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EXCHANGE OF BONDED HYDROGEN IN AMORPHOUS SILICON BY DEUTERIUM

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ABSTRACT

We show that bonded hydrogen in a-Si:H is readily exchanged by atomic deuterium when exposed to a deuterium plasma discharge. The effective diffusion coefficient for the D,H exchange 10^{-14} cm^2/sec at 160°C, is comparable to that of interstitial hydrogen in c-Si.

Compositionally modulated amorphous semiconductors have proven to be a powerful new tool to study the growth and structure of amorphous semiconductors and their interfaces. This motivated us to use neutron scattering to investigate superlattices consisting of alternating layers of amorphous hydrogenated silicon (a-Si:H) and amorphous deuterated silicon (a-Si:D). We grew the a-Si:H/a-Si:D multilayers by plasma assisted chemical vapor deposition using SiH_4 and SiD_4 for the reactive gases. While we did succeed in observing coherent neutron scattering in the multilayers [1], the intensities of the Bragg peaks were one to several orders of magnitude smaller than expected for abrupt H/D interfaces, indicating that the interfaces were smeared out on a scale of ~200Å.

In this paper we provide evidence that smearing of the interfaces is due to an exchange of bonded H and D by rapidly diffusing interstitial atomic H and D. The source of the atomic H and D is the plasma discharge. The exchange reaction D + SiH $\rightleftarrows$ H + SiD, which we believe to be responsible for the H,D mixing, is analogous to isotopic exchange processes that have been studied extensively in organic molecules [2]. To verify the H/D exchange mechanism we exposed a-Si:H to a D_2 plasma and then determined by IR-spectroscopy and by SIMS profiling that D has replaced some of the bonded H in the amorphous network. From neutron scattering, IR and SIMS experiments we deduce an effective diffusion coefficient for the D,H exchange process.

NEUTRON SCATTERING IN a-Si:H/a-Si:D SUPERLATTICES

a-Si:H/a-Si:D multilayers were made by RF(13.56 MHz) plasma assisted CVD in a capacitive reactor with SiH_4 and SiD_4 exchanged periodically in the reactor, at a flow rate of 3 cc/min and pressure of 30 mtorr. The plasma was interrupted for 15 sec during the gas exchange to minimize cross contamination. The substrates, 2 inch diameter, 1/8 inch thick, optically polished quartz discs with a RMS surface roughness of ~ 5Å, were mounted on the anode of the reactor, held at 180°C. The deposition rate was ~1Å/sec. The repeat distance d_r and the number of bilayers were chosen so that the multilayer film thickness was about ~ 1μm. The nominal thicknesses of the a-Si:H and a-Si:D layers (given by product of deposition time and deposition rate) were equal.

To determine the average concentration and bonding configuration of H and D we measured the IR absorption spectra of the multilayers deposited on polished c-Si substrates. The IR stretching bands for the multilayers with d_r = 95Å are shown in Fig. 1. The absorption peak at 1440 cm^{-1} corresponds to the monodeuterium Si-D stretching vibration. The width of the Si-D peak is narrower by a factor $1/\sqrt{2}$ and the amplitude is smaller by a factor of

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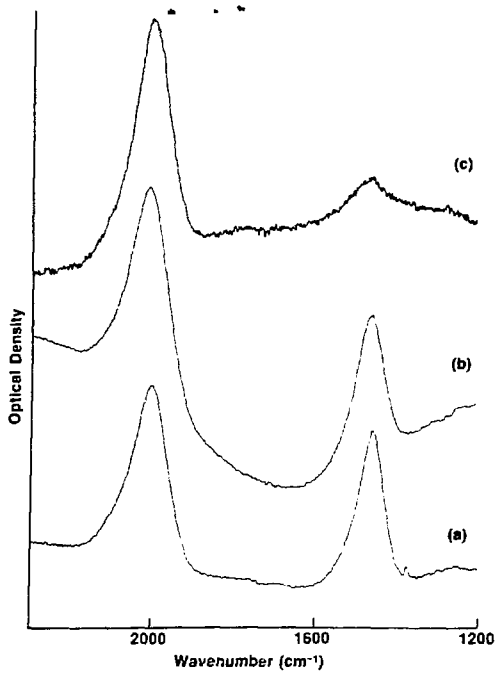

Fig. 1. IR absorption spectra of the Si-H and Si-D stretch bands vs wave number: (a) a-Si:H/a-Si:D superlattice with d_r - 95Å; (b) 50 layers of a-Si:H 200Å thick, 150 sec D_2 plasma; (c) 7 layers of a-Si:H 1000Å thick, 813 sec D_2 plasma.

