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Photoelectron Spectra of Hydrogenated Amorphous Silicon

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uv-induced and x-ray-induced photoelectron spectra have been taken on hydrogenated amorphous silicon prepared *in situ* by reactive sputtering. Hydrogen-induced features in the *a*-Si valence-band region have been identified by comparison with spectra and calculations appropriate to the adsorption of hydrogen onto Si surfaces. Films sputtered at room temperature show peaks related to Si multiply bonded to hydrogen, while deposition at 300°C or above is mainly causing the formation of singly bonded SiH groups.

When hydrogen is incorporated into amorphous silicon (*a*-Si) either by preparing films from a glow-discharge plasma of silane¹ (SiH₄) or by reactively sputtering the material in an Ar-H₂ mixture,^{2,3} the dangling bonds believed to be present at the inner surfaces of microvoids or multivacancies are saturated by hydrogen atoms attached to them.⁴ This conjecture is supported by the reduction in the electron-spin-resonance signal^{5,7} and the presence of Si-H vibrational modes observed in the infrared absorption.^{7,8} The presence of hydrogen is therefore essential for the substitutional doping of *a*-Si either by glow discharge⁹ or by sputtering techniques,¹⁰ which has enabled the construction of solar cells based on *a*-Si.¹¹ This exciting possibility has triggered an increasing number of investigations on the electronic and transport properties of *a*-Si with H concentrations that exceed those necessary to merely saturate dangling bonds.^{3,8} In this Letter we report the photoemission spectra of *a*-Si with varying degrees of hydrogenation. The H-induced additional structure in the *a*-Si valence band can

be explained by an incorporation of H into the *a*-Si network, the main configurations being SiH and SiH₃. These results have been derived by comparing our spectra with experiments and calculations of H chemisorbed on Si single-crystal surfaces. A reduction in width of the Si valence band up to 1 eV suggests a partial destruction of the Si network for H concentrations in excess of approximately 10%.

Photoelectron spectra of *a*-Si:H were measured with a resolution of 0.3 eV using He I (21.2 eV) and He II (40.8 eV) radiation for the valence-band region, while Al K α (1486.6 eV) x rays were employed to obtain core-level spectra at a resolution of 1.1 eV.

The samples were prepared *in situ* (base pressure 1×10^{-9} Torr) by dc sputtering from a single-crystal Si target (50 Ω cm, *n* type, 18 mm diam) in a mixture of Ar and H₂. Depending on the deposition temperature T_D , substrates of Cu ($T_D > 300^\circ\text{C}$) or W ($T_D > 300^\circ\text{C}$) were used. The distance between target and substrate was about 4 cm, and the deposition angle was 45°. The sput-

ter gas premixed from high-purity Ar (99.9997%) and H₂ (99.999%) flowed at a rate of ~ 0.1 l/h through the discharge region at a pressure between 10^{-1} and 10^0 Torr. The H₂ concentrations quoted are partial H₂ pressures determined with a membrane gauge in the mixing system. Despite a low deposition rate of only 3–15 Å/min, sputtering times of 1–3 h were sufficient to obtain films for the photoemission measurements.

The cleanliness of the *a*-Si films was checked *in situ* by XPS (x-ray photoemission spectroscopy) scans covering the range of 0–1000 eV binding energy. Signals from the O 1s and N 1s levels disappeared after prolonged sputtering times. Oxygen and nitrogen concentrations below 2% did not contribute discernibly to the valence-band spectra. In a few cases an argon concentration of no more than 1% was detected.

Figures 1(a) (He I) and 1(b) (He II) show the valence-band spectra of a series of samples, sputtered with 0%, 10%, and 50% H₂ in the sputtering gas. Binding energies are given with respect to the Fermi energy E_F of a clean metal substrate. *a*-Si prepared without hydrogen exhibits a prominent peak 2 eV below E_F , due to Si 3*p*-derived states in both spectra. Further weak valence-band emission between 5 and 12 eV can be dis-

tinguished in the He II spectrum [Fig. 1(b)].

Taking the lower cross section of Si 3*s*-derived states into account,¹³ this agrees well with the XPS spectra of *a*-Si by Ley *et al.*¹⁴ The position of the Fermi level coincides to within 0.1 eV with the top of the valence band.

With the incorporation of hydrogen a new peak labeled *A* in Figs. 1(a) and 1(b) around 6 eV develops. The area under this peak is approximately proportional to the H₂ concentration in the sputtering gas. Its position shifts from 5.9 to 6.2 eV between H₂ concentrations of 10% and 50%, respectively. At the same time the width increases from 1.2 eV full width at half-maximum (FWHM) to 1.9 eV (see Fig. 1). A second broader peak (2.5 eV FWHM), *B* in Fig. 1(b), can be distinguished in the He II spectrum only. Its distance from peak *A* increases from 4.3 eV in the 10% spectrum to 5.0 eV in the 50% spectrum. This last feature is masked by the background of inelastically scattered electrons in the 21.2-eV spectra.

