

# 行政院國家科學委員會專題研究計畫成果報告

第三、五族雜質在矽、鍺晶面上氣相生長之原子與電子結構研究

計畫編號：NSC 88-2112-M-009-005

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## 一、中文摘要

我們利用掃描探針式電子穿隧顯微(STM) 微同步輻射光電子能譜來研究單一原子解析度以下的矽單晶(100)面在磷化學氣相沉積生長過程，對氣體分子吸附後所產生之表面化學反應作了原子解析度下的即時觀察[1]。實驗結果顯示在室溫下，三氫化磷以分子吸附，分解為  $\text{PH}_2$ ，在 700K 左右再分解為 P-P dimers。在 850K 附近磷與矽合氫混合雙體，1040 K 以雙磷開始由矽單晶(100)表面熱解離。

關鍵詞：同步輻射應用研究、超高真空、光電子能譜學、氣相沉積長晶

## Abstract

This study [1] investigates the adsorption and thermal decomposition of phosphine ( $\text{PH}_3$ ) 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  $\text{PH}_2$  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  $\text{PH}_3$  into  $\text{PH}_2$ , converts  $\text{PH}_2$  to P-P dimers, and causes the desorption of  $\text{PH}_3$ . 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、緣由與目的

Most silicon epitaxy uses the chemical vapor deposition (CVD) technique. In silicon CVD processes, phosphine ( $\text{PH}_3$ ) 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

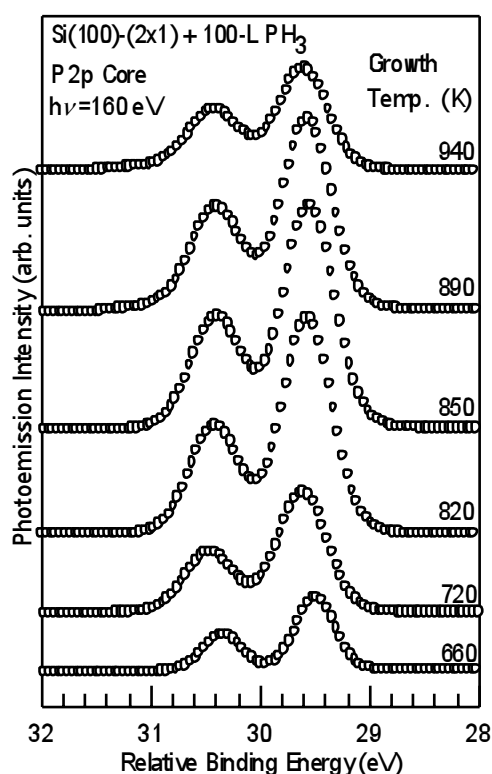
desorption, and low-energy electron diffraction measurements. On the basis of thermal desorption spectroscopy, that investigation contended that  $\text{PH}_3$  adsorption on  $\text{Si}(100)-(2\times 1)$  at room temperature is largely molecular with a sticking coefficient of near unity and annealing  $\text{PH}_3$ -saturated surface caused partial dissociation of  $\text{PH}_3$  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  $\text{PH}_3$  adsorption on  $\text{Si}(100)$  at 300 K. Wang also demonstrated that the  $\text{Si}(100)$  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  $\text{PH}_3/\text{Si}(100)$  system using high-resolution electron energy loss spectroscopy. They concluded that most of the phosphine adsorbs dissociatively on the  $\text{Si}(100)-(2\times 1)$  surface to produce  $\text{PH}_n$  ( $n=1, 2$ ) and H species as low as 100 K, in contrast to the above mentioned nondissociative adsorption model. According to their TPD data,  $\text{PH}_3$  desorption peaks appear at 485 K and 635 K, and  $\text{H}_2$  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  $\text{PH}_3$  on  $\text{Si}(100)-(2\times 1)$ . Experimental results indicate that the growth of phosphorus on  $\text{Si}(100)$  using phosphine involves several reaction steps.

### 三、結果與討論

#### A. Phosphorus growth

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 the P  $2p$  core levels for phosphine adsorption on  $\text{Si}(100)$  at various adsorption temperatures as indicated.

As Fig. 2(a) reveals, the photoemission intensity indicates that maximum P coverage takes place at phosphine adsorption temperature of  $\sim 850$  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  $\sim 27\%$  from the clean Si(100)-(2x1) surface (bottom spectrum in Fig. 1(a)).

