Effects of oxidation on surface band-gap states in a-Si:H

K. Winer* and L. Ley

Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, 7000 Stuttgart 80, Federal Republic of Germany

We use total-yield photoelectron spectroscopy in combination with the Kelvin probe to study changes in the work function and the distribution of occupied band-gap states upon oxidation of undoped and slightly boron-doped a-Si:H surfaces. We find that the work function changes rapidly upon activated oxygen exposure for both undoped and boron-doped surfaces corresponding to large (up to 0.3 eV) changes in the surface band bending. The Fermi energy becomes pinned 4.55 eV below the vacuum level by a large density ($> 1 \times 10^{12}$ cm^{-2}) of oxygen-induced surface band-gap states for activated oxygen exposures above 100×10^{-6} Torr s. The origin of these oxygen-induced surface gap states is discussed.

I. INTRODUCTION

A detailed knowledge of the distribution and nature of band-gap states is required to fulfill the technological promise of hydrogenated amorphous silicon (a-Si:H). Despite intensive efforts towards this end,[1] several fundamental issues concerning these states remain poorly understood. Among these are the nature of surface gap states in a-Si:H and, in particular, the effects of adsorbates on the properties of the clean a-Si:H surface. An understanding of these issues is important for the interpretation of any method employed to investigate gap states where sizable surface or interface contributions might be expected. Because thin (< 1.0 μm) a-Si:H films are often the subject of investigation, this latter category includes almost all methods. Furthermore, the presence of intrinsic or adsorbate-induced states at the a-Si:H surface can strongly influence the electronic properties of a-Si:H–metal or –semiconductor interfaces, possibly to the detriment of the desired application.[2]

The question of how the initial oxidation of a-Si:H proceeds has some relevance for device applications and is certainly of fundamental interest, yet few studies of the initial stages of a-Si:H oxidation have been carried out. Ley et al.[3] have compared the initial oxidation of clean crystalline silicon (c-Si) and a-Si:H surfaces by monitoring the core peaks in the x-ray photoelectron (XPS) spectra of the respective surfaces during oxygen exposure. They found that for exposure to unactivated O$_2$, no appreciable oxygen signal appeared in the XPS core spectrum of a-Si:H for exposures up to 10^6 langmuirs (L) (1 L $= 1 \times 10^{-6}$ Torr s), while the equivalent of a monolayer of oxygen formed on the clean c-Si surface after $\sim 4 \times 10^4$ L. On the other hand, exposure to activated oxygen (ion gauge filament on during exposure) produced a monolayer of oxygen on the a-Si:H surface after 1×10^5 L, only ~ 30 times higher than the 3×10^3 L exposure required for monolayer coverage on c-Si. It is clear from their study that activated oxygen exposures above $\sim 10^3$ L lead to the oxidation of the a-Si:H surface.[3]

Although estimates of the surface-state density in a-Si:H have been made with a variety of methods,[4,5] little

direct information concerning the distribution or behavior of intrinsic or oxygen-induced surface states in a-Si:H has been available. Yet some of the effects of oxidation on band-gap states in a-Si:H have been investigated. Derrien et al.[6] studied the electron energy losses of sputter-cleaned and oxidized a-Si:H surfaces under illumination. The light-induced changes in the loss spectra of the oxidized a-Si:H sample at 163 K, absent at 300 K and for the sputter-cleaned surface, were interpreted as arising from electronic transitions to an empty and a partially filled band of oxygen-induced surface states lying in the band gap 1.1 and 0.5 eV away from the valence-band edge, respectively. Their results indicate that oxidation introduces states into the band gap. However, Frye et al.[7] found that the surface defect density of 1-μm-thick a-Si:H films inferred from photothermal deflection spectroscopy (PDS) measurements decreased by a factor of 4 after deposition of ~ 100 Å of silicon oxide on the surface. Foller et al.,[8] based on contact potential difference and surface photovoltage measurements of a-Si:H films, determined that the density of surface states remained unchanged after oxidation. A comparison of these results shows that a consistent view of the effects of oxidation on gap states in a-Si:H is lacking.

