

Atomic arrangement and electron band structure of $\text{Si}(1\ 1\ 1)\text{-}\beta\text{-}\sqrt{3} \times \sqrt{3}\text{-Bi}$ reconstruction modified by alkali-metal adsorption: *ab initio* study

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Abstract

Using *ab initio* calculations, atomic structure and electronic properties of $\text{Si}(1\ 1\ 1)\sqrt{3} \times \sqrt{3}\text{-Bi}$ surface modified by adsorption of 1/3 monolayer of alkali metals, Li, Na, K, Rb and Cs, have been explored. Upon adsorption of all metals, a similar atomic structure develops at the surface where twisted chained Bi trimers are arranged into a honeycomb network and alkali metal atoms occupy the T_4 sites in the center of each honeycomb unit. Among other structural characteristics, the greatest variation concerns the relative heights at which alkali metals reside with respect to Bi-trimer layer. Except for Li, the other metals reside higher than Bi layer and their heights increase with atomic number. All adsorbed surface structures display similar electron band structures of which the most essential feature is metallic surface-state band with a giant spin splitting. This electronic property allows one to consider the $\text{Si}(1\ 1\ 1)\sqrt{3} \times \sqrt{3}\text{-Bi}$ surfaces modified by alkali metal adsorption as a set of material systems showing promise for spintronic applications.

Keywords: surface reconstructions, electronic band structure, DFT calculations

(Some figures may appear in colour only in the online journal)

1. Introduction

Metal/silicon reconstructions (i.e. silicon surfaces covered with monoatomic and submonoatomic layers of metals) have attracted considerable attention due to variety of structural and electronic properties. The Bi/Si(1 1 1) is a vivid example of such a system. Two reconstructions with a $\sqrt{3} \times \sqrt{3}$ periodicity are known to be formed upon Bi adsorption onto Si(1 1 1) surface [1–5]. The first one (denoted usually as $\alpha\text{-}\sqrt{3} \times \sqrt{3}\text{-Bi}$ phase contains 1/3 ML (1 monolayer (ML) = $7.8 \times 10^{14} \text{ cm}^{-2}$) of Bi atoms occupying the T_4 sites on Si(1 1 1). The second

one (denoted as $\beta\text{-}\sqrt{3} \times \sqrt{3}\text{-Bi}$ phase) incorporates 1 ML of Bi atoms arranged into the trimers according the milkstool model [4]. The $\beta\text{-}\sqrt{3}$ phase is of special current interest due to the recent discovery of a giant Rashba-type spin splitting of its surface-state band [6–8]. This property of $\text{Si}(1\ 1\ 1)\text{-}\beta\text{-}\sqrt{3}\text{-Bi}$ (as well as that of a very similar $\text{Ge}(1\ 1\ 1)\text{-}\beta\text{-}\sqrt{3}\text{-Bi}$ phase [9–12]) has been thoroughly investigated. These studies have contributed much for understanding peculiarities of Rashba effect at semiconductor surfaces with a hexagonal symmetry. However, the following drawback of this interesting system should be emphasized. The spin-split surface-state band in

$\beta\sqrt{3}$ -Bi phase is *non-metallic*, while bearing in mind spintronics applications one needs *metallic* spin-split bands to ensure considerable spin transport. Recently it has been demonstrated that adding 1/3 ML Na to the Si(1 1 1)- $\beta\sqrt{3}$ -Bi alters its atomic and electron band structure. As a result, the forming 2D Bi–Na compound displays a metallic spin-split band [13]. It is of interest to see if the same result can be achieved with the other alkali metals (AM) and elucidate common and peculiar features of the various Bi–AM 2D compounds on Si(1 1 1).

In the present paper, we report on the results of the first-principles calculations of atomic and electronic structures of 2D compounds formed upon adsorption of 1/3 ML of alkali metals, Li, Na, K, Rb and Cs, onto Si(1 1 1)- $\beta\sqrt{3} \times \sqrt{3}$ -Bi surface.

2. Calculation details

Our calculations were based on density functional theory (DFT) as implemented in the Vienna *ab initio* simulation package VASP [14, 15] using a planewave basis and the projector-augmented wave approach [16] for describing the electron-ion interaction. The generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) [17] has been used for the exchange correlation (XC) potential. Relativistic effects, including spin-orbit interaction (SOI), were taken into account. To simulate the Bi–AM reconstructions on Si(1 1 1) we use a slab consisting of 6 bilayers (BL) of silicon. Hydrogen atoms were used to passivate the Si dangling bonds at the bottom of the slab. Both bulk Si lattice constant and the atomic positions of adsorbed atoms and atoms of Si layers within the three BLs of the slab were optimized including SOI self-consistently. The silicon atoms of deeper layers were kept fixed at the bulk crystalline positions.

