Electronic Structure of Partially Hydrogenated Si(100)-(2 × 1) Surfaces Prepared by Thermal and Nonthermal Desorption

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The electronic structure of partially hydrogenated Si(100)-(2 × 1) surfaces, prepared by controlled thermal annealing and nonthermal photon stimulated desorption of fully hydrogenated Si(100) surfaces, has been investigated by using valence band photoemission. Thermal and nonthermal desorption are found to produce very specific electronic surface structures. This led us to the discovery of two specific surface states having binding energies of 1.0 and 0.7 eV associated with the isolated Si dimers and single Si dangling bonds, respectively.

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In recent years, the hydrogen-terminated Si(100) surface has emerged as the ideal surface for the fabrication of functionalized surfaces [1]. The ability to selectively remove hydrogen from these fully nonreactive surfaces by using the tip of the scanning tunneling microscope (STM) [2–4] or by laser irradiation [5] enables one to pattern reactive areas. Adsorption of appropriate atoms or molecules into these patterned areas may then lead to the fabrication of the desired functionalized features [1,6]. However, an important prerequisite is to understand and to control the electronic and atomic structures of the dehydrogenated Si(100) areas. Indeed, this is crucial not only to be able to characterize the various stages of the dehydrogenation but, moreover, to investigate the reactive properties of the dehydrogenated areas.

So far, electronic structure studies have been limited to the clean and fully hydrogenated Si(100) surface. It is well known that the clean Si(100) surface reconstructs to form 2 × 1 dimer rows [7]. The two adjacent dangling bonds form a π bonding within the same Si-Si dimer. The electronic coupling between adjacent Si-Si dimers results in a further reconstruction and the appearance of alternatively buckled dimers within the dimer rows [8]. The interdimer coupling induces the energetic splitting of the dangling bond surface states [9,10]. Hydrogen, adsorbing on the silicon surface, affects both intradimer coupling (when hydrogen saturates one of the dimer dangling bonds) and interdimer coupling (when hydrogen saturates both dangling bonds of a dimer surrounded by clean dimers). As a consequence, the dangling bond surface states of the partially hydrogenated Si(100)-(2 × 1):H surface are expected to be quite different from those of the clean surface.

In this Letter we report the first photoemission study of the surface states of the partially hydrogenated Si(100)-(2 × 1) surfaces. We took advantage of using two separate methods, namely, thermal annealing and nonthermal photon stimulated desorption, for producing specific partially hydrogenated Si(100) surfaces. Very different electronic structures are produced by these two methods. This enables one to unambiguously characterize two specific electronic surface states, which have been assigned to the isolated Si dimers and single Si dangling bonds.

All the experiments were performed *in situ* in an ultrahigh vacuum chamber with a base pressure of 2×10^{11} Torr. The hydrogenation of the clean silicon sample (p-type boron-doped Si(100), $\rho = 1\ \Omega$ cm) was done at 650 K by using the method described elsewhere [11]. The synchrotron radiation from Super-ACO in Orsay was used either as an undispersed light source (zero order of the monochromator) for photodesorption experiments or as a monochromatic photon source for electron photoemission studies. Two separate methods were used for preparing the partially hydrogenated surface. First, hydrogen was thermally desorbed from the hydrogenated surface by resistive heating of the sample. The Si sample was rapidly heated up to a certain temperature; this temperature was maintained during 1 min. Then the sample was cooled down to room temperature and photoemission spectra (PES) were recorded. Second, hydrogen was desorbed from the hydrogenated surface at room temperature using unmonochromatized synchrotron radiation (from the visible range to about 250 eV). Valence band photoemission spectra were recorded at a photon energy of 40 eV and normalized to the beam intensity. The linear polarization of the photon beam is in a plane perpendicular to the surface. The incident and emission angles were chosen to be 68° and 22°, respectively (referred to the normal of the surface).