In this report, we describe the effects of oxygen adsorption on the distribution of surface band-gap states in undoped and slightly boron-doped a-Si:H on the basis of total-yield photoelectron spectroscopy and Kelvin probe measurements. The combination of these two methods allows us to monitor changes in the gap state distribution at the surface that accompany changes in the work function and electron affinity. In the next section, we give a brief introduction to total-yield photoelectron spectroscopy and explain how we extract the occupied densities of states from the measured yield spectra. In Sec. III we describe the sample preparation conditions. In Sec. IV we present the results of the total-yield measurements including the occupied densities of states for clean undoped and slightly boron-doped a-Si:H, both before and after oxidation. We also show the behavior of the surface-state density and the Fermi energy as a function of activated oxygen exposure. In Sec. V we discuss our results. We

conclude that activated oxygen creates new surface states in the gap of a-Si:H similar to the bulk states observed after incorporation of oxygen into the a-Si:H network, and that oxidation proceeds immediately upon exposure to activated oxygen.

II. TOTAL-YIELD PHOTOELECTRON SPECTROSCOPY

Total-yield photoelectron spectroscopy allows a direct, spectroscopic determination of the density of occupied band tail and defect states in the gap of a-Si:H with a minimum of well-founded assumptions. In total-yield monochromatic light $(3.7 \leq \hbar\omega \leq 6.4$ eV) excites photoelectrons from the sample surface into the vacuum, all of which are collected regardless of their kinetic energy. The resulting total-yield spectrum $Y(\hbar\omega)$, defined as the number of emitted electrons per incident photon, is proportional in amorphous materials to the convolution of the occupied initial g_v and empty final g_c densities of states weighted with the square of an average dipole transition matrix element $R^2(\hbar\omega)$,[9]

$$Y(\hbar\omega) \propto \hbar\omega R^2(\hbar\omega) \int_{E_{vac}}^{\infty} g_v(E - \hbar\omega) g_c(E) dE , \quad (1)$$

where E_{vac} is the energy at the vacuum level, which defines the zero of energy in total yield. The density of final states g_c, located between 0 and ~ 2 eV above the vacuum level, is known to be essentially flat and featureless in a-Si:H.[9] If we assume the final density of states to be exactly constant, we can remove g_c from the integral in Eq. (1). Furthermore, the square of the average matrix element $R^2(\hbar\omega)$ is proportional to $(\hbar\omega)^{-5}$ above a photon energy of 3.4 eV.[10] Therefore, the occupied density of states is a simple function of $\hbar\omega$, $Y(\hbar\omega)$, and its energy derivative $Y'(\hbar\omega)$;

$$g_v(\hbar\omega) \propto (\hbar\omega)^3 [4Y(\hbar\omega) + \hbar\omega Y'(\hbar\omega)] . \quad (2)$$

The density of states at the Si $3p$ valence-band peak maximum is estimated to be 2.5×10^{22} states/(eV cm^3) $(5 \times 10^{22}$ atoms/cm$^3 \times 2$ states/atom divided by a band width of 4 eV). Therefore we normalize $g_v(\hbar\omega)$ to 1×10^{22} states/(eV cm^3) at a photon energy of 6.2 eV, corresponding to a point in the valence band about halfway down from the Si $3p$ maximum. We estimate that the density of states we determine using this procedure is accurate to within a factor of 2. Further details concerning the total-yield method are given elsewhere.[11]

III. SAMPLE PREPARATION

Thin (0.3 μm) a-Si:H films were deposited in a standard ultrahigh-vacuum (UHV) system (base pressure $\leq 10^{-8}$ mbars) onto polished stainless-steel substrates by capacitive rf (13.56 MHz) glow discharge decomposition of pure silane or diborane diluted in silane ([B$_2$H$_6$]/[SiH$_4$] $= 10^{-5}$) for the doped films. Other deposition parameters were substrate temperature 230 °C, gas flow rate 5 cm^3/min at standard temperature and pressure, gas pressure 0.3 mbar, and rf power density 50 mW/cm^2. Directly after the deposition, the samples were transferred under UHV to a connecting UHV analysis chamber (base pressure $\leq 5 \times 10^{-10}$ mbars) for the Kelvin probe and

