Abstract

This study [1] investigates the adsorption and thermal decomposition of phosphine (PH$_3$) on the Si(100)-(2x1) surface. The adsorption species, dissociation reactions, atomic ordering, and surface morphology of the phosphine/Si(100) surface at temperatures between 300 and 1060 K are examined by scanning tunneling microscopy (STM) and high-resolution core-level photoemission spectroscopy employing synchrotron radiation. The P 2p core level spectra clearly indicate that phosphine molecularly adsorbs at room temperature and partially dissociates into PH$_2$ and H on the time scale of minutes at low (<0.2 ML) coverages. An exposure of more than 15 Langmuirs (L, 1 Langmuir=10$^{-6}$ Torr s) of phosphine on the Si(100)-(2x1) surface at room temperature produces a saturated and disordered surface. The total amount of P on the saturated surface is about 0.37 monolayers as calibrated by the P 2p photoemission intensity. Successive annealing of the saturated surface at higher temperatures converts PH$_3$ into PH$_2$, converts PH$_2$ to P-P dimers, and causes the desorption of PH$_3$. These processes become complete at ~700 K, and the resulting surface is a H/Si(100)-(2x1) surface interspersed with one-dimensional P-P islands. Desorption of hydrogen from that surface occurs at ~800 K, and is accompanied by partial displacement of P with Si atoms on the substrate. At 850 K, the Si(100) surface, interspersed with 0.22 ML of 2-D islands, is a random alloy of nominal 0.5 ML Si-P heterodimers and 0.5 ML Si-Si dimers.

Keywords: Synchrotron Radiation Research, Ultrahigh Vacuum, Photoelectron Spectroscopy, Surface Physics, Chemical Vapor Deposition (CVD), Scanning Tunneling Microscopy (STM)

二、缘由與目的

Most silicon epitaxy uses the chemical vapor deposition (CVD) technique. In silicon CVD processes, phosphine (PH$_3$) is frequently added to the Si source gas for in situ n-type doping during the deposition. Yu, Vitkavage, and Meyerson explored the interaction between phosphine and the Si(100) surface using X-ray photoelectron spectroscopy, temperature programmed...
desorption, and low-energy electron diffraction measurements. On the basis of thermal desorption spectroscopy, that investigation contended that PH3 adsorption on Si(100)-(2x1) at room temperature is largely molecular with a sticking coefficient of near unity and annealing PH3-saturated surface caused partial dissociation of PH3 at 475 K and hydrogen desorption at 675 K.

Their results further indicated that the maximum phosphorus coverage, close to 1-ML at 823 K and 0.25 ML at 300-673 K. By employing STM, Wang et al. observed two varieties of protrusions directly on top of a single Si-Si dimer at the initial stage of PH3 adsorption on Si(100) at 300 K. Wang also demonstrated that the Si(100) surface consists of P-P dimers at maxima (one full monolayer) phosphorus coverage, and a nearly random alloy of P-P, Si-Si, and Si-P dimers at less than monolayer phosphorus coverage. Colaianni, Chen, and Yates carefully examined the PH3/Si(100) system using high-resolution electron energy loss spectroscopy. They concluded that most of the phosphine adsorbs dissociatively on the Si(100)-(2x1) surface to produce PHn (n=1, 2) and H species as low as 100 K, in contrast to the above mentioned nondissociative adsorption model. According to their TPD data, PH3 desorption peaks appear at 485 K and 635 K, and H2 at 685 K and 770 K.

In light of the above developments, this study presents STM and synchrotron radiation core-level photoemission spectroscopy data for the thermal reactions of PH3 on Si(100)-(2x1). Experimental results indicate that the growth of phosphorus on Si(100) using phosphine involves several reaction steps.

According to Fig. 1, exposure of phosphine at 660 K results in a relatively sharp P 2p line shape. While containing only a pair of spin-orbit-split peaks, the spectrum presumably corresponds to phosphorus emissions from a single bonding environment.

