Photoemission spectroscopy of ultrathin hydrogenated amorphous silicon layers

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Photoemission spectroscopy of ultrathin hydrogenated amorphous silicon films on silicon oxide show that the interfaces are atomically abrupt. The Si $3p$ valence band is already developed in monolayer-thick islands. The absence of quantum-size effects associated with holes indicates that the Si $3p$ wave functions are localized on a scale of a few angstroms. The range of the Si $2p$ core-hole–exciton interaction is estimated to be 6 Å.

A subject of fundamental importance in the study of the electronic structure of solids is the transition from clusters of few atoms to monolayer islands to a three-dimensional solid. We have carried out such studies on hydrogenated amorphous silicon (a-Si:H) in the form of ultrathin films deposited on silicon oxide (a-SiO$_x$:H), using photoemission spectroscopy as a tool. The critical factors which make these experiments possible are that a-Si:H forms an atomically abrupt interface with a-SiO$_x$:H, and that there are large differences in the optical gaps (1.7 eV in a-Si:H compared with 9 eV in a-SiO$_x$:H) and in the Si $2p$ core-level binding energies of the two materials. This enables one to separate accurately the photoemission spectra of the a-Si:H overlayer from the a-SiO$_x$:H substrate. Our motivation for this work was to study quantum-size effects in a-Si:H layers resulting from the confinement of electrons and holes by the potential barriers formed by the vacuum/a-Si:H and a-Si:H/a-SiO$_x$:H interfaces. Previous evidence for quantum-size effects came from the large blue shift in the optical absorption edge and photoluminescence observed in superlattices[1-3] and individual ultrathin films.[4,5] However, in those experiments it was not possible to separate the individual contributions to the blue shift from the valence band and from the conduction band. Photoemission measurements on the other hand are more direct and allow one to determine separately the quantum shift of the valence band. In addition, from the size dependence of the L_{23} absorption edge, information is obtained on the range of the core-hole–exciton interaction.

Heterojunctions of a-Si:H on a-SiO$_x$:H were made by plasma-assisted chemical vapor deposition. The substrates, polished stainless steel, were held at ~240° C mounted on the anode of a 13.6-MHz capacitive reactor. For the a-Si:H layers we used pure SiH$_4$ and the a-SiO$_x$:H layers were made[6] with a mixture of 2% SiH$_4$ in N$_2$O. A 400-Å buffer layer was deposited on top of the steel substrate, followed by a 60-Å a-SiO$_x$:H layer and the a-Si:H overlayer. The compositions of thick layers of a-Si:H and a-SiO$_x$:H determined by Rutherford backscattering (RBS) and ^{15}N nuclear resonant reaction measurements were SiH$_{0.1}$ and SiO$_{1.9}$H$_{0.08}$, respectively. The plasma was turned off for several seconds before depositing the overlayer to allow the gases to be completely exchanged. To achieve precise timing in the deposition of the overlayer we used a Tesla coil to ignite the plasma. After the deposition the reactor was pumped down to its base pressure of 5×10^{-9} Torr and the sample was transferred under ultrahigh-vacuum (UHV) to the measurement chamber. The photoemission was measured with light from the uv ring at the National Synchrotron Light Source, Brookhaven National Laboratory, monochromatized using an extended-range grasshopper monochromator and the electrons were detected with a cylindrical-mirror analyzer (CMA). The beam line is described in more detail elsewhere.[7] The combined resolution of the monochromator and CMA was 0.3 eV.