total-yield measurements. The samples were exposed to activated (ion gauge filament on) research grade (99.9995%) dry oxygen, which was passed directly from the O$_2$ gas canister through a precision leak valve and was pumped out by a turbomolecular pump during exposures. The contact potential difference (CPD) between the samples and a calibrated Mo reference electrode was measured with the Kelvin probe both before and after each exposure to oxygen. The work function (the Fermi energy with respect to the vacuum level) derived by this method is accurate to within ±10 meV.

IV. RESULTS

In Fig. 1 we show the occupied densities of states $g_v(\hbar\omega)$ extracted from the measured yield spectra according to Eq. (2) of clean undoped, clean boron-doped, and oxidized a-Si:H. The spectra are plotted as a function of photon energy, which is identical to the binding energy with respect to the vacuum level. All three spectra are characterized by a linear valence-band edge between 5.6 and 6.0 eV,[11] an exponential valence-band tail, and a band of defect states centered near 5.0 eV. The dramatic decrease in the density of defect states near 5.0 eV photon energy and the shift of the Fermi energy by 0.5 eV towards the valence-band edge with boron incorporation is due to the removal of near-surface defect states intrinsic to the clean, undoped a-Si:H surface and the subsequent depinning of the Fermi energy.[11] This exposes the intrinsic valence-band tail which is found to be exactly exponential over more than 3 orders of magnitude in the density of states with an inverse logarithmic slope $E_0 = 45$ meV, in excellent agreement with the results of dispersive transport measurements.[12]

The adsorption of increasing amounts of activated oxygen gradually increases the occupied defect density of
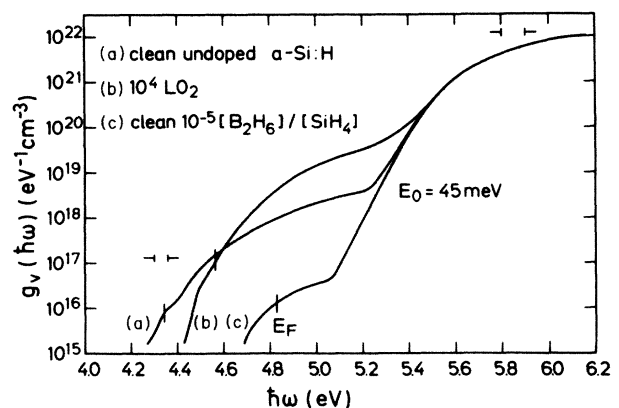

FIG. 1. Occupied densities of states extracted from the measured yield spectra according to Eq. (2). The Fermi energy for each spectrum is marked by a vertical bar. The sharp decrease in the defect density of states beyond the Fermi energy is due to the effect of the Fermi distribution, which limits the occupation of states near E_F. Horizontal bars mark the bandwidth of the incident light that imposes an upper limit to the spectral energy resolution. E_0 is the inverse logarithmic slope of the exponential valence-band tail.

states in the gap of both undoped and boron-doped a-Si:H, and shifts the Fermi energy to a point midway between the clean undoped, and boron-doped a-Si:H extremes. Exposure of clean a-Si:H to 10^4 L activated oxygen, the highest exposure in our investigation, results in a maximum density of defect states corresponding to 2×10^{19} states/(eV cm^3) averaged over the probe depth (~ 40 Å, Ref. 11) of the method. This is an order of magnitude higher than the maximum intrinsic defect density $(2 \times 10^{18}$ eV^{-1} cm$^{-3})$ as measured in an ~ 40 Å surface layer on clean undoped a-Si:H.

