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EXPERIMENTAL ELUCIDATION OF HYDROGEN LOCAL DENSITY OF STATES IN HYDROGENATED AMORPHOUS SILICON

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Ultraviolet and X-ray photoemission spectroscopies (UPS and XPS) are used to study the valence band in device quality hydrogenated amorphous silicon films (s-Si:H). Their results are combined to obtain estimated information about the hydrogen local density of states (HLDOS). The monohydride bonding configuration and the occurrence of interhydride bonding between H atoms are confirmed by the experimental data.

Recent demonstrations of the drastic changes in the properties of amorphous silicon (a-Si) by virtue of hydrogenation have stimulated many experimental studies. Its scientific attractions include a continuously adjustable band gap, a usable carrier life time and diffusion length, efficient optical transitions and the versatility of incorporating either n- or p-type dopants. This exciting possibility has triggered many researchers to investigate on the nature of the role played by H_2 in deciding the electronic and transport properties of a-Si:H. Von Roedern et al. [1] have used photoemission studies and observed hydrogen induced features between approximately 5 and 11 eV below the top of the valence band. In the conduction band the photoconductivity data of Moustakas et al. [2] suggest the formation of the Si:H antibonding states. The hydrogen local densities of states have been calculated by Ching et al. [3–6] for several possible types of Si:H bonding configuration, each of them being embedded in an a-Si cluster. These are SiH_x ($x=1, 2, 3$) units, a $(SiH)_2$ chain fragment, a $(SiH_2)_2$ fragment and SiH–HSi, a broken Si–Si bond with two H atoms taking the place of the broken bond. In this Letter we report our concerted effort on photoemission measurements of a-Si:H at different incident energies and show how the information contained in these spectra effectively reflects the hydrogen induced electronic structure (HIES) which is compatible with the theoretically estimated partial density of states [3–6].

Photoelectron spectroscopy provides direct information about the energy distribution of the occupied states in solids. Energy distribution curves of valence electrons are, aside from cross sectional effects, true replicas of the valence band density of states (VBDOS) and thus reflect, in our case, the changes in the electronic structure of silicon upon amorphization or incorporation of H into its lattice. We have measured the photoemission spectra of hydrogenated a-Si films prepared by conventional plasma CVD from silane hydrogen mixture. The pressure in the preparation chamber and the RF power density of the discharge were maintained at 1.0 Torr and 60 mW/cm^2 respectively. The substrates used were stainless steel for photoemission measurements, corning 7059 for optical and electrical measurements and c-Si wafer for infrared absorption measurements. The samples were transferred into the vacuum generators ESCA 3 system immediately.

The photoemission spectra were taken in a vacuum better than 5×10^{-10} Torr. The oxygen, carbon and nitrogen contaminations in these films, as monitored by their respective X-ray photoemission signatures from their core levels, were maintained below 0.5% using low energy argon ions. MgKα X-rays (1253.6 eV) and He II radiation (40.8 eV) were used to study the electronic states in the valence band region of a-Si:H. The electrical and optical properties

