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Effect of hydrogen on the density of gap states in reactively sputtered amorphous silicon

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The density of states near midgap and the hydrogen content have been measured on a number of reactively sputtered a-SiH$_x$ films prepared at different hydrogen partial pressures. The density of states near midgap is observed to decrease exponentially with increasing hydrogen partial pressure to less than 10^{15} states cm^{-3} eV^{-1}. The data are interpreted in terms of a simple kinetic model of the H incorporation in the a-Si network.

Various measurements[1–4] indicate that amorphous silicon hydride prepared by glow discharge decomposition of silane can have a residual density of states in the middle of the gap of order 10^{15} states cm^{-3} eV^{-1}. Although there is a large technological incentive to reduce the density of these states even further, very little is known about their origin. For example, it is not known whether the residual density of states is intrinsic, characteristic of the amorphous state, or extrinsic, due to impurities, a few unsaturated dangling bonds or to new states introduced by exotic bonding configurations of the hydrogen.

In this paper we describe the first measurements of the density of localized states near midgap in thin films of reactively sputtered hydrogenated amorphous silicon (a-SiH$_x$) as a function of hydrogen content. The density of gap states was determined from differential capacitance-voltage and ESR measurements, and the hydrogen content was inferred from the infrared absorption spectra. The effect of the hydrogen in the sputtering plasma on the density of states and the hydrogen content is discussed in terms of a simple kinetic model of the H incorporation. An advantage of sputtering compared to glow discharge is that one can vary the H content in the films simply by adjusting the partial pressure of hydrogen (P_H) in the argon sputtering gas without changing any of the other deposition parameters. Thus, the effect of hydrogen in eliminating or creating defects can be probed independently of the other deposition conditions.[5]

The a-SiH$_x$ films were prepared by rf sputtering of a polycrystalline target at a power density of 1.5 W/cm^2, a substrate temperature of 275 °C, an Ar pressure of 5 mT and variable P_H. The capacitance measurements were made on films deposited on glass substrates that had been first coated with a layer of NiCr and 500 Å of a-SiH$_x$ doped with phosphorous.[5] These layers formed an ohmic contact to the undoped a-SiH$_x$. A Schottky barrier contact was made to the front surface of the a-SiH$_x$ film by evaporating 100-Å Pd or Pt dots 2 or 8.5 mm^2 in area. The films for the infrared absorption spectra were deposited on high-purity single-crystal silicon. The position of the Fermi level in the bulk was determined through conductivity studies on both Schottky barrier structures and coplanar configurations.

In a-SiH$_x$ the width of the space-charge region is determined by the density of states near midgap. Unlike conventional crystalline semiconductors the junction capacitance of a-SiH$_x$ Schottky diodes does not give an accurate measure of the width of the depletion region because of series resistance and trap ionization effects.[6] However, changes in the width of the depletion region with applied bias can be inferred from capacitance measurements and can be used to map out the potential distribution near the metal-semiconductor interface provided the built-in potential, V_0, is known.[7]

The built-in potential at the metal-semiconductor interface is equal to the difference between the height of the potential barrier at the interface and the activation energy of the conductivity in the semiconductor. Our studies of the Schottky diodes reported in this paper indicate that the barrier height of the Pd and Pt contacts as well as the conductivity activation energy increase by about 0.2 eV with increasing P_H so that the built-in potential is approximately independent of hydrogen content having a value of about 0.35 eV for Pd and 0.43 eV for Pt. In any event the results reported here are relatively insensitive to the size of the built-in potential. To a first approximation an external bias has the effect of raising (or lowering) the built-in potential by an amount equal to the applied voltage, and expanding (or contracting) the depletion region, following the contour of the zero-bias potential distribution. Thus by plotting the applied bias against the corresponding change in the width of the depletion region determined from the capacitance, one can map out the potential distribution near the interface. The capacitance measurements were made with a lock-in amplifier and a 5-mV test signal in the frequency range in which the change in capacitance with bias was independent of frequency.[7] For the samples at the highest P_H, this frequency range