The photoemission bands [Figs. 1(a) and 1(b)] were assigned as follows. The bands in the 0–1.5 eV binding energy range (shown as shadow areas) were assigned to the dangling bond surface states [9]. The other bands were assigned to the hydrogen induced surface states (bands at 3.6, 4.2, 5.8, and 10.1 eV), Si-Si dimer bond (band at 2.3 eV), Si bulk states (band at 7.5 eV) [10], and oxygen traces (band at 6.8 eV) [12]. It is known that hydrogen adsorption at 650 K does not affect Si-Si dimer bonds [11]. We normalized the PES using the 2.3 eV band intensity. Hydrogen desorption by thermal annealing is accompanied

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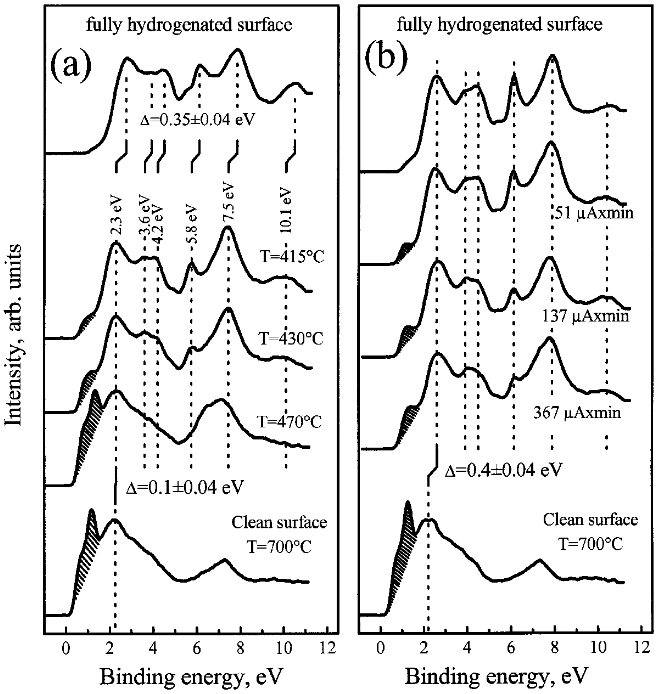

FIG. 1. Photoemission spectra of the Si(100)-(2 × 1):H surface as a function of (a) annealing temperature and (b) irradiation dose (annealed clean surface is shown for comparison). The irradiation dose was calculated by multiplying the irradiation time with the photoemission current of a gold mesh monitoring the photon flux.

by a decreasing of the Si-H bands and simultaneously by the appearance of dangling bond surface states [Fig. 1(a)]. This produces also changes in band bending, which can be explained as follows. It was shown previously that, during hydrogen adsorption on silicon, hydrogen is incorporated into the subsurface region [13], producing B-H complexes [14] and, by this way, deactivating boron dopant atoms [15]. As a result, the Fermi level moves upward to the middle of the band gap. The B-H complexes are thermally less stable than Si-H bonds [13]. Thus, in our case [Fig. 1(a)] under mild annealing ($t = 415$ °C) the reverse process occurs: B-H complexes are decomposed and boron dopant atoms are reactivated. The corresponding downward movement of the Fermi level to its bulk position causes the 0.35 ± 0.04 eV shift. Further annealing induces hydrogen desorption from the surface, Si-H bonds are decomposed, and dangling bonds induce an additional band bending. However, this process is accompanied by further hydrogen evolution from the subsurface region [16] inducing an additional boron atom reactivation. Thus, the observed shift of 0.1 ± 0.04 eV [Fig. 1(a)] represents the net band bending changes due to the surface dangling bond (upward band bending) and boron reactivation (downward band bending). On the irradiated silicon surface [Fig. 1(b)] no changes in band bending were observed during the irradiation. The synchrotron irradiation, as a nonthermal process, has no influence on subsurface hydrogen. The band bending changes, induced by a small amount of dangling bonds produced by irradiation, were beyond our detection limit.

