Thermal reactions of disilane on Si(100) studied by synchrotron-radiation photoemission

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H-terminated Si(100) surfaces were formed by saturation exposure of Si(100) to disilane at room temperature. Annealing these surfaces to progressively higher temperatures resulted in hydrogen desorption. This process, of basic importance to the growth of Si by atomic layer epitaxy using disilane, was studied by synchrotron-radiation photoemission. The Si 2*p* core-level line shape, the position of the Fermi level within the band gap, the work function, and the ionization potential were measured as a function of annealing temperature. These results revealed two steps in the thermal reaction preceding the recovery of the clean surface. The dihydride radicals on the surface are converted to monohydride radicals at 500–610 K, and the monohydride radicals decompose at 700–800 K.

I. INTRODUCTION

Silicon vapor-phase epitaxy using disilane (Si_2H_6) as the source gas has attracted much attention in both fundamental and applied research of crystal growth.[1–6] Compared with other commonly used source gases such as silane (SiH_4), dichlorosilane (SiH_2Cl_2), trichlorosilane ($SiHCl_3$), and silicon tetrachloride ($SiCl_4$), disilane offers the benefit of much lower growth temperatures.[3,7] This is related to the lower activation energy for dissociative chemisorption of disilane due to relative weakness of the Si-Si bond in the Si_2H_6 molecule.[8] The use of disilane also allows the practical implementation of atomic layer epitaxy on Si(100).[3,6] In this process, the starting Si surface is saturated by disilane exposure resulting in a H-terminated surface. The amount of Si adsorbed is about $\frac{1}{2}$ monolayer, which is limited by the available dangling-bond sites on the clean surface. The terminating hydrogen on the surface is then desorbed by thermal annealing or light illumination, and the surface reverts back to clean Si(100)-(2×1). This cycle of desorption followed by adsorption results in a quantized deposition of Si. Repeating this cycle, therefore, allows a precise control of the thickness of the growth.

This study is an attempt to better understand the thermal desorption process of H_2 from Si(100) after saturation exposure to disilane at room temperature. The details of the adsorption of disilane on Si(100) at room temperature and below have been investigated recently by multiple internal reflection infrared spectroscopy.[9] The results show that disilane adsorbs molecularly at temperatures below 90 K. Above 120 K, SiH_3 radicals are formed as a result of the dissociation of Si_2H_6. The SiH_3 radicals become unstable at higher temperatures and further decompose into SiH_2 and H. The H atom released reacts with a nearby Si dangling bond to form SiH. Exposure of Si(100) to disilane at room temperature mostly results in SiH and SiH_2 radicals on the surface. In our study of the desorption process, we employed synchrotron-radiation photoemission to examine the evolution of the line shape of the Si 2*p* core level. Hydrogen-induced changes and shifts of the line shape were observed, and can be attributed to chemical shifts of the core level and band bending. The work function of the sample was simultaneously determined from the photoemission bandwidth. The work function and the band bending measurements together yielded the ionization potential of the sample. All of these results combine to show the presence of two well-defined steps of thermal reaction preceding the recovery of the clean surface. These two steps can be associated with the decomposition of SiH_2 radicals to form SiH radicals, and the decomposition of SiH to form pure Si on the surface. Our results are thus consistent with recent temperature-programmed desorption measurements[10] in which two broad peaks are found, suggesting the presence of a two-step thermal reaction. Our results also corroborate and complement a recent scanning tunneling microscopy (STM) measurement[6] in which the formation of monohydride and the desorption of H_2 were inferred from the observation of certain features in the images.