We have subtracted the exponential portions of the valence-band tails from the spectra in Fig. 1 and we plot the remaining occupied defect densities of states on a linear scale in Fig. 2. The extent of the exponential part of the occupied density of states in the spectrum of oxidized a-Si:H shown in Fig. 1 is limited and the derived shape of the defect band towards higher energies may therefore not be unique. However, small variations of the slope of the exponential tail used to extract the defect band in Fig. 2(b) do not significantly affect the position of the oxygen-induced occupied defect band. The shape of the two defect bands is similar (roughly Gaussian) with full widths at half maximum of 0.4 eV. The defect band maximum is shifted 0.15 eV toward the valence-band edge (to higher photon energy) upon oxidation, which is smaller by 0.1 eV than the corresponding shift of the Fermi energy. Because the detailed shape, intensity, and position of the maximum of the oxygen-induced defect band are different from those of the intrinsic near-surface defect band of clean, undoped a-Si:H, the defects responsible for the respective bands probably have different origins.

The occupied defect densities of states of boron-doped a-Si:H after various activated oxygen exposures are shown in Fig. 3. The evolution of the oxygen-induced de-
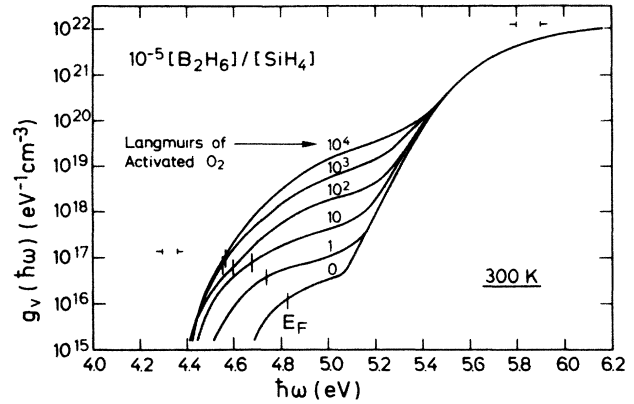
FIG. 3. Evolution of the occupied density of states of boron-doped a-Si:H with increasing activated oxygen exposure.

fect distribution is most easily observed for the boron-doped film because the large density of intrinsic surface states present on clean, undoped a-Si:H has been largely removed. The adsorption of increasing amounts of activated oxygen steadily increases the number of occupied defect states in the gap and at the same time shifts the Fermi level away from the valence-band edge toward the middle of the gap. The Fermi level becomes pinned after ~ 100 L activated oxygen exposure at 4.55 eV but the defect band continues to grow monotonically with further oxidation. Beyond 100 L activated oxygen exposure, the occupied density of states of both the undoped and the boron-doped a-Si:H surfaces respond similarly to increasing oxygen adsorption.

Knowing the width of the defect bands (0.4 eV) and assuming a 40-Å probe depth for the total-yield measurements,[11] we can determine the occupied surface-state density as a function of activated oxygen exposure [Fig. 4(a)]. The density of surface states present on clean, undoped a-Si:H is 3×10^{11} states/cm^2, in good agreement with other estimates of a-Si:H surface-state densities.[3,4] The surface-state density on the clean boron-doped surface $(3 \times 10^9$ cm$^{-2})$ is 2 orders of magnitude lower. The surface-state density in undoped a-Si:H begins to increase only after the first 30 L of activated oxygen is adsorbed because of the already high density of intrinsic surface defect states present on the clean surface. The increase of the density of surface states with oxygen adsorption is much more rapid for the boron-doped sample where the majority of (occupied) intrinsic surface states has been removed. In this case, the surface-state density increases as the $\frac{2}{3}$ power of the exposure up to the first 100 L, where the surface-state density $(\sim 2 \times 10^{11}$ cm$^{-2})$ approaches that of the clean undoped a-Si:H surface, and more slowly thereafter. Although the maximum occupied surface-state density induced by oxygen adsorption in our study $(3 \times 10^{12}$ cm$^{-2})$ is an order of magnitude higher than that on the clean undoped a-Si:H surface $(3 \times 10^{11}$ cm$^{-2})$, it is still 2 orders of magnitude lower than that $(4 \times 10^{14}$ cm$^{-2})$ inferred on clean, cleaved c-Si (111) reconstructed surfaces.[13] This is presumably because of the presence of hydrogen at the surface of a-Si:H, although the disor-
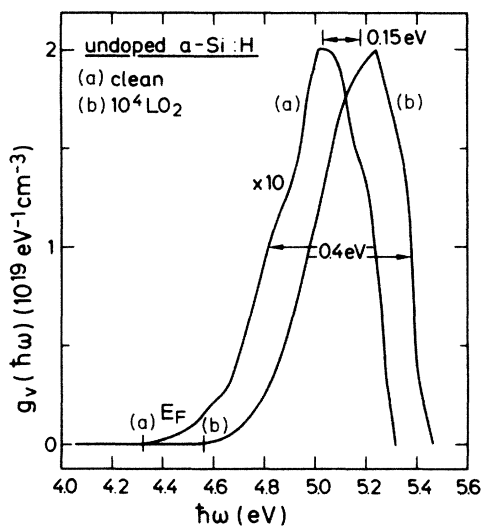
FIG. 2. Occupied density of defect states of clean undoped a-Si:H before and after oxidation. The spectra are obtained by subtracting the exponential part from the density of states in Fig. 1. Note the linear scale.

