Supplementary information

In order to understand the surface band states, we further calculated the band-decomposed charge density distributions at $\bar{\Gamma}$ point near the Fermi level for Ca/Si(111)-3×2 and Ba/Si(111)-3×2 surfaces. As shown in Fig. S1(b) and S2(b), for each case the first conduction bands (CB_1) have π^* antibonding character between p_z orbital of the surface Si(C) and Si(D) atoms. The corresponding charge distribution are mainly contributed by the surface Si(C) and Si(D) atoms, while the charge contributions of Si atoms in the second layer and metal atoms are small. Meanwhile, for the first and second valence bands (VB_1 and VB_2) we find that there are no charge contribution from Si atoms in the topmost layer and metal atom, and all charge distribution are contributed by the bulk Si atoms. Similar to CB_1, the third valance bands (VB_3) are primarily contributed by the d_{xy} orbital of metal adatom and the p_x orbital of surface Si(A) and Si(B) atoms. These results clearly indicate that CB_1 and VB_3 are the surface states, while the VB_1 and VB_2 are not. Therefore, the surface band gap are between CB_1 and VB_3 bands, and the corresponding values are estimated to be 1.65 and 1.66 eV for Ca and Ba, respectively. These values are in good agreement with the experimental data of 1.7 eV for Sr/Si(111)-(3×2) surface. [1]

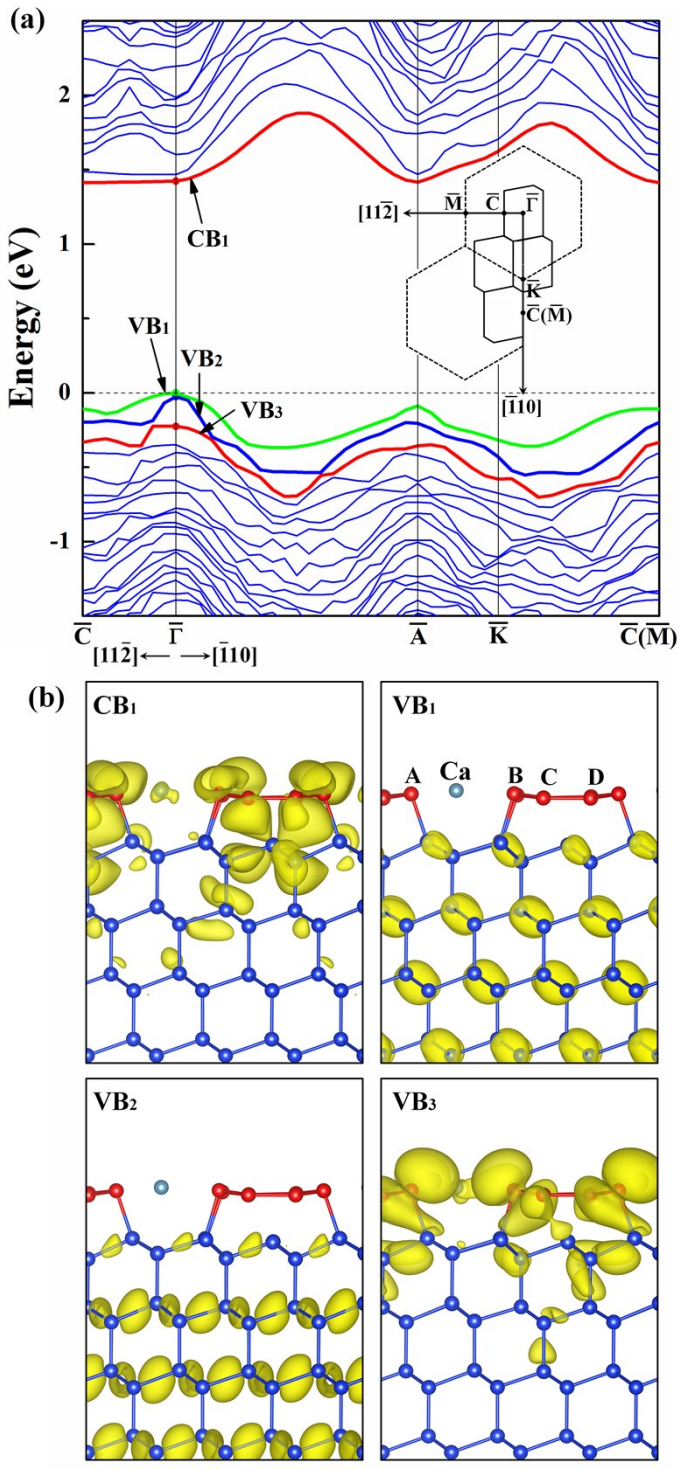

FIG. S1: (a) Calculated electronic band structure of Ca/Si(111)-3×2 surface using HSE06 functional. Horizonal dotted line gives the Fermi level that is set to zero. (b) The band-decomposed charge density distributions at $\bar{\Gamma}$ point. VB_1, VB_2 and VB_3 represent the first, second and third valence band, respectively, and CB_1 represent the first conduction band. The color spacing is 0.005 e/Å^3. The Si atoms in the first layer

are plotted in red, the other Si atoms are in blue, and the AEM atoms are in grey.