II. EXPERIMENTAL DETAILS

The photoemission experiments were performed using synchrotron radiation at Aladdin, the 1-GeV storage ring at the Synchrotron Radiation Center of the University of Wisconsin-Madison. The incoming photon flux was monitored by measuring the photocurrent from an Au wire mesh placed in the photon beam path. The photoelectrons emitted from the sample were collected and analyzed by a larger, angle-integrating hemispherical analyzer with a pass energy of 5 eV. The overall instru-

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mental energy resolution was better than 0.15 eV. The Si(100) samples, $0.4 \times 1.2 \times 0.04$ cm^3 in size, were cut from an *n*-type, phosphorus-doped commercial wafer with a resistivity in the range of 1–60 Ω cm. The misalignment of the wafer is about 0.4°. Following a well-established procedure for preparing clean and ordered (2×1) surfaces, each sample was outgassed for several hours at 900 K and flashed to ~1500 K for ~10 s. Pure disilane gas was introduced into the chamber via a precision leak valve at a pressure of 5×10^{-8} Torr. During the exposure, the ion gauge was turned off to avoid exciting the disilane molecules. The dosing pressure was monitored using the ion-pump current, which was previously calibrated against the ion gauge. The pressure readings of the ion gauge were corrected by the gauge sensitivity to disilane, which is 2.4 relative to air.[2] Successive annealing of the disilane-saturated sample was accomplished by ac resistive heating of the sample; each annealing lasted 60 s. The substrate temperature was inferred from the heating power, which was calibrated in an independent experiment using a very small thermocouple attached to the front of an identical test sample.

III. RESULTS

Figure 1(a) shows a surface-sensitive Si 2*p* core-level spectrum (circles) for clean Si(100)-(2×1) and its least-squares fit (curve through the circles) with three decomposed components (curves labeled *B*, *S*, and *S'*). The photon energy used is 140 eV. The fitting was carried out in the usual manner.[11,12] The three components, each bearing a pair of spin-orbit-split peaks, are assumed to have the same Voigt line shape (convolution of a Gaussian and a Lorentzian). The *B* component corresponds to bulk emission. The *S* component accounts for the small peak (or shoulder) located at about −0.51 eV relative to the *B* component, and is derived from surface atoms (with dangling bonds). The *S'* component is not visually resolved from the *B* component, but its presence has been verified in previous studies.[11,13,14] It has been associated with emission from the second-layer atoms, but this interpretation has not been universally accepted.[13,14] This uncertainty, however, does not affect our discussion in the following.

Figure 2 shows Si 2*p* core-level spectra for the starting clean Si(100)-(2×1) surface and the same surface exposed to 15-L (1 L$=10^{-6}$ Torr s) disilane at 300 K followed by progressive annealing to higher temperatures as indicated. The binding-energy scale is referred to the *B* component of the clean surface. At this dose, the surface is saturated by disilane, as the line shape does not change any more upon further exposure to 60 L. It is clear from a visual inspection of the second spectrum from the bottom in Fig. 2 that exposure to disilane at room temperature causes the line shape to move toward higher binding

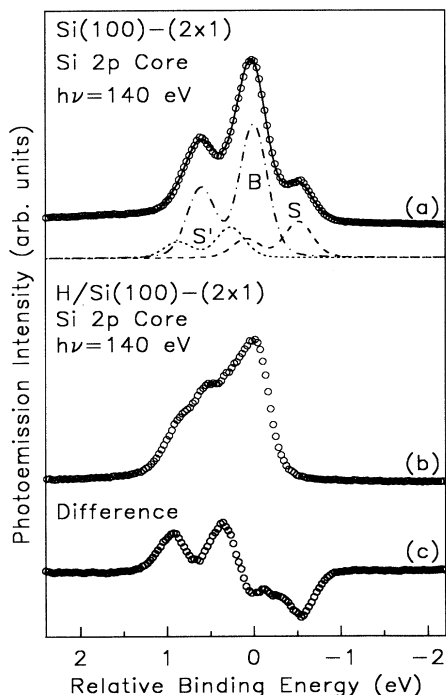

FIG. 1. (a) Photoemission spectrum (circles) for the Si 2*p* core level of the clean Si(100)-(2×1) surface. The photon energy used is 140 eV. The solid curve is a fit to the spectrum. The curves labeled *S*, *S'*, and *B* are the results of a decomposition into individual components. The *B* component is derived from the bulk; *S* and *S'* are surface related. (b) Photoemission spectrum for the H/Si(100)-(2×1) monohydride surface obtained by annealing the disilane saturated Si(100)-(2×1) surface at 670 K. (c) Difference of the above two spectra, (b)−(a).