3. Results and discussion

Let us consider first atomic reordering of the Si(1 1 1)- $\beta\sqrt{3}$ -Bi surface upon AM adsorption. Remind that pristine Si(1 1 1)- $\beta\sqrt{3}$ -Bi surface reconstruction is built of Bi trimers. The Bi atoms occupy positions close to the on-top (T_1) sites on the bulk-like Si(1 1 1) surface; the Bi trimers are centered at the T_4 sites and reside 2.7 Å higher than top Si atoms; the Bi–Bi bond length (i.e. the trimer side) equals 3.1 Å (figure 1(a)). Recent results of the *ab initio* random structure search for adsorption of 1/3 ML Na onto the Si(1 1 1)- $\beta\sqrt{3}$ -Bi surface [13] have proved that the most stable configuration is the one where Na atom occupies the T_4 site (figure 1(b)). In the present study, the calculations were performed for three adsorption geometries, namely when alkali metal is placed in between Bi trimers either in the T_4 or H_3 sites and when it is placed in the center of the Bi trimer. Similarly to Na, all other alkali metals were found to prefer occupying the T_4 site in between the Bi trimers. When AM atom is placed in the H_3 site, the Bi atoms reorder to form trimers centered at the H_3 sites. This configuration is less stable than the T_4 one by 0.2–0.3 eV, depending on the particular AM. The configuration

with AM in the Bi-trimer center appears to be the most energetically unfavorable.

For all metals, AM adsorption produces a same effect on the size and orientation of the Bi trimers. They increase in size from 3.1 Å to 3.4 Å (the new size being almost the same for all cases) and become twisted with respect to $\langle 1\bar{1}0 \rangle$ directions. The rotation angle is maximal (23.2°) for the case of Na and minimal (17.6°) for Li. Upon these transformations, Bi atoms become arranged into a honeycomb network of chained trimers. While the height of the Bi trimers above the top Si(1 1 1) layer for all AM adsorbates is almost the same being close to that (2.7 Å) for the pristine Si(1 1 1)- $\beta\sqrt{3}$ -Bi surface, the relative height of AM atoms with respect to Bi-trimer layer depends on the AM species. Among them, the light element Li is the only one that resides lower (by 0.5 Å) than Bi atoms. The other AM atoms are located higher than Bi layer and their relative height is greater for the heavier atoms, namely it increases from 0.6 Å for Na to 2.3 Å for Cs. Thus, the calculation results imply that the basic atomic arrangement of all AM-modified Si(1 1 1)- $\sqrt{3}$ -Bi surfaces is very similar with the most essential variation concerning the height at which AM atom resides with respect to Bi atomic layer.

Figures 2(b)–(f) shows calculated electron band structures for AM-modified Si(1 1 1)- $\sqrt{3}$ -Bi surfaces with that for the pristine Si(1 1 1)- $\sqrt{3}$ -Bi surface (figure 2(a)) given for a reference. In agreement with the recent experimental and theoretical results [6–8], the most prominent electronic feature of the pristine Si(1 1 1)- $\sqrt{3}$ -Bi surface is occurrence of the hole-like surface-state band at \bar{M} (denoted S_1) with a giant spin splitting below the Fermi level. In addition, one can also notice a presence of the unoccupied spin-split band at $\bar{\Gamma}$ (Σ_1) above the Fermi level. As none of these bands crosses the Fermi level, the Si(1 1 1)- $\sqrt{3}$ -Bi surface exhibits semiconducting properties. Modification of the Si(1 1 1)- $\sqrt{3}$ -Bi surface by AM adsorption changes substantially its electron band structure. This change in the band structure occurs mainly owing to the charge transfer from AM to the Bi layer while the potential change in the silicon layers is weak and thus the electric field effect in the slab [18] can be neglected. Comparing band structures before and after AM modification, these changes can be visualized as follows. The S_1 band goes down in the \bar{M} point to the greater binding energies for Li (slightly) and for Na (greatly), but it goes up for K, Rb and Cs. The split value of S_1 band decreases for all AM adsorbates (especially, for Na). For all metals, except Li, the surface character of the deeper spin-split bands significantly enhances and they become closer to the S_1 band (especially, for heavy alkali metals, K, Rb and Cs). As for the unoccupied Σ_1 band, the shape of its dispersion changes significantly. Around the $\bar{\Gamma}$ point the band goes up to the higher energies, while at \bar{M} point it goes down into the bulk band gap. Going down, the band crosses the Fermi level that makes the surface metallic. Electron filling of the metallic Σ_1 band depends on how deep the band protrudes below the Fermi level and this is slightly different for different metals. In all cases, the Σ_1 band is spin-split and its momentum splitting Δk_{\parallel} and energy splitting ΔE_F near the Fermi level depends both on the band shape and location of the band with respect to the Fermi level. The maximal splitting values, $\Delta k_{\parallel} = 0.053$