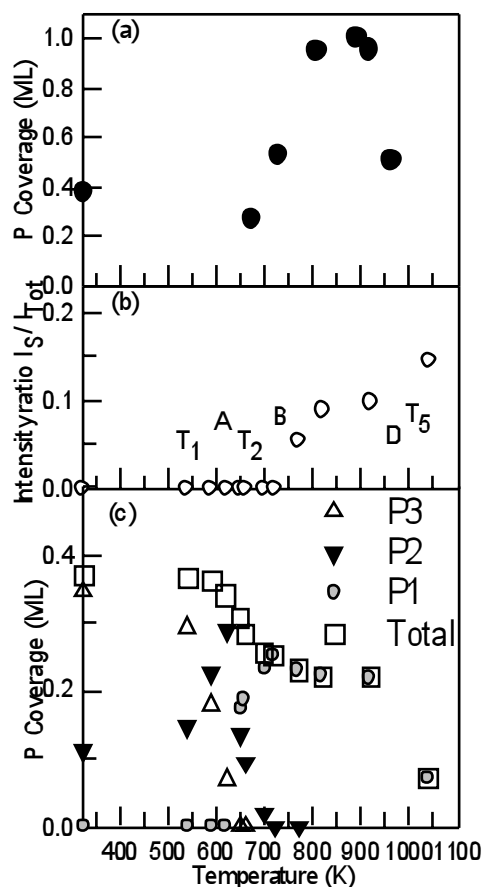
FIG. 2. (a) Phosphorus coverage obtained from Fig. 1. (b) Intensity ratio of the S component and the total intensity of Si  $2p$ , and (c) photoemission intensity for the P0 (circles), P2 (filled triangles), P3 (open triangles) components and the sum of the three components (rectangles) of P  $2p$  as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

### B. Annealing of $\text{PH}_3$ adsorbed Si(100)-(2x1) surfaces

Fig. 2(b) plots the intensity ratio,  $I_S/I_{\text{Tot}}$ . 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  $\text{PH}_3$  may alternatively take place via insertion of  $\text{PH}_2$  into a dimer bond. In this bonding configuration, the phosphorus atom in a  $\text{PH}_2$  radical form covalent bonds with two neighboring Si atoms and two H atoms. The fifth valence electron can resonantly form the second valence bond with one of the two neighboring Si atoms and,

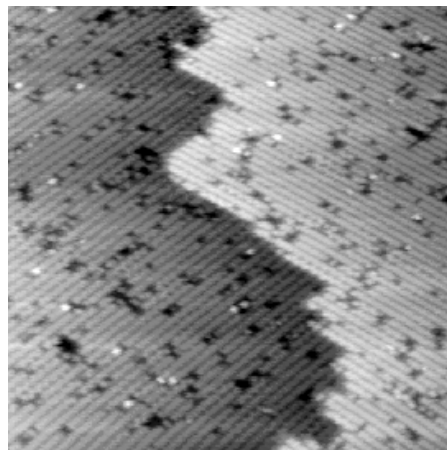


possibly, prevents the two Si from further  $\text{PH}_3$  adsorption. The dissociated H may then attach itself to a nearby Si dangling bond. The overall reaction is energetically favorable since dimer bond breaking requires  $\sim 2.3$  eV, while H termination of dangling bonds releases  $\sim 3.6$  eV. In configuration B, an adsorbed phosphorus atom consumes three free Si sites, thereby leading to the low ( $\sim 0.37$  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  $\text{PH}_3$  species gradually dissociate into  $\text{PH}_2$  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  $\text{PH}_3$  since a previous TPD study reveals a small  $\text{PH}_3$  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  $\text{PH}_2$  and H consume three surface sites, resulting in 0.33 ML P coverage at most. The excess adsorbed  $\text{PH}_3$  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 ( $\sim 580$  K), the surface consists of both  $\text{PH}_2$  and  $\text{PH}_3$  species and is still highly disordered, as illustrated in Fig. 4(a).

FIG. 3. STM images of the Si(100) surface after exposure to a small amount of  $\text{PH}_3$  at room temperature. The sample bias used was  $-2.3$  V.



