Comparison of thermal reactions of phosphine on Ge(100) and Si(100) by high-resolution core-level photoemission

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Abstract

The thermal decomposition processes of phosphine (PH3) on a Ge(100)-2 × 1 surface at temperatures between 325 and 790 K were investigated and compared with those on Si(100)-2 × 1. High-resolution synchrotron radiation core-level photoemission spectra indicates that, at room temperature, phosphine molecularly adsorbs on the Ge(100)-2 × 1 surface, however on the Si(100)-2 × 1 it partially dissociates into PH2 and H. Successive annealing of the PH3-saturated Si(100) and Ge(100) surfaces at higher temperatures similarly converts PH3 into PH2 and PH2 to P. P atoms form stable P-P and/or P-Si dimers on Si(100) above 720 K, but exhibit complex bonding configurations on Ge(100). © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

During the chemical vapor deposition (CVD) of Ge, Si1-x alloys and heterostructures as well as silicon films [1,2], phosphine (PH3) is frequently added to Si and Ge source gases for in situ n-type doping. The adsorption, fragmentation, and subsequent hydrogen desorption processes which occur during the interaction of phosphine with the Si(100) surface have received much attention [3–10]. In contrast, to our knowledge, the interaction of phosphine with the Ge(100) surface has yet to be studied.

Yu et al. [3,4] contended that, on the basis of thermal desorption spectroscopy (TPD), at room temperature PH3 adsorption on Si(100)-2 × 1 is primarily molecular and annealing the PH3-saturated surface caused partial dissociation of PH3 at 475 K and hydrogen desorption at 675 K. Colaianni et al. [7] examined the PH3/Si(100) system applying high-resolution electron energy loss spectroscopy (HREELS). However, they concluded that much of the phosphine adsorbs dissociatively on the Si(100)-2 × 1 surface to produce both PHn (n = 1, 2) and H species as low as 100 K. Hamers and coworkers [8] employed Fourier transform infrared spectroscopy (FTIR) and proved that the degree of dissociation of adsorbed PH3 on Si(100) depends upon the flux and coverage during exposure. Lin et al. [10], employing core-level photoemission and scanning tunneling microscopy, found that at room temperature phosphine molecularly adsorbs and only at low (<0.2 ML) coverage PH3 partially dissociates into PH2 and H. Successive annealing of the PH3-saturated
surface to higher temperatures converts PH$_3$ into PH$_2$, PH$_2$ to P–P and P–Si dimers below 700 K.

Therefore, this study presents results of photoemission on thermal reactions of PH$_3$ on both the Ge(1 0 0)-2 × 1 and Si(1 0 0)-2 × 1 surfaces. Although silicon and germanium are both group IV semiconductors with the same diamond crystal structure, they have a slightly different chemical reactivity. Both clean Si(1 0 0) and Ge(1 0 0) surfaces also have the same 2 × 1 dimer structures. Therefore, a comparison of the thermal interaction of PH$_3$/Si(1 0 0) and PH$_3$/Ge(1 0 0) provides valuable information regarding the influence of structural and/or chemical reactivity on the atomic processes during CVD. Experimental results indicate that at room temperature, the PH$_3$ adsorption is molecular on Ge(1 0 0)-2 × 1, however partially dissociative on the more reactive Si(1 0 0)-2 × 1 surface. Subsequent conversion of PH$_3$ to PH$_2$ and P at higher annealing temperatures reacts similarly on both surfaces. After all H desorbs from the surfaces, however, the deposited P exhibits more complex bonding configurations on Ge(1 0 0) than it does on Si(1 0 0).

2. Experimental details

The photoemission experiments were performed in a μ-metal shielded UHV system utilizing a 1.5-GeV synchrotron radiation source in Hsinchu, Taiwan. Light from the storage ring was dispersed by a 6-m spherical grating monochromator. Photoelectrons were collected and analyzed by a 125 mm hemispherical analyzer. The overall energy resolution was less than 150 meV. The Si(1 0 0) samples were sliced from boron-doped wafers with an electrical resistivity of around 10 Ω cm. Si(1 0 0) samples’ cleaning involved outgassing at ~900 K for ~12 h followed by brief DC heating to ~1450 K. The Ge(1 0 0) sample was prepared by several cycles of sputtering with Ar$^+$ ions and annealing. Phosphine (ultrahigh purity grade) was introduced into the chamber through a precision leak valve. The dosing pressure (~2 × 10$^{-8}$ Torr) was monitored by an ionization gauge not directly facing the sample. The samples were annealed by passing currents through them and their temperature was measured with an infrared pyrometer. Each annealing lasted for 60 s.

