First-Principle Study of Phosphine Adsorption on Si(001)-2×1-Cl

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This paper presents a DFT study for phosphine adsorption on a Si(001)-2×1 surface covered by a chlorine monolayer, including adsorption on local defects, i.e. mono- and bivacancies in the adsorbate layer (Cl, Cl2), and combined vacancies with removed silicon atoms (SiCl, SiCl2). Activation barriers were found for the adsorbing PH3 to dissociate into PH2+H and PH+H2 fragments; it was also established that phosphine dissociation on combined vacancies is possible at room temperature. If there is a silicon vacancy on the surface, phosphorus settles in the Si(001) lattice as PH (if the vacancy is SiCl) or as PH2 (if the vacancy is SiCl2). This paper suggests a method to plant a separate phosphorus atom into the silicon surface layer with atomic precision, using phosphine adsorption on defects specially created on a Si(001)-2×1-Cl surface with an STM tip.

I. INTRODUCTION

Developing atomic-scale nanoelectronic components, in particular building blocks for the quantum computer on nuclear spins of phosphorus in Si1, requires methods for incorporating single impurity atoms into silicon. STM lithography — to date, the most precise method of manipulating a solid surface — offers such a possibility by creating or deleting atomic structures with pinpoint impacts of a scanning tunneling microscope (STM) tip. In Ref.1, a chemisorbed hydrogen monolayer is used as the resist for a Si(001)-2×1 surface. First the mask is prepared by electron-stimulated desorption of selected hydrogen atoms with an STM tip, then phosphine (PH3) is adsorbed on the masked surface, with PH3 adsorbing only to places free of hydrogen. As this surface is heated to 350°C, the phosphine molecule dissociates, and a phosphorus atom is incorporated into the Si(001)-2×1 atomic lattice.

Chlorine monolayer on a silicon surface may also be considered as a resist for STM lithography. The difference between the chlorine and hydrogen monolayers is most pronounced in thermal desorption experiments: SiCl2 compound removes from the Si(001)-2×1-Cl surface2,3, while hydrogen desorbs from Si(001)-2×1-H as H2 molecule.4 Therefore, one can expect that as a result of electron-stimulated desorption of chlorine atom from monolayer, atomic defects containing a silicon vacancy will be created by STM tip.

The aim of the work is to study PH3 interaction with Si(001)-2×1-Cl surface (with and without vacancies) in order to predict the possibility to utilize chlorine resist for phosphorus incorporation into silicon lattice. Phosphine adsorption on clean Si(001) surface is a broadly discussed (see Ref.2 and Refs. therein) and well-researched topic. Adsorption of phosphine on hydrogenated Si(001) surface with defects was considered for studying the incorporation of phosphorus atom into the silicon lattice.5 However, no effort has to our knowledge been spent so far on phosphine interaction with a Si(001) surface whose electron structure was modified by chemisorbed chlorine.

This paper presents the results of theoretical inquiries into PH3 adsorption on an ideal chlorinated Si(001)-2×1 surface and the same surface with local defects — Cl, Cl2, SiCl, and SiCl2 vacancies. We have created DFT models of atomic structures containing a PH3 molecule and PH2 and PH dissociation fragments; established the most beneficial atomic configurations for each of these defects; mapped the possible ways of PH3 dissociation; and found the corresponding activation barriers. On the basis of this data, we discuss the process of implanting a phosphorus atom into a silicon lattice as a result of phosphine adsorption on atomic defects in Si(001)-2×1-Cl.

II. METHOD

Spin polarized calculations were made on the basis of the density functional theory (DFT) as provided by the VASP software package.6 We used generalized gradient approximation (GGA), PBE exchange correlation functionals,7,8 and Grimme corrections to van der Waals interactions.9 The Si(001)-2×1 surface was modeled by periodic 4×4 cells. Each cell contained eight silicon atomic layers, the three bottom layers are fixed. Chlorine atoms and a phosphine molecule were placed on the top of the slab, while the bottom surface was covered with hydrogen. The slabs were separated by a vacuum spacing of 15 Å.

