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HREELS and UPS Studies of PH_3 and PD_3 on Si(110)

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Abstract

The interaction of PH_3 with $\text{Si}(110)$ has been studied at temperatures between 120 and 880 K by UPS and HREELS. The results of HREELS measurements suggest that PH_3 molecularly adsorbs on the silicon surface at 120 K with three distinct loss peaks at 60, 130 and 296 meV, corresponding to $\nu(\text{Si-P})$, $\delta(\text{PH}_3)$ and $\nu(\text{PH}_3)$, respectively. Heating of the surface to 300 K resulted in the dissociation of PH_3 , producing SiH , PH and PH_2 species, with loss peaks near 263, ~270 and 288 meV, respectively. Further heating to 570 - 760 K caused a total loss of the 288 meV peak and the sharpening of the 263 and 270 meV peaks. At the highest surface temperature studied, 880 K, new loss peaks near 56 and 130 meV appeared. The combination of the UPS and HREELS data suggests that these loss peaks were due to the P_4 molecule adsorbed on $\text{Si}(110)$. The HREELS study of PD_3 was carried out to confirm the EELS assignments of PH_x . However, the heating of the adsorbed PD_3 resulted in the desorption, rather than the decomposition of PD_3 . This finding reveals the importance of the tunneling effect which appears to dominate the chemistry of PH_3 on $\text{Si}(110)$.

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1. Introduction

Various phosphorus compounds have been employed for semiconductor doping and chemical vapor deposition (CVD) of thin films such as InP. Phosphine (PH_3), one of the smallest stable P-compounds, has been used most commonly as a CVD source molecule [1-3]. Many studies have been made to elucidate the mechanisms of PH_3 adsorption and decomposition on different metal surfaces, such as Rh(100) [4], Rh/ Al_2O_3 [5], Ag(111) [6], Pt(111) [7], Ni(100) [8] and polycrystalline Fe [9] under UHV conditions. Some experiments have also been conducted on silicon surfaces, including polycrystalline silicon [10], Si(111) [11,12], and Si(100) [13].

At low temperatures, PH_3 may either molecularly adsorb or dissociatively adsorb on various surfaces, depending on the nature of surfaces. After thermal treatments, elementary phosphorus was observed. From the results of an XPS study, Yu et al. [13] suggested that PH_3 binds nondissociatively to Si(100) at room temperature. However, the HREELS (high resolution electron energy loss spectroscopy) results of PH_3 exposed on Si(111) [12] have indicated that mainly PH_2 and H were present on the surface at temperatures as low as 80 K.

In order to understand the interaction of PH_3 with the other low index silicon surface, we have investigated the interaction of PH_3 with the Si(110) surface. The results of this study, using HREELS and

UPS (ultraviolet photoelectron spectroscopy), are reported here. Our results indicate that, initially, PH_3 molecularly adsorbed on $\text{Si}(110)$ at 120 K; as the surface temperature was increased, H, PH, PH_2 and P species appeared on the $\text{Si}(110)$ surface. When the surface was annealed at 880 K, the final product of P_4 was identified by HREELS and UPS. A Similar HREELS of PD_3 on $\text{Si}(110)$ was also carried out in order to confirm the PH_3 peak assignments. PD_3 was, however, noted to be more stable than PH_3 on the $\text{Si}(110)$ surface. The heating of the surface resulted in the desorption rather than the decomposition of the adsorbed PD_3 molecule. This interesting observation can be understood in terms of the well-known tunneling effect associated with the fragmentation of hydrides.

2. Experimental Procedures

The experiments were performed in a UHV system (Leybold Co.) with a base pressure of 4×10^{-11} torr, as described earlier [14]. Briefly, the HREEL spectrometer was operated with an electron beam which has a primary energy of $E_p = 5$ eV and a resolution of ΔE (FWHM) = 10 meV in the straight-through mode. UPS data was collect with a He II (40.8 eV) light source using a He-discharge lamp; the CMA detector was employed on the retard mode with a fixed pass energy of $\Delta E/E = \text{constant}$.