3. Results

Figs. 1(a) and 2 depict P2p core-level spectra, respectively, for Ge(1 0 0) and Si(1 0 0) surfaces after saturation exposure of phosphine at ~325 K, followed by successive anneals to higher temperatures. Fig. 1(b) displays the Ge 3d spectra corresponding to Fig. 1(a). High-resolution core-level photoemission spectroscopy allows the distinction of surface atoms in inequivalent sites and in different chemical bonding configurations by binding energy shifts [11]. The line shape of the Ge 3d core level (the bottom spectra in Fig. 1(b)) for the clean Ge(1 0 0)-2 × 1 surface has been studied previously [12,13] and is similarly analyzed herein based upon a least-squares analysis. The fit involves two spin–orbit-split components, one bulk (B) and one surface component (S), riding on a smooth polynomial background [12]. After dosing 60-L PH$_3$ onto the Ge(1 0 0)-2 × 1 surface at 325 K, the P2p integrated intensity (not presented here) indicates a saturated surface. The S component of the Ge 3d dissipates. The line shape of the PH$_3$-saturated Ge(1 0 0) surface (bottom spectrum of Fig. 1(a)) displays only one discernible spin–orbit-split component (labeled GP$_3$), which corresponds to a specific surface adsorption species. In contrast, the line shape of the PH$_3$-saturated Si(1 0 0) surface (bottom spectrum of Fig. 2) exhibits three distinct peaks and is therefore analyzed with two spin–orbit-split components, SP$_2$ and SP$_3$, as indicated. Previous studies [7,8] revealed vibrational bands in HREELS and FTIR adsorption peaks for PH$_3$ and SiH surface species upon the phosphine adsorption on Si(1 0 0)-2 × 1 at room temperature. This indicates that at least to some extent, adsorbed PH$_3$ radicals subsequently dissociate into PH$_2$ and H. The dissociated H may then become attached to a nearby Si dangling bond. Since Si–Si dimer bond breaking requires ~2.3 eV, the overall reaction is energetically favorable, while H termination of a dangling bond releases ~3.6 eV [14]. The relative binding energy of the SP$_2$ component is lower than that of SP$_3$ by 0.54 eV. Owing to that
trihydrides generally exhibit a higher chemical shift than dihydrides do [12,15]. The SP$_3$ and SP$_2$ components of Fig. 2 can be readily assigned to signals from the PH$_3$ and PH$_2$ surface species, respectively. The Ge(1 0 0)-2 × 1 and Si(1 0 0)-2 × 1 surfaces have similar surface electronic properties associated with their common 2 × 1 dimer structure. Also, germanium has a weaker chemical reactivity than silicon does. Therefore, the GP$_3$ component is attributed to the PH$_3$ species and without further fragmentation PH$_3$ molecularly adsorbs on the Ge(100)-2 × 1 close to room temperature.

Annealing the PH$_3$-saturated Si(100) surface above 540 K yields an increase in the SP$_2$ peak at the expense of SP$_3$ in the core-level spectra (Fig. 2). The P 2p spectrum during 620 K annealing chiefly consists of a single (SP$_2$) component as the transformation progresses. The transposition of the SP$_3$ and SP$_2$ peaks demonstrates further conversion of PH$_3$ to PH$_2$ and indicates that at 620 K, PH$_2$ is the primary surface species. In the P 2p core-level
spectra of the PH$_2$/Ge(100) system (Fig. 1(a)), a new component (GP$_2$) gradually appears between 450–600 K and eventually becomes predominating upon annealing at 615 K, a temperature at which the SP$_2$ component (and its associated PH$_2$ species) prevails on the PH$_3$/Si(100) system. The binding energy difference of 0.59 eV between the GP$_3$ and GP$_2$ components is similar to that between SP$_3$ and SP$_2$, thereby indicating that although only the PH$_3$ species is initially present on the Ge(100)-2 × 1 surface at 325 K, GP$_2$ is similarly derived from the PH$_2$ surface species and the PH$_3$ species converts to PH$_2$. Notably, during temperature increase of 620 K, the integrated intensity of P 2p of Fig. 2(a) remains roughly the same, but that of Fig. 1(a) decreases by 50%. Since hydrogen on PH$_2$ naturally hinders the P-indiffusion, this phenomena indicates that upon annealing, a large amount of molecularly adsorbed PH$_3$ desorbs and the bonding between the molecular-adsorbed PH$_3$ and the Ge(100) surface is weak.