dered amorphous network may lead to a lower surface-state density than on the corresponding crystalline surface even in the absence of hydrogen.[14]

With the adsorption of oxygen, the Fermi energy moves rapidly from its extreme positions for the clean surfaces to a point between these extremes [Fig. 4(b)]. The Fermi energy becomes pinned above 100 L activated oxygen exposure at a point 4.55 eV below the vacuum level in both the undoped and boron-doped films. The Fermi energy shifts observed in this study upon exposure of a-Si:H to activated oxygen are due solely to changes in the work function and are not due to changes in the electron affinity χ. We monitor changes in χ through changes in the position of the valence-band edge (assuming a constant energy gap), which does not shift upon activated oxygen exposure within the 10-meV accuracy of our method. This implies that all of the oxygen-induced Fermi energy shifts (work function changes) observed here result from a corresponding change of the surface band bending.

From our earlier measurements[11] we concluded that the Fermi level is unpinned and close to midgap in the slightly boron-doped sample. The decrease in the work function upon exposure of the slightly boron-doped sample to oxygen corresponds thus to a downward bending of
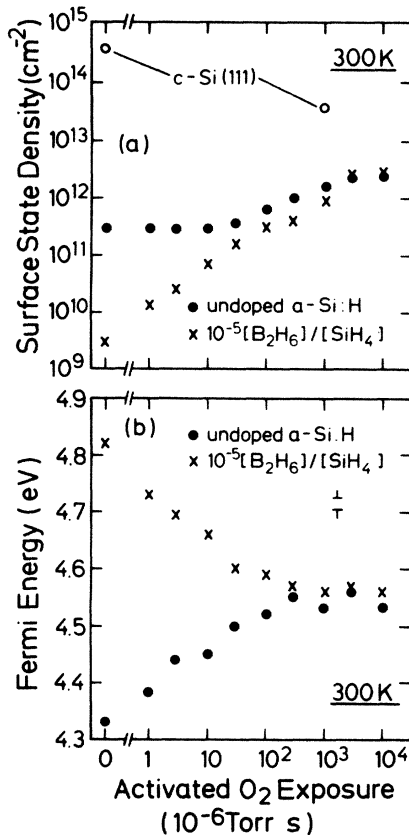

FIG. 4. Variation of (a) the surface-state density and (b) the Fermi energy of undoped and slightly boron-doped a-Si:H films with activated oxygen exposure. The points for c-Si (111) in (a) are taken from Ref. 15.

the bands by up to 0.27 eV. By the same token, the clean undoped sample starts out with a downward band bending of ~ 0.5 eV, which is reduced by 0.25 eV after an exposure to 10^4 L activated oxygen. This argument holds because of the negligible change in the bulk Fermi level with slight boron doping. The 0.25-eV difference in work function between the two pinning positions on clean and oxidized undoped a-Si:H measured here agrees in sign and magnitude with the 0.15-eV upward band bending upon oxidation of clean undoped a-Si:H earlier measured by Ley et al.[3] using conventional photoemission (XPS) methods.

