Comparison of thermal reactions of phosphine on Ge(1 0 0) and Si(1 0 0) by high-resolution core-level photoemission

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Abstract

The thermal decomposition processes of phosphine (PH_3) on a Ge(1 0 0)-2 × 1 surface at temperatures between 325 and 790 K were investigated and compared with those on Si(1 0 0)-2 × 1. High-resolution synchrotron radiation core-level photoemission spectra indicates that, at room temperature phosphine molecularly adsorbs on the Ge(1 0 0)-2 × 1 surface, however on the Si(1 0 0)-2 × 1 it partially dissociates into PH_2 and H. Successive annealing of the PH_3-saturated Si(1 0 0) and Ge(1 0 0) surfaces at higher temperatures similarly converts PH_3 into PH_2 and PH_2 to P. P atoms form stable P–P and/or P–Si dimers on Si(1 0 0) above 720 K, but exhibit complex bonding configurations on Ge(1 0 0). © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

During the chemical vapor deposition (CVD) of Ge_xSi_{1-x} alloys and heterostructures as well as silicon films [1,2], phosphine (PH_3) 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(1 0 0) surface have received much attention [3–10]. In contrast, to our knowledge, the interaction of phosphine with the Ge(1 0 0) surface has yet to be studied.

Yu et al. [3,4] contended that, on the basis of thermal desorption spectroscopy (TPD), at room temperature PH_3 adsorption on Si(1 0 0)-2 × 1 is primarily molecular and annealing the PH_3-saturated surface caused partial dissociation of PH_3 at 475 K and hydrogen desorption at 675 K. Colaianni et al. [7] examined the PH_3/Si(1 0 0) system applying high-resolution electron energy loss spectroscopy (HREELS). However, they concluded that much of the phosphine adsorbs dissociatively on the Si(1 0 0)-2 × 1 surface to produce both $PH_n (n = 1, 2)$ 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 PH_3 on Si(1 0 0) 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 PH_3 partially dissociates into PH_2 and H. Successive annealing of the PH_3-saturated

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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 P 2p 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 P 2p 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_n 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
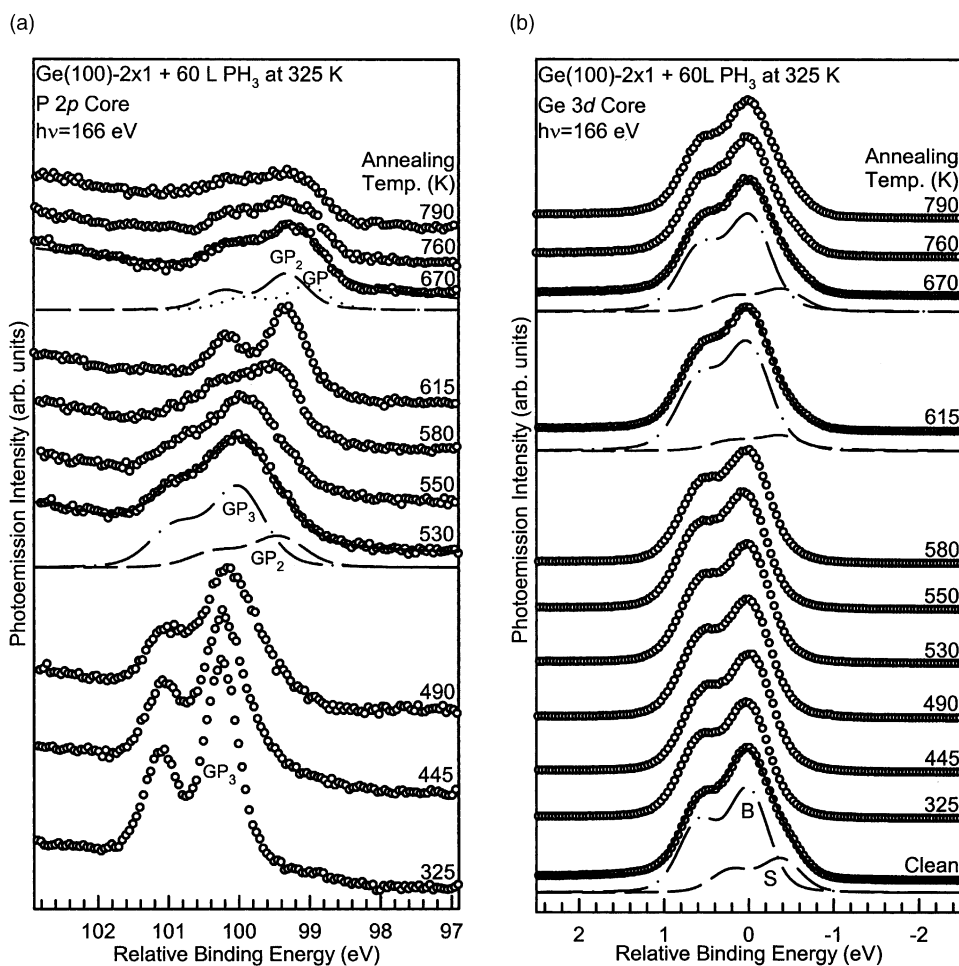
(a)

(b)