All the remaining of P 2p spectra in Fig. 1 also exhibit one spin-orbit-split component although their line shapes broaden. The normalized integrated intensities of P 2p spectra in Fig. 1 account for the relative abundance of surface phosphorus atoms at various adsorption temperatures, and are plotted in Fig. 2(a).

FIG. 1. Photoemission spectra (circles) for the P 2p core levels for phosphine adsorption on Si(100) at various adsorption temperatures as indicated.

三、結果與討論
A. Phosphorus growth
As Fig. 2(a) reveals, the photoemission intensity indicates that maximum P coverage takes place at phosphine adsorption temperature of ~850 K, which corresponds to previous studies. The intensity of the maximum coverage is nominally 1 ML. Correspondingly, the total amount of P coverage on room-temperature phosphine saturated Si(100) surface is 0.37 ML.

At growth temperatures between 790 and 890 K, the line shapes of Si 2p core closely resemble each other. The P/Si interface related (Sp) component has a binding energy shift from the B component by 0.49 eV to the higher binding energy side. The normalized total Si 2p intensity after 100-L phosphine adsorption at 850 K decreases by ~27% from the clean Si(100)-(2x1) surface (bottom spectrum in Fig. 1(a)).

FIG. 2. (a) Phosphorus coverage obtained from Fig. 1. (b) Intensity ratio of the S component and the total intensity of Si 2p, and (c) photoemission intensity for the P0 (circles), P2 (filled triangles), P3 (open triangles) components and the sum of the three components (rectangles) of P 2p as a function of annealing temperature.

B. Annealing of PH$_3$ adsorbed Si(100)-(2x1) surfaces

Fig. 2(b) plots the intensity ratio, $I_S/I_{Tot}$. After annealing at 1040 K for 60 s, the intensity ratio is 0.15, which is slightly lower than the value of 0.18 for the original clean surface. Figure 2(c) plots the intensity of the P3, P2, P0 components, and the sum of these three components as a function of annealing temperature. Figure 2 contains four temperature ranges, denoted as A, B, C, and D, in which one or more curves show significantly steeper slopes. Such behavior implies certain transitions or reactions. The relevant temperatures define these ranges are the following: $T_1$=540 K, $T_2$=620 K, $T_3$=700 K, $T_4$=820 K, and $T_5$=920 K.

C. Room temperature adsorption behavior

Figure 3 shows that most adsorption features appear on top of a single dimer. This observation suggests that the dissociation of PH$_3$ may alternatively take place via insertion of PH$_2$ into a dimer bond. In this bonding configuration, the phosphorus atom in a PH$_3$ radical form covalent bonds with two neighboring Si atoms and two H atoms. The fifth valance electron can resonantly form the second valence bond with one of the two neighboring Si atoms and,
possibly, prevents the two Si from further PH$_3$ adsorption. The dissociated H may then attach itself to a nearby Si dangling bond. The overall reaction is energetically favorable since dimer bond breaking requires ~2.3 eV, while H termination of dangling bonds releases ~3.6 eV. In configuration B, an adsorbed phosphorus atom consumes three free Si sites, thereby leading to the low (~0.37 ML) saturation phosphorus coverage at room temperature.

**D. Transition A**

The onset of transition A at $T_1$ is characterized by a rise of the P2 signal at the expense of P3, as depicted in Fig. 2(c). During this transition, the molecularly adsorbed PH$_3$ species gradually dissociate into PH$_2$ and H as indicated by Eq. (2). Figure 2(c) also reveals that the total P coverage drops slightly during the transition. This drop is likely attributed to partial desorption of nondissociated PH$_3$ since a previous TPD study reveals a small PH$_3$ desorption peak at 485 K. As mentioned in Sec. IVA, the P coverage on room-temperature saturated Si(100) surface is 0.37 ML. However, configuration B suggests that dissociated PH$_2$ and H consume three surface sites, resulting in 0.33 ML P coverage at most. The excess adsorbed PH$_3$ of 0.04 ML would have to desorb intact into space, which corresponds to the reduction from 0.37 to 0.34 ML as shown in Fig. 2(c). Upon 620 K annealing, the P 2p core consists essentially of a single (P2) component with some broadening possibly due to vibrational excitations as well as a slight amount of the arising P0 component. Half way through the transition A (~580 K), the surface consists of both PH$_2$ and PH$_3$ species and is still highly disordered, as illustrated in Fig. 4(a).
FIG. 4. STM images of the Si(100) surface after annealing to (a) 580 K, (b) 630 K, (c) 730 K, (d) 840 K, and (d) 1060 K. The sample is Si(100)-(2x1) saturated by 20-L PH$_3$ exposure at room temperature. The scanned areas are 100x300 Å$^2$ for (a, e) and 200x300 Å$^2$ for (b, c, and d). The sample bias used was +2.5 V for (a-d) and −2 V for (e). A monoatomic step can be discerned around the upper right corner in (c).

