close to the band edges because of their competition with the monotonic (but steep) increase of the conductance due to tunneling into the bands. These reasons, and the suggestion that in *a*-Si and *a*-Ge the conductance represents the integrated density of states,[11,41] make us believe that it is the detection of the structure in the tunneling characteristics rather than the monotonic density of states which is responsible for the tunneling characteristics observed in *a*-Si and *a*-Ge. This suggestion is supported by Gray's work,[1] which showed that when the impurity band lies close enough to the band edge and the impurities concentration is high enough, the features associated with tunneling into the impurity band are smeared.

In the present paper we have shown that a nonmonotonic states distribution does exist in *a*-Si:H. The present evidence is much more convincing than the field-effect results[30,39] for the following reason: The field-effect measurements have too low a sensitivity to determine unambiguously the existence of a peak in the density of states[43,44] and the peaks are thus derived as a result of the interpretation of the experimental data.[45] Here, in contrast, the existence of a peak in the density of states is borne out by the *raw data*, as shown in Figs. 7 and 8. Considering the fact that our experimental procedure has yielded no structure in the tunneling characteristics of *a*-Si (in agreement with many previous works[7-17]), but has yielded a conspicuous structure for *a*-Si:H, one should surmise that this structure is a feature of *a*-Si:H. The interpretation of the tunneling characteristics in the present paper is only in association of their structure with a certain energy ($E_c - 0.45$ eV) and a certain states density ($\approx 5\times10^{18}$ cm^{-3}eV^{-1}). This interpretation of the tunneling results is supported by the ac conductance and capacitance given here (Fig. 8), as well as by previous works in which other methods have been used.[39]

Considering the agreement between the interpretation of the tunnel conductance (the structure in Fig. 7 which is frequency independent) and the interpretation of the ac conductance (the peak in Fig. 8 which is frequency dependent), we should point out, in regard to Fig. 10, that the simple relation $N = N_S^{3/2}$ does not necessarily present the exact N. A more proper procedure would be to consider[21,22] $N = N_S/l$, where l is the voltage-dependent width of the space-charge region. Unfortunately, this width is not known since we know neither the distribution of bulk states nor the distribution of surface states. If we assume, however, that the data of Fig. 8 are associated solely with bulk states, that these states are uniformly distributed throughout the gap, and that the existence of donors and free carriers can be neglected, we find that $l \simeq 200$ Å and that at the density-of-states peak, $N = 1.7\times10^{18}$ cm^{-3}eV^{-1}. Since a justification of all these assumptions is beyond the scope of the present paper, we have preferred to use here[31] the more transparent $N = N_S^{3/2}$ relation. As can be seen, the two estimates for N from N_S differ only by a factor of 4. If indeed all the states sensed are bulk states, then it seems that N can be trusted to be within this factor. These estimates from the ac conductance and capacitance measurements (Figs. 8 and 10) are in good agreement with the order of magnitude estimate ($N = 5\times10^{18}$ cm^{-3}eV^{-1}) which is made from the tunneling measurements (Fig. 7).

While there is no quantitative theory for tunneling into impurity bands, the method used here for the determination of N_S from the ac conductance and capacitance is well established for crystalline semiconductors.[4,6] In these materials the simple interpretation of the corresponding data is possible since, except for shallow donor levels, no other states are expected to be present in the bulk. In amorphous semiconductors, where there are many states both on the surface and in the bulk, these measurements,[46,47] just as the field-effect measurements,[48,49] are associated with "true" surface states as well as with states in the space-charge region of the bulk.[43] Hence, generally, all these electrical surface measurements cannot distinguish between surface and bulk states. Naturally, the results become harder to resolve the higher the bulk density of states within E_g.

In fact, it was reported[47] that for an *a*-Si:H material which apparently has a relatively low density of surface and bulk states, the *C*-*V* characteristics are similar to those found in *c*-Si, MOS devices.[21] Moreover, the differences between the *C*-*V* characteristics shown here (Fig. 8) and those reported in Ref. 47 are of the same type as those found between various *c*-Si, MOS devices.[18,21] (A detailed comparison between the present results and those reported in Ref. 47 will be given in a forthcoming paper.) The absence of structure in the C-V characteristics presented in Ref. 47 is by no means an evidence against the presence of the peak E_x in the density of states. We have shown[50] that if the a-Si:H material is of high enough resistivity, yielding a long enough characteristic time τ (see Sec. II), the structure in both the ac-conductance characteristic and in the capacitance characteristic will not be observed. This structure is revealed, however, upon illumination (which increases the carrier concentration and therefore decreases τ), since the photoexcitation enables a recombination-generation process at experimentally accessible test-signal frequencies. The observed structure was shown to correspond to E_x in both the G-V and the C-V characteristics.[50] The fact that this structure was found for doped as well as for undoped a-Si:H indicates that the peak in E_x always exists. Moreover, the fact that we have observed the corresponding structure in many a-Si:H alloys, which were prepared under different conditions,[50] and that the peak in the density of states was concluded from the various field-effect measurements[34,39] leaves very little doubt that E_x is an "intrinsic" and universal property of the a-Si:H system. In addition to the establishment of this universality, the present tunneling measurements indicate that the peak in E_x is associated with a peak in the bulk density of states and that these states extend to the surface. Other indirect evidence for this is provided by the many luminescence studies on this material.[51,52]

The above conclusion does not settle the quantitative question of how many of the states are bulk states and how many are surface states. It seems, however, in view of the order-of-magnitude agreement between our various estimates of the density of states at E_x that, within this accuracy, the density of surface states does reflect the bulk density of states.[31] It should be stressed that this may not be the case since the surface is sensitive to its environment.[43] Indeed, the integrated density of surface states in a-Si:H was reported to be relatively low[53,54] or relatively high,[55] depending on the method of measurement and the samples' configuration.