The PH3 adsorption energy was calculated as the difference between the total energy of a chlorinated surface Si(001)-2×1-Cl with the adsorbate (E_{PH_3+surf}) and the total energies of the Si(001)-2×1-Cl surface (E_{surf}) and a PH3 molecule in the gaseous phase (E_{PH_3}):

\[ E_a = E_{PH_3+surf} - E_{surf} - E_{PH_3}. \] (1)

The underlying assumption was that the atomic defects had been created on the Si(001)-2×1-Cl before the PH3 adsorption (e.g., with an STM tip), therefore equation (1) did not include the energy spent on creating them.

Activation barriers (E_{act}) were calculated using the NEB (nudged elastic band) method provided within VASP.
III. RESULTS AND DISCUSSION

Since there are no studies of phosphine adsorption on chlorinated silicon surface, we tested our calculation method on a well-studied PH$_3$/Si(001)-c(4×2) system. The ground state of an atomically clean Si(001) surface is the c(4×2) reconstruction, in which dimers in neighboring rows are tilted in opposite directions. Our values for Si interatomic distances in a dimer (2.36 Å) and the dimer tilt angle (18°) on a clean Si(001)-c(4×2) surface are in good agreement with experimental data and other calculations (see, e.g., Refs. therein). It is known that at room temperature, PH$_3$, as it adsorbs on a Si(001), dissociates into PH$_2$ + H in the first stage of the reaction, with the PH$_2$ + H adsorption energy on Si(001) calculated theoretically somewhere between −1.88 eV and −2.29 eV (see ref. and Refs. therein). Our calculated value $E_a = −2.03$ eV is in good agreement with previous calculations and with an experimental estimate of −1.8 eV made in Ref. on the basis of thermal-desorption spectroscopy data. Distance $d$ from a P atom to the nearest Si atom was 2.28 Å, from a dissociated H atom to the Si atom $d$(Si-H) = 1.50 Å, from a P atom to the H atom in the PH$_2$ fragment $d$=1.44 Å ($d$(P-H) = 1.43 Å in a free PH$_3$ molecule).

A. PH$_3$ adsorption on Si(001)-2×1-Cl

After a Si(001) surface is chlorinated, the c(4×2) reconstruction is partially removed and changed into the (2×1) reconstruction. Our calculated value for the bond length $d$(Si-Cl) is 2.07 Å, which is in agreement with both experimental and theoretical data. The distance between the Si atoms in a dimer increases by 0.07 Å after chlorine adsorption ($d$(Si-Si) = 2.43 Å). We also calculated the energies and activation barriers for phosphine adsorption and dissociation for an ideal (defect-free) Si(001)-2×1-Cl surface and for the same surface with vacancy defects Cl, Cl$_2$, SiCl and SiCl$_2$. For the ideal surface, we looked at two PH$_3$ adsorption scenarios: the molecules adsorbs on top of or under the chlorine layer. For a defected surface (Cl, Cl$_2$, SiCl, SiCl$_2$ vacancies), we looked at PH$_3$ adsorption and dissociation in all possible scenarios, of which only those were included in the paper whose final state is more preferable than the initial state.

1. Defect-free Si(001)-2×1-Cl

The adsorbed PH$_3$ molecule remains close to the surface (Fig. 1a). There is almost no interaction with chlorine ($E_a = −0.01$ eV), and the distance from the P atom to the nearest Cl atom is 3.63 Å. The molecule is adsorbed without any activation barrier and does not dissociate.