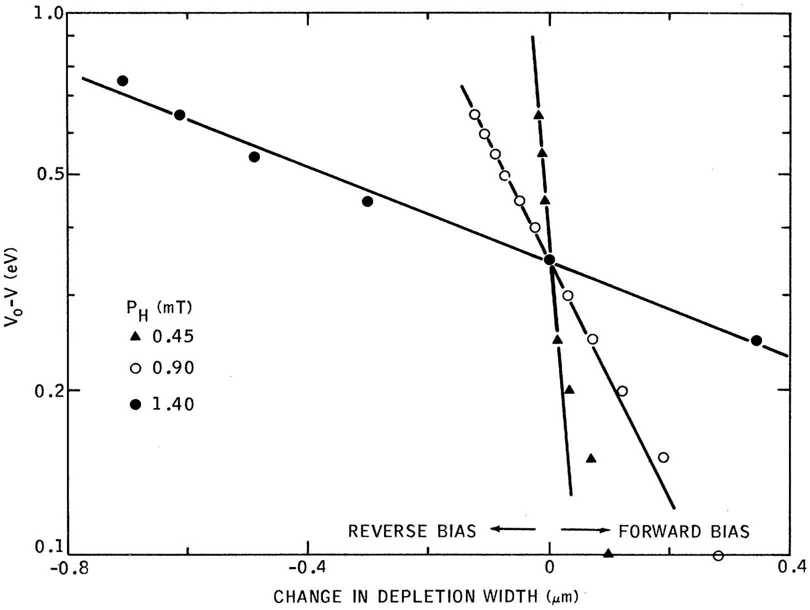

FIG. 1. Potential distribution in three different films of hydrogenated *a*-Si near a Pd contact, determined by the capacitance voltage technique discussed in the text. The potential profiles are obtained from a plot of the change in depletion width (plotted along the x axis) induced by an applied bias V, plotted on the y axis as $V_0 - V$ where V_0 is the built-in potential.

was below 1 Hz at room temperature. For experimental convenience these samples were measured at 50–100 °C where higher-frequency measurements were possible.

The measured potential distributions are plotted in Fig. 1 for samples prepared at low, intermediate, and high P_H. Note that the potential distributions become progressively flatter with increasing H content. In order to compare films prepared under different conditions, we assume that the density of states between the Fermi level E_F and $E_F - V_0$ is a constant. This density of states leads[8] to an exponential depletion region with characteristic width $X_0 = \sqrt{\epsilon/Ne}$ where ϵ is the dielectric constant and N ($\text{cm}^{-3}\,\text{eV}^{-1}$) is the density of states. The parameter X_0 can be estimated from the slope of the experimental potential distributions in Fig. 1. This slope reflects an average density of states between E_F and $E_F - V_0$. The corresponding densities of states for a series of samples prepared at different P_H are plotted in Fig. 2. Also plotted in Fig. 2 is the ESR spin density measured on a thick sample (5 μm prepared at $P_H = 0.5$ mT). Although the spin density is not strictly comparable to the density of states, it can be compared by dividing by the width of the spin distribution. Plausible estimates for the width of the distribution (0.3–1.0 eV) bring the spin density into satisfactory agreement with the capacitance data.

The relative amount of bonded hydrogen in the present films has been inferred from the integrated intensity under the Si–H vibrational modes. Figure 3

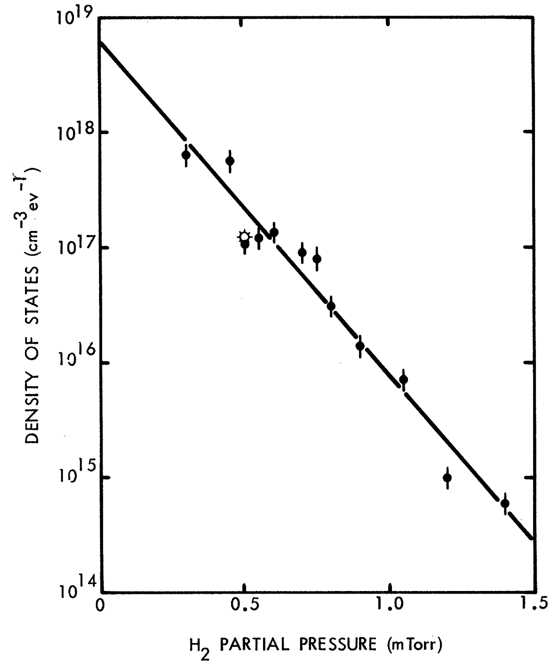

FIG. 2. Density of gap states as a function of hydrogen partial pressure. The error bars indicate the reproducibility of the measurements, and the solid line is a least-squares fit to the data. The point indicated by the symbol (✡) is the ESR spin density ($1.1 \times 10^{17}\ \text{cm}^{-3}$).

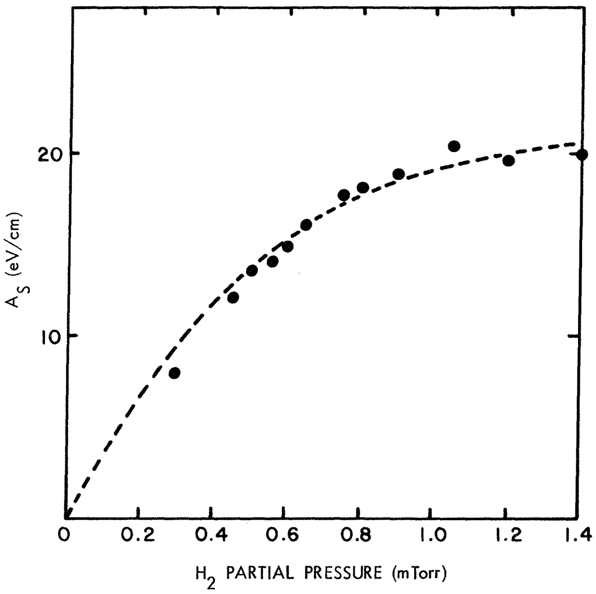

FIG. 3. Dependence of the integrated intensity of the Si–H stretching mode on the partial pressure of hydrogen. The dashed line is a fit to the data based on Eq. (3) as discussed in the text.

shows the integrated intensity under the ir absorption associated with the Si–H stretching vibration vs P_H. In addition, infrared data indicate that the bonding configuration of hydrogen changes with P_H. For example, the modes at 2100 and 890 cm^{-1} attributed to dihydride configurations[5] increase relative to the mode at 2000 cm^{-1} associated with monohydride configurations, with increasing P_H.