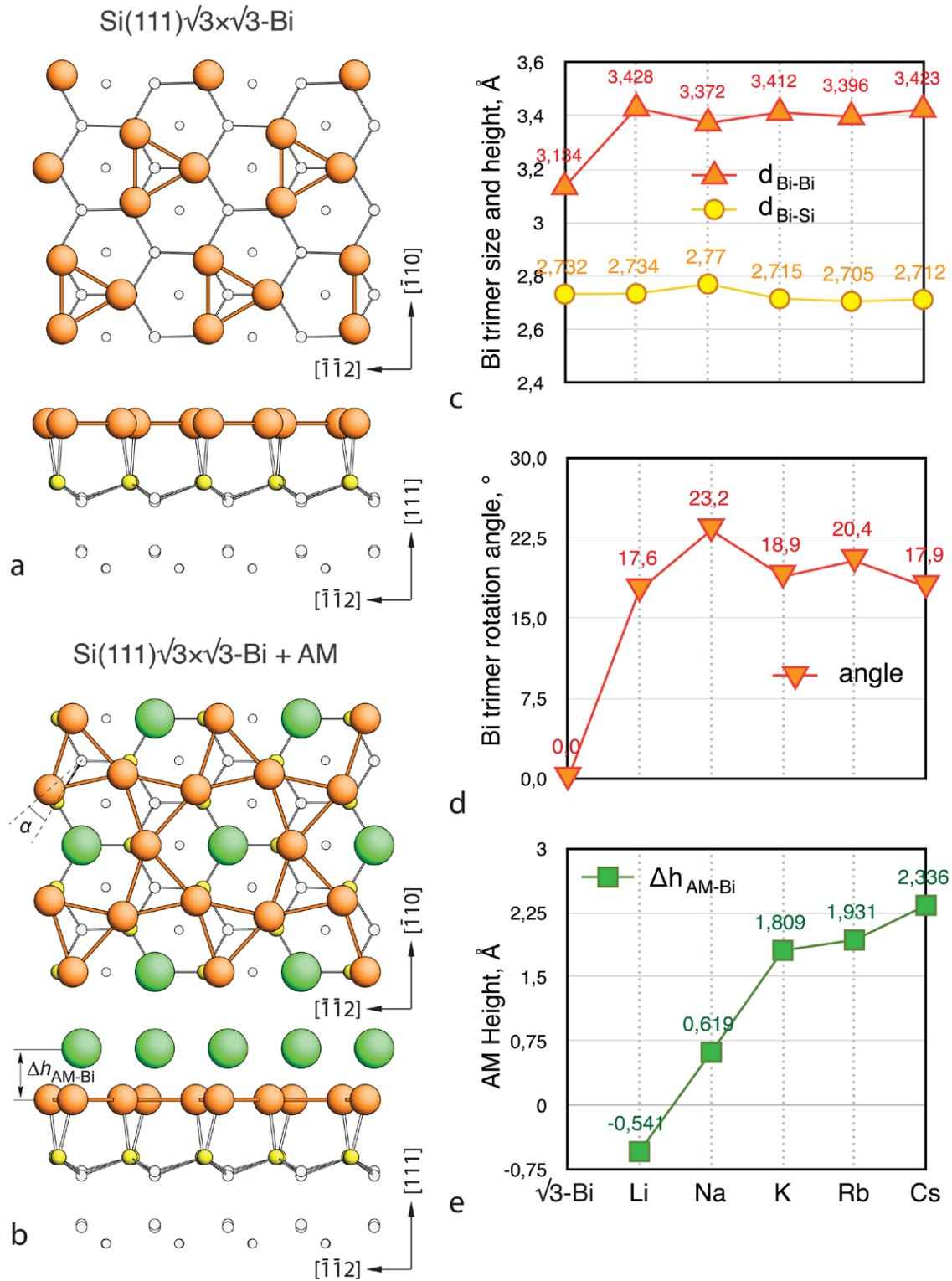


Figure 1. Structural properties of the $\text{Si}(1\ 1\ 1)\sqrt{3} \times \sqrt{3}\text{-Bi}$ surface modified by AM adsorption. Structural models of the (a) pristine and (b) AM-modified $\text{Si}(1\ 1\ 1)\sqrt{3} \times \sqrt{3}\text{-Bi}$ surfaces. Bi atoms are shown by orange circles, alkali metal atoms by green circles, top Si atoms by yellow circles, Si atoms of the deeper layers by small white circles. Calculated structural characteristics, (c) size (red triangles) and height (yellow circles) of Bi trimers, (d) rotation angle of Bi trimers, (e) relative height of AM atoms with respect to Bi-trimer layer for AM = Li, Na, K, Rb and Cs.

\AA^{-1} and $\Delta E_F = 255$ meV, are for Rb adsorbate and minimal, $\Delta k_{\parallel} = 0.049$ \AA^{-1} and $\Delta E_F = 173$ meV, are for Li and Na, respectively. It should be remarked, however, that in reality these values might be somewhat different. The reason is that