The Si $2p$ core-level spectra for the Si on SiO$_x$ heterojunctions with different overlayer thicknesses are shown in Fig. 1. The thicknesses of the overlayers were taken to be equal to the product of deposition time and deposition rate where the deposition rate (1.0 Å/s) was determined from *in situ* optical reflectivity measurements on thick films. The growth of the a-Si:H overlayer manifests itself by an abrupt (within the first monolayer) chemical shift of the overlayer photoemission peak to a binding energy 3.7 eV below that of the a-SiO$_x$:H underlayer. This chemical shift is due to the different Si coordination in the two materials, four nearest Si neighbors in the a-Si:H overlayer, compared to four nearest O neighbors in the a-SiO$_x$:H underlayer (on the average 0.9-eV chemical shift per oxygen bond). H bonded to Si gives rise to a much smaller chemical shift, i.e., ~0.3 eV per Si—H bond.[8] The near total absence of any suboxide-derived Si $2p$ structure in Fig. 1 indicates that the interface is atomically abrupt and that the Si:H overlayer is bonded to the SiO$_x$:H underlayer almost exclusively through Si—Si bonds. The large lattice mismatch between the two materials results in dangling bonds at the Si/SiO$_x$ interface which are passivated by H. Evidence for extra hydrogen bonded at the interface comes from ir spectroscopy of a-Si:H/a-Si:O$_x$:H superlattices.[9] Hydrogen also terminates the a-Si:H/ vacuum interface.[8]

The overlayer thickness can be determined directly from the attenuation of the intensity of the underlayer peak. From considerations of the photoelectron detection
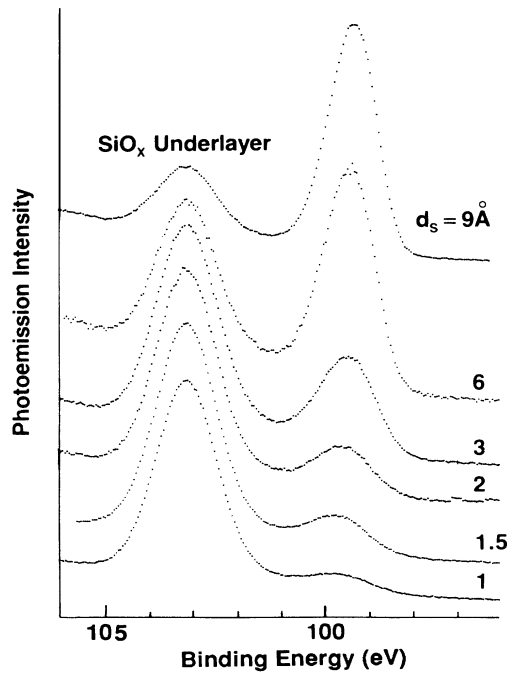
FIG. 1. Binding energy of Si $2p$ core levels for Si on SiO_x measured at 125-eV photon energy. Thickness d_S of a-Si:H overlayers are indicated.

geometry, the overlayer intensity I_S and underlayer intensity I_0 are given by

$$I_S = M_S N_S \lambda_S \int \cos\theta [1 - \exp(-d_S/\lambda_S \cos\theta)] d\omega , \qquad (1)$$

$$I_0 = M_0 N_0 \lambda_0 \int \cos\theta \exp[-d_S/\lambda_S \cos\theta] d\omega , \qquad (2)$$

where M is the optical matrix element, N is the density of Si atoms, λ is the electron escape depth, d_S the overlayer thickness, θ the angle between the direction of electron escape path and the normal to the film. The integration is over the acceptance cone of the CMA. To eliminate systematic variations in photoemission intensity arising from misalignment of sample, or change in the beam position or CMA, we have plotted the ratio I_S/I_0 versus overlayer thickness in Fig. 2(a). The solid curve in Fig. 2(a) was calculated from Eqs. (1) and (2) using the escape depth as an adjustable parameter. The best fit value, $\lambda_S = 4.5$ Å, is in agreement with published values[8] for the escape depth in a-Si:H at a kinetic energy of 25 eV. The good agreement between experimental and calculated values of I_S/I_0 confirms that the deposition rate for the ultrathin films is the same as for thick films determined by the *in situ* optical measurements. Moreover, it also indicates that for $d_S > \lambda_S$ the overlayer is continuous and uniform, since for an island structure I_S/I_0 would exhibit a linear rather than the observed exponential dependence on d_S. On the other hand, for $d_S < \lambda_S$ the ratio I_S/I_0 is insensitive to the film structure and an island structure gives equally good fit to the data.

