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PREPARATION OF HIGHLY PHOTOCONDUCTIVE AMORPHOUS SILICON BY rf SPUTTERING*

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The photoconductivity of hydrogenated rf sputtered amorphous Si has been determined as a function of the partial pressure of hydrogen in the sputtering gas and of deposition temperatures up to 450°C. The data can be used to choose conditions for preparing material with large photoresponse and small defect state density.

Amorphous Si and Ge prepared by rf sputtering is known[1] to possess a large number of dangling bonds and reconstructed dangling bonds which give rise to states in the gap between the conduction and valence bands. This defect state density, N_g, may be reduced by (1) annealing or deposition at high temperatures,[2,3] which presumably heals and reorganizes the network, or (2) the addition of controlled amounts of hydrogen to the argon sputtering gas, which, by compensating dangling bonds, shifts states from the gap deep into the valence band. The latter method was used in this laboratory[4] in an extensive investigation of a-Ge which led to successful doping of both a-Ge and a-Si and the fabrication of Schottky barriers and p-n junctions with good rectification characteristics.[5]

At first thought, it might appear that the maximum reduction of states in the gap would be obtained for substrate temperatures that are as high as is possible without inducing crystallization, and for hydrogen incorporation that saturates the dangling bonds. When our preliminary investigations suggested that this approach was oversimplified, we undertook a systematic examination of various properties of a-Si prepared for substrate temperatures, T_s, between 25 and 450°C and hydrogen partial pressures, p_H, between 0 and 5×10^{-3} Torr. We shall demonstrate that interpretation of the results involves two important considerations: (1) at fixed p_H, the atomic incorporation of H decreases for T_s greater than about 250°C; (2) it is probable that the energy of the Si-H antibonding states occurs roughly at the bottom of the a-Si conduction band, so that these states increasingly influence all band edge and gap processes as the atomic incorporation of H is increased.

Details of our sputtering system and measurement techniques have been published elsewhere.[4] In this paper we shall rely for the most part on the results of photoconductivity measurements to infer the changes of N_g. The dark transport measurements have also been published elsewhere[6] and will now be briefly summarized. As T_s is increased from 25 to 540°C at zero p_H, the conductivity decreases by only a factor of five and remains unactivated up to 250°C. Thus N_g remains large, implying that reorganization of the network at 540°C is not sufficient in itself to remove a significant fraction of the defect state density. When p_H is increased, the conductivity decreases by orders of magnitude and is activated over a wide temperature range above room temperature. This is obviously consistent with a reduction of N_g as a result of the compensation of dangling bonds by hydrogen.

Figure 1 shows the effect of varying T_s on the room temperature photoconductivity of films

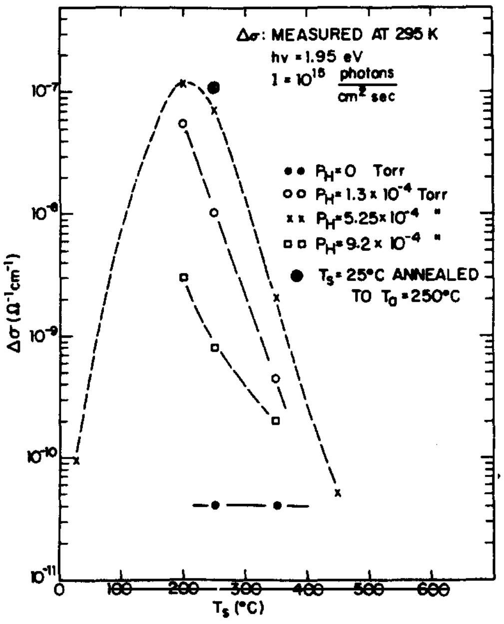

Figure 1. Room temperature photoconductivity vs T_s for samples prepared at different p_H.

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prepared at different p_H. The initial increase in $\Delta\sigma$ with T_s is consistent with the removal of states in the gap and is believed to be the result of two effects: (1) some network reorganization, which, however, cannot be great because of the results described in the previous para graph, and (2) an increase with T_s, at relatively low T_s, of the probability that H atoms will migrate on the growing surface to sites where they compensate incipient dangling bonds or incipient reconstructed bonds. However, we observe that the photoresponse goes through a maximum at a temperature between 200 and 250°C. We believe this to be a result of the increasing likelihood at higher T_s that the H will be unable to bond into the Si network, so that less hydrogen is incorporated into the film for a given p_H. A number of separate experiments are now in progress to test this hypothesis directly, but the evidence from transport[6] and ESR studies[7] points to the same conclusion. Recent measurements on Si prepared by silane decomposition also indicate that hydrogen evolution begins at temperatures as low as 250°C.[8] Also shown in the figure is the photoconductivity of one room temperature deposited film annealed for 1 hour at 250°C, which indicates that, in this temperature range, the effect of annealing is very similar to that of deposition at high temperature.