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of the films, simultaneously produced at different substrates like corning 7059 glass or crystalline Si wafer, are summarized in table 1. We have presented UPS and XPS experimental data on the VBDOS for device quality a-Si:H (prepared at $T_s = 300°C$ and having properties as in table 1) in figs. 1a and 1b respectively. For comparison we have also presented our experimental data on the XPS VBDOS for crystalline silicon and pure amorphous silion in figs. 1c and 1d respectively. The inset in fig. 1 shows the valence and O 1s core level spectra of an unhydrogenated a-Si film whose surface is oxidized. The strength of the O 1s line at 532 eV binding energy (fig. 1f) corresponds to a coverage of 0.03 monolayers of oxygen. The O 2p derived states show up at 6.7 eV (O_I) and at 11.8 eV (O_{II})(fig. 1f). One can observe a close resemblance in the spectra of a-Si:H (fig. 1a) and oxidized a-Si (fig. 1e) as far as the hydrogen or oxygen induced structures are concerned. Fig. 1g pictures our UPS experimental data on the VBDOS for pure amorphous silicon. The oxygen ontamination level as estimated from XPS in the a-Si:H films under examination is similar to that shown in fig. 1g. Now on examining the spectra in figs. 1c and 1d one finds that peak I′ (p-like states) moves slightly upward in energy with reference to E_F as compared to peak I in c-Si. In addition, a single featureless peak III′ appears probably due to the merger of peaks II and III. It may, however, be noted that peak III′ in a-Si (fig. 1d) appears at the same energy (9.2 eV) as that of peak III in c-Si (fig. 1c). Moreover peaks I′ and III′ (fig. 1d) are broader than peaks I and III in fig. 1c. The disappearance of peak II in a-Si has been attributed to the diminishing of the sharp maximum in the VBDOS of c-Si, due to the flat bands near L and X in the Brillouin zone [7]. Suh a change is expected due to the loss of long range order in a-Si.

One major advantage of using X-ray photoelectron spectroscopy (XPS) to study the effect of hydrogen on the silicon site density of states in a-Si:H is that it directly reflects the partial density of states of silicon sites (Si LDOS) since the partial hydrogen 1s cross section is negligibly small at energies beyond 120 eV [8]. Fig. 1b depicts only the partial silicon density of states (Si LDOS) in a-Si:H, whereas fig. 1a reflects the total density of states in the valence band of a-Si:H.

Allan and Joannopoulos [9] have investigated the effects of bulk-like and surface-like surroundings on the electronic density of states of a variety of Si–H bonding configurations in a-Si:H using a cluster Bethe lattice approach. They predict two fundamentally different bonding patterns for the device grade a-Si:H films with different consequences for the doping mechanism, that are consistent with the available ultraviolet photoemission spectroscopy data (UPS). These are:

(1) H atoms bonded in microcrystalline regions, and

(2) clusters of mono-hydrides (SiH) in a continuous random network.

The first prediction supports the idea of Phillips [10] that hydrogenation of a-Si leads locally to the formation of crystalline regions with hydrogenated boundaries. Should this picture apply to the device grade a-Si:H, our XPS measurements, which are sensitive to the Si LDOS only, would resemble those of c-Si (fig. 1c) and exhibit peaks II and III. This is, however, not the case as depicted by fig. 1b, which is qualitatively similar to fig. 1d. Further our laser Raman results on the specimen under investigation show no detectable features near 520 cm^{-1} (characteristic of c-Si). So it is evident from our measurements that hydrogenation does not induce crystallization in a-Si:H.

Table 1
Electrical and optical properties of the hydrogenated amorphous silicon (a-Si:H) film used for photoemission experiments.

Dark conductivity (σ_D)	2×10^{-10} $(\mathrm{Ohm\,cm})^{-1}$
Light conductivity (σ_L) (AM 1 illumination)	5×10^{-5} $(\mathrm{Ohm\,m})^{-1}$
Dark conductivity activation energy (E_{act})	0.85 eV
Optical bandgap (E_{opt})	1.72 eV
Bonded hydrogen content	8.35%
H_2 bonding mode (from IR measurements)	Si–H
Mid-gap density of states (SCLC measurements)	$< 10^{16}\ \mathrm{cm}^{-3}\,\mathrm{eV}^{-1}$

