

First-Principles Study of the Adsorption of PH₃ on Ge(001) and Si(001) Surfaces

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Using a first-principles pseudopotential method we have compared the adsorption and dissociation of the common *n*-type dopant molecule PH₃ on the Si(001)-(2×1) and Ge(001)-(2×1) surfaces. We find that the dissociated state is energetically more favourable than the molecular state by 1.70(0.81) eV, whereas the latter is 0.58(0.25) eV more stable than the system composed of the free silicon(germanium) surface and PH₃(g). The chemisorbed system is characterised by elongated Si-Si(Ge-Ge) dimers that are symmetric in the dissociative case and asymmetric in the molecular case and by the fact that the Si(Ge)-PH₂ as well as the PH₃(ads) groups retain the pyramidal geometry of the phosphine molecule. Our dissociative adsorption model is further supported by our calculated vibrational modes, which are in good agreement with available experimental works.

Precise control of doping is important for the fabrication of novel semiconductor devices with decreasing dimensions. Due to its chemical simplicity, phosphine gas is a very common *in situ n*-type dopant source in chemical vapour deposition (CVD) or gas-source molecular-beam epitaxy of SiGe films [1, 2]. One of the problems related with the use of phosphine as a dopant is the resultant decrease of the growth rate, degrading the throughput of the device processing. In order to elucidate this issue, the interaction of phosphine with the silicon and germanium surfaces has been the focus of many experimental works [1-7], involving different techniques. Due to its technological importance in the production of ultra-large-scale integrated circuits, the interaction process of phosphine with the silicon surface concentrates the majority of experimental studies so far. In a general sense the experimental results suggest that phosphine is molecularly adsorbed on one side of a Si (or Ge) dimer at room temperature. For low PH₃ coverages [≤ 0.18 monolayers (ML)], the molecule dissociates into PH₂ and H, with PH₂ and H at different sides of the Si or Ge dimer. For higher coverages, only a small amount of PH₃ dissociates due to the lack of empty dangling bonds. The experimental observation of molecular adsorption on the Si(001) surface is also corroborated by available theoretical works [5, 8]. However, no theoretical investigations for the adsorp-

tion of phosphine on the Ge(001) surface are available so far. Despite the great number of experimental works and some theoretical efforts for the interaction of phosphine with the silicon surface, little is known about details of the adsorption, dissociation and local geometry resulting from the interaction of phosphine with the germanium surface. This information is essential for a complete understanding of the doping mechanism.

The surface was modelled in a super-cell geometry, with an atomic slab of eight Si or Ge layers and a vacuum region equivalent to eighth atomic layers. The theoretical bulk lattice constant of 5.42 Å for Si and 5.74 Å for Ge was used in the surface calculations. On the top side of the slab we placed the PH₃ molecule in different configurations, and the back surface was passivated by H atoms arranged in a dihydride structure. The pseudopotentials for Ge, Si, P, and H were derived by using the scheme of Troullier and Martins [9] and the electron-electron exchange correlation was considered by using GGA [10]. The single-particle orbitals were expressed in a plane-wave basis up to the kinetic energy of 16 Ry and four special **k** points were used for the Brillouin-zone summation. The atoms were assumed to be in their fully relaxed positions when the forces acting on the ions were smaller than 0.005 eV/Å. The pathway from the gas-phase molecule to the ad-

sorbed state, and from the adsorbed state to the dissociated state was obtained by using a constraint dynamics scheme in which atomic movement along the pathway is a response to forces in a local region around it. The vibrational modes were calculated by using the frozen-phonon approach. In our calculations for the dynamical properties only the adsorbed system (PH_3 or PH_2+H) and the Si or Ge dimer atoms were allowed to vibrate.

It is now well established that, at low temperatures, the (001) surface of silicon and germanium exhibits a $c(4\times 2)$ reconstruction. This changes to a (2×1) reconstruction at room temperature, therefore the majority of experiments on the adsorption of phosphine are performed on the Si(001) or Ge(001)- (2×1) reconstructions (see for example Ref. [4, 5]). For this reason we will only consider the (2×1) reconstruction throughout this paper. We have determined the equilibrium geometries of the phosphine adsorbed Si and Ge(001) surfaces for the molecular (i.e. PH_3 bonded at one side of the Si(Ge) dimer as in Fig. 1(a)) and dissociated (i.e. PH_2 and H bonded to different components of the dimer as in Fig. 1(b)) models. The bridge configuration (i.e. PH_3 bonded to both Si(Ge) atoms on the Si-Si (Ge-Ge) dimer) early proposed by Wang and co-workers [3] will not be discussed in this work as we have already shown that it does not correspond to a stable adsorption configuration [8].