In view of the above discussion, which concludes that the E_x peak in the density of states is a characteristic and universal property of the a-Si:H system, it appears worthwhile to speculate about the particular defect which is associated with this peak. The first possibility is that the hydrogen incorporated into the silicon has not removed all dangling bonds and that E_x is associated with residual dangling bonds. The argument against this suggestion is that the concentration of hydrogen is much higher than the concentration of dangling bonds in a-Si and that the concentration of states around E_x (see above) is much higher than the unpaired spin density[56] (5×10^{15} cm^{-3}) found by ESR measurements. One is led then to conclude that the states around E_x are due to spin-paired defects. This conclusion is generally agreed upon in the many recent theoretical works[57-61] which discuss the nature of gap states in the a-Si:H system.

The most fundamental question concerning the gap states in a-Si:H is whether the states are due to defects which are already present in a-Si (Refs. 57 and 58) or whether these states are due to Si–H bonds.[59,60] *A priori*, both possibilities are reasonable since, on the one hand, removal of the many dangling bonds enables the detection of the spin-paired states (which are of relatively low concentration in a-Si) while, on the other hand, there are many Si–H bonds which may yield states in the gap. As for the states associated with the E_x peak, which are the subject of the present discussion, no definite or rigorous answer was given. However, suggestions were made according to the above two possibilities. Adler[57] has suggested that E_x is associated with a T_2^0 (doubly-bonded neutral) Si defect, while Fisch and Licciardello[59] have suggested that E_x is associated with a three-center Si–H–Si bond. A more recent calculation by Allan and Joannopoulos[61] has concluded that there is a clustering of states associated with both Si defects and Si–H bonds at about 0.6 eV below E_c. Hence, theoretical considerations have not yet pointed conclusively as to the nature of the states around E_x.

The theoretical inconclusiveness and the lack of experimental results which can distinguish between the various suggestions leads one to speculate about the defect associated with E_x by comparisons with similar systems. In particular, the defects in the bulk and on the surface of c-Si have been studied in detail both experimentally[19,62] and theoretically.[63] Indeed, Spear[64] and Mott, Davis, and Street[42] have compared the results on a-Si:H with results associated with defects known to exist in c-Si, while Phillips[65] has compared the results on a-Si:H with information on c-Si surfaces. In regard to the E_x and E_y energy levels, Spear[64] has pointed out that these levels are very close to those of a divacancy in c-Si. Mott *et al.*[42] have noticed the fact that the divacancies yield spin-paired states as expected from states which remain in c-Si after the incorporation of hydrogen (see above). We believe that further comparison with experimental data on c-Si lends support to the attribution of the E_x and E_y levels to states which result from divacancies

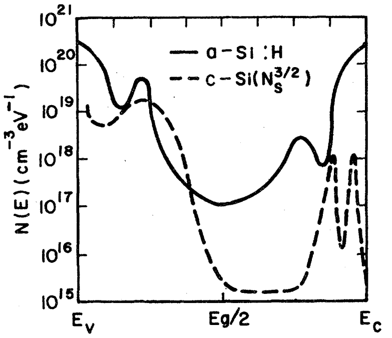

FIG. 12. Comparison of the bulk density of states of a-Si:H as determined by field-effect measurements (Ref. 29) and the c-Si "bulk" density of states $N_S^{3/2}$ as determined (dashed curve) from measurements of the surface density of states N_S (Ref. 6).

or from some bridging bonds of types present in c-Si bulk[64] or c-Si surface.[63] We have pointed out already[31,50] that the incorporation of phosphorous or arsenic enhances the E_x peak, while it is known that in c-Si the vacancy-phosphorous complex has an energy level around the level E_x. Here we would like to point out that electrical surface measurements on both c-Si surfaces and a-Si:H surfaces yielded similar results. Measurements on MOS structures[4,6,66] of c-Si have shown that there are always two major peaks in $N_S(E)$, one close to E_c and the other close to E_v. Both peaks result from the same defect[62] (as in Spear's suggestion[64] for a-Si:H), and (as may be the case with our results[50]) when the density of states becomes high the peak close to E_c is still very sharp, while the one close to E_v is broadened considerably.[6] It was found that the density of the corresponding surface states decreases with H_2 annealing.[24,62]

In Fig. 12 we make a comparison between the $N(E)$ derived from field-effect measurements[30] on a-Si:H and the surface-states density N_S obtained[6] from the ac-conductance measurements on c-Si. To set the scale we again use $N_S^{3/2}$ for the comparison. The similarity between the results on a-Si:H and the results on c-Si (Ref. 6) is quite remarkable. It is apparent that, apart from the typical amorphous band tailing, the surface-states distribution in c-Si is much the same as the $N(E)$ distribution in a-Si:H.

In conclusion, in view of the comparison of data on c-Si and on a-Si:H it is believed that the peak in the density of states at E_x is associated with a divacancy-type defect. The existence of this peak was shown here to be the universally most conspicuous feature of the states distribution in a-Si:H.

Note added in proof. The temperature dependence of the peak shown in Fig. 8 is the same as that of the electrical conductivity, while that of the feature shown in Fig. 7 is much stronger. These findings (see Sec. II) support the interpretation given here concerning recombination and hopping conduction in the corresponding cases.

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