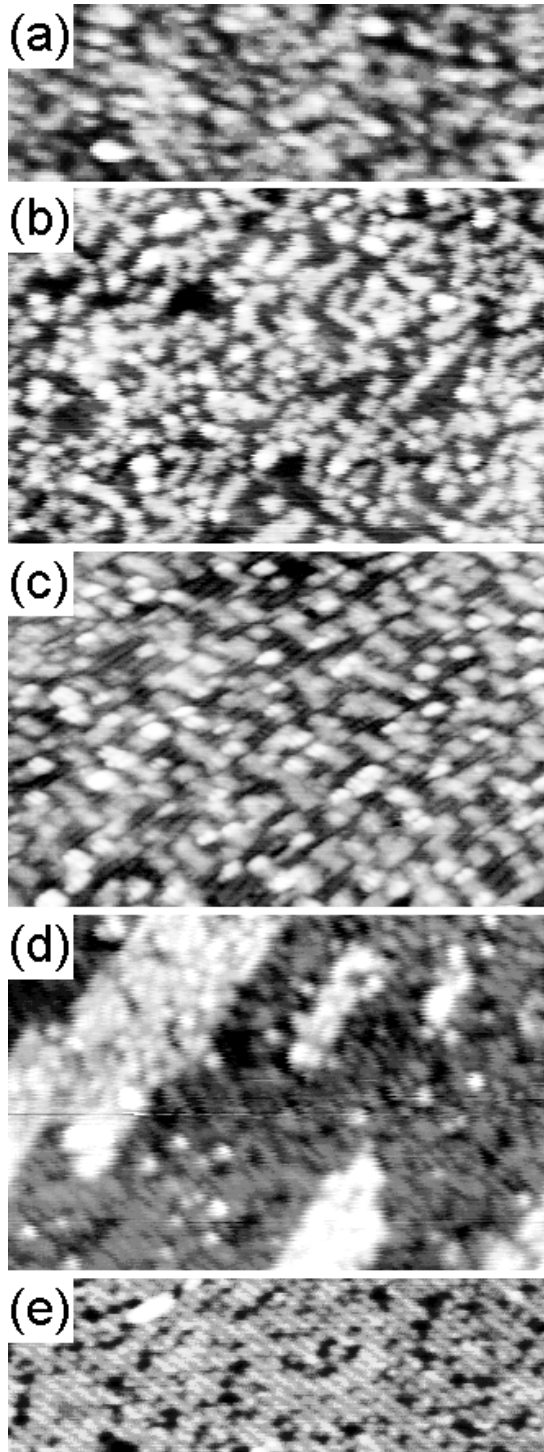


FIG. 4. STM images of the Si(100) surface after annealing to (a) 580 K, (b) 630 K, (c) 730 K, (d) 840 K, and (e) 1060 K. The sample is Si(100)-(2x1) saturated by 20-L  $\text{PH}_3$  exposure at room temperature. The scanned areas are  $100 \times 300 \text{ \AA}^2$  for (a, e) and  $200 \times 300 \text{ \AA}^2$  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  $\text{PH}_3$ -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)  $\text{Si}_2\text{H}_2$  monohydride structure. Owing to that the desorption maximum of  $\text{H}_2$  from  $\text{Si}_2\text{H}_2$  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  $\text{Si}_2\text{H}_2$  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  $\text{PH}_2\text{D}$  and  $\text{PH}_3$  desorption peaks at 635 K are observed on a Si(100) surface partially covered with D species before  $\text{PH}_3$  exposure, Colaianni *et al.* contended that phosphine desorption arises from  $\text{PH}_2+\text{H}$  recombination. Colaianni *et al.* also observed a  $\text{H}_2$  desorption peak at 685 K and fully removal of  $\text{PH}_2$  scissor mode and the P-H stretching mode in HREELS spectra at 650 K, indicating that  $\text{PH}_2$  (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  $\text{PH}_3$  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  $\text{PH}_2$  fragments desorb from the surface.

*photoemission and scanning-tunneling-microscopy study, Surf. Sci., 424, 7(1999).*

#### 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  $\text{PH}_3$  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  $\text{Si}_2\text{H}_2$  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  $\text{PH}_3$  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  $\text{PH}_3$  exposure at  $\sim 800$  K, and all surface sites are available for phosphorus, leading to the maximum P coverage of  $\sim 1$ ML.

#### 五、參考文獻

- [1] Deng-Sung Lin, Tsai-Shain Ku, and Tzeng-Jiuh Sheu, *Thermal reactions of phosphine with Si(100): A combined*