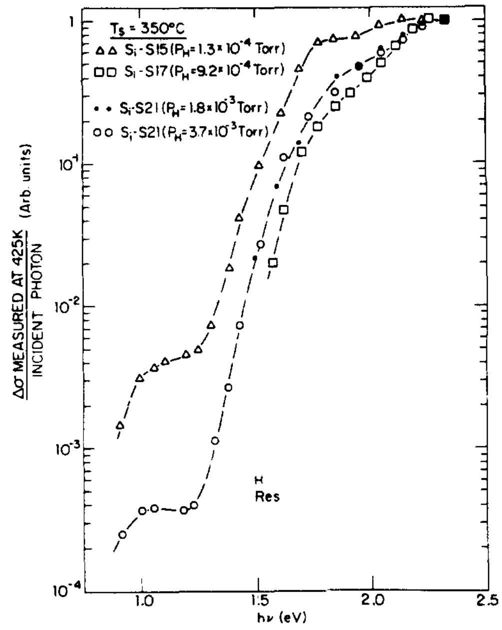

Figure 2. Spectral dependence of photoconductivity per incident photon for films prepared at T_s = 350°C and different p_H.

Figure 2 shows the spectral dependence of the photoconductivity per incident photon, $\Delta\sigma$, for films prepared at T_s = 350°C and different p_H.

$$\Delta\sigma(\nu) \propto \mu(\nu)\tau(\nu)\eta(\nu)\{1 - \exp(-\alpha t)\}$$

where ν is the optical frequency, μ the microscopic mobility, τ the recombination time, η the quantum efficiency, α the absorption coefficient and t the sample thickness. In the spectral region where all of the light is absorbed and $\{1-\exp(-\alpha t)\}$ tends to unity, the magnitude of the photoconductivity depends strongly on p_H. Since this dependence is related to the transport and recombination of the photogenerated carriers in the main bands, we have chosen to normalize $\mu\tau\eta$ to unity at 2.4 eV. The photoconductivity edge, defined in this way, shifts initially to higher photon energies and then reverses with increasing p_H. The initial blue shift of the edge is consistent with a reduction of N_g which it is natural to associate with the removal of dangling bonds. The subsequent shift of the edge to smaller photon energies is attributed to an increase in the density of gap states close to the conduction band edge. We speculate that these are the Si-H antibonding states and we offer simple but nevertheless strong evidence for their position in energy. It is known that H adsorbed on a crystalline Si surface yields Si-H bonding states some 5 eV below the top of the crystalline valence band,[9] and it is further known from theoretical studies[10] that the bonding state-antibonding state energy difference in SiH_4 and related molecules is about 7.0 eV. If we assume that these numbers are good enough for a rough estimate of the energetic position of the Si-H antibonding state, then we find an energy very close to the bottom of the conduction band, which is consistent with the observed behavior of the photoconductivity edge at high p_H. We are currently growing thick films for optical absorption measurements to provide an unambiguous test of the inferences drawn from shifts in the photoconductivity edge.

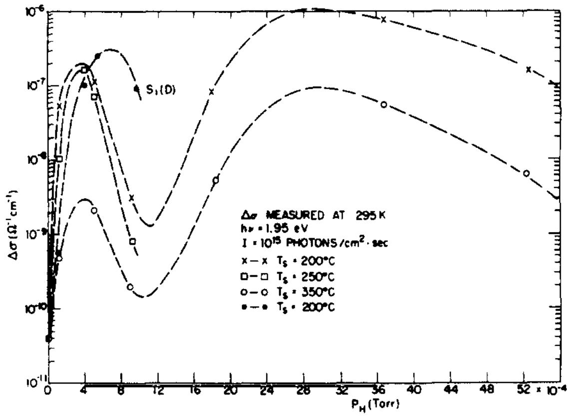

Figure 3. Room temperature photoconductivity vs p_H for films prepared at different T_s. Si(D) denotes a series of films prepared with deuterium instead of hydrogen at T_s = 200°C.

Figure 3 shows the magnitude of the room temperature photoconductivity of hydrogenated and deuterated films prepared at different T_s as a function of p_H. It can be seen that the T_s = 200°C and T_s = 350°C curves which span the entire p_H range have two maxima with the second slightly higher than the first. At present we do not have an accurate determination of hydrogen actually incorporated into the film, but we estimate from the strength of the Si-H absorption in the infrared[4] that the first peak corresponds to approximately 6 at. % and the second to perhaps a factor 3 or 4 higher. The initial growth of photoconductivity with p_H is again consistent with the removal of recombination centers by compensation of dangling bonds. The subsequent structure in the figure requires a different explanation.