Concomitant with the appearance of peaks *A* and *B* we observe a gradual recession in the leading edge of the photoemission spectra that reaches 1.0 eV for the samples prepared with 50% H₂ in the gas. The top of the valence band determined by the intercept of the steepest descent of the leading edge with the base line moves by 0.8 eV in the same direction. These shifts are not accompanied by a change in the position of the Si core levels relative to E_F . The binding energies of these levels remain constant to within 0.2 eV. This implies that we are not dealing with a shift of the Fermi level relative to an otherwise unchanged distribution of energy levels in the Si:H system, but rather with a depletion of states at the top of the Si valence band and a Fermi level that remains unchanged with respect to the inner potential of the Si matrix.

Spectra different from those described above were obtained by sputtering *a*-Si in an atmosphere containing 10% H₂ onto a substrate held at 350°C (Fig. 2). The two H-induced peaks are now at 5.3 (peak *C*) and 7.5 eV (peak *D*) below E_F . They are fully developed with an H₂ concentration of 10% and more H₂ in the sputtering gas did not change the spectra. The top of the valence band recedes simultaneously by 0.4 eV. This corresponds to the shift of the sample prepared at room temperature with 10% H₂.

The H incorporated in *a*-Si can be driven out by annealing.¹⁵ In Fig. 3 we show the changes in the spectrum of a sample prepared at room

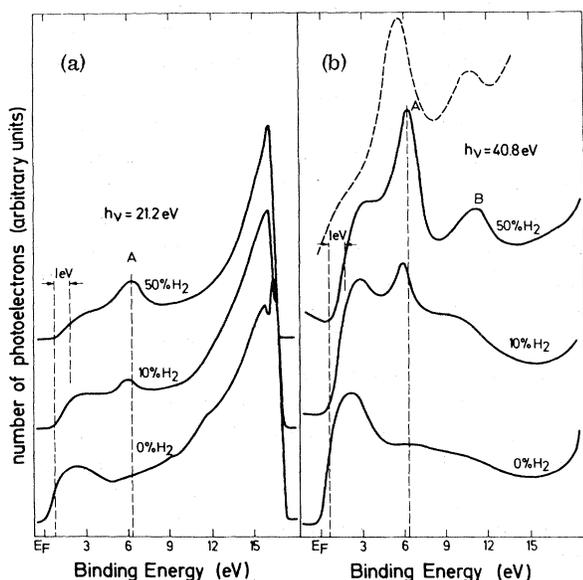


FIG. 1. (a) He I (21.2 eV), and (b) He II (40.8 eV), induced valence-band spectra of *a*-Si films prepared by reactive sputtering in an argon-hydrogen atmosphere. The H₂ concentrations given are those of the sputter gas. The dashed curve reproduces the electronic structure of hydrogen adsorbed onto the Si(111) surface in the form of SiH₃ as calculated in Ref. 12.

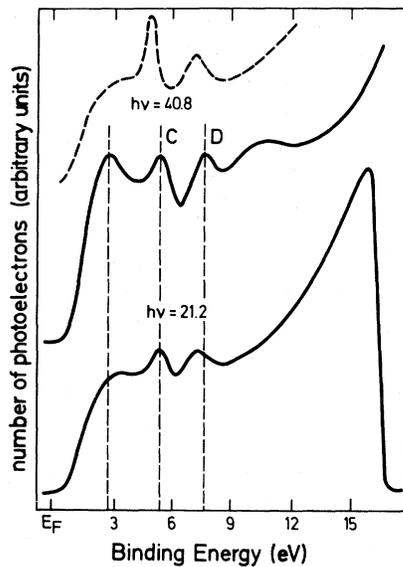


FIG. 2. He I and He II photoemission spectra of α -Si sputtered with 10% H_2 in the sputtering gas onto a substrate held at 350°C . The dashed curve reproduces the electronic structure of hydrogen adsorbed onto the Si(111) surface in the form of SiH as calculated in Ref. 12.

temperature containing the equivalent of 50% H_2 upon annealing at a temperature of 400°C . The decrease in the intensity of peak A is accompanied by a rapid evolution of H_2 gas as monitored with a mass spectrometer. At the same time, states at the top of the valence bands reappear and the leading edge is continuously shifted up towards its position in pure α -Si. After 30 min at 400°C we recorded spectrum *b* in Fig. 3 that corresponds approximately to a hydrogen concentration of 10%. Unlike the corresponding spectrum in Fig. 1(a) we now observe two new features: a peak C at 5.5 eV and a hump D centered 1.9 eV below C. We take that as an indication that the dehydrogenation of α -Si at elevated temperatures tends to produce the same structure as the sample deposited at 350°C in Fig. 2. The dehydrogenation of the samples deposited at 350°C proceeds without any observable change in the position of peaks C and D.