This variation in H content and the exponential decrease in the density of states with increasing H partial pressure in Fig. 2, can be understood if we postulate that the measured gap states are due to dangling silicon bonds. This postulate is supported by the good agreement between the measured density of states and the ESR data both at 0.5 mT and at zero H pressure, where the extrapolated density of states of about 10^{19} $cm^{-3}\,eV^{-1}$ is consistent with the spin density in unhydrogenated *a*-Si.[9] During the film growth process, a potential dangling bond at the growing surface of the film, will either capture an H atom or be covered up by the shower of Si atoms raining down. Once the dangling bond is covered by a layer of silicon atoms it is unlikely to capture a hydrogen and it becomes an electronically active defect. The capture rate of hydrogen atoms by dangling bonds will be given by the product $\sigma\theta FN$, of σ the capture cross section of the dangling bond for hydrogen, θ the sticking coefficient, F the hydrogen flux onto the surface of the growing film, and N the number of dangling Si bonds. For a given film growth rate R (monolayers/sec), the dangling bond will have on the average a time of $1/R$ in which to capture an H atom before it is sealed up by an overlayer of silicon. The time dependence of the number of dangling bonds N on the growing surface of the film will be given by

$$\frac{dN}{dt} = -\sigma\theta FN \quad . \tag{1}$$

If N_0 is the number of dangling bonds present in the absence of hydrogen, then after the cutoff time $1/R$ the number surviving is given by

$$N(1/R) = N_0 \exp(-\sigma\theta F/R) \quad . \tag{2}$$

Equation (2) predicts an exponential decrease in the density of dangling bonds with increasing H partial pressure since the H flux F is expected to be proportional to the partial pressure of H_2. Although it is not clear which species of hydrogen (molecule, atom, ion) is the important one, the density of all of these species is expected to scale with the H partial pressure, provided the argon pressure is high compared to the H pressure. For lack of more detailed information, we will use for F the flux of H_2 molecules in a hypothetical neutral gas at the same temperature and pressure. We find $F = AP_H$ where $A = 1.1 \times 10^{18}$ $cm^{-2}\,sec^{-1}\,mTorr^{-1}$. The constants N_0 and $\sigma\theta/R$ can be inferred from the intercept and slope of the line through the data on the density of states near midgap, shown in Fig. 2. If we use 10^{-16} cm^2 for σ and the experimental value for R of about 1 monolayer/sec, then the measured slope gives a sticking coefficient $\theta = 0.06$. this small sticking coefficient is reasonable in light of the fact that only a fraction of the hydrogen ($\lesssim 10\%$) in our sputtering plasma is dissociated.[10] The more abundant molecular hydrogen is not expected to eliminate dangling bonds.

Since the density of dangling bonds in the absence of H is much smaller than the actual H content of the hydrogenated material,[5] it is clear that only a small fraction of the incorporated H eliminates potential dangling bonds. Most of the H bonds to other sites. We can estimate a sticking coefficient of these sites for H using the same kinetic model of the film growth process. In this model the integrated intensity under the Si–H stretching mode A_s (assumed to be proportional to the concentration of bonded hydrogen[11]) will be given by

$$A_s = A_{\max}[1 - \exp(-\sigma\theta' F/R)] \quad , \tag{3}$$

where $A_{\max}$ should reflect the maximum amount of H that can be incorporated into the lattice. By fitting the data in Fig. 3 with Eq. (3), we find that the H sticking coefficient is $\theta' = 0.02$ if we use the same capture cross section (10^{-16} cm^2) as for the dangling bond sites. The fact that the sticking coefficient inferred from the H content is smaller than that inferred from the density of gap states may mean that most of the hydrogen has a high probability of being displaced by Si during the film growth process, or that the H is incorporated into reconstructed dangling bonds. The sticking coefficient for these sites is likely to be smaller than for true dangling bonds, because the hydrogen incorporation involves bond breaking. In this interpretation the bulk of the hydrogen is incorporated into sites that in the absence of hydrogen are reconstructed dangling bonds and do not have a spin or contribute states near midgap.

In conclusion, we have measured the density of gap states (by a capacitive technique and by ESR) and the hydrogen content in a series of sputtered a-SH$_x$ films prepared at different hydrogen partial pressures, and found the data to be in remarkable agreement with a simple kinetic model of the film growth process. The lowest density of states observed (7×10^{14} states/cm^3 eV) is the lowest value yet reported for reactively sputtered a-SiH$_x$. We have identified the states in midgap with Si dangling bonds, rather than impurities or other structural defects. Also, the results demonstrate that the residual density of states in the middle of the gap in our films is not due to special forms of hydrogen bonding[12] or modifications of the network resulting from hydrogen incorporation.

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