the experimental E_F can depends on surface imperfections. For example, in order to tie the calculated band structures to the experimental ARPES spectra for pristine $\text{Si}(1\ 1\ 1)\sqrt{3}\text{-Bi}$ and Na-modified $\text{Si}(1\ 1\ 1)\sqrt{3}\text{-Bi}$ it is necessary to shift the

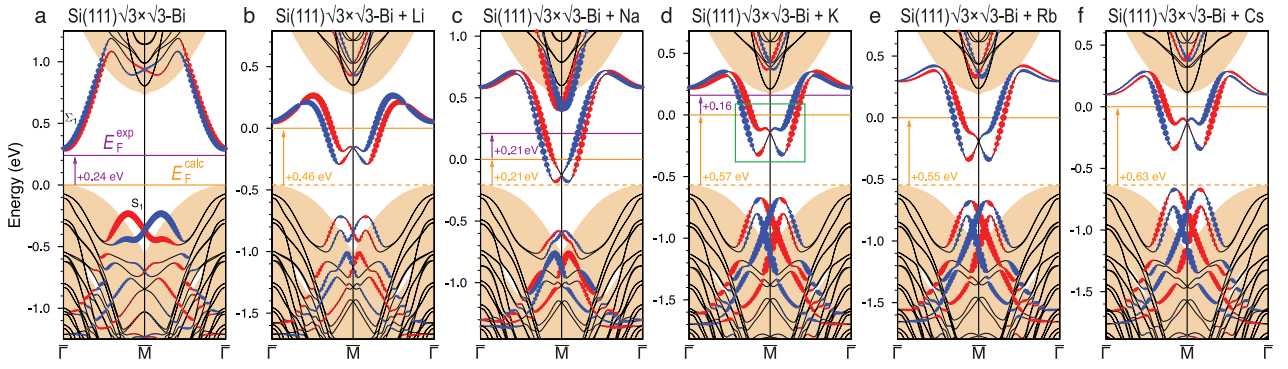


Figure 2. Calculated electron band structure of (a) pristine $\text{Si}(111)\sqrt{3}\times\sqrt{3}\text{-Bi}$ surface and the $\text{Si}(111)\sqrt{3}\times\sqrt{3}\text{-Bi}$ surface modified by adsorption of (b) Li, (c) Na, (d) K, (e) Rb and (f) Cs. The bands with opposite spin orientation are highlighted by blue and red circles. The size of the circle corresponds to the strength of the surface character summed over all orbitals at a particular k_{\parallel} value. Shaded region indicates projected bulk bands. Location of calculated and experimental Fermi levels are indicated by orange and violet lines, respectively.