Our results are relevant for the incorporation of H into the Si network rather than for the initial stages of hydrogenation that lead to the saturation of internal dangling bonds. This is substantiated by the fact that the peak near 6 eV becomes detectable only for H_2 concentrations in the sputtering gas in excess of 5%. To saturate the dangling bonds which give rise to the high density of

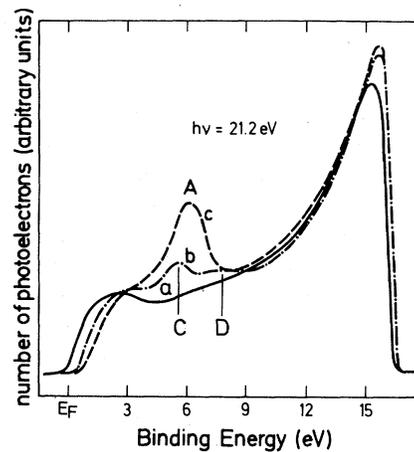


FIG. 3. Changes in the valence-band structure of α -Si (50% H_2 , spectrum *a*) upon annealing at 400°C . Spectrum *b* was obtained after 30 min at 400°C . Spectrum *c* is that of pure α -Si.

states in the gap, less than 6% H_2 in the sputtering gas is necessary, as derived from conductivity measurements.^{3,10} Therefore we argue that the appearing peak structure arises from the hydrogen incorporation into the Si network.

The silicon-hydrogen bonds give rise to a two-peak structure, which can also be seen in the spectra of SiH_4 and $\text{Si}_n\text{H}_{2n+2}$.^{16,17} The explanation of our results is facilitated by theoretical and experimental studies of hydrogen chemisorption onto single-crystal Si surfaces. Studies of the Si(111) surface by Pandey, Sakurai, and Hagstrum¹² show a trihydride- (SiH_3 -) configured hydrogen chemisorption to this surface. Both tight-binding^{12,18} and pseudopotential¹⁹ calculations of the density of states of such a hydrogenated surface show two peaks, called A and B in Ref. 12, arising from the SiH_3 arrangement. Our peaks A and B [Fig. 1(b)] correspond well to these [see dashed line in Fig. 1(b)]. The half-width of our peak A (1.9 eV) is smaller than that of Pandey, Sakurai, and Hagstrum¹² at (2.8 eV); on the other hand, the half-width of our peak B (2.5 eV) is greater than his (1.5 eV). The distance between peaks A and B is 5.0 eV in our experiment and 4.0 in their experiment. Peak widths and the distance between peaks A and B are determined by the H-H interaction; hence these differences are reasonable since the interaction in a single-crystal surface layer should differ from that in amorphous bulk material. We conclude that the incorporation of hydrogen into samples sputtered at room temperature results

in a SiH_3 coordination (at least if sufficient hydrogen is present). Dihydride bands (SiH_2) have been observed in infrared experiments.⁸ Their A - B splitting²⁰ should be about 1.6 eV and hence they do not seem to give the main contribution to the observations of Fig. 1(b).

By comparison with the theoretical work we conclude that peak A arises from the H 1s and the Si 3p orbitals, and peak B from the H 1s and Si 3s states. The latter corresponds to antibonding s states interacting with the Si-Si bond from the first- and second-neighboring Si atoms. This can be deduced from the charge distribution calculations in Ref. 19 and from the work in Ref. 17.

Peaks C and D in our samples deposited at 350°C correspond to similar peaks observed during the adsorption of hydrogen on the Si(100) surface. They have been identified as due to the formation of a Si monohydride phase on the (100) surface,²⁰ an assignment that is supported by calculations of the monohydride phase on Si(111).^{18,19}

There appears to be a chemical equilibrium between the hydrogen content of the sputtering gas and the SiH or SiH_3 concentration, respectively. At low temperatures the formation of SiH_3 is favored whereas at high temperatures the equilibrium is shifted towards the formation of SiH bonds. During the desorption of hydrogen from the low-temperature phase, we observe in addition to a decomposition of the SiH_3 phase a gradual transformation of some of the SiH_3 radicals into those of the SiH type (peaks C and D in Fig. 3).