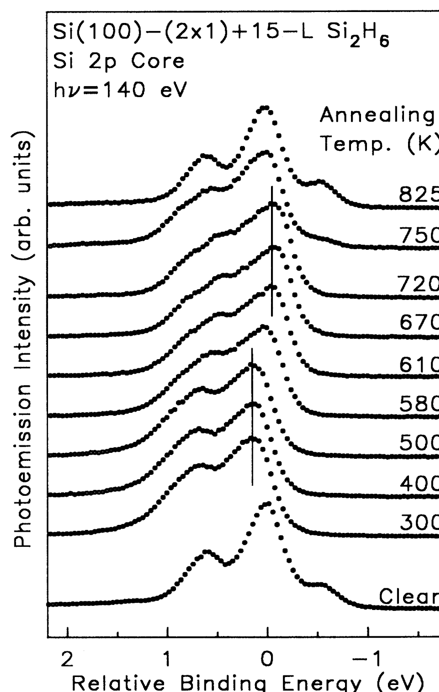

FIG. 2. Si 2*p* core-level spectra for the starting clean Si(100)-(2×1) surface and the same surface exposed to 15-L disilane at 300 K followed by progressive annealing to higher temperatures as indicated. The photon energy used is 140 eV. The relative binding energy is referred to the *B* component of the clean surface. The vertical lines are reference lines showing the energy shifts of the line shape.

energies (left in the figure). Furthermore, the shoulder characteristic of the S component disappears, and the remainder of the line shape broadens significantly. Upon annealing to higher temperatures T, the line shape remains the same until T exceeds about 500 K, beyond which the line shape changes (for example, see the valley between the two main peaks) and shows an overall shift toward lower binding energies. This evolution of the line shape saturates at about 610 K, and it remains unchanged until $T=700$ K is reached. The line shape then evolves and moves back toward higher binding energies, and finally returns to the original position and shape at $T=800$ K and beyond, indicating that the surface has been restored to the original, clean state. These results are quite reproducible. The first set of data was taken in October of 1991, and the date shown in Fig. 2 was taken in March of 1993. The two sets look essentially identical.

The overall shifts of the line shape seen in Fig. 2, as revealed by referencing to the vertical lines, are too large to be accounted for by H-induced chemical shifts alone, as the bulk emission is the largest contribution in the line shape. The sample was electrically grounded during the photoemission measurements. Thus the Fermi level remains at the same position in the spectra for all measurements, while the valence bands and core levels can shift due to band bending changes. To separate out this effect, we also took bulk-sensitive Si $2p$ core-level spectra using 108-eV photons (not shown here to save space).[15] The surface emission, which is affected by the chemical shifts of surface atoms, is minimal in these spectra. Without the interference from the surface emission, the shifts of the bulk emission can then be deduced easily, giving the band bending changes. The bulk Si $2p_{3/2}$ core-level component is known to be at 98.74 eV below the valence-band maximum (VBM).[11] The measured band bending shifts thus allow us to deduce the position of the Fermi level within the energy gap of Si for various annealing temperatures.[16] The results are shown in Fig. 3(a). The Fermi level for the clean surface is at 0.45 eV above the VBM.[16] After saturating the surface with disilane at room temperature, the Fermi level moves up to 0.53 eV. As the annealing temperature increases, it moves down to 0.34 eV first, and then recovers to the clean value of 0.45 eV.

The work function as a function of annealing temperature was also measured. This was deduced from the position of the cutoff of the secondary electron background in the photoemission spectra. The results are shown in Fig. 3(b). By combining the work-function and band bending measurements, we have also deduced the changes of the ionization potential (the energy difference between the vacuum level and the VBM). The results are shown in Fig. 3(c).