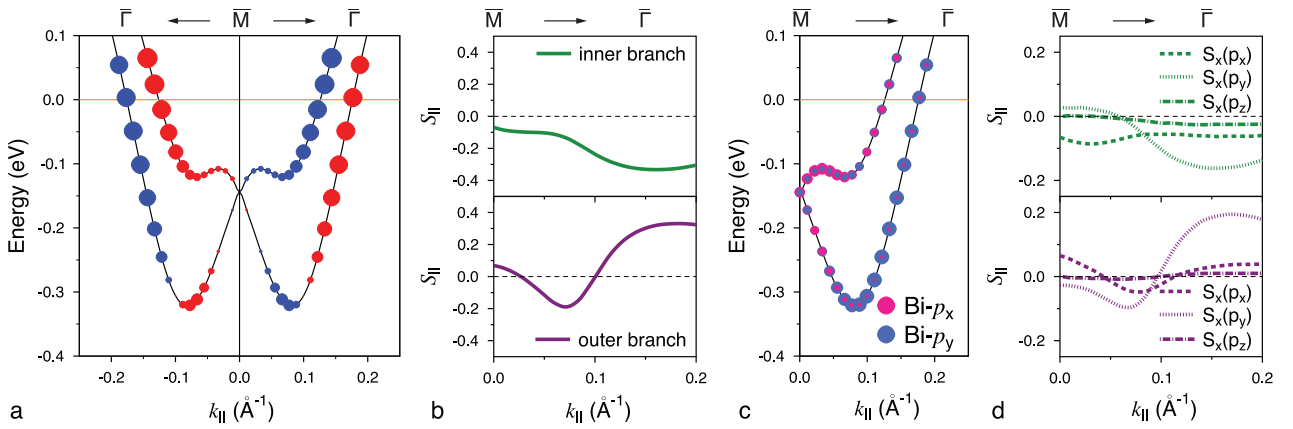


Figure 3. (a) Magnified view of the metallic \bar{M} surface state on K-adsorbed $\text{Si}(111)\beta\text{-}\sqrt{3}\text{-Bi}$ surface (see green rectangle in figure 2(d)); (b) The in-plane spin component S_x as functions of k_{\parallel} along the $\bar{M} - \Gamma$ direction for inner (top) and outer (bottom) branches of the spin-split \bar{M} surface state; (c) Orbital composition of the surface state; (d) Orbital-projected S_x as functions of k_{\parallel} for inner (top) and outer (bottom) branches of the spin-split surface state.

the calculated Fermi level up by 240 and 210 meV, respectively [13] while for K-modified $\text{Si}(111)\sqrt{3}\text{-Bi}$ this shift is 160 meV [19].

In contrast to the pristine $\text{Si}(111)\sqrt{3}\times\sqrt{3}\text{-Bi}$ surface, where both occupied \bar{M} surface state (S_1) and unoccupied $\bar{\Gamma}$ surface state (Σ_1) have typical Rashba-like spin structure, i.e. inner and outer branches have opposite in-plane spin orientation, which change their sign when k is replaced by $-k$, all AM-modified surfaces demonstrate unusual overturn of the spin sign in the vicinity of band apices (both in the metallic and in the occupied surface states). As an example, the magnified view of the metallic surface state of the K-modified $\text{Si}(111)\sqrt{3}\text{-Bi}$ is shown in figure 3(a) where one can clearly see that at $k_{\parallel} > 0.1 \text{ \AA}^{-1}$ far from the \bar{M} point ($k_{\parallel} = 0$ here is the \bar{M} point) the spin structure of the surface state is typical Rashba-like while at $k_{\parallel} < 0.1 \text{ \AA}^{-1}$ the in-plane spin in the outer branch changes its sign. The detailed behavior of the S_x spin component as functions of k_{\parallel} for inner and outer branches of the surface state is demonstrated in figure 3(b). Both $S_x(k_{\parallel})$ curves have peculiarities at $k_{\parallel} \simeq 0.1 \text{ \AA}^{-1}$. The curve of the inner branch