The increase in the occupied surface-state density upon activated oxygen exposure correlates well with the Fermi energy shift for the boron-doped film. There is a rapid decrease in the Fermi energy for low exposures which levels off above 100 L, just where the surface-state density begins to increase beyond its intrinsic value (3×10^{11} cm^{-2}) on clean undoped a-Si:H. It is clear that the pinning of the Fermi energy for higher oxygen exposures is due to the high density of oxygen-induced occupied surface states. This behavior is opposite to the effect of oxygen on the clean (degenerate n type) c-Si surface.[15] In the latter case, the adsorption of 10 L O_2 has little effect on the position of the Fermi energy. However, the adsorption of 10^3 L O_2 reduces the density of surface states in the gap by a factor of 10 and depins the Fermi energy, which shifts by 0.6 eV to nearly its bulk position just below the conduction-band edge.[15]

V. DISCUSSION

It is instructive to compare our results for the initial oxidation of a-Si:H with the corresponding results for the clean, cleaved c-Si (111) surface. In the latter case, pairing of broken bonds on the reconstructed surface gives rise to two bands of surface states, one filled and one empty,[13] which lie in part in the forbidden gap between the conduction and valence bands.[15] The density of occupied surface states is equal to half the number of surface silicon atoms ($\frac{1}{2} \times 8 \times 10^{14}$ atoms/$cm^2 \approx 4 \times 10^{14}$ states/cm^2). This is 2 orders of magnitude larger than the highest oxygen-induced occupied surface defect density ($\approx 3 \times 10^{12}$ states/cm^2) observed on a-Si:H in this study. The adsorption of 1000 L O_2 onto the clean, cleaved c-Si surface removes at least 90% of the occupied intrinsic surface gap states.[15] Oxygen removes these states by bonding to surface silicon atoms. The strong Si—O bond increases the binding energy of the formerly occupied surface gap states, pushing them out of the gap and into the valence band proper. The net effect of oxidation on c-Si is thus a reduction in the density of occupied surface gap states, which depins the Fermi level and reduces the surface band bending. The occupied density of intrinsic surface gap states on clean, undoped and clean, boron-doped a-Si:H is 3 and 5 orders of magnitude, respectively, lower than that of the clean, cleaved c-Si surface. We are thus in the position to observe oxygen-induced surface gap states in a-Si:H at a very low concentration. These states might conceivably be present in c-Si as well but would be obscured by the much higher density of intrin-

sic surface states.

Before we consider the origin of the oxygen-induced surface gap states, let us estimate the oxygen coverage and the Si—O bonding configurations of the a-Si:H surface, drawing from the comparative photoemission study of the oxidation of c-Si and a-Si:H by Ley et al.[3] According to their work, an activated oxygen exposure of 10^4 L leads to the equivalent of half a monolayer of oxygen on a-Si:H, i.e., a surface oxygen density of $\sim 4 \times 10^{14}$ cm^{-2}. The observed occupied surface gap state density at this coverage is only 3×10^{12} cm^{-2}. This means that only one out of a hundred adsorbed oxygen atoms leads to an occupied surface gap state. The creation of surface gap states is thus not representative of the electronic structure associated with the adsorption of the majority of oxygen on a-Si:H, although these states have a profound influence on the electronic properties of the a-Si:H surface.

The low efficiency with which occupied surface gap states are created makes it difficult to offer a conclusive explanation for their origin. A possible clue comes again from the comparative oxidation study of Ley et al.[3] They determined the average stoichiometry x of the SiO$_x$ units that are involved in the bonding of oxygen on the crystalline and amorphous silicon surfaces. The value x is defined as [O]/[Si]$_{ox}$, where [O] and [Si]$_{ox}$ refer to the surface concentration of oxygen and oxidized silicon (attached to one or more oxygen) atoms, respectively. For c-Si, x was found to be equal to one for oxygen coverages below a monolayer. This value is in accord with the bonding of oxygen on c-Si in terms of Si-O $\cdots$ O-Si peroxyl groups, where the ratio [O]/[Si]$_{ox}$ remains unity as long as the surface is not completely covered with oxygen.[16] On differently prepared a-Si:H surfaces, x remains well below one and approaches $x \approx 0.75$ for an a-Si:H film comparable to the samples studied here after an exposure to 10^4 L activated oxygen. A stoichiometry x less than one implies that at least some of the oxygen atoms are bonded to more than one Si atom. An oxygen atom in a bridging configuration bonds to two Si atoms and the average stoichiometry of the Si-O units would thus be $x = 0.5$.

