Magnetism on the boron-doped Si(111)-$\sqrt{3} \times \sqrt{3}$ surface

Chang-Youn Moon, Daejin Eom, and Ja-Yong Koo
Quantum technology institute, Korea Research Institute of Standards and Science, Yuseong, Daejon 34113, Republic of Korea

Abstract

We investigate the possible magnetism on the Si(111)-$\sqrt{3} \times \sqrt{3}$ surface, which is stabilized for highly boron-doped samples, by using first-principles calculations. When the silicon adatom on top of a boron atom is removed to form a defect structure, three silicon dangling bonds are exposed generating half-filled doubly degenerate energy levels in the band gap which stabilizes a local magnetic moment of 2 $\mu_B$. When there are many such defect structures adjacent one another, they are found to align antiferromagnetically. However, we demonstrate that the ferromagnetism can be stabilized by adjusting the number of electrons in defects, suggesting a possibility towards spintronic applications of this unique silicon surface structure.

PACS numbers: 71.15 Mb, 71.55.Cn, 71.70.Gm, 75.30.Hx

Keywords: Density-Functional Theory, silicon, defect, exchange interaction, ferromagnetism, spintronics

*Electronic address: cymoon@kriss.re.kr
I. INTRODUCTION

Exploiting the spin as well as charge degrees of freedom of materials in information processing, nowadays often referred to as spintronics, composes one of the major parts of modern day condensed matter physics and materials science, as it is considered as a promising candidate to overcome the limiting factors of conventional semiconductor technologies based on utilizing only the charge degree of freedom. Materials used for this purpose should be magnetically ordered, in most cases ferromagnetically, which can produce the spin-polarized current. The majority of efforts to obtain a magnetically ordered state has been made using conventional magnetic materials containing 3d-active elements such as Mn, Fe, Co, etc., as the strong intra-atomic Coulomb interaction within localized 3d orbitals tends to induce the local magnetic moment. In these materials, the magnetic elements are periodically ordered to form a crystal or at least incorporated as impurities as in the case of diluted magnetic semiconductors, mostly with compound semiconductors such as ZnO, TiO2, and GaAs, etc., as host [1–3].

Meanwhile, magnetism originating purely from atomic s and/or p orbitals has not been reported very often, with past few studies mostly based on the carbon-based nanostructures [4–6]. If a magnetic ordering can be realized in a technologically more mature and versatile material such as silicon, spintronic applications would develop much faster and in more diverse ways. Authors of the present paper has been studying peculiar structural and electronic properties of the Si(111)-√3 × √3 surface, which is stabilized for highly boron-doped samples [7]. In this surface, a top silicon atom, or silicon adatom (Si_{ad}), is triply coordinated with other silicon atoms underneath which in turn are bonded to a boron atom below [8] (see Fig. 1). It was found that the position of Si_{ad} is the key to switching between two very distinct quantum states, with which the possible application to a very high-density memory device was demonstrated using the scanning tunneling microscopy (STM) technique [9]. Regarding Si_{ad}, further interesting question would be what happens when we remove a Si_{ad} leaving three adjacent partially-filled dangling bonds of underneath silicon atoms, which seems promising for holding a large local magnetic moment.

In the present work, we perform a theoretical study of the magnetic properties of boron-doped Si(111)-√3 × √3 surface using first-principles calculations based on the density-functional theory. Si_{ad} vacancy (V_{Si_{ad}}), a defect structure with the missing Si_{ad}, has three
dangling-bond orbitals from each of the three silicon atoms, which are filled with two electrons in total. Spin-polarized calculation reveals that a net magnetic moment of 2 $\mu_B$, which is equally distributed over the three dangling-bond orbitals, is stabilized for an isolated V$_{Siad}$. When there are series of the defect structures adjacent with one another, the anti-parallel arrangement of magnetic moments turns out to be more stable than the parallel alignment, as expected for the exchange interaction among half-filled orbitals. We further investigate the doping dependence of the exchange interaction between the defects, and find that the hole doping enhances the relative stability of the ferromagnetic (FM) ordering with respect to that of the antiferromagnetic (AFM) ordering, and over 0.1 hole per defect eventually the FM state becomes more stable than the AFM one. Our result suggests a new possibility for the spintronic application of silicon, the most well understood and widely used conventional semiconductor.