A study of interaction between ammonia (NH$_3$) and a Si(001)-2×1 chlorinated surface demonstrated that embedding of an NH$_2$ fragment instead of a chlorine atom is possible (with formation of HCl molecule) if NH$_3$ is incorporated under the chlorine layer. Our calculated energy values for PH$_3$ on-top adsorption (−0.01 eV, Fig. 1a), PH$_3$ adsorption under the chlorine layer between Si dimer rows (0.40 eV, Fig. 1b), and the adsorption of a PH$_2$ fragment bound to a Si atom with a HCl molecule close to the surface (0.42 eV, Fig. 1c), are close to values reported in Ref. for the energies of initial (−0.02 eV), transitional (0.40 eV) and final (0.45 eV) states of substituting NH$_2$ instead of a Cl atom with HCl molecule formation. This suggests that the transitional state energies of NH$_3$ and PH$_3$ on Si(001)-2×1-Cl may also be approximately the same. Our calculated initial, transitional, and final state PH$_3$ adsorption energies, and activation barrier data from Ref. bring us to a conclusion that a PH$_2$ fragment can only be placed on Si(001)-2×1-Cl instead of a Cl atom if it overcomes the activation barrier of ≈1.6 eV. Thus, reaction of substitution a PH$_2$ fragment instead of a Cl atom on an ideal Si(001)-2×1-Cl surface is endothermic ($E_a > 0$ in the final state) and unfavorable.

2. Si(001)-2×1-Cl with a single vacancy in a chlorine monolayer

As a phosphine molecule is adsorbed into a single vacancy in a chlorine monolayer on Si(001)-2×1-Cl, PH$_3$ takes the place vacated by a chlorine atom (Fig. 2a). There is no activation barrier for phosphine adsorption. The calculated Si-P bond length is 2.31 Å, distance $d$(P-H) = 1.41 Å.

Phosphine, dissociating in a single chlorine vacancy to produce a PH fragment, also necessarily produces an H$_2$ molecule (Fig. 2b) because there are no more chlorine-free places on the surface. This PH + H$_2$ dissociation
is unfavorable because the adsorption energy of this system ($E_a = -0.21$ eV) is smaller than the energy of the adsorbed PH$_3$ molecule ($E_a = -0.91$ eV).

3. **Si(001)-2×1-Cl with a double vacancy in a chlorine monolayer**

Figure 3a shows a PH$_3$ molecule adsorbed on a Si-Si dimer free of chlorine atoms. A phosphorus atom is bound to one of the silicon atoms. The Si-P bond length is 2.30 Å ($d$(P-H) = 1.41 Å); the adsorption energy is $-1.37$ eV; there is no activation barrier (Fig. 3a). However, a phosphine molecule in a double chlorine vacancy can dissociate into PH$_2$ and H fragments and thus create the most energetically favorable state ($E_a = -2.37$ eV, Fig. 3b). The dissociation process goes through an intermediate state shown in Fig. 3b and requires an activation energy of 0.25 eV. While on a clean Si(001)-c(4×2) surface, PH$_2$ dissociates further into PH or PH$_3$, it is not preferable for it to do so on a chlorinated surface because there are no unoccupied space for the hydrogen atoms. Nonetheless, there is yet another state with a negative adsorption energy (Fig. 3c), in which a PH fragment occupies a bridge position over the Si-Si dimer ($d$(Si-P) = 2.29 Å), while the remaining hydrogen atoms form an H$_2$ molecule. This state ($E_a = -1.30$ eV) is less preferential than phosphine molecule adsorption ($E_a = -1.37$ eV). From this adsorption site, the phosphorus atom can (in principle) migrate to the position between two silicon dimers, so that the P atom is bound to three Si atoms (one Si atom of each dimer and one Si atom of underlying layer) and H atom remains on the free silicon atom. Note, this position is the most favorable on a clean silicon surface. However, in the presence of only one chlorine-free Si dimer, this state is less favorable than those shown in Fig. 3 because one of the Si atoms bound to P is also bound to one chlorine atom. This is in agreement with the finding that three free dimers on a Si(001)-c(4×2) surface are required for full phosphine dissociation.