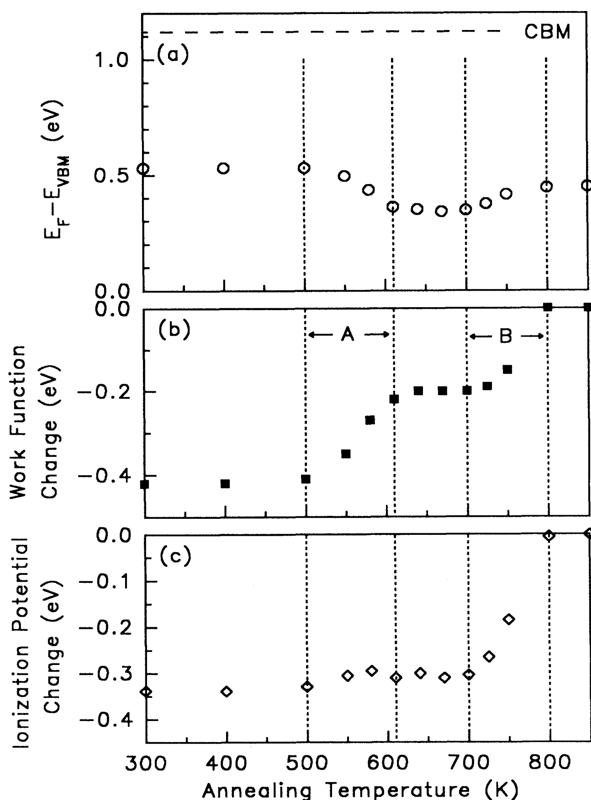

FIG. 3. (a) Fermi-level positions in the Si band gap, (b) work-function changes, and (c) ionization potential changes for various annealing temperatures of the Si(100)-(2×1) surface exposed to 15-L disilane at 300 K. The work-function and ionization potential changes are shown relative to the clean surface. Two transitions A and B are indicated by the vertical dotted lines.

IV. DISCUSSION

As mentioned above, the line shape in Fig. 2 goes through two transitions, the first one at 500–610 K, and the second one at 700–800 K. We will refer to these two transitions as A and B. The line shapes remain unchanged before, in between, and after the two transitions. The two transitions are also evident in Fig. 3, where they are indicated by vertical dashed lines. Thus there are three states of the system. Before transition A, the system remains in the room-temperature saturated state. Between the two transitions, the system is in an intermediate state. After transition B, the system is the clean Si(100)-(2×1) surface. A very important feature of the data in Fig. 2 is the absence of the S component in both the room-temperature saturated state and the intermediate state. This means that all of the dangling bonds on the clean Si(100)-(2×1) remain saturated by H before and after transition A. This puts a rather stringent constraint on any model for the desorption pathway.

As mentioned earlier, infrared studies show that room-temperature adsorption results in mostly SiH_2 and SiH radicals on the surface. The most straightforward interpretation of our data, which is consistent with the commonly proposed pathway,[3,4] is that transition A corresponds to the conversion of dihydride to monohydride radicals:

$$2SiH_2 \rightarrow Si_2H_2 + H_2(g) \;, \qquad (1)$$

where Si_2H_2 denotes a silicon-monohydride dimer on the surface and $H_2(g)$ denotes a hydrogen molecule released from the surface into the gas phase. During this desorption process, no Si dangling bonds are generated, which is confirmed by our data. Transition B should then correspond to the decomposition of the monohydride radicals:

$$Si_2H_2 \rightarrow Si_2 + H_2(g) , \quad (2)$$

where Si_2 denotes a Si dimer on the surface. Ideally, saturation exposure of Si_2H_6 (saturation of all dangling bonds) should result in $\frac{1}{2}$ ML (monolayer) of SiH_2 radicals on the surface from the decomposition of SiH_3, and $\frac{1}{2}$ ML of SiH from the reaction of the original clean surface Si atoms with the released H. Thus the net deposition of Si should be approximately $\frac{1}{2}$ ML, and this is consistent with recent STM and film-thickness measurements.[3,4] Based on this model, the amount of hydrogen evolved from the surface should then correspond to 1/2 and 1 ML (in terms of surface Si atoms) for transitions A and B, respectively. This factor of 2 difference in the amount of hydrogen desorbed from the surface was indeed observed by temperature-programmed desorption.[10] Thus all of the experimental evidence so far points to the validity of the model summarized by Eqs. (1) and (2) above. As far as we know, no other models exist that are compatible with all of the experimental data.