II. COMPUTATIONAL DETAIL

Our first principles calculations are based on the density functional theory with the PAW potential [10, 11] as implemented in the VASP code [12, 13]. Electronic wave functions are expanded with plane waves up to a cutoff energy of 318 eV. A slab structure of 10 silicon monolayer thick (16 Å) which consists of $2 \times 2$ primitive units of the $\sqrt{3} \times \sqrt{3}$-surface structure including 4 boron atoms, is constructed to mimic the Si (111) surface, where the dangling bonds on the bottom silicon layer are passivated by hydrogen atoms. A vacuum region of about 7 Å separates the slab and its periodic images along the surface normal direction. We adopt the experimental lattice constant in determining the in-plane supercell dimensions, and all the surface structures studied in this work are fully relaxed both for spin-unpolarized and polarized calculations if not indicated otherwise, except for the silicon atoms on the bottom layer representing the rigidity of the bulk region. The K-point sampling is performed on a $8 \times 8 \times 1$ Monkhorst-Pack grid [14].

III. RESULT AND DISCUSSION

Fig. 1 depicts the atomic structure of Si(111)-$\sqrt{3} \times \sqrt{3}$ surface, which is stable for highly boron-doped silicon [7]. Every boron atom, substitutionally located on the third
atomic layer, is accompanied by a Si$_{ad}$ sitting directly above. A hole generated by the substitutional boron compensates an electron from the lone-pair orbital of Si$_{ad}$, leaving the orbital empty and making the surface structure energetically stable and chemically inert. If a Si$_{ad}$ is removed to form V$_{Si_{ad}}$ by a suitable mean, e.g., the STM tip manipulation [9], three silicon atoms on the second atomic layer are exposed to the vacuum with a dangling-bond orbital of each atom, pointing up perpendicular to the surface plane as illustrated in Fig. 1(b).

With the $C_{3v}$ symmetry, the three dangling-bond orbitals in V$_{Si_{ad}}$ form two-fold degenerate molecular orbital ($E$) energy levels inside the band gap of silicon. As one electron is captured by an acceptor state generated by the nearby boron, two electrons are left for the molecular orbitals and hence the $E$ orbitals are half-filled, as represented by a peak structure across the Fermi level ($E_F$) in the calculated spin-unpolarized density of states (DOS) in Fig. 2(b). Since two electrons occupy the doubly degenerate orbitals which are spatially localized, the Hund’s coupling dictates the total spin of electrons to be maximized, resulting in a triplet state with a magnetic moment of 2 $\mu_B$. Indeed, our spin-polarized calculation leads to the exchange splitting between spin-up and spin-down states inside the band gap as shown in Fig. 2(b). The gain of the total energy by this spin polarization is 187 meV, which lies in the typical energy range of Hund’s coupling. The calculated spin density, which is defined as the difference between charge densities of spin-up and spin-down states, is displayed in Fig. 2(a). It clearly shows that the spin density profile is symmetrically distributed over the three silicon atoms, with some additional weight on the boron atom (in opposite sign) and other silicon atoms nearby. Because of the missing Si$_{ad}$, the exposed three silicon atoms are pulled down from the original positions with Si$_{ad}$ and form nearly planar $sp^2$ bondings with the surrounding atoms. As a consequence, the spin density becomes almost atomic $p_z$-like. Therefore, we conclude that a local magnetic moment of 2 $\mu_B$ is formed on a defect structure made by removing a Si$_{ad}$.

Although the formation of a local magnetic moment in this single defect structure is fascinating itself and possibly can serve as a new platform for the quantum spin device application, it is also of importance and interest to understand how the spin moments would align when there are many of them in such a case where rather an extended area of polarized spins is desirable. To dig out this matter, we build V$_{Si_{ad}}$ defects in a row adjacent one another, and perform spin-polarized calculations to get a FM solution where
all the magnetic moments are in the same direction (Fig. 3(a)) as well as an AFM solution where spin directions alternate from one site to the next (Fig. 3(b)). It turns out that the AFM alignment is energetically more favorable than the FM alignment by 36 meV per supercell containing 2 V_{Siad}. This can be understood as a result of direct exchange interactions between the local magnetic moments in half-filled localized defect orbitals, where anti-parallel spin alignment is required for the electrons to hop between neighboring defect orbitals to gain in the kinetic energy while observing the Pauli exclusion principle [15]. As typical for the direct exchange, the interaction is very short-ranged and the AFM state is only 8 meV more stable than the FM state for V_{Siad}’s at the next-nearest neighbor distance, which is estimated from a calculation using a larger supercell (4 × 2 units of √3 × √3 surface structure). Because the exchange splitting of defect states in an isolated V_{Siad} results in fully occupied majority spin orbitals and empty minority spin orbitals as we see in Fig. 2(b), the band structure from the series of the localized V_{Siad} orbitals is found to have a band gap.