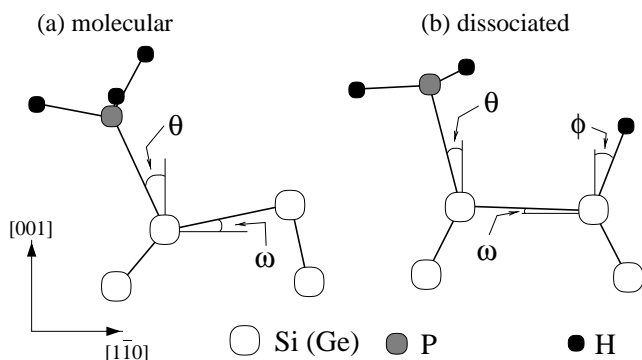


Figure 1. Schematic side view of the molecular and dissociated adsorption models for PH_3 on $X(001)-(2\times 1)$, where $X = \text{Si}$ or Ge .

We have found that the dissociative adsorption model, shown in Fig. 1(b), is energetically more favourable than the molecular state (Fig. 1(a)) by 1.70 eV for Si and 0.81 eV for Ge. Our first-principles calculations also show that the molecularly adsorbed system is 0.58 eV for Si and 0.25 eV for Ge more stable than the system composed of the free surface and $\text{PH}_3(\text{g})$, suggesting that the molecularly adsorbed system corresponds to a meta-stable configuration. This is in agreement with experimental observations of a

molecular adsorption followed by the dissociation under low coverage exposure (see, for example, Ref. [7]). In Fig. 2 we present the energy diagram obtained for a probable dissociative pathway considering a lower coverage adsorption. Along the path from the gas-phase PH_3 (I) to the molecularly adsorbed state (II), there is no adsorption barrier. This spontaneous process is mainly due to the energetically favourable hybridization between the lone-pair state of PH_3 and the empty dangling bond state of the down atom on the Si or Ge dimer. The energy barrier for the adsorbed molecular phase PH_3 (II) to dissociate into PH_2 and H (IV) was found to be 0.31 eV for Si but 0.72 eV for Ge. The peak of the dissociation barrier corresponds to a transition state represented in Fig. 2 (III).

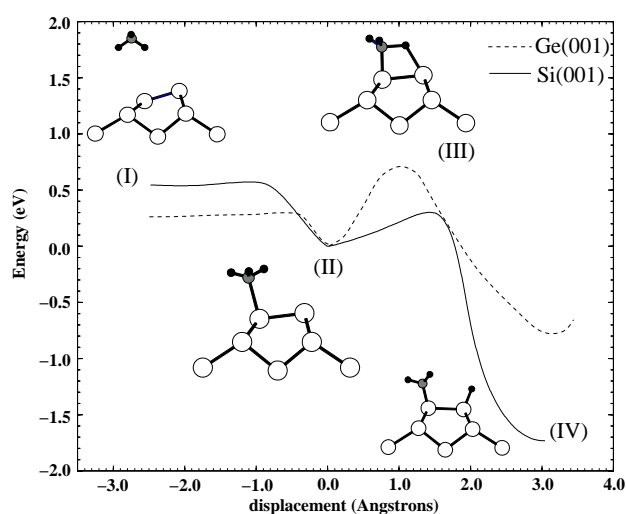


Figure 2. Calculated energy barrier diagram for the dissociative adsorption process of PH_3 on $X(001)-(2\times 1)$, where $X = \text{Si}$ or Ge : (I) corresponds to $X(001)-(2\times 1) + \text{PH}_3(\text{gas})$; (II) corresponds to $X(001)-(2\times 1) + \text{PH}_3(\text{ads})$ (molecular adsorption); (III) corresponds to the transition state and (IV) corresponds to $X(001)-(2\times 1) + \text{PH}_2(\text{ads}) + \text{H}(\text{ads})$ (dissociative adsorption)

Considering the phenomenological approach in the form of the Arrhenius equation [11], with the choice for the A-factor between $10^{13} - 10^{15} \text{ s}^{-1}$, we have estimated that, for complete dissociation, an activation barrier of 0.31 eV (0.72 eV) corresponds to a thermal activation in the range 104–120 K (241–278 K). This is consistent with the experimental dissociation of PH_3 on the silicon surface even at 100 K [4] observed at low coverage. Our results also indicate that, for the germanium surface, the phosphine molecule dissociates at room temperature. However, as shown in Fig. 2, for the Ge based system desorption is more favourable than the dissociation process. We would like to re-emphasise that the energy barrier presented here does not necessarily correspond to the experimentally observed process, as

a great number of different pathways may be allowed during the dissociation of the molecule.