Fig. 1. Photoemission spectra (○) of (a) the P 2p and (b) the Ge 3d core levels for the Ge(1 0 0)-2 × 1 surface exposed to 60-L PH₃ at 325 K followed by progressive annealing to higher temperatures as indicated. The solid curves are fit to the spectra. The curves labeled GP₃, GP₂, GP, S, and B are the results of decompositions into individual components, each having a pair of spin–orbit-split peaks. The relative binding energy of Ge 3d core levels refers to the Ge $3d_{5/2}$ line of the bulk (B) component of the clean Ge(1 0 0)-2 × 1 surface. To eliminate the band bending effect, the relative binding energy of P 2p refers to the corresponding Ge $3d_{5/2}$ line of the B component.

trihydrides generally exhibit a higher chemical shift than dihydrides do [12,15], the SP₃ and SP₂ components of Fig. 2 can be readily assigned to signals from the PH₃ and PH₂ 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 GP₃ component is attributed to the PH₃ species and without further fragmentation PH₃ molecularly

adsorbs on the Ge(1 0 0)-2 × 1 close to room temperature.

Annealing the PH₃-saturated Si(1 0 0) surface above 540 K yields an increase in the SP₂ peak at the expense of SP₃ in the core-level spectra (Fig. 2). The P 2p spectrum during 620 K annealing chiefly consists of a single (SP₂) component as the transformation progresses. The transposition of the SP₃ and SP₂ peaks demonstrates further conversion of PH₃ to PH₂ and indicates that at 620 K, PH₂ is the primary surface species. In the P 2p core-level
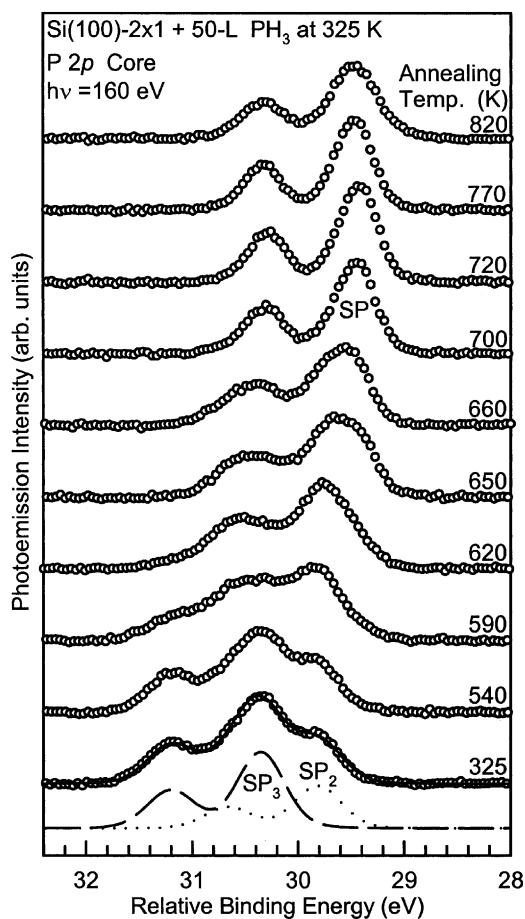
Fig. 2. Photoemission spectra (○) of the P 2p core levels for the Si(1 0 0)-2 × 1 surface saturated with a 50-L PH_3 dose at 325 K followed by progressive annealing to higher temperatures as indicated. The fit (—) and the decomposed individual SP_2 and SP_3 components for the bottom spectrum are also shown. The relative binding energy scale refers to the corresponding Si $2p_{3/2}$ line of the B component [10].

spectra of the PH_3/Ge(1 0 0) 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(1 0 0) 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(1 0 0)-2 × 1 surface at 325 K, GP_2 is simi-

larly 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(1 0 0) 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_2 scissor mode and the P–H stretching mode [8], thus, suggesting that no P–H bond exists on the Si(1 0 0) 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 P 2p 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 β_1 desorption peak (∼800 K) on the H/Si(1 0 0)-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(1 0 0) system above 620 K illustrates an apparently different evolution in the P 2p line shapes. Unlike the PH_3/Si(1 0 0) system, the P 2p spectra obtained after >615 K annealing of the PH_3-saturated Ge(1 0 0) 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(1 0 0), 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(1 0 0)-2 × 1 reveals H_2 desorption maximum at ~600 K [16].

As previously mentioned, the phosphorus atoms on Si(1 0 0) 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(1 0 0) surface. Bottomley et al. [17] studied the 20-min annealing effects on P-doped Ge(1 0 0) samples at 880 K and found that P atoms segregate towards the surface and form GeP_3 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(1 0 0) like other similar systems, such as As, Sb/Si(1 0 0), Ge(1 0 0) do.

4. Summary

High-resolution core-level photoemission spectroscopy clarified the thermal reactions of phosphine on the Si(1 0 0)-2 × 1 and Ge(1 0 0)-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 adsorbs on both the Si and Ge(1 0 0) surfaces at room temperature, however on Si(1 0 0), it partially dissociates into PH_2.
2. On both Si(1 0 0) and Ge(1 0 0), surface PH_3 species gradually convert into PH_2. At ~620 K, this reaction is complete. Much of the adsorbed PH_3 species desorbs into vacuum on the PH_3-saturated Ge(1 0 0) upon annealing.
3. PH_2 species converts into P and forms a stable partial P-terminated surface on Si(1 0 0) between 720 and 920 K. On the contrary, the P 2p core level spectra on Ge(1 0 0) display a broad line shape and therefore indicate that P atoms exhibit multiple chemical bonding configurations.

Acknowledgements

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