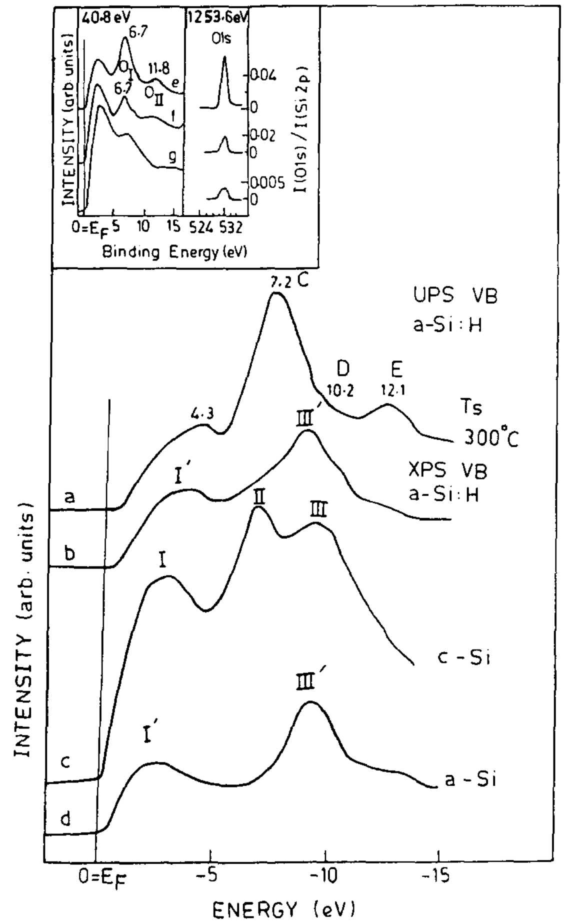

Fig. 1. The experimental valence band density of states spectra for device quality a-Si:H. (a) XPS spectra of a-Si:H. (b) UPS spectra of the same a-Si:H. (c) XPS spectra of c-Si filed in ultra-high vauum. (d) XPS spectra of pure amorphous silicon. (e)–(f) The inset shows the valence of O 1s core level spectra of an unhydrogenated a-Si film whose surface is oxidized. (g) UPS spectra of pure amorphous silicon (same as in (d)). The zero of the energy scale corresponds to E_F. I(O 1s)/I(Si 2p) = 0.02 corresponds to 0.03 monolayers (ML) of oxygen coverage.

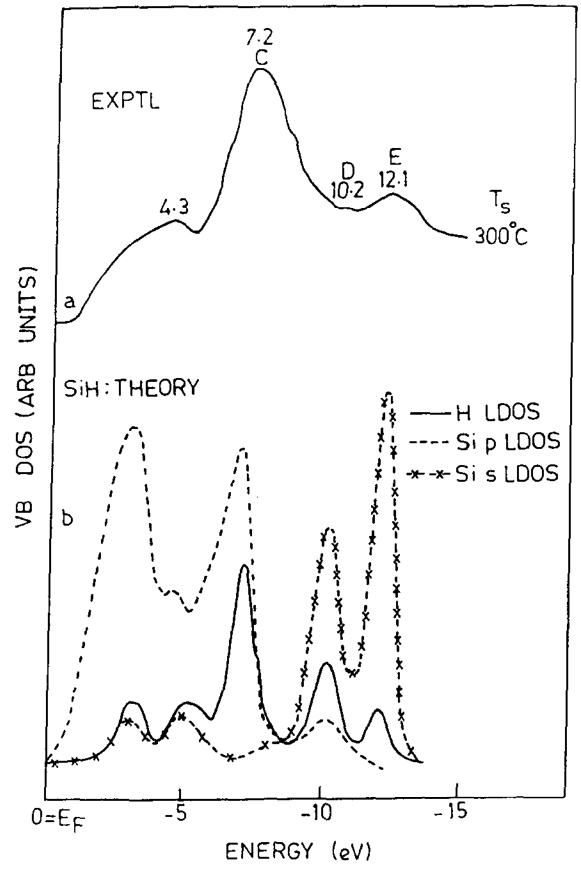

Fig. 2. (a) He II valence band spectra of hydrogenated amorphous silicon films prepared at 300°C. (b) Calculated local density of states for an a-Si : H_x cluster ontaining only Si–H units by Ching et al. [5]. All the theoretical urves have been shifted by 1 eV towards the low energy side.