$\text{Si}(110)$ samples from Virginia Semiconductor Co. were cut into $1.5 \times 1.0 \text{ cm}^2$ and mounted onto a sample holder with two Ta clips. After being rinsed with HF, the crystal was cleaned by successive

annealing to >1470 K under UHV conditions until no carbon impurity can be detected by HREELS. Surface temperature was monitored by the combination of pyrometer, temperature-resistance calibration curve, and Pt-chromel thermocouple under different temperature ranges as reported elsewhere [14].

PH_3 (electronic grade, 2% in He, MG industries) was dosed directly into the chamber through a 3.2 mm SS tubing, about 4 cm from the crystal. PD_3 was prepared in vacuo as follows. Dried Ca_3P_4 (Aldrich Co.) was placed in a 100 ml 3-neck round-bottom flask, which was prebaked and connected in series to 3 traps maintained at 195, 195 and 77 K. After thorough pumping and degassing, 80% D_3PO_4 in D_2O (Aldrich Co.) was slowly introduced into the sample flask through an evacuable dropping funnel. The first two dry ice traps (195 K) were used to remove vaporized D_2O ; PD_3 was collected at the final liquid nitrogen trap (77 K). Final purification was made by distilling the 77 K condensate from 195 K to 77 K. FTIR analysis of the purified PD_3 showed no detectable impurities and the D-atom enrichment was determined to be about 95%.

3. Results and Discussion

3.1. HREELS of PH_3

Figure 1 shows the temperature dependence of the HREEL spectra of 1.8 L PH_3 dosed on a Si(110) surface obtained under the specular mode. Immediately after dosing at 120 K, three loss peaks at 60, 130 and 296 meV were observed; these peaks may be

assigned to be $\nu(\text{Si-P})$, $\delta(\text{PH}_3)$, and $\nu(\text{PH}_3)$ vibrations, respectively. When the surface was warmed up to 300 K, the intensities of the peaks at 130 and 296 meV associated with the PH_3 vibrations were greatly attenuated, while the shoulder around 87 meV and the two new peaks at 263 and 288 meV appeared. Earlier Lu et al. [5] showed, in their transmission IR absorption measurement for PH_3 adsorbed on $\text{Rh/Al}_2\text{O}_3$, that PH_2 and PH stretching vibration frequencies at about 2270 cm^{-1} (281 meV) and 2230 cm^{-1} (276 meV) could be identified. Accordingly, we assigned the 288 meV peak as the PH_2 stretching vibration $\nu(\text{PH}_2)$, and the 263 meV peak as the Si-H vibration, perhaps with some contribution from the PH stretching vibration. Because of our instrument resolution ($\approx 80\text{ cm}^{-1}$ or 10 meV), we cannot distinguish these two peaks clearly. The $\nu(\text{PH}_2)$ peak at 288 meV is close to that assigned by Chen et al. [12], 280 meV for PH_2 on $\text{Si}(111)$.

As the surface was further annealed at 670-760 K, the 288 meV peak almost disappeared entirely, while the 263 meV peak increased and, at the same time, shifted to 260 meV with a shoulder appearing at 270 meV, which may be assigned to the PH stretching vibration. In the meantime, the Si-PH_x peak at 87 meV decreased significantly and new peaks at 56 and 130 meV started to grow.

When the surface was annealed at 880 K, the latter two peaks became more distinct; these two peaks were tentatively assigned as P_4 stretching vibrations. Because they compared quite favorably with the two gas-phase IR peaks of P_4 at 58 and 133 meV reported by Gutowsky et al. [16].

It should be mentioned at this juncture that an earlier TPD experiment of PH_3 on $\text{Si}(111)\text{-(7\times7)}$ by Taylor et al. [11] suggested that P_2 , instead of P_4 , may be formed as a gas-phase product. The stretching frequencies of gaseous P_2 or P_2H_4 [17] are approximately 98 meV. Chen et al. [12] has shown that at temperatures higher than 850 K, only allotropes of phosphorus were left on the surface. Due to intensity problems, they cannot identify the products.