Further evidence that Si on SiO_x forms an atomically abrupt interface is provided by the photoemission measurements of the valence band shown in Fig. 3. The peak
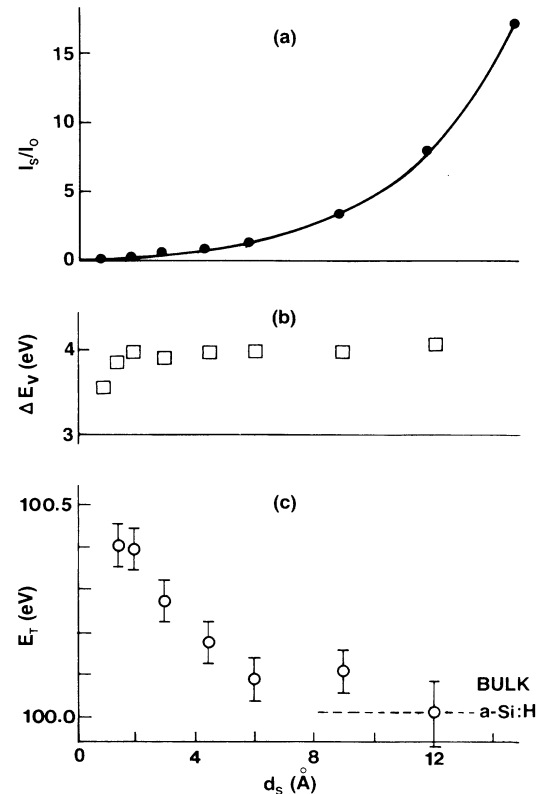

FIG. 2. (a) Ratio of Si-overlayer to SiO_x-underlayer integrated intensities I_S/I_0, as a function of overlayer thickness d_S. (b) Offset between a-Si:H and a-SiO_x:H valence bands ΔE_v as a function of a-Si:H overlayer thickness d_S. (c) L_{23} absorption edge energy E_T in a-Si:H as a function of a-Si:H overlayer thickness d_S.
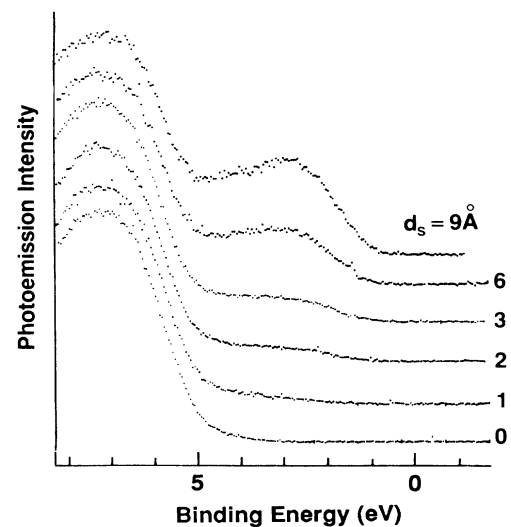

FIG. 3. Photoemission EDC's showing the top of the valence band of Si on SiO_x heterojunctions for different a-Si:H overlayer thicknesses d_S measured at 125-eV photon energy. Also shown is valence band of a-SiO_x:H ($d_S = 0$). Energies are measured relative to the Fermi energy.