The most intriguing observation is that during the thermal annealing the shape of the dangling bond surface states changes drastically. Indeed, the initially observed smooth shoulder in the low binding energy part of the PES is gradually transformed into the sharp high-intensity peak having another shoulder with slightly lower energy [Fig. 1(a)]. We suggest that this is a manifestation of the specific surface states of the partially hydrogenated surface. For a quantitative analysis, each photoemission spectrum in Fig. 1(a) was shifted to remove any influence of band bending. Then, the spectrum of the fully hydrogenated surface was subtracted. The resulting dangling bond surface states of the partially hydrogenated surface are shown in Fig. 2(a) as a function of coverage. The H coverage (θ_{H}) was calculated assuming isothermal annealing at each temperature. The kinetic parameters of H desorption were taken from Ref. [17]. The accuracy of the temperature measurements was assumed to be ±10 °C. To analyze these surface states we assumed that the H-perturbed surface states are superimposed on the surface states of the clean surface. The surface states corresponding to the clean surface are shown in the inset of

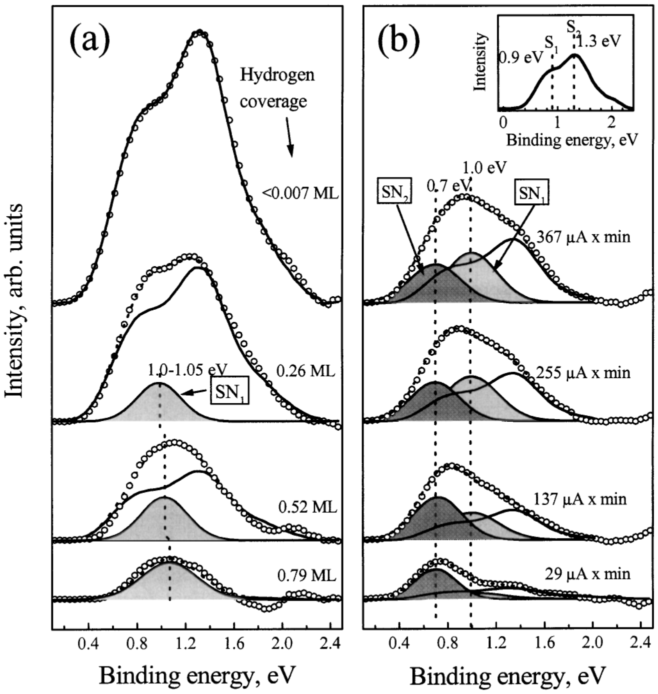

FIG. 2. Surface states of the partially hydrogenated Si(100)-(2 × 1):H surface prepared by (a) thermal annealing and (b) synchrotron irradiation. The open circles and dotted lines represent the experimental and simulated spectra, respectively. The filled areas represent the surface states of isolated Si dimers (light grey) and of single Si dangling bonds (dark grey). The solid curves represent the scaled surface states of the clean surface. Inset: the surface states of the clean surface.

Fig. 2(b). Thus, each spectrum in Figs. 2(a) and 2(b) was deconvoluted using the following equation:

$$I(E) = A_0 \times I(E)_{c1} + A_1 \times \exp[-(E - x_1)^2/2\omega_1^2], \quad (1)$$

where $I(E)$ is the intensity of the simulated spectrum as a function of the binding energy E, $I(E)_{c1}$ is the spectrum of the clean surface, A_0 is the fraction of the clean surface, A_1, x_1, and ω_1 are the intensity, energy position, and width of the new H-perturbed surface state, respectively. The simulation was done using best-fit criteria while four parameters A_0, A_1, x_1, and ω_1 varied independently. All the photoemission spectra could be well fitted with the surface state SN_1 at ~1 eV as shown in Fig. 2(a). We suggest that the SN_1 state represents isolated Si dimers, i.e., the Si dimers surrounded by double-occupied SiH-SiH dimers in dimer rows (Fig. 3). This SN_1 band is believed to correspond to the π orbital of the isolated Si dimers and is free of any interdimer coupling effect. At high H coverage the SN_1 state dominates the spectrum [Fig. 2(a)] suggesting that most of the clean Si dimers are isolated from each other. Our observation agrees well with the results of direct dangling bond counting using scanning tunneling microscopy [18]. Buehler and Boland [18] observed that only clean Si dimers randomly distributed between double-occupied SiH-SiH dimers exist on the surface at high coverage [$\theta_H \cong 0.98$ ML (monolayer)]. At lower hydrogen coverage [Fig. 2(a)] the fraction of isolated Si dimers decreases and coupled Si dimers (S_1 and S_2 states) dominate.