For the spintronic application purpose, the FM alignment would be more suitable because it can be a source of spin-polarized electrons. As demonstrated above, the half-filled orbitals prefer the AFM exchange coupling and the electron localization (band gap). On the other hand, the fractional filling of orbitals facilitates electron delocalization (partially-filled bands) and the FM state can be stabilized to maximize the Hund’s coupling energy among the hopping electrons, while the kinetic energy gain is the same between FM and AFM alignments because the electron hopping is allowed for both spin alignments in this partially filled orbital case. To test this possibility, we investigate the stability of spin alignments as a function of the hole doping, considering that many extra boron dopants other than those in the third layer of the √3 × √3 surface can exist near the surface in this highly boron-doped system. The result is shown in Fig. 3(c). Here we consider not only the fully relaxed structure for each spin alignment and doping level, but also the lattice structure fixed to that from the spin-umpolarized calculation with no doping, to separate the purely electronic exchange interaction from the lattice relaxation effect. In the fixed lattice case, the FM state is less stable than the AFM state by 52 meV for zero doping. On the other hand, the relative stability of the FM state increases with hole doping, and over around 0.25 hole per defect the FM state becomes the ground state. The maximum stability of the FM state is found to be 29 meV at around 0.9 hole per defect. This doping level is close to 0.5 electron per orbital in doubly degenerate majority-spin energy levels (see Fig. 2(b)),
where the electron itinerancy (delocalization) is maximized. This is the best condition for the FM state to be stabilized with a purely electronic origin such as the electron hopping and Hund’s coupling. Meanwhile, the effect of lattice relaxation is to further stabilize the FM state, indicated by the overall downward shift of the curve with the lattice relaxation in Fig. 3(c). Consequently, a doping as small as 0.1 hole per defect can drive the system into the FM state, and at around 0.6 hole per defect the maximum stability of 39 meV is reached. At this doping level, the total magnetization of the system is reduced to 1.4 $\mu_B$ per defect, and the system is metallic with a finite DOS for the majority spin channel at $E_F$ as shown in Fig. 3(d). In contrast, the DOS value at $E_F$ for the minority spin channel is very small, resulting in the spin polarization, defined as $P(E) = \frac{\rho_\uparrow(E) - \rho_\downarrow(E)}{\rho_\uparrow(E) + \rho_\downarrow(E)}$, estimated to be 73% for $E = E_F$, being close to the half-metallicity or 100% spin polarization at $E_F$.

Our results show that a FM cluster of $V_{\text{Si}}$ defects can be formed when the Si(111)-$\sqrt{3} \times \sqrt{3}$ surface is doped with holes, whereas the AFM coupling among magnetic moments is stable for the intrinsic surface. The FM state can be stable up to $\sim 390$ K ($\sim 39$ meV) with a net magnetic moment of 1.4 $\mu_B$ per $V_{\text{Si}}$ site at a doping level of 0.6 hole per defect. This amount of doping level can be considered to be feasible when we take into account a possibility of the existence of many extra boron atoms near the surface in this highly boron-doped surface, as mentioned earlier. Moreover, the FM state is highly spin-polarized at $E_F$, making this system ideal for the spintronic applications such as a source of the spin-polarized current in a nanometer-sized device. Noteworthy is that silicon is also suitable as a channel material for the spin transport [16–18] with the long spin relaxation time and large spin diffusion length due to a weak spin-orbit coupling of this material. Thus, a FM defect cluster on a silicon surface would be very promising for the comprehensive spin device applications. Finally, the electron doping might have a similar effect with the hole doping, that is, stabilizing the FM coupling of defects. However, the electron doping would fill unoccupied minority spin orbitals above $E_F$ of the undoped system, which is close to bulk conduction band minimum (CBM) in our DFT calculation (see Fig. 2(b)). These doped electrons can be delocalized by spilling into the bulk conduction band states instead of being localized inside the defect orbital, and, therefore, the mechanism of doping-driven stabilization of the FM state might not work. On the other hand, this scenario can possibly be an artifact of the DFT calculation because the energy position of CBM is underestimated as usual for DFT calculations. An appropriate band gap correction scheme, such as using
hybrid exchange-correlation functionals [19], would predict a reliable behavior of the spin alignment with the electron doping, which we leave as a future work.

IV. CONCLUSIONS

In conclusion, we investigate a possibility of magnetic activities on the Si(111)-$\sqrt{3} \times \sqrt{3}$ surface by using the first-principles calculation. Removing an Si$_{ad}$ generates doubly-degenerate local defect states consisting of three silicon dangling-bond orbitals, which holds a local magnetic moment of 2 $\mu_B$. While these local moments tend to align anti-parallel in the intrinsic surface, hole doping is found to enhance the stability of the FM alignment. The maximum relative stability of the FM state with respect to the AFM state is 39 meV implying that the FM state is stable up to 390 K for the 0.6 hole doping per defect, with a local magnetic moment of 1.4 $\mu_B$. Moreover, the FM state exhibits a high spin polarization value at $E_F$, making the system promising for the spintronic applications.