4. **Si(001)-2×1-Cl with a combined SiCl vacancy**

In phosphine adsorption into combined vacancies in which both silicon and chlorine have been removed, a phosphine molecule approaching such a Si(001)-2×1-Cl surface may create a single bond either with a lower-layer silicon atom (Fig. 4a) or with the remaining silicon atom of a broken dimer (Fig. 4b) because PH$_3$ can not create bonds to two Si atoms. There is no activation barrier in both cases but the latter option is more preferable (its $E_a = -1.09$ eV against the former option’s $E_a = -0.79$ eV). Bonded to the top Si atom (Fig. 4c), the phosphine molecule dissociates into PH + H$_2$ (Fig. 4d) with almost no activation barrier ($E_{act} = 0.02$ eV). If the phosphine molecule is bonded to a lower-layer silicon atom (Fig. 4b), its dissociation results in the same final state (Fig. 4c) but only over an activation barrier of 0.13 eV (Fig. 4d). The structure in which the PH fragment is incorporated into the silicon lattice and an H$_2$ molecule is formed (Fig. 4d) is the most preferable ($E_a = -2.64$ eV, phosphorus bond lengths to two lower-layer silicon atoms are 2.32 Å, to the dimer Si atom 2.37 Å, to the hydrogen atom 1.42 Å).

5. **Si(001)-2×1-Cl with a combined SiCl$_2$ vacancy**

As for a SiCl vacancy, the phosphine molecule is adsorbed into a SiCl$_2$ vacancy either through bonding to a lower-layer silicon atom (Fig. 5a), or occupying a position close to a silicon atom in broken dimer (Fig. 5b). Nei-
Figure 4: Structures (top view and side view) and adsorption energies of phosphine and its fragments into a combined SiCl vacancy on Si(001)-2×1-Cl: (a) PH$_3$ molecule adsorbed on lower-layer silicon atom; (b) intermediate state in the process of PH$_3$ dissociation into PH + H$_2$ (c); (d) PH$_3$ molecule adsorbed on the remaining silicon atom of a broken dimer. Another process has an activation barrier. A PH$_3$ molecule in a SiCl$_2$ vacancy can transfer one hydrogen atom to the broken-bond silicon atom, while the remaining PH$_2$ fragment can meanwhile form two bonds to silicon atoms from the lower layer (Fig. 4b). The adsorption energy is minimal in this state ($E_a = -2.66$ eV), the Si-P bond lengths are Å ($d$(P-H) = 1.42 Å). PH$_3$ dissociation into PH$_2$ + H requires activation energies of 0.11 eV (Fig. 4b) and 0.50 eV (Fig. 4c), respectively. Note that the reaction paths with the HCl molecule formation are less favorable than the pathways with the H$_2$ formation for the Si(001)-2×1-Cl surface with Cl, Cl$_2$, and SiCl vacancies.

Figure 5: Structures (top view and side view) and adsorption energies of phosphine and its fragments into a combined SiCl$_2$ vacancy on Si(001)-2×1-Cl: (a) PH$_3$ molecule bound to a lower-layer silicon atom; (b) intermediate state between (a) and (c); (c) the most preferable state after PH$_3$ dissociation into PH$_2$ and H; (d) PH$_3$ molecule bound to a broken-bond dimer silicon atom; (e) intermediate state between (d) and (c).

Figure 5: Structures (top view and side view) and adsorption energies of phosphine and its fragments into a combined SiCl$_2$ vacancy on Si(001)-2×1-Cl: (a) PH$_3$ molecule bound to a lower-layer silicon atom; (b) intermediate state between (a) and (c); (c) the most preferable state after PH$_3$ dissociation into PH$_2$ and H; (d) PH$_3$ molecule bound to a broken-bond dimer silicon atom; (e) intermediate state between (d) and (c).

B. Incorporating a phosphorus atom into the Si(001) lattice

If hydrogen resist is used on Si(001), it is only possible to plant a phosphorus atom on a Si(001) surface with an error of several lattice spacings because three free silicon dimers are required for PH$_3$ dissociation, and as the surface is heated up, any of the neighboring substrate atoms may be substituted by phosphorus atom. This precision is sufficient to create a single electron transistor to read the qubit state but not to create a network of qubits, where phosphorus atoms must be incorporated exactly into the positions of specifically selected silicon atoms. In Refs. 16,19, it was demonstrated that, if two neighboring phosphorus atoms are not located precisely along high-symmetry directions on a silicon surface (diverging from that line by one or several lattice spacings), the exchange interaction between them oscillated and decreased exponentially, which is a serious problem in the way of creating a two-qubit register of a quantum computer.