at 7-eV binding energy corresponds to the O $2p$ states[10] and the shoulder at the low binding energies corresponds to the Si $3p$ states[11] of the Si overlayers. The measurements were made at 125 eV because at this photon energy the Si $2p$ states are emphasized over the O $2p$ states. The curves were shifted slightly in energy to align the O $2p$ peaks. In this way small variations due to Fermi-level shifts and variations due to irreproducibility in monochromator setting are eliminated. The a-Si:H valence band is brought out more clearly by subtracting the SiO$_x$ underlayer signal from the heterojunction signal. This is shown in Fig. 4, where we also show for comparison the top of the valence band of bulk a-Si:H. In Fig. 2(b) we have plotted the offset energy ΔE_v between the a-Si:H and the a-SiO$_x$:H valence-band maxima as a function of Si overlayer thickness. The valence-band maximum is defined by the intersection of the dashed lines as illustrated in Fig. 4 for one of the heterojunctions. We find that ΔE_v = 3.95 ± 0.08 eV independent of overlayer thickness, except for the thinnest overlayer $(d_S = 1$ Å) where ΔE_v starts to decrease. Within the experimental uncertainty the same offset energy $(\Delta E_v = 4.0$ eV) was obtained for the interface formed by a-SiO$_x$:H overlayer on top of a-Si:H. Because the offset energy ΔE_v and the shape of the energy distribution curves (EDC's) in the overlayers do not change with layer thickness we conclude that the Si $3p$ valence band is already developed in the thinnest overlayer and that the wave functions are strongly localized. To obtain a more quantitative measure of the localization of the wave functions requires knowledge of the structure of the a-Si:H overlayers. It is reasonable to expect that
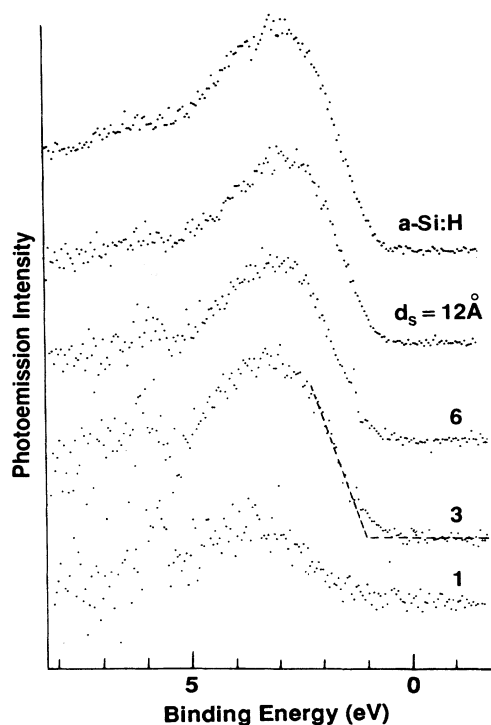
the thinnest a-Si:H layers consist of monolayer islands with lateral dimensions of several atoms forming Si—Si bonds with the a-SiO$_x$:H underlayer, and with H atoms terminating all dangling bonds. The spatial extent of the Si $3p$ wave function in that case can be no more than 1–2 atomic spacings.

The 4.0-eV offset in the valence bands, gives rise to a deep potential well for both electrons and holes in the a-Si:H overlayer. The absence of any variation in the valence-band offset with overlayer thickness in Fig. 2(b) leads us to conclude that quantum shifts due to confinement of the holes in the potential well are smaller than our experimental uncertainty of 80 mV. The absence of quantum shifts is, in fact, a consequence of the strong localization of the hole wave functions. Therefore, we take the large blue shift of ~0.4 eV observed in the optical absorption and photoluminescence of ultrathin ~10-Å a-Si:H layers[2,4,5] as evidence for quantum shift of the conduction band with wave functions for electrons that are extended on a scale of a few nanometers. Recognizing the fact that extended wave functions are associated with low effective mass and small density of states, our interpretation is consistent with calculations by Zdetsis, Economu, Papaconstantopoulus, and Flytzanis,[12] who find that the density of states at the top of the valence band is about an order of magnitude higher than the density of states at the bottom of the conduction band. Moreover, a large ratio of hole to electron masses is also consistent with the fact that the extended-state electron mobility in a-Si:H (13.6 cm^2/ V sec) is more than an order of magnitude larger than that of holes[13] (0.6 cm^2/V sec).