Now comparing figs. 1b and 1a, one observes additional features C, D and E in fig. 1a. These features are explained as hydrogen induced structures in the VBDOS by earlier workers [1,7,8]. We have presented our UPS VBDOS spectra along with the calculated LDOS of Si and H for an a-Si:H cluster having only siH units by Ching et al. [5,6] in fig. 2. The agreement with the measured spectra is seen to be good, if one assumes that the leading two peaks in the HLDOS are masked by the strong Si 3p emission between 0 and 5 eV. Peak C is attributed to the characteristic signature of Si 3p–H 1s bonding. Von Roedern et al. [1] have attributed peak D to Si 3s–H 1s bonding which is seen to be weak in our measured spectra. The origin of peak E is still under debate, since a number of other calculations on monohydride configurations give two peaks in reasonable agreement with C and D but fail to reproduce peak E [11–13]. We resolve this mystery through our experimentally determined hydrogen induced elecronic structure (HIES), which we explain in the subsequent portion of this Letter.

The Si valence band consists of 3p and 3s portions with relative photoemission cross sections given by $\sigma_s/\sigma_p \sim 3.4$ in the XPS regime and $\sigma_s/\sigma_p \sim 1$ in the

UPS regime respectively. In the case of amorphous silicon (fig. 1g) Si 3p states show up as a leading peak at approximately 4 eV from E_F. The Si 3s derived states and hybridized 3s–3p states form a rather broad and structureless band between 6 and 14 eV from E_F. Also from various theoretical calculations on a-Si:H clusters [1,7,8], it is known that hydrogen induced states in the valence band ocur at approximately beyond 5 eV from E_F. In the light of the above facts we have adopted the following normalization procedure for comparing our measured XPS and UPS VBDOS spectra. The UPS spectrum has been scaled in such a way that there is a maximum overlap between the XPS and UPS VBDOS in the approximate energy range 0–3 eV. Then to derive information about the hydrogen induced electronic structure (HIES) in a-Si:H we have computed (1) the difference of the UPS spectra (fig. 1a) and the XPS spectra (fig. 1b) and (2) the ratio of the UPS spectra (fig. 1a) to the XPS spectra (fig. 1b). Both the difference and the ratio spectra are shown along with the theoretical HLDOS curves of Ching et al. in figs. 3a and 3b respectively. Since our XPS spectra purely reflect only the Si partial density of states irrespective of the H_2 content, figs. 3a and 3b should either reflect peaks which are comparable to the HILDOS or exhibit a featureless spectrum if the peaks C, D and E seen in fig. 1a and fig. 2a have a different origin than H_2 induced features. Indeed fig. 2a shows four peaks at 4.5, 7.1, 10.3 and 12.2 eV whereas fig. 3b shows corresponding peaks at 5.1, 7.1, 11.1 and 12.7 eV respectively. It is also seen that the features in the difference spectra (fig. 3a) are much broader and weaker than those in the ratio spectra (fig. 3b). The hydrogen induced features that occur in the energy range beyond 5 eV from E_F, due to Si 3s–H 1s interactions or between Si-3s–3p hybridized state and H 1s interactions, are suppressed in the difference spectra by the enhanced Si 3s contribution (cross sectional effects) of our XPS spectra. This artifact is passed over by taking the ratio spectra (fig. 3b) which clearly show the well defined sharp hydrogen induced electronic structure (HIES) representation of the hydrogen occupied states as compared to difference spectra [1]. We have also presented the calculated HLDOS spectra for various monohydride configurations in figs. 3c–3e. It is evident from fig. 3, that fig. 3b can easily unfolded as a linear combination of figs. 3c–3e with appropriate weight factors reflecting the presence of the particular clusters (SiH, $(SiH)_2$ or $(SiH)_n$) in the continuous random network of silicon. The possibility that such hydrogen clusters exist is, of course, a very real