In Table I we present our calculated structural parameters obtained for the molecular and dissociated adsorption models of PH_3 on $\text{Si}(001)$ and $\text{Ge}(001)-(2\times 1)$ as well as some available theoretical data [5] for the silicon based system. Our results are in good agreement with the first-principles calculations by Kipp *et al* [5]. Upon the adsorption of phosphine, while for the silicon based system the dimers get elongated by $\sim 6\%$, for the germanium based system, we observe that the dimer elongation is much smaller: $\sim 2\%$. In both cases, for the molecular adsorption the Si-Si and Ge-Ge dimer retains its asymmetric configuration, while for the dissociated system it becomes almost symmetric. For the molecular model we calculated a Si-P (Ge-P) bond length of 2.35 Å (2.49 Å) in contrast to a much smaller value of 2.27 Å (2.38 Å) obtained for the dissociated model. The weakening of the Si-P (Ge-P) bond observed for the molecular model is probably related to charge transfer from phosphorus to silicon and germanium. With respect to the surface normal, we calculated the inclination of the Si-P (Ge-P) bond as $\theta=25.6^\circ$ (30.5°) for the molecular model, but only 13.5° (15.4°) for the dissociated model. We believe that this difference arises from the difference of the dimer tilt angles between the molecular and dissociated cases. In addition, we have found that the PH_3 as well as the $\text{PH}_2\text{-Si}(\text{Ge})$ species preserve the trigonal character of the free molecule.

Table I. Structural parameters for the molecular and dissociated adsorption models of PH_3 on $\text{X}(001)-(2\times 1)$, where $\text{X} = \text{Si}$ or Ge . The symbols are explained in Fig. 1.

bond leng. (Å)	molec.		dissoc.	
	X=Si	X=Ge	X=Si	X=Ge
X-X	2.38	2.57	2.39	2.54
X-P	2.35	2.49	2.27	2.38
X-H			1.51	1.57
P-H	1.45	1.46	1.46	1.46
bond ang. ($^\circ$)				
X-X (ω)	12.0	15.4	1.4	0.7
X-P (θ)	25.6	30.5	13.5	26.1
X-H (ϕ)			20.7	20.4
H-P-H	99.4	98.5	92.5	91.4

For calculating the zone-centre optical phonon frequency modes we set up a 36×36 eigenvalue problem, and only selected modes that describe a pronounced surface character. The results for our calculated zone-centre vibrational modes for stretch, bend and scissors

modes are presented in Table 2. The decrease of the X-P stretch mode as X changes from Si to P is consistent with the mass trend generally observed. The strongest experimental indication of the dissociative character of the interaction of phosphine with the silicon surface is the detection of Si-H stretch mode immediately after exposing $\text{Si}(001)$ to PH_3 , as suggested by Shan *et al* [6]. Our first-principles calculations further support this dissociative adsorption model as we have identified the Si-H stretch mode at 2049 cm^{-1} , in very good agreement with the experimental values obtained using HREELS [4] (2100 cm^{-1}) and FTIS [6] (2097 cm^{-1}).

In summary, we have performed *first principles* calculations for the atomic structure and dynamical properties of the adsorption of PH_3 on the $\text{Si}(001)-(2\times 1)$ and $\text{Ge}(001)-(2\times 1)$ surfaces. We find that the dissociated state is energetically more favourable than the molecular state by 1.70(0.81) eV, whereas the latter is 0.58(0.25) eV more stable than the system composed of the free silicon(germanium) surface and $\text{PH}_3(\text{g})$. We have presented the energy diagram obtained for a possible reaction pathway from the gas-phase PH_3 to the molecularly adsorbed state and then to the dissociated state, and estimate that the complete dissociation occurs at temperatures around 110 K for silicon and 240 K for germanium. The chemisorbed system is characterised by elongated Si-Si(Ge-Ge) dimers that are symmetric in the dissociative case and asymmetric in the molecular case and by the fact that the Si(Ge)- PH_2 as well as the $\text{PH}_3(\text{ads})$ groups retain the pyramidal geometry of the phosphine molecule. Our dissociative adsorption model is further supported by our calculated vibrational modes, which are in good agreement with available experimental works.

Table II. Zone center vibrational modes, in cm^{-1} , for the dissociated adsorption models of PH_3 on $\text{X}(001)-(2\times 1)$, where $\text{X} = \text{Si}$ or Ge .

	P-H	X-H	P-H	X-H	X-P
	stretch	stretch	scissors	bend	stretch
X=Si	2162	2049	955	628	467
X=Ge	2105	1949	961	553	324

Acknowledgments

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