We next turn to the L_{23} absorption edge which is due to transitions from Si $2p$ core levels to unoccupied conduction-band states modified by core-hole excitonic effects. Partial yield measurements of the L_{23} edge in the Si/SiO$_x$ overlayers in Fig. 5 show that the a-Si:H L_{23} edge (indi-

Fig. 4. Same as Fig. 3, but after subtraction of the photoemission from the a-SiO$_x$:H underlayer.
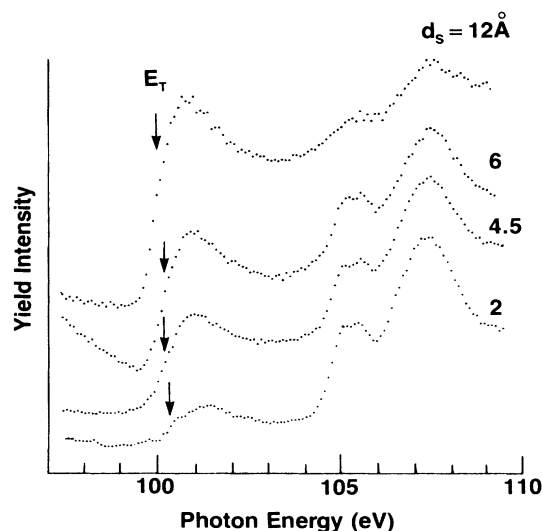

FIG. 5. L_{23} absorption edge as a function of photon energy for Si on SiO$_x$ heterojunctions with different a-Si:H overlayer thicknesses. The arrows indicate the a-Si:H L_{23} absorption edge energy E_T.

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cated by arrows) is well resolved from the underlayer a-SiO$_x$:H exciton peak[14] (105 eV) and conduction-band edge[14] (107 eV), once again demonstrating the abruptness of the interfaces. In overlayers with $d_S \gtrsim 6$ Å the absorption edge is centered at 100.0 eV, which is close to the value reported for thick films.[8,9,11,15] As d_S is reduced below 6 Å the absorption edge moves abruptly to higher energies. This is shown clearly in Fig. 2(c) where we have plotted the absorption threshold energy E_T (defined as the energy at which the absorption edge assumes half its value) vs d_S.

In thick a-Si:H and a-Si films as well as in c-Si the exciton peak is merged with the conduction band because of the relatively small 0.1–0.3-eV exciton binding energy.[8,9,11,15] As we decrease the a-Si:H layer thickness d_S we expect the conduction-band edge to move up in energy due to the quantum-size effects, but as long as the range of the excitonic interaction d_{ex} is small compared to d_S we expect the exciton edge E_T to remain unshifted. When d_S becomes smaller than d_{ex} the exciton becomes two dimensional and we expect E_T to shift together with E_c to higher energies. The above arguments are based on an analogy with the behavior of valence hole excitons.[16] While we are unable to resolve in Fig. 5 any shift in E_c relative to E_T we associate the abrupt rise in E_T for $d_S \leq 6$ Å with a transition from three-dimensional to two-dimensional behavior of the core-hole–exciton interaction with $d_{ex} = 6$ Å. This value of d_{ex} is consistent with the exciton binding energy $E_{ex} = 0.3$ eV observed in a-Si:H. This can be seen from the scaling relation $E_{ex}d_{ex}^2 = 4 E_R r_B^2$ for the hydrogenic model of the exciton, where $E_R = 13.6$ eV is the Rydberg energy and $r_B = 0.52$ Å is the Bohr radius.

In conclusion, photoemission spectroscopy shows that a-Si:H on a-SiO$_x$:H forms an atomically abrupt interface. The offset between the valence bands of a-Si:H and a-SiO$_x$:H is 4.0 eV. From the fact that the offset energy is independent of a-Si:H overlayer thickness down to monolayer dimensions we conclude that the quantum shift of the valence-band edge is vanishingly small because the Si $3p$ wave functions are strongly localized. From the dependence of the L_{23} absorption edge energy on a-Si:H layer thickness, we infer that the range of the core-hole–exciton interaction is 6 Å.

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