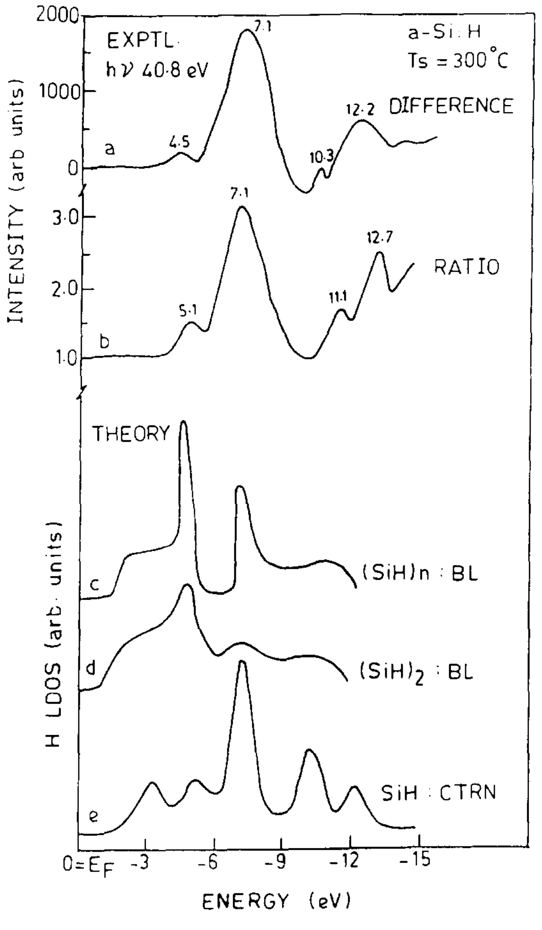

Fig. 3. (a), (b) Estimated experimental hydrogen occupied sites spectra of a hydrogenated amorphous silicon film prepared at 300°C. (c), (d) Calculated HLDOS in an a-Si:H_x cluster by Allan and Joannopoulos for different bonding geometries [2]. BL – Bethe lattice. (e) Calculated HLDOS in an a-Si:H_x cluster having Si-H units only, by Ghing et al. [5]. CTRN – continuous tetrahedral random network. All the theoretical curves have been shifted by 1 eV towards the low energy side.

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[1] This procedure is more appropriate for analyzing the complex photoemission data from various orbitals having significantly varying photoemission cross sections in the energy range under consideration.

one. Their presence has been postulated independently by Shanks et al. [14] based on IR spectrosopy and Reimer et al. [15] based on NMR studies.

The observed peaks in fig. 3b at 5.1 eV, 7.1 eV and 11.1 eV are in good agreement with both the earlier calculations of Ching et al. [4,5] and many other workers [11–13] on various Si:H bonding configurations and also with the experimentally observed H_2 induced peaks in the UPS spectra for the device quality films by Von Roedern et al. [1]. This supports Allan and Joannopoulos' [9] second prediction, i.e. clusters of monohydride (SiH) are present in the continuous random network of Si in the device quality a-Si:H films.

The peak at 12.7 eV in fig. 3b arises from the interhydride bonding between H atoms in the neighbouring (SiH) lusters. Such an explanation is compatible with the calculated results of Ching et al. [5] for an a-Si:H_x cluster containing SiH_2–SiH_2 fragments of varying Si–Si distance embedded in a continous random network. They observe a peak at approximately 14 eV below the valence band maximum in their calculations. The interhydride bonding intensifies upon contracting nearby the Si–Si bond length. Thus the shorter the Si–Si bond length the larger the intensity of the peak near 14 eV and consequently the gap states are better developed as per their calculations. They have also observed the reversal of this phenomenon upon lengthening the Si–Si bond in their model cluster. Thus we feel that the concerted efforts on similar measurements of hydrogen induced electronic structure on device quality films under various treatments might shed light on even the unsolved mystery of H_2, in altering the transport properties of a-Si:H, more particularly, on the origin of the S.W. effect. Experimentation along these lines is in progress in our laboratory. We have also performed extensive measurements of the HIES on a variety of a-Si:H films with different hydrogen contents. Elaborate discussions on such results along with a comprehensive study of earlier work on the photoemission experiments on a-Si:H are being communicated separately.

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