In Fig. 2, the intensity of the SP$_2$ component decreases at temperature exceeding 620 K, while a new feature appears on the lower binding energy side, ≈0.29 eV relative to SP$_2$. The spectrum consists of just one relatively sharp spin–orbit-split component (labeled SP) upon 720 K annealing for 1 min. At >650 K, HREELS spectra reveals full removal of PH$_3$ scissor mode and the P–H stretching mode [8], thus, suggesting that no P–H bond exists on the Si(100) surface. This lack of P–H bonds indicates that at this temperature range, all PH$_2$ species undergo thermal decomposition to P and H and P2p in P–P and/or P–Si dimers contributes to the SP component. Furthermore, as a H$_2$ desorption peak was observed at a temperature near the $\beta_1$ desorption peak (≈800 K) on the H/Si(100)-2 × 1 surface [15], the H released from PH$_2$ species may then produce Si–H bonds. Energy positions, intensities and line shapes of the P 2p spectra remain roughly the same between 720–920 K, therefore indicating that all surface P atoms contribute to the same SP component.

The PH$_3$/Ge(100) system above 620 K illustrates an apparently different evolution in the P 2p line shapes. Unlike the PH$_3$/Si(100) system, the P 2p spectra obtained after >615 K annealing of the PH$_3$-saturated Ge(100) surface are broad. Upon annealing at 670 K (at which temperature the SP component in Fig. 2 emerges), the line shape can be analyzed in terms of two components, that is, a new feature (labeled GP) and a GP$_2$ component. The binding energy shift of −0.29 eV between the GP and GP$_2$ components is also similar to that between the SP$_2$ and SP components. This finding strongly indicates that, similar to the SP component on PH$_3$/Si(100), after H dissociation from the PH$_2$ species, GP originates from P atoms.
Fig. 1(b) also shows that the S component in the Ge 3d spectrum begins to reappear upon 615 K annealing. The intensity of the S component measures the surface areas that consist of clean Ge–Ge dimers. The intensity increase of the S component indicates that dissociated hydrogen in Ge–H form desorbs at >615 K since TPD from the H/Ge(100)-2 × 1 reveals H₂ desorption maximum at ~600 K [16].

As previously mentioned, the phosphorus atoms on Si(100) in the form of P–P or P–Si dimers contributes to a single P 2p core-level component (Fig. 2). However, the P 2p spectra for 760 and 790 K annealing in Fig. 1(a) exhibit broad line shapes, thereby indicating that multiple phosphorus chemical bonding configurations coexist on the P/Ge(100) surface. Bottomley et al. [17] studied the 20-min annealing effects on P-doped Ge(100) samples at 880 K and found that P atoms segregate towards the surface and form GeP₃ three dimensional nanometer scale islands and elemental phosphorus in the subsurface regions. This result and our observation of broad P 2p line shapes indicate that surface P atoms do not form a simple passivated phosphorus layer on Ge(100) like other similar systems, such as As, Sb/Si(100), Ge(100) do.

4. Summary

High-resolution core-level photoemission spectroscopy clarified the thermal reactions of phosphine on the Si(100)-2 × 1 and Ge(100)-2 × 1 surfaces. Typically, these reactions occur during in situ doping of Si and SiGe CVD. Based upon the results herein, the followings have been concluded:

1. Initially, phosphine molecularly adsors on both the Si and Ge(100) surfaces at room temperature, however on Si(100), it partially dissociates into PH₂.
2. On both Si(100) and Ge(100), surface PH₃ species gradually convert into PH₂. At ~620 K, this reaction is complete. Much of the adsorbed PH₃ species desorbs into vacuum on the PH₃-saturated Ge(100) upon annealing.
3. PH₂ species converts into P and forms a stable partial P-terminated surface on Si(100) between 720 and 920 K. On the contrary, the P 2p core level spectra on Ge(100) display a broad line shape and therefore indicate that P atoms exhibit multiple chemical bonding configurations.

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