3.2. HREELS of PD_3

In order to confirm the peak assignments for PH_3 on the $\text{Si}(110)$ surface, we also measured the HREEL spectra of PD_3 at different temperatures. Fig. 2 shows the HREELS of 1.1 L PD_3 exposed on the $\text{Si}(110)$ surface. After dosing PD_3 at 120 K, two peaks clearly appeared at 92 and 218 meV, corresponding to the PD_3 bending and PD_3 stretching vibrations, respectively [7]. However, when the surface was annealed to 550 K, the PD_3 EELS signals disappeared totally, suggesting that the PD_3 molecule desorbed completely from the surface without a detectable decomposition product as was observed in the case of PH_3 . This observation could only be accounted for by the assumption that the energy barrier for PD_3 dissociation is higher than that for the desorption process. The fact that the dissociation of adsorbed PH_3 does occur clearly suggests the importance of the tunnelling effect for the light phosphine molecule.

3.3. UPS of PH₃

Figure 3 shows a series of UPS results of 1.8 L PH₃ on Si(110). All the spectra were plotted as the difference between the dosed and post-annealed surface and the clean surface. After dosing PH₃ at 120 K, the Si(110) valence states (Fig. 3f) at about 3 eV were reduced, and two major features located at 7.2 and 12.2 eV below the Fermi level were observed (fig. 3a). According to the UPS study of PH₃ on Ag(111) by Zhu and White [6], the energy separation between P(3s) 4a₁ and P-H 2e band was 5.0 eV. This agrees exactly with our results. However, the peak around 4.0 eV due to 5a₁ P lone pair was very weak; according to gas-phase He II UPS result of PH₃ by Bock [18], it should be about 3 eV lower in binding energy than that of the 2e peak.

When the surface was annealed at 270-590 K, a shoulder at 10.7 eV started to grow. Based on the result of Greenlief et al. [4] for PH₃ on Rh(100), P(3p) resulting from the partial dissociation of PH₃ should be contributed to the 10.7 eV peak. After the surface was annealed at 670 K, the 4a₁ band intensity began to decrease, and the 4.0 eV 5a₁ band structure became stronger. The valence state of Si(110) at 2.0 eV was reestablished again, while the transition due to PH_x (x=1,2) grew weaker, which evidently resulted from the desorption of these species from the surface.

As the annealing temperature reached 870 K, a new peak appeared at 13.2 eV, and the 7.2 eV peak shifted to 6.9 eV. The energy difference between the two peaks was about the same as that

of the P_4 gas-phase He II UPS result measured by Brundle et al. [19], who assigned those two peaks to be $2e$ and $5t_2$, respectively.

4. Conclusions

The thermal stability of PH_3 on Si(110) has been studied with HREELS and UPS. PH_3 was found to molecularly adsorb on the Si(110) surface at 120 K. When the surface was warmed up to 300 K, the PH_3 molecule started to dissociate into PH and PH_2 as indicated by the disappearance of both the 130 meV $\delta(PH_3)$ and 296 meV $\nu(PH_3)$ frequencies and the growth of the peaks near 263 meV due to Si-H and P-H stretching frequencies, and the appearance of the 288 meV peak due to the PH_2 stretching vibration. When the surface was further annealed at 670-760 K, PH_2 and probably PH began to fragment further, as indicated by the decrease of the 288 meV peak and the shifting of the 263 meV peak to 260 meV, with a shoulder appearing at 270 meV. Finally at 880 K, the P species left on the Si(110) surface was concluded to be in the form of P_4 . The result of a parallel experiment with PD_3 showed that the PD_3 adsorbed on Si(110) at 120 K undergoes desorption, rather dissociation, when the surface was heated up to 550 K. This result reveals clearly the importance of the tunnelling effect, which is responsible for the dissociation of the PH_3 molecule as described above.

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Figure Captions

Fig. 1. HREELS spectra (from bottom to top) of clean Si(110), and PH_3 exposed Si(110) surface at 120 K and after heating to various temperatures then cooling to 120 K. The initial exposure was 1.8 L.

Fig. 2. HREEL Spectra (from bottom to top) of clean Si(110), and PD_3 exposed Si(110) surface at 120 K, and after heating to 550 K then cooling to 120 K. The initial exposure was 1.1 L.

Fig. 3. He (II) (40.8 eV) photoelectron Spectra of (f) clean Si(110), (a) - (e) 1.8 L PH_3 exposed Si(110) at 120 K and after heating to various temperatures then cooling to 120 K.