$1/\sqrt{2}$ than the monohydride Si-H peak at 2000 cm^{-1}. Thus the intensity of the Si-D peak is a factor 1/2 lower than the intensity of the Si-H peak. Since the matrix elements for the Si-D vibrations are a factor of 1/2 smaller than for Si-H [3], it follows that the average concentrations of H and D in the multilayer are equal.

The neutron scattering experiments were made at the Brookhaven National Laboratory High Flux Beam Reactor using a triple-axis spectrometer in the elastic scattering mode to produce a monochromatic neutron beam of λ = 4.05Å. Figure 2 shows the reflection intensity versus wave number $Q = 4\pi \sin\Theta)/\lambda$ for the multilayer with d_r = 235Å, where Θ is the angle of incidence of the neutron beam. The spectrum exhibits a prominent first order Bragg reflection at Θ = 1.22 but no higher order Bragg peaks were observed in this nor in two other multilayers we looked at with d_r = 95 and 160Å. Using a Fe/Ge multilayer as a calibration standard we determined that the reflection peak in Fig. 3 corresponds to an integrated reflectance of 2.5×10^{-5} and the reflectances of the other two multilayers were both 4×10^{-8}.

The integrated intensity of the first order Bragg reflectance R for an ideal multilayer with abrupt H/D interfaces and equal sublayer thickness is given by [4]

$$R = (\lambda/2L)A \tan A \qquad (1)$$

$$A = (2/\pi)Ld_r(\ell_D - \ell_H)N \qquad (2)$$

where L is the multilayer thickness, $\ell_H = -0.374\ cm^{-12}$ and $\ell_D = 0.667 \times 10^{-12}\ cm^{-12}$ are the neutron scattering lengths of H and D respectively and $N = 7.3 \times 10^{21}\ cm^{-3}$ is the density of H and D in the H/D multilayers determined from the intensity of the IR stretching bands. From Eqs. 1 and 2. We calculate $R = 4.04 \times 10^{-4}$, for $d_r = 235$. This is more than an order of magnitude larger than the measured reflectance and for the smaller d_r multilayers the discrepancy between calculated and measured R is four orders of magnitude. The low intensity of the Bragg reflections suggest that the H and D are intermixed.

If we assume that the mixing of bonded H and D is due to diffusion of interstitial atomic H and D, the source of which is the plasma discharge, we can estimate from our data a value for the diffusion coefficient d. During the growth of the a-Si:D layer, D from the plasma diffuses through the growing a-Si:D layer to reach the underlaying a-Si:H layer where it displaces H. During the growth time t of the a-Si:D layer, D diffuses a length $\sqrt{(td)}$. If the diffusion length $\sqrt{(td)}$ is smaller than the sublayer thickness, tr, where r is the deposition rate, than D and H will be spatially separated. The deposition time which roughly divides multilayers with intermixed H and D from multilayers with separated H and D is given by the relation $\sqrt{(td)} = rt$ or $d = r^2t$. Substituting r = 1Å/sec and t = 100 sec, we obtain $d \approx 10^{-14}\ cm^2/sec$.

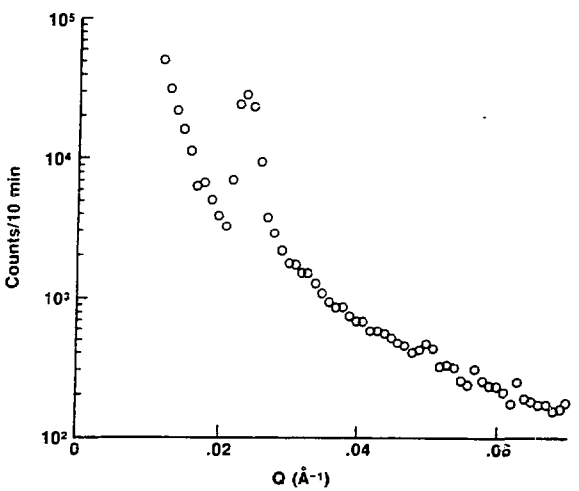

Fig. 2. Neutron scattering intensity vs wave number Q for a-Si:H/a-Si:D superlattice with $d_r = 235Å$.

EXCHANGE OF BONDED H BY PLASMA GENERATED D

To test the idea that the intermixing of H and D is due to interstitial atoms diffusing into the network from the plasma we exposed a-Si:H layers to a D_2 plasma. Figure 3 shows Secondary Ion Mass Spectroscopy (SIMS) profile of a multilayer made by depositing a 1000Å a-Si:H layer at 160°C and exposing it at 160°C for 813 sec to a D_2 plasma (40 mtorr, 10 watt RF power) and repeating the process periodically for another six times. Figure 3 clearly demonstrates that H was displaced by D resulting in a compositionally modulated structure. We also made a multilayer consisting of 50 layers of a-Si:H each 200Å thick, exposed to the D_2 plasma for 150 sec. While in this case SIMS and IR also indicated a substantial

concentration of D in the multilayer no modulation in the concentration was observed. The IR spectra of the two multilayer films are shown in Fig. 2b and 2c.