C. Transition B

Transition B is characterized by a rapid transformation of the P2 component to P0 and a large (about 25%) reduction of total surface phosphorus coverage. Figures 4(b) and 4(c) display the STM images taken after annealing of the room-temperature PH$_3$-saturated surface to the temperatures near the beginning and the end of transition B. Figure 4(b) indicates that the adsorption fragments on the surface after 630 K annealing are still disordered, although some chainlike structure is present. Upon further annealing at 730 K, most adsorption fragments line up into short one-dimensional trains, as Fig. 4(c) depicts. The trains are orthogonal to the dimer rows on the substrate. The substrate dimer rows resemble the (2x1) Si$_2$H$_2$ monohydride structure. Owing to that the desorption maximum of H$_2$ from Si$_2$H$_2$ is about 800 K, the annealing temperature of 730 K is not sufficiently high to desorb hydrogen atoms from the surface. Therefore, the substrate dimer rows in Fig. 4(c) may be readily attributed to Si$_2$H$_2$ dimers. The reduction in P-coverage during transition B correlates with the finding of the molecular phosphine desorption feature at 635 K in TPD spectra. Since both PH$_2$D and PH$_3$ desorption peaks at 635 K are observed on a Si(100) surface partially covered with D species before PH$_3$ exposure, Colaianni _et al._ contended that phosphine desorption arises from PH$_3$+H recombination. Colaianni _et al._ also observed a H$_2$ desorption peak at 685 K and fully removal of PH$_2$ scissor mode and the P-H stretching mode in HREELS spectra at 650 K, indicating that PH$_2$ (a) undergoes thermal decomposition to P and H near 650 K. Above evidence cumulatively suggests that the dimer-chain
features in Fig. 4(c) are P-P dimers. All three hydrogen atoms on an adsorbed PH$_3$ molecular are released at $\sim$700 K. Therefore, as expected, the P coverage is only 0.25 ML, which corresponds to the measured photoemission intensity in Fig. 2(c). Again, the excess PH$_2$ fragments desorb from the surface.

D. Transition C

During transition C (between 700 and 820 K), the saturation phosphorus coverage surges rapidly from minimum to maximum, as depicted in Fig. 2(a). Also, according to Fig. 2(b), the S component of the Si 2p spectra for the annealed Si(100) surface initially saturated by PH$_3$ at room temperature, recovers half of its intensity. Owing to that the S component in Si 2p spectra characterizes the dimer atoms, its gradual reappearance suggests the hydrogen desorption from Si$_2$H$_2$ monohydrides. The observation of this reaction temperature region fairly corresponds to the $\beta_1$ desorption state centered at 780 K for monohydride Si surface in the TPD spectra. As mentioned in Sec. IVC, all hydrogen on adsorbed PH$_3$ molecules are released at $\sim$700 K and, along with phosphorus, terminate all surface sites. Therefore, as expected, the P coverage is at the minimum value of only 0.25 ML during phosphine exposure at 700 K, which correlates with the measured photoemission intensity in Fig. 2(a). In contrast, all hydrogen desorbs immediately upon PH$_3$ exposure at $\sim$300 K, and all surface sites are available for phosphorus, leading to the maximum P coverage of $\sim$1ML.

五、参考文献