Overcoordination of chalcogens in amorphous networks is a commonly observed phenomenon.[17] Let us therefore assume that oxygen can bind on the a-Si:H surface to one, two, or three silicon atoms with probabilities α, β, and γ, respectively. This leads to the following two equations for α, β, and γ:

$$\alpha + \tfrac{1}{2}\beta + \tfrac{1}{3}\gamma = 0.75 \tag{3}$$

and

$$\alpha + \beta + \gamma = 1 . \tag{4}$$

If we further make the plausible assumption that only one of these configurations causes the observed surface gap states, we have as a third condition that one of the probabilities equals 0.01. The three conditions allow the following solutions: $\alpha = 0.49$, $\beta = 0.50$, and $\gamma = 0.01$ or $\alpha = 0.66$, $\beta = 0.01$, and $\gamma = 0.33$. We dismiss the second solution because we do not expect bridging oxygen (the β configuration), which is the most stable Si—O

configuration, to introduce new states in the gap. Therefore threefold-coordinated surface oxygen atoms (represented by γ) are, within this scenario, responsible for the oxygen-induced occupied surface gap states observed on a-Si:H. This is certainly plausible because the stronger bonds (SiO, Si$_2$O) lead to occupied states further into the valence band.[15,18]

Overcoordination of oxygen requires that one electron be placed in an antibonding orbital. It is conceivable that rehybridization lowers this antibonding orbital sufficiently so that its energy falls in the band gap of a-Si:H and can thus be directly identified with the observed oxygen-induced occupied surface gap states. Alternatively, a mechanism similar to the valence alternation pair in chalcogenide glasses might be operative.[19] This means that the threefold-coordinated oxygen [O^0(3)] transfers the antibonding electron to a weak Si—Si bond creating two dangling bonds, one of which is doubly occupied. Energetically this process is possible when the bonding energy of a weak Si—O bond exceeds the Si—Si bond energy (1.84 eV) augmented by the effective correlation energy U (≤ 0.3 eV) that is necessary to place the extra electron into one of the dangling bond states. The so-created dangling bonds are then observed as the new gap states in our experiment.

The above equations can also be satisfied by setting $\gamma = 0$ so that only singly or doubly coordinated surface oxygen configurations are considered. However, one cannot then explain why only 1% of the oxygen atoms lead to occupied surface gap states, unless hydrogen is somehow involved. Hydrogen can also form chemical bonds with adsorbed oxygen atoms. The formation of Si—O—H clusters may then also lead to occupied surface gap states. The results of total yield cannot distinguish between these two possible origins for the oxygen-induced surface states. However, either Si-O or Si-O-H units terminating into the vacuum would form a surface dipole layer which should lead to a change in the electron affinity.

The fact that neither the position nor the shape of the valence-band edge changes with surface oxidation (see Fig. 3) shows that the photoemission threshold and therefore the electron affinity χ is essentially unaffected by oxygen adsorption (again assuming a fixed band gap). This places an upper limit on the surface dipole density μ which affects χ through the potential drop across the dipole layer according to

$$\Delta \chi = \mu / \epsilon_s \epsilon_0 \tag{5}$$

where $\Delta \chi$ is the change in the electron affinity and ϵ_s is the static dielectric constant in the surface layer. We take $\Delta \chi = 10$ meV, the smallest change resolvable in the total-yield spectra and $\epsilon_s \approx 6$ (the average between $\epsilon_s = 12$ for a-Si:H and $\epsilon_s = 1$ for vacuum) and obtain an upper limit of 3.3×10^{12} electrons Å/cm^2 for the surface dipole density.