has a kink whereby the magnitude of $S_x(k_{\parallel})$ at large and small k_{\parallel} differ by a factor of three. The curve of the outer branch has the sign opposite to that at large k_{\parallel} . Such a behavior of $S_x(k_{\parallel})$ is related to peculiarities in the orbital composition of the surface state near the \bar{M} point. The surface state mainly come from p_x and p_y orbitals of Bi with negligible contribution from $\text{Bi-}p_z$ and K orbitals. As can be seen in figure 3(c), in the inner branch at large k_{\parallel} the band is contributed mainly by p_y orbitals with admixture of p_x ones while at $k_{\parallel} < 0.1 \text{ \AA}^{-1}$ p_x orbitals dominate. In the outer branch the p_x Bi orbitals prevail over p_y at small k_{\parallel} and they nearly disappear at $k_{\parallel} \simeq 0.1 \text{ \AA}^{-1}$ whereupon the band becomes almost completely composed by $\text{Bi-}p_y$ orbitals. These changes in the orbital symmetry of the surface state results in the behavior of the orbital-projected spin, as can be seen in figure 3(d). In the vicinity of $k_{\parallel} \simeq 0.1 \text{ \AA}^{-1}$ in both inner and outer branches p_y -projected in-plane spin change the sign with respect to that at large k_{\parallel} -vectors. At the same time, the relatively large magnitude of $S_x(p_x)$ at $k_{\parallel} < 0.1 \text{ \AA}^{-1}$ in the inner branch is responsible for the fact that at small k_{\parallel} the magnitude of total S_x of the inner branch substantially decreases

but does not change sign. In the outer branch the magnitude of $S_x(p_x)$ is smaller and thus, the total S_x is mainly provided by the p_y -projected spin.

4. Conclusion

In conclusion, results of the present *ab initio* calculations demonstrate that adsorption of 1/3 ML of alkali metals, Li, Na, K, Rb and Cs, onto the Si(1 1 1) $\sqrt{3} \times \sqrt{3}$ -Bi surface results in the formation of the 2D alloyed layers having a basically common structure. It contains twisted chained Bi trimers which are arranged into a honeycomb network and alkali metal atoms occupying the T_4 sites in the center of each honeycomb unit. All alloys have similar, albeit not quantitatively identical, electron band structures, which the most essential feature is occurrence of the metallic spin-split electron-like surface-state band \bar{M} . The latter demonstrates a significant electron filling and giant spin splitting. Thus, the Si(1 1 1) $\sqrt{3}$ -Bi reconstructions modified by alkali metals can be considered as a set of material systems with a promise for spintronic applications. From this viewpoint, their thorough experimental studies are greatly demanded.

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References

- [1] Wan K J, Guo T, Ford W K and Hermanson J C 1992 *Surf. Sci.* **261** 69
- [2] Shioda R, Kawazu A, Baski A A, Quate C F and Nogami J 1993 *Phys. Rev.* **48** 4895
- [3] Nakatani S, Takahashi T, Kuwahara Y and Aono M 1995 *Phys. Rev.* **52** R8711
- [4] Miwa R H, Schmidt T M and Srivastawa G P 2003 *J. Phys.: Condens. Matter* **15** 2441
- [5] Kuzumaki T, Shirasawa T, Mizuno S, Ueno N, Tochiwara H and Sakamoto K 2010 *Surf. Sci.* **604** 1044
- [6] Gierz I, Suzuki T, Frantzeskakis E, Pons S, Ostanin S, Ernst A, Henk J, Grioni M, Kern K and Ast C R 2009 *Phys. Rev. Lett.* **103** 046803
- [7] Sakamoto K et al 2009 *Phys. Rev. Lett.* **103** 156801
- [8] Frantzeskakis E, Pons S and Grioni M 2010 *Phys. Rev.* **82** 085440
- [9] Hatta S and Aruga T 2009 *Phys. Rev.* **80** 113309
- [10] Ohtsubo Y, Hatta S, Iwata M, Yaji K, Okuyama H and Aruga T 2009 *J. Phys.: Condens. Matter* **21** 405001
- [11] Ohtsubo Y, Hatta S, Yaji K, Okuyama H, Miyamoto K, Okuda T, Kimura A, Namatame H, Taniguchi M and Aruga T 2010 *Phys. Rev.* **82** 201307
- [12] Hsu C H, Chang H R, Chuang F C, Liu Y T, Huang Z Q, Lin H, Ozolinš V and Bansil A 2014 *Surf. Sci.* **626** 68
- [13] Gruznev D V et al 2014 *Sci. Rep.* **4** 4742
- [14] Kresse G and Hafner J 1993 *Phys. Rev.* **47** 558
- [15] Kresse G and Joubert D 1999 *Phys. Rev.* **59** 1758
- [16] Blöchl P E 1994 *Phys. Rev.* **50** 17953
- [17] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
- [18] Krukowski S, Kempisty P and Strak P 2013 *J. Appl. Phys.* **114** 143705
- [19] Our result, unpublished