Acknowledgments

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT (2016R1C1B1014715).

[1] S. B. Ogale, Adv. Mater. 22, 3125 (2010).
[2] M. H. N. Assadi, D. A. H. Hanaor, J. Appl. Phys. 113, 233913 (2013).
[3] B. T. Jonker, Y. D. Park, B. R. Bennett, H. D. Cheong, G. Kioseoglou, and A. Petrou, Phys. Rev. B 62, 8180 (2000).
[4] Y.-H. Kim, J. Choi, K. J. Chang, and D. Tomanek, Phys. Rev. B 68, 125420 (2003).
[5] Y.-W. Son, M. L. Cohen, and S. G. Louie, Nature (London) 444, 347 (2006).
[6] Y.-W. Son, M. L. Cohen, and S. G. Louie, Phys. Rev. Lett. 97, 216803 (2006).
[7] V. V. Korobtsov, V. G. Lifshits, and A. V. Zotov, Surf. Sci. 195, 466 (1988).
[8] I.-W. Lyo, E. Kaxiras, and Ph. Avouris, Phys. Rev. Lett. 63, 1261 (1989).
[9] C.-Y. Moon, D. Eom, and J. Y. Koo, Nano Lett. 15, 398 (2015).
[10] P. E. Blochl, Phys. Rev. B 50, 17953 (1994).
[11] G. Kresse and J. Joubert, Phys. Rev. B 59, 1758 (1999).
[12] G. Kresse and J. Furthmüller, Comput. Mater. Sci. 6, 15 (1996).
[13] G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).
[14] H. J. Monkhorst and J. D. Pack, Phys. Rev. B 13, 5188 (1976).
[15] C.-Y. Moon, B.-C. Min, J. H. Lee, J. Chang, and H. J. Choi, Phys. Rev. B 90, 235305 (2014).
[16] B.-C. Min, K. Motohashi, C. Lodder, and R. Jansen, Nat. Mater. 5, 817 (2006).
[17] I. Appelbaum, B. Huang, and D. J. Monsma, Nature (London) 447, 295 (2007).
[18] S. P. Dash, S. Sharma, R. S. Patel, M. P. de Jong, and R. Jansen, Nature (London) 462, 491 (2009).
[19] J. Paier, M. Marsman, K. Hummer, G. Kresse, I. C. Gerber, and J. G. J. Angyan, Chem. Phys. 124, 154709 (2006).
FIG. 1: (Color online) (a) Atomic structure of the Si(111)-$\sqrt{3} \times \sqrt{3}$ surface. Only top few layers are shown for clarity. An imaginary line joining a boron atom and the Si$_{ad}$ atom on top of it defines the surface normal direction, while in-plane primitive unit vectors are shown with arrows. The supercell geometry used in this study contains $2 \times 2$ units of the in-plane primitive cell. (b) Schematics depicting the perfect surface atomic arrangement (upper structure) and V$_{\text{Si}_{ad}}$ (lower structure) after removing a Si$_{ad}$, exposing the silicon dangling-bond orbitals. Note that Si$_{ad}$ is represented in a color different from that of other silicon atoms for clarity, although both are the same silicon species.
FIG. 2: (Color online) (a) Isosurface plot of the calculated spin density in an isolated $V_{Siad}$ defect. Yellow isosurface represents the density of the majority spin state, while cyan color is for the minority spin density represented by negative values, with absolute value of 0.0013 $e/\AA^3$ for both spin density isosurface. (b) Total DOS of the surface containing an isolated $V_{Siad}$ defect. The upper panel is from the spin-unpolarized calculation with doubly-degenerate defect levels inside the band gap denoted by a shaded area, and the lower panel from the spin-polarized calculation with majority and minority spin defect levels split by an exchange energy.
FIG. 3: (Color online) Isosurface plot of the calculated spin density showing (a) the FM alignment (b) the AFM alignment of local defect magnetic moments. (c) Total energy difference between the FM and AFM states per supercell containing 2 $V_{\text{Siad}}$ defects. For the fixed lattice case, all the calculations are done using the same atomic structure obtained by fully relaxing the 2-$V_{\text{Siad}}$-defect structure in a spin-unpolarized calculation, while in the relaxed structure case the full structure optimization is taken for each spin alignment and the doping level. Negative value of the energy difference represents that the FM state is more stable than the AFM state. (d) Spin-resolved DOS of the FM state for the doping level of 0.6 hole per defect. At $E_F$, DOS values for the opposite spin directions differ considerably, resulting in a large value of spin polarization of 73 % (see the text).