Atomic level investigation of boron and phosphorus chemical vapor deposition on Si, Ge surfaces (II)

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chemical vapor deposition; silicon; Germanium

(STM)

(100)

(100)

Abstract

The thermal decomposition processes of phosphine (PH$_3$) on a Ge(100)-2x1 surface at temperatures between 325 and 790 K were investigated and compared with those on Si(100)-2x1. High-resolution synchrotron radiation core-level photoemission spectra indicates that, at room temperature phosphine molecularly adsorbs on the Ge(100)-2x1 surface, however on the Si(100)-2x1 it partially dissociates into PH$_2$ and H. Successive annealing of the PH$_3$-saturated Si(100) and Ge(100) 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(100) above 720 K, but exhibit complex bonding configurations on Ge(100).

Keywords: phosphine; photoemission;

During the chemical vapor deposition (CVD) of Ge$_x$Si$_{1-x}$ alloys and heterostructures as well as silicon films, 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(100) surface have received much attention [1-8]. In contrast, to our knowledge, the interaction of phosphine with the Ge(100) surface has yet to be studied.

Yu, Vitkavage, and Meyerson [1,2] contended that, on the basis of thermal desorption spectroscopy (TPD), at room temperature PH$_3$ adsorption on Si(100)-2x1 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, Chen, and Yates [5] examined the PH$_3$/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)-2x1 surface to produce both PH$_n$ (n=1, 2) and H species as low as 100 K. Hamers *et al.* [6] employed Fourier transform infrared spectroscopy (FTIR) and proved that the degree of dissociation of adsorbed PH$_3$ on

Si(100) depends upon the flux and coverage during exposure. Lin, Ku, and sheu [8], 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 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(100)-2x1 and Si(100)-2x1 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(100) and Ge(100) surfaces also have the same 2x1 dimer structures. Therefore, a comparison of the thermal interaction of PH_3/Si(100) and PH_3/Ge(100) 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(100)-2x1, however partially dissociative on the more reactive Si(100)-2x1 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(100) than it does on Si(100).

Figures 1 and 2 depict P 2p core-level spectra, respectively, for Ge(100) and Si(100) surfaces after saturation exposure of phosphine at ~325 K, followed by successive anneals to higher temperatures. Figure 1(b) displays the Ge 3d spectra corresponding to Fig. 1). The line shape of the PH_3-saturated Ge(100) surface (bottom spectrum of Fig. 1) 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(100) 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 [5,6] revealed vibrational bands in HREELS and FTIR adsorption peaks for PH_n and SiH surface species upon the phosphine adsorption on Si(100)-2x1 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. 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 [11,13], 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 GP$_3$ component is attributed to the PH_3 species and without further fragmentation PH_3 molecularly adsorbs on the Ge(100)-2x1 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_3/Ge(100) system (Fig. 1), 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 PH3/Si(100) system. The binding
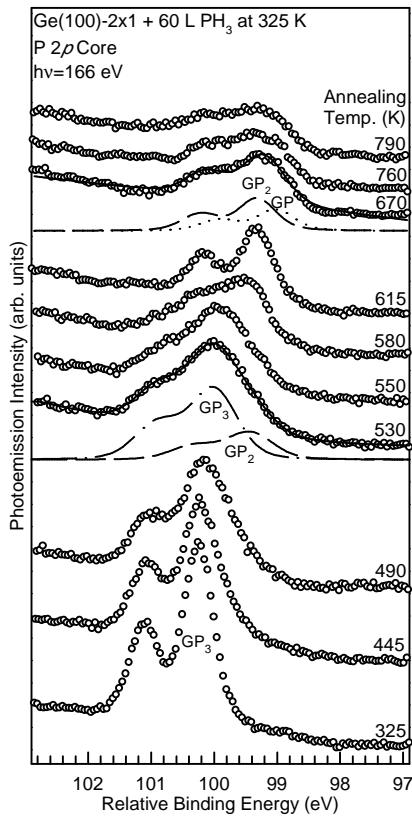
energy difference of 0.59 eV between the GP$_3$ and GP$_2$ components is similar to that between SP$_3$ and SP$_2$, thereby indicating that although only the PH$_3$ species is initially present on the Ge(100)-2x1 surface at 325 K, GP$_2$ is similarly derived from the PH$_2$ surface species and the PH$_3$ 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 decreases by 50%. This phenomena indicates that upon annealing, a large amount of molecularly adsorbed PH$_3$ desorbs, therefore, 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, ca 0.29 eV relative to SP$_2$. The spectrum consists of just one relatively sharp spin-orbit-split component (labeled SP) upon 720
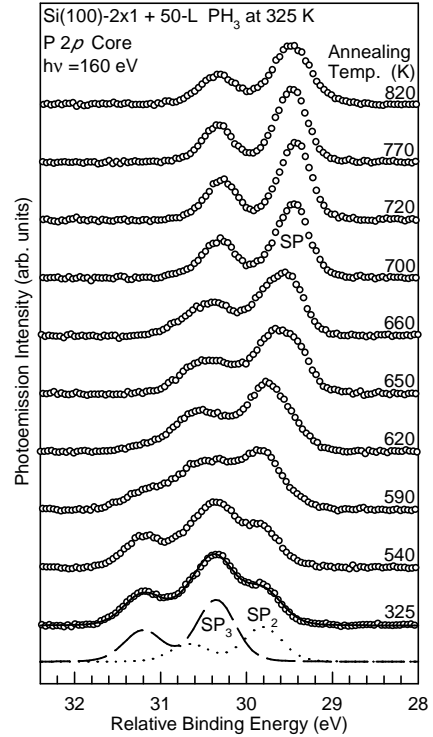
K annealing for one minute. At >650 K, HREELS spectra reveals full removal of PH$_2$ scissor mode and the P-H stretching mode [6], thus, suggesting that no P-H bond exists on the Si(100) surface. This lack of P-H bonds indicates that at this temperature range, all PH$_2$ species undergo thermal decomposition to P and H and 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(100)-2x1 surface [11], 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)

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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. Figure 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)-2x1 reveals H$_2$ desorption maximum at ~600 K [15].

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-K and 790-K annealing in Fig. 1 exhibit broad line shapes, thereby indicating that multiple phosphorus chemical bonding configurations coexist on the P/Ge(100) surface. Bottomley *et al.* [16] studied the 20-minute annealing effects on P-doped Ge(100) samples at 880K 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(100) like other similar systems, such as As, Sb/Si(100), Ge(100) do.

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