We suggest a procedure for incorporating phosphorus atoms into the top Si(001)-2×1 layer with atomic precision. It is based on two operations. The first one is STM lithography on Si(001) surface with a chlorine monolayer used as the resist to create atomic defects containing a silicon vacancy. We believe that there is a controlled way to create vacancies with silicon atoms for Si(001)-2×1-Cl surfaces. The second operation is phosphine adsorption on defects containing silicon vacancies. According to our calculations summarized below, phosphine adsorption on such defects results in incorporating a phosphorus atom exactly into the site previously occupied by a silicon atom removed with an STM tip.

As phosphine is adsorbed onto a perfect Si(001)-2×1-Cl surface, there is little interaction between the gas and the chlorine monolayer because the PH$_3$ adsorption energy is close to zero (−0.01 eV). A phosphine molecule dissociation, so that the PH$_2$ fragment is put into the place of a chlorine atom and an HCl molecule is formed, is endothermic process and requires an activation energy of about ∼ 1.6 eV, which makes this process unfavorable at room temperature.

If there is a single vacancy in the chlorine monolayer, the phosphine molecule settles into the vacant place and
does not dissociate. If there is a double vacancy in the chlorine monolayer, i.e. the phosphine molecule is adsorbed onto a free Si-Si dimer, it dissociates into PH$_2$ and H at room temperature (the activation energy is 0.25 eV). In this case P atom incorporation into silicon surface layer requires two additional Si dimers free from Cl atoms and heating to 350 °C.

At room temperature, phosphine adsorption onto a Si(001)-2×1-Cl surface with combined vacancies (SiCl or SiCl$_2$) results in phosphine dissociation, with the fragments taking the most favorable positions: PH in the SiCl vacancy, PH$_2$ + H in the SiCl$_2$ vacancy. The adsorption into the SiCl and SiCl$_2$ vacancies ($E_a = -2.64$ eV and $E_a = -2.66$ eV, respectively) are more preferable than into the Cl and Cl$_2$ vacancies ($E_a = -0.91$ eV and $E_a = -2.37$ eV, respectively). Thus, it is possible to incorporate a phosphorus atom into a silicon lattice at room temperature as part of a PH fragment adsorbed on a SiCl vacancy or PH$_2$ fragment adsorbed on a SiCl$_2$ vacancy without undesirable heating, which is not possible if chemisorbed hydrogen is used as the resist.

The resulting surface is Si(100) under a chlorine monolayer, with phosphorus atoms embedded in the silicon lattice. One or two hydrogen atoms may be bound with each phosphorus atom. To use these phosphorus atoms as quantum computer elements (such as registers, wiring, or convertors), chlorine and hydrogen should be removed, and a sufficiently thick crystalline silicon layer (25 to 50 nm) should be grown on top of the surface enough to minimize the impact of the surface on computing operations.

**IV. CONCLUSIONS**

On the basis of DFT modeling, we studied phosphine adsorption on Si(001)-2×1-Cl surface, including surface with Cl, Cl$_2$, SiCl, and SiCl$_2$ vacancies. We have demonstrated that it is possible to incorporate a phosphorus atom into the silicon lattice if phosphine is adsorbed into defects with a silicon vacancy. We found that phosphorus is best positioned to occupy the vacant place in the lattice as part of a PH fragment in a SiCl vacancy (Fig. 4) or as part of a PH$_2$ fragment in a SiCl$_2$ vacancy (Fig. 5). Phosphine molecules adsorbed on a chlorinated defect-free Si(001)-2×1-Cl surface are not bound to silicon.

Our calculations confirm that it is possible to incorporate a phosphorus atom precisely into a specific place of the silicon lattice on Si(001)-2×1 through a chemisorbed chlorine monolayer mask. As we have demonstrated, operationally this requires a specific type of vacancies on the Si(001)-2×1-Cl surface, and we expect STM lithography to create specific types of defects to be developed.