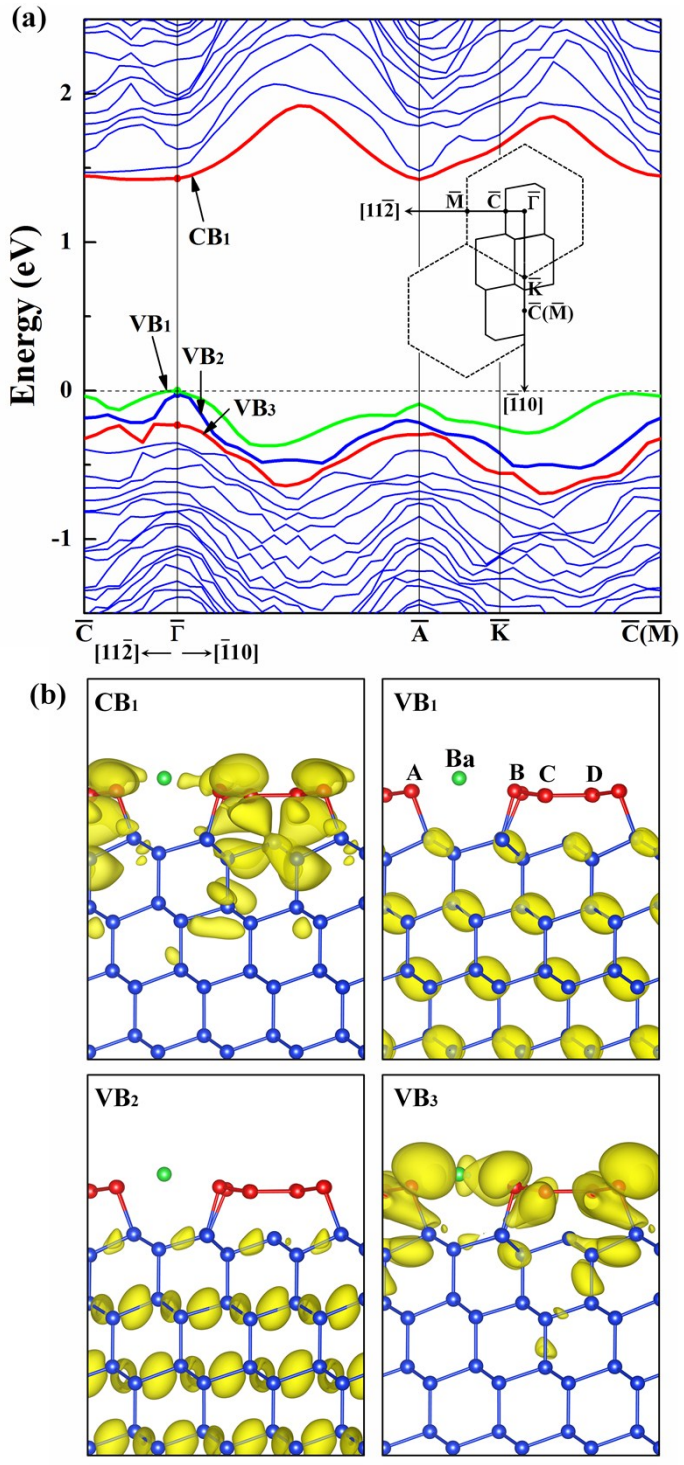

FIG. S2: (a) Calculated electronic band structure of Ba/Si(111)-3×2 surface using HSE06 functional. Horizonal dotted line gives the Fermi level that is set to zero. (b) The band-decomposed charge density distributions at $\bar{\Gamma}$ point. VB_1, VB_2 and VB_3 represent the first, second and third valence band, respectively, and CB_1 represent the

first conduction band. The color spacing is 0.005 e/Å^3. The Si atoms in the first layer are plotted in red, the other Si atoms are in blue, and the AEM atoms are in green.

REFERENCES

[1] W. H. Du and J. J. Yang, *Surf. Sci*., 2016, **653**, 222.