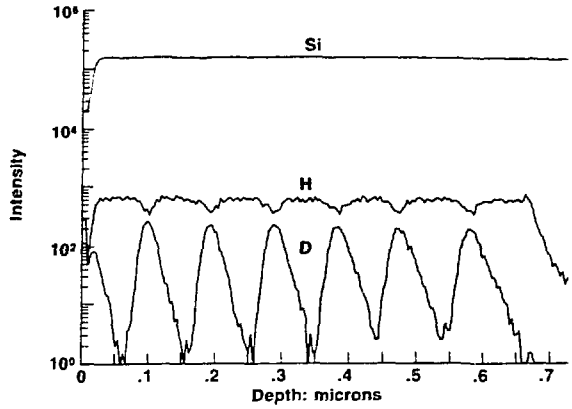

Fig. 3. SIMS depth profile of 7 layers of a-Si:H 1000Å thick, each exposed to 833 sec D_2 plasma.

From the IR and SIMS measurements we draw the following conclusions: (1) Bonded H is exchanged by bonded D. This follows from the fact that the Si-H and Si-D bonding configuration of H and D (monohydride and monodeuterium) and the sum of the concentrations of H and D are the same as the bonding configuration and concentration of H in a-Si:H untreated with D_2 plasma. (2) The D_2 plasma did not result in any etching of the a-Si:H layers. (3) The rate limiting step in the D, H exchange is diffusion. This follows from the fact that the concentration of D in the thin a-Si:H layers (Fig. 2b) is much larger than in the thick layers (Fig. 2c) and that H in the 1000Å a-Si:H layers was displaced only to a depth of ~250Å (Fig. 3). (4) The H/D interface formed when a-Si:H deposited on the deuterated layer is appreciably more abrupt than the opposite interface. The cause of this asymmetry we believe is that dehydrogenation of the deuterated layer is impeded by the growth of the a-Si:H layer through which the atomic H must diffuse to reach the deuterated layer. Moreover the concentration of atomic H in the SiH_4 plasma may be smaller than the concentration of atomic D in the D_2 plasma. (5) The fact that the modulation in the H,D concentrations does not change significantly with depth indicates that once the plasma front has moved away from the underlaying layers mixing of D and H ceased.

To estimate a diffusion coefficient for the D,H exchange, we note that in the 1000Å a-Si:H layers the SIMS data shows that H was replaced by D to a depth of ~ 250Å in a time of 813 sec. This corresponds to a diffusion coefficient $d \approx (2.5 \times 10^{-6})^2/813 \approx 10^{-14}$ cm^2/sec. In the 200Å a-Si:H layers IR data shows that half the H was replaced by D in 150 sec. If we assume that the diffusion length was 100 Å then $d \approx (10^{-6})^2/150 \approx 10^{-14}$ cm^2/sec. Both of the above values agree with d estimated from the neutron scattering data.

The above value for the diffusion coefficient for D,H exchange is orders of magnitude larger that for bonded hydrogen i.e. 10^{-20} cm^2/sec for undoped[5] a-Si:H (extrapolated to 160°C) and 10^{-16} cm^2/sec for B doped[6] a-Si:H. Diffusion of bonded H is much slower because of the energy required for bond breaking while in the case of the D,H exchange, no expenditure in energy is required, apart from the requirement of overcoming a finite but probably small kinetic barrier.

The transport and D,H exchange in a-Si:H bears close analogy to diffusion of H in B doped c-Si, where similar magnitude diffusion coefficients were observed[7,8]. It should be noted however that there are also important differences between the two systems. In c-Si there is long range order and the interstitial H is trapped at impurity sites whose denisty is ~ 10^{19} cm^{-3}. In a-Si:H there is only short range order, thre are two diffusing species, D as well as the displaced H and there are ~ 10^{21} bonding sites. Moreover to derive rigorously the diffusion coefficient for interstitial H and D and the rate constant for D,H exchange requires solution of the coupled diffusion equation for H and D with the proper boundary conditions. We will report the solution of these equations and the temperature dependence of the D,H diffusion coefficient of interstitial D in a-Si:H in a future paper.

In conclusion we have shown that bonded H in a-Si:H can be exchanged with D by exposing the a-Si:H film for a D_2 plasma. The diffusion of interstitial D is of comparable rate to diffusion of H in crystalline Si. This work opens up an interesting new approach to study transport of H in a-Si:H and other hydrogenated semiconductors and insulators.

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