Street et al.[20] have observed a broad luminescence peak centered near 1.1 eV due to bulk oxygen introduced into the a-Si:H network during deposition. They interpreted the luminescence as arising from localized transitions directly associated with oxygen atoms. Further-

more, they proposed that the active oxygen centers are not associated with twofold-coordinated oxygen atoms, but rather with singly or threefold-coordinated oxygens which form charged defects.[20] The luminescence results are consistent with the increase in the occupied surface-state density in a-Si:H upon oxygen adsorption and the interpretation that these states arise from threefold-coordinated oxygen atoms bound to surface silicon atoms. However, it is not clear that the oxygen defects observed in luminescence and by total yield are necessarily the same.

Michelson et al.[21] have observed an increase in the bulk defect density of a-Si:H after oxygen ion implantation. They observed a shift in the "dangling bond" peak after implantation of ~0.1 eV toward the valence-band edge, just as we observe with total yield after adsorption of activated oxygen. They also observed a new feature in their deep level transient (DLTS) spectra ~0.3 eV above (toward the conduction-band edge) the unimplanted defect peak which they interpreted as arising from a shift of the intrinsic "dangling bond" energies due to the electronegativity of backbonded oxygen atoms. We do not observe such a feature in our total-yield spectra. This may be due to the negligible number of backbonded oxygens expected at such low coverages. However, the fact that the bulk defect band shifts towards the valence-band edge and increases in intensity with oxygen implantation just as the surface defect band does after oxygen adsorption suggests that the defects responsible for this behavior, whether in the bulk or on the surface, are probably the same.

Finally, the fact that oxygen chemisorption occurs immediately upon exposure of the a-Si:H surface to activated oxygen has profound consequences for any attempts to study the surface properties of a-Si:H. One can no longer assume that a-Si:H surfaces are essentially inert in all environments, although they are for unactivated O_2 exposure.[3] Ion sputtering and annealing of a-Si:H, for example, is not an effective method for the production of clean a-Si:H surfaces. Apart from possible loss of hydrogen, implantation of unwanted impurities, and unknown damage caused by the impinging ions, the oxygen detection limit for Auger electron spectroscopy (~0.1 at. %),

which is one of the most sensitive elemental analysis techniques compatible with UHV, is simply not low enough to ensure the complete absence of oxygen from the surface. Given the extreme sensitivity of a-Si:H surface properties to oxygen contamination, studies of these properties employing this cleaning procedure are most probably being carried out on surfaces with a substantial chemisorbed oxygen concentration, and consequently their results will not be characteristic of the clean a-Si:H surface.

VI. SUMMARY AND CONCLUSIONS

The present study has shown that the initial adsorption of activated oxygen on clean, undoped or slightly boron-doped a-Si:H leads to the creation of a band of occupied surface gap states centered 5.15 eV below the vacuum level. The density of these new states reaches $\sim 3 \times 10^{12}$ cm^{-2} for an oxygen coverage corresponding to $\sim 4 \times 10^{14}$ oxygen-atoms cm^{-2}; i.e., only one out of a hundred adsorbed oxygen atoms leads to an occupied surface gap state. Despite their low density (relative to the intrinsic surface states on c-Si), the new oxygen-induced surface states cause up to an ~0.3 eV change in the surface band bending and lead to the pinning of the Fermi energy 4.55 eV below the vacuum level. These results confirm earlier observations that the oxidation of a-Si:H occurs immediately upon exposure to activated oxygen. They also highlight the fundamental difference between the surfaces of c-Si and a-Si:H. In c-Si, the high intrinsic density of surface states is reduced upon oxidation, causing a depinning of the Fermi level. Because of the extremely low intrinsic surface-state density in a-Si:H, oxidation produces new surface states in the gap which pin the Fermi level. The low intrinsic surface-state density on clean a-Si:H provides an ideal system with which to study extremely small effects of adsorbates on the surface electronic properties of disordered semiconductors.

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*Present address: Xerox Palo Alto Research Center, 3333 Coyote Hill Road, Palo Alto, CA 94304.

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