We now discuss the surface states of the partially hydrogenated surface prepared by photon-stimulated desorption [Fig. 1(b)]. As shown in Fig. 2(b) we were not able to fit properly the surface states using the S_1, S_2 and SN_1 surface states only. We suggest that, due to the different preparation procedure, another specific surface state appears on the surface. From our simulation, this specific surface state, marked as SN_2, is found to exist at 0.7 eV on the irradiated surface [Fig. 2(b)]. Most probably this SN_2 state originates from the single Si dangling bonds produced by H desorption (Fig. 3). These unpaired dangling bonds were observed on the thermal annealed surface (at room temperature) neither in our experiments nor in other studies [19]. The main reason is that hydrogen thermally desorbs from the Si(100) surface by the concerted mechanism leaving paired dangling bonds on the surface [7]. At elevated temperatures the paired dangling bonds become separated. However, they pair back into the thermodynamically favorable π-bonded configuration during the cooling down [19]. By contrast, on the irradiated surface, such a redistribution of unpaired dangling bonds cannot occur due to the low mobility of dangling bonds at room temperature [19].

In order to check the reliability of our analysis and deconvolution of the surface states we compared the amounts of Si dimers deduced from the photoemission spectra with those calculated from the analysis of hydrogen distribution on the partially hydrogenated surface [Figs. 4(a) and 4(b)]. The symbols in Figs. 4(a) and 4(b) represent the amounts deduced from the surface state analysis [Figs. 2(a) and 2(b)] as follows. Amounts of coupled Si dimers (θ_{coup}) on thermal annealed surface [squares in Fig. 4(a)] were taken as A_0 values obtained from Eq. (1). Amounts of isolated Si dimers (θ_{isol}) were determined from the SN_1 integral intensities. Considering that the photoemission cross section of various Si dimers can differ significantly, the SN_1 integral intensity was scaled to fulfil the condition $\theta_{\text{coup}} + \theta_{\text{isol}} + \theta_H = 1$ for $\theta_H = 0.79$ ML.

On the photon irradiated surface, amounts of coupled Si dimers [squares on Fig. 4(b)] were taken as A_0 values obtained from Eq. (1). Amounts of isolated Si dimers were found from the SN_1 intensities using the scaling factor determined previously. The amounts of single Si dangling

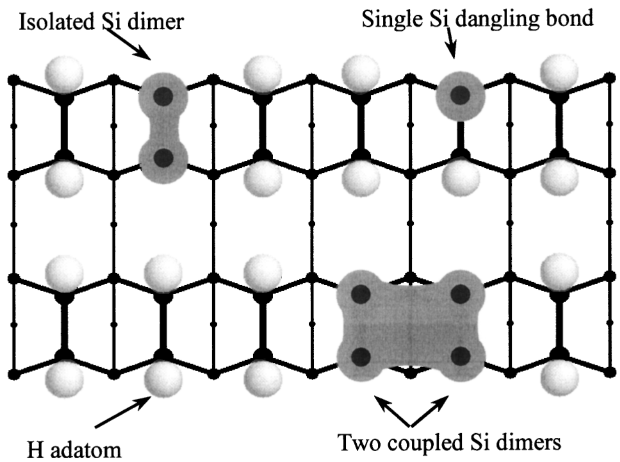

FIG. 3. Schematic representation of Si dimers on the partially hydrogenated Si(100)-(2 × 1):H surface.