In Fig. 3, the Fermi level, work function, and ionization potential exhibit changes at the two transitions. The Fermi-level position of a semiconductor surface is usually determined by the energies of intrinsic surface states and/or surface defects. Flatband conditions are rather rare. The Fermi level of the clean Si(100)-(2×1) surface appears to be pinned by defects, even though the defect density is rather low.[17] Recent theoretical calculations and experiments with the monohydride surface suggest that there are no intrinsic surface states within the gap,[18,19] and thus the measured Fermi-level position shown in Fig. 3(a) is also likely pinned by surface defects. This defect pinning will affect both the band bending and the work function. The ionization potential, on the other hand, is not sensitive to a small population of surface defects. Figure 3(c) shows that the ionization potential is smaller by about 0.3 and 0.34 eV for the monohydride phase and the mixed dihydride-monohydride phase, respectively, compared to the clean surface. This implies a change in the surface dipole layer due to hydrogen termination, with the hydrogen being on the positive charge side of the added dipole layer. This is opposite to what one might expect intuitively, since hydrogen is more electronegative than Si. However, replacing the dangling bonds on the clean surface by Si-H bonds involves both structural modifications (such as the unbuckling of the dimers) and charge redistributions, which can lead to nontrivial dipole layer changes. Theoretical studies are needed for a detailed understanding of this observation.

We have attempted to analyze the line shapes of the Si $2p$ core level for the hydrogen-covered surfaces as shown in Fig. 2 by employing the same assumption as for the clean surface, namely three components with the same line shape but different energy positions and different intensities. The results of the fit are unsatisfactory in that certain features of the line shapes just cannot be reproduced, and the deviations are significantly larger than what we get for the clean surface. Undoubtedly, we can get a better fit by using more components, but the meaning of the results will be highly questionable in the present case. It is not surprising that the observed line shape is fairly broad for the mixed monohydride-dihydride phase, as multiple components are expected in this case. However, the monohydride phase also shows a broad line shape with subtle features. Figure 1(b) shows in detail this line shape after a 670-K anneal; it is clear that the broad shoulder at 0.5–1 eV actually consists of two shoulders with a long tail to higher binding energies. These and other features cause trouble in the curve fitting. It is quite possible that the line shape is complicated by subsurface shifts and by vibrational overtones;[20] we just cannot reliably extract the information from the data. To get a rough idea of the chemical shift, in Fig. 1(c) we show the difference spectrum obtained by subtracting the spectrum in Fig. 1(a) from that in Fig. 1(b). Before the subtraction, the two spectra are aligned using the bulk-sensitive spectra, so the band bending offset is taken care of. The negative peaks in Fig. 1(c) correspond to the S component of the clean surface removed by hydrogen termination, and the positive peaks on the higher-binding-energy side should mainly reflect the chemically shifted components. A chemical shift of ~0.3 eV can be inferred from this spectrum.

V. SUMMARY

Progressive annealing of a disilane-saturated Si(100)-(2×1) surface shows two steps in the thermal reaction and desorption of H_2, which can be related to the sequential decomposition of SiH_2 and SiH radicals. An intermediate phase is observed between 610 and 700 K, which is identified as the monohydride phase. These reactions and phases are examined by core-level photoemission and measurements of the band bending and work-function changes. Our results are in excellent agreement with recent measurements by STM, temperature-programmed desorption, and electron-energy-loss spectroscopy.

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