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1. Kane, B. E. A Silicon-based Nuclear Spin Quantum Computer. *Nature* 1998, 393, 133–137.
2. O’Brien, J. L.; Schofield, S. R.; Simmons, M. Y.; Clark, R. G.; Dzurak, A. S.; Curson, N. J.; Kane, B. E.; McAlpine, N. S.; Hawley, M. E.; Brown, G. W. Towards the Fabrication of Phosphorus Qubits for a Silicon Quantum Computer. *Phys. Rev. B* 2001, 64, 161401R.
3. Szabó, A.; Engel, T. Etching of Si Surfaces With Hot Chlorine Beams: Translational and Vibrational Excitation of the Incident Chlorine Particles. *J. Vac. Sci. Technol. A* 1994, 12, 648–657.
4. Andryushcheokin, B. V.; Eltsov, K. N.; Kuzmichev, A. V.; Shevylyuga, V. M. Electron-induced Interaction of Condensed Chlorine with Si(100). *Phys. Wave Phen.* 2010, 18, 303–304.
5. Sinniah, K.; Sherman, M. G.; Lewis, L. B.; Weinberg, W. H.; Yates, J. T. Jr.; Janda, K. C. Hydrogen Desorption from the Monohydride Phase on Si(100). *J. Chem. Phys.* 1990, 92, 5700–5711.
6. Warschikow, O.; Curson, N. J.; Schofield, S. R.; Marks, N. A.; Wilson, H. F.; Radny, M. W.; Smith, P. V.; Reusch, T. C. G.; McKenzie, D. R.; Simmons, M. Y. Reaction Paths of Phosphine Dissociation on Silicon (001). *J. Chem. Phys.* 2016, 144, 014705.
7. Kresse, G.; Hafner, J. Ab initio Molecular Dynamics for Liquid Metals. *Phys. Rev. B* 1993, 47, 558–561.
8. Kresse, G.; Furthmuller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B* 1996, 54, 11169–11186.
9. Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* 1996, 77, 3865–3868.
10. Grimme, S.; Semiempirical GGA-type Density Functional Constructed with a Long-Range Dispersion Correction. *J. Comput. Chem.* 2006, 27, 1787–1799.
11. Jonsson, H.; Mills, G.; Jacobsen, K. W. Classical and Quantum Dynamics in Condensed Phase Simulations; World Scientific: Singapore, 1998.
12. Yokoyama, T.; Takayanagi, K. Anomalous Flipping Motions of Buckled Dimers on the Si(001) Surface at 5 K. *Phys. Rev. B* 2000, 61, R5078–R5081.
13. Monch, W. *Semiconductor Surfaces and Interfaces*; Springer-Verlag: Berlin, 2001.
14. Lange, B.; Schmidt, W. G. Ammonia Adsorption on Cl/Si(001): First-Principles Calculations. *Surf. Sci. 2008*, 602, 1207–1211.
15. Colaianni, M. L.; Chen, P. J.; Yates, J. T. Jr. Unique Hydride Chemistry on Silicon–PH$_3$ Interaction with Si(100)-(2×1). *J. Vac. Sci. Technol. A* 1994, 12, 2995–2998.
16. Lee, Ji Young; Kang, Myung-Ho. First-Principles Study of the Cl and Br Adsorbed Si(100) Surfaces *Phys. Rev. B* 2004, 69, 113307.
17. Watson, T. F.; and Weber, B.; House, M. G.; and Büch,
H.; Simmons, M. Y. High-Fidelity Rapid Initialization and Read-Out of an Electron Spin via the Single Donor $D^-$ Charge State. *Phys. Rev. Lett.* **2015**, *115*, 166806.

18 Koiller, Belita; Hu, Xuedong; Das Sarma, S. Exchange in Silicon-Based Quantum Computer Architecture. *Phys. Rev. Lett.* **2002**, *88*, 027903.

19 Gamble, John King; Jacobson, N. Tobias; Nielsen, Erik; Baczewski, Andrew D.; Moussa, Jonathan E.; Montaño, Inés; Muller, Richard P. Multivalley Effective Mass Theory Simulation of Donors in Silicon *Phys. Rev. B* **2015**, *91*, 235318.