With the addition of very large amounts of hydrogen, there will be a gradual transition in the structural short range order from essentially pure amorphous silicon at one extreme to a Si-H alloy at the other. The argument that the Si-H antibonding state energy lies near the bottom of the a-Si conduction band therefore has increasing significance at high hydrogen incorporations, since the thermopower measurements indicate that the predominant carriers are electrons. Thus, if these states are the initial states for recombination, there will be an increased probability of radiationless recombination with a high energy phonon going into the Si-H vibration. This may be the explanation for the decrease in photoresponse between $p_H = 4 \times 10^{-4}$ and $p_H = 9 \times 10^{-4}$ Torr. This idea gains additional support from the fact that the $p_D = 9.2 \times 10^{-4}$ Torr deuterated film has a much higher photoconductivity than the corresponding hydrogenated specimen; since the phonon energy $\hbar\omega$ of the Si-D localized vibrations is smaller than that of the Si-H ones, they provide a less efficient route for multi-phonon recombination.

This hypothesis cannot, however, account for the second peak at higher p_H. There is some evidence from the dc transport and also the photoconductivity response time that significant changes in both transport and trapping mechanisms occur in films deposited at very high p_H. Our understanding of these changes is not adequate at this time to attribute the second maximum in the photoconductivity to any one of these or other possible effects.

From these data we conclude that the conditions for preparing rf sputtered a-Si with the lowest N_g represent an optimization of both deposition temperature and hydrogen partial pressure. Certainly for our apparatus and overall deposition parameters, raising T_s indefinitely at zero p_H and raising p_H indefinitely at $T_s = 25°C$ does not produce the lowest N_g. It is likely that, regarded solely from the point of view of minimizing N_g, a useful bounded area in the T_s- p_H plane may be defined. Thus $T_s = 250°C$ and $p_H = 4 \times 10^{-4}$ Torr, which correspond to the first photoconductivity maximum in Figure 3, may be an example of a suitable choice. It follows that a larger p_H, but still at $T_s = 250°C$, would not be expected to increase, and might even decrease, the overall state density in the gap, even although these conditions do lead to a deterioration in photoconductive response. One test of the efficacy of the preparation conditions in reducing N_g is afforded by the shift of the Fermi level with addition of n or p type dopant. We have, in fact, doped a-Si at $T_s = 250°C$ and $p_H = 4 \times 10^{-4}$ Torr. The data indicate that the movement of the Fermi level is significantly greater than that reported in our previous paper,[4] for the same partial pressures of dopant gas (PH_3 or B_2H_6). We propose to repeat the doping procedure under conditions corresponding both to the minimum and the second maximum of photoconductivity in Figure 3.

Of course, from a more pragmatic point of view - although not unmindful of the likely correlation between photocarrier recombination time and N_g - the best combination of conditions for some applications might be taken to correspond to those giving the two peaks in the photoconductivity of Figure 3, whatever the detailed (and as yet poorly established) reasons for them. This is the case, for example, in investigating the practicality of hydrogenated sputtered a-Si as a potential solar cell material. The dark conductivity of hydrogenated Si is very low ($\sigma(300\ K) \sim 10^{-9}$ to $10^{-10}\ \Omega^{-1}\ cm^{-1}$), and therefore the internal resistance of a photocell would be very high. However, if the material is very photoconductive, the internal resistance under illumination by sunlight is likely to decrease to acceptable values. This point of view suggests a program of research that concentrates attention on the preparation conditions corresponding to the maxima in photoconductivity in Figure 3 in seeking possible devices, while at the same time endeavors to sort out the fundamental arguments involving reduction of N_g, alteration of state density in the conduction band, mobilities and recombination times which give the double maxima in the first place.

In conclusion, we have shown that optimization of choice of T_s and p_H, rather than extreme values of either or both parameters, gives the maximum reduction of density of states in the pseudogap and the best photoresponse. However, the detailed behavior of the photoresponse as a function of H incorporation raises new questions about the role of Si-H antibonding states in transport and recombination. It is also clear that we need to consider with care the changing atomic arrangement and the electronic structure of the material as it evolves from H-compensated Si into a Si-H alloy. Until this is done in a systematic way, the conclusions drawn from experiments such as those described here should be viewed as preliminaries to the new investigations they suggest.

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