For an estimate of the amount of hydrogen incorporated we compare the surface spectra with ours. The relative size of the SiH_3 surface peaks of Pandey, Sakurai, and Hagstrum (Ref. 12) and ours is about the same. A mean escape depth of the 21.2-eV photoelectrons²¹ between 4 and 12 Å corresponds to a Si:H ratio of 33% to 50%. A similar hydrogen concentration should therefore be present in our samples. These results are to be compared with the infrared and Raman data of Brodsky, Cardona, and Cuomo (Ref. 8). Samples deposited at room temperature show all three vibrational modes of the SiH, SiH_2 , and SiH_3 configurations, and the amount of H incorporated is estimated to be up to 50%. Samples deposited above 250°C have only a SiH coordination. Annealing experiments by Brodsky *et al.*¹⁵ on samples with higher H concentrations show a desorption of H_2 when heated to 470°C, but in this case mainly hydrogen out of SiH_3 and SiH_2 positions, and not SiH, is driven out, a process similar to that observed in our photoemission spectra.

The shift in the leading edge upon hydrogenation is enough to account for the increase in the fundamental gap from 1.8 eV in a -Si to about 2.5 eV in the most heavily hydrogenated a -Si.²² The Fermi level is seen to move at the same time from a position close to the valence-band edge towards the center of the gap. The loss of states at the band edge is in good agreement with the results of Ref. 17: A reduction in the band width with reduced Si concentration was observed in a number of gaseous polysilane ($\text{Si}_n\text{H}_{2n+2}$) molecules. This suggests that in our trihydride phase a large part of the Si network has been destroyed and that the model of a highly cross-linked polymer of polysilane chains⁸ is a good description of this material.

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Specific Heats of Superconducting Splat-Cooled "Amorphous" $\text{La}_{1-x}\text{Au}_x$ Alloys

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Specific-heat measurements from 1.3 to 6.2 K provide new information about superconductivity in an "amorphous" transition-metal system, $\text{La}_{1-x}\text{Au}_x$. These measurements indicate some qualitative differences between "amorphous" transition metals and simple amorphous metals such as Bi, Ga, Pb, and Sn.

Since the discovery^{1,2} of superconductivity in amorphous metals in the early 1950's, a large amount of experimental data and at least a qualitative understanding of the influence of the absence of long-range order on superconductivity in the simple (nontransition) metals have been developed. For the simple metals the properties of the amorphous phase are described reasonably well by a close-packed structure similar to the liquid metal, an electronic structure consistent with the free-electron model, a softened phonon spectrum, and a sharply enhanced electron-phonon coupling at low frequencies.³ The softened phonon spectrum and enhanced electron-phonon coupling cause the simple amorphous metals to be very strong-coupling superconductors with ratios of energy gap to transition temperature, $2\Delta(0)/k_B T_c$, as high as 4.5 and electron-phonon coupling parameters λ as large as 2.4. Bergmann⁴ has attributed the enhanced strong coupling to the availability of additional phase space for electron-phonon scattering because the need to conserve crystalline momentum is eliminated in an amorphous structure. Such an explanation may be expected to be universal and one would suspect that amorphous transition metals also would be strong-coupling superconductors. Aside from the experiments by Collver and Hammond⁵ to study T_c for amorphous transition-metal alloy films there are very few experimental studies of these interesting materials. The very limited experimental data suggest that highly disordered amorphous transition metals may differ considerably from the simple amorphous metals; e.g., measurements for disordered V films indicate a positive Hall coefficient,⁶ and preliminary results from

tunneling experiments with highly disordered Nb_3Si films do not indicate strong-coupling behavior.⁷

We report measurements of the low-temperature specific heats (1.3–6 K) for two different "splat-cooled" $\text{La}_{1-x}\text{Au}_x$ alloys ($x = 0.20$ and 0.24) in the composition range for which the samples are reported to be amorphous.⁸ Analysis of the specific-heat data provides considerable new information about the properties of these unusual "amorphous" transition metals: (1) The large jump in the specific heat near 3.5 K indicates that superconductivity in these splat-cooled foils is a bulk property. The agreement of the heat-capacity transition temperature T_c and transition width ΔT_c with previous resistive measurements establishes that those previous studies⁸ also deal with bulk properties. (2) The heat-capacity measurements indicate the presence of a small amount of a second phase with a superconducting transition temperature $T_c \sim 2$ K which was not previously observed by either resistivity or x-ray measurements. (3) A fit of the normal-state data by $C_v = \gamma T + \beta T^3$ provides a value of γ from which the electronic density of states $N(0)$ may be determined and a value of β from which the Debye temperature θ_D , which characterizes the phonon spectrum, may be determined. (4) The magnitude of the jump in the specific heat, which is very close to that expected for a weak-coupling BCS superconductor, suggests that these materials are relatively weak-coupling superconductors in contrast to the very strong-coupling simple (nontransition) amorphous metals. (5) T_c and θ_D may be used with the McMillan⁹ expression to estimate the electron-phonon coupling parameter