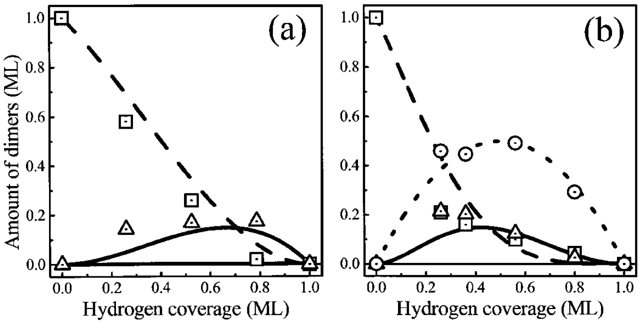

FIG. 4. Distribution of Si dimers on the partially hydrogenated surface prepared by (a) thermal annealing and (b) photon irradiation. The squares, triangles, and circles represent the amounts of coupled Si dimers, isolated Si dimers, and single Si dangling bonds, respectively, as deduced from the analysis of the surface states [Figs. 2(a) and 2(b)]. The dashed, solid, and dotted lines represent statistically calculated amounts of the coupled Si dimers, isolated Si dimers, and single Si dangling bonds, respectively.

bonds (θ_{single}) were obtained from the SN_2 integral intensities. The SN_2 integral intensity was scaled considering that $\theta_{\text{coup}} + \theta_{\text{isol}} + \theta_{\text{H}}^2 + \theta_{\text{single}} = 1$ when the irradiation dose was 29 μA min. The H coverage at each irradiation dose was calculated from the intensity of the 5.8 eV Si-H band [Fig. 1(a)].

For comparison with experimental values, the θ_{single}, θ_{isol}, and θ_{coup} values were calculated statistically assuming that hydrogen atoms occupy randomly Si dangling bonds.

$$\begin{aligned} \theta_{\text{single}} &= 2\theta_{\text{H}}(1 - \theta_{\text{H}}), \\ \theta_{\text{isol}} &= (1 - \theta_{\text{H}})^2[1 - (1 - \theta_{\text{H}})^2]^2, \\ \theta_{\text{coup}} &= 1 - \theta_{\text{H}}^2 - \theta_{\text{single}} - \theta_{\text{isol}}. \end{aligned} \tag{2}$$

At room temperature, the hydrogen atoms are not mobile on the surface. Thus, we used Eqs. (2) to calculate the amounts of dimers in the case of photon-stimulated desorption [Fig. 4(b)]. By contrast, Eqs. (2) fail to describe properly the dimer distribution on the thermal annealed surface where thermal redistribution of dangling bonds takes place. When cooling down, the dangling bonds are rearranged into π-bonded paired configuration, so that single Si dangling bonds no longer exist on the surface. Assuming a random distribution we obtain

$$\begin{aligned} \theta_{\text{isol}} &= \theta_{\text{H}}^2(1 - \theta_{\text{H}}), \\ \theta_{\text{coup}} &= (1 - \theta_{\text{H}})(1 - \theta_{\text{H}}^2). \end{aligned} \tag{3}$$

Thus, we used Eqs. (3) to calculate the amounts of dimers on the thermally annealed surface [Fig. 4(a)]. A good correspondence between statistically calculated (lines) and experimentally obtained (symbols) amounts of dimers was obtained for both thermally annealed [Fig. 4(a)] and irradiated [Fig. 4(b)] surfaces. This suggests that the random distribution of dangling bonds assumption is valid in our case. However, the limited experimental accuracy may not be sufficient to completely exclude an interaction between isolated Si dimers [20]. These results mean that the surface state analysis and deconvolution properly describe the dynamics of the surface states as a function of H coverage. The finding of two specific dangling bond surface states with binding energies of 1.0 and 0.7 eV is also supported by scanning tunneling spectroscopy (STS) data [7]. Indeed, STS showed occupied state features at 0.9 and 0.5 eV when the STM tip was positioned over an isolated Si dimer and a single Si dangling bond, respectively.

In conclusion, various types of partially hydrogenated Si(100)-(2 × 1) surfaces were prepared by thermal annealing and nonthermal photon-stimulated desorption. The investigation of the resulting surface states by valence band photoemission led us to the discovery of specific surface states with binding energies of 1.0 and 0.7 eV corresponding to isolated Si dimers and single Si dangling bonds, respectively. The validity of the whole procedure has been inferred by comparing the experimental and statistically calculated dimer distributions as a function of the total hydrogen coverage. Monitoring these specific surface states by valence band photoemission is expected to become a very powerful method for characterizing properly the various stages of patterning and functionalization of H-terminated Si(100) surfaces.

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