Supporting Information

First-principles study of O_2 and H_2O adsorption on Mg_3Sb_2(10-11) surface

Juan Li, Kai Han, Bing Sun, Lianzhen Cao, Shuai Zhang*

School of Physics and Electronic Information, Weifang University, Weifang 261061, China

Table S1 The total energies, adsorption energies, adsorption heights, shortest Mg-O and Al-O bond lengths of O_2 adsorption at different sites of Al-doped 3×3×2 Mg_3Sb_2 (10-11) slab.

Adsorption sites	E_{slab} (eV)	E_{ads} (eV)	$h_{Mg_3Sb_2(10\text{-}11)\text{-}O}$ (Å)	$d_{Mg\text{-}O}$ (Å)	$d_{Al\text{-}O}$ (Å)
Bridge	-239.92	-1.61	0.031	2.03	1.84
Top1	-240.12	-1.82	0.035	1.95	1.80
Top2	-237.24	1.10	0.077	1.94	6.90
Hollow	-235.84	2.50	0.078	3.57	5.57

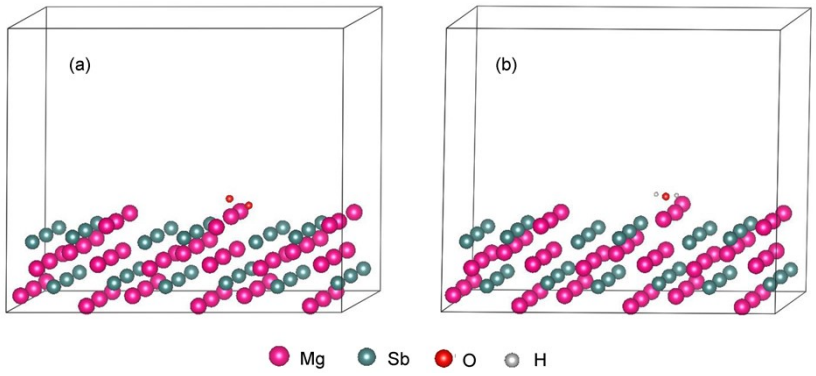

Fig. S1 The most stable adsorption configurations of (a) O_2 and (b) H_2O at B1 site of 3×3×2 Mg_3Sb_2 (10-11) slab.

Estimation of surface energy

The 3×3×2 surface is used for surface energy calculations. When the surface is stoichiometric, surface energy can be calculated by [1]:

$$\sigma = \frac{1}{2A}(E_{slab} - n\mu^{bulk}_{Mg_3Sb_2}) \quad (1)$$

where E_{slab} is the total energy of the relaxed slab, A is the surface area, $\mu^{bulk}_{Mg_3Sb_2}$ is the chemical potential of bulk Mg_3Sb_2 and n is the number of Mg_3Sb_2 formula units in the slab. $\mu^{bulk}_{Mg_3Sb_2}$ is calculated to be -17.53 eV. E_{slab} is estimated to be -223.12 eV for Mg_3Sb_2 (10-11) with Mg termination. Based on equation (1), the surface energy of stoichiometric (10-11)-Mg surface is calculated to be 2.18 J/m^2.

When the surface is non-stoichiometric, the chemical potential of the excess atoms should be subtracted in surface energy calculation, which is expressed as [1-3]:

$$\sigma = \frac{1}{2A}(E_{slab} - n\mu_{Mg_3Sb_2}^{bulk} - (N_{Sb} - \frac{2}{3}N_{Mg})\mu_{Sb}^{slab}) \quad (2)$$

where N_{Sb} and N_{Mg} are the numbers of Sb and Mg atoms in slab, respectively, and μ_{Sb}^{slab} is the chemical potential of Sb atom in slab. E_{slab} is estimated to be -304.24 eV for Mg_3Sb_2 (10-11) with Sb termination. In equilibrium, the chemical potential of a given atomic species is the same in all its phases which are in contact, therefore, the chemical potential of excess atom can be regarded as the same as that of other atoms, and can be expressed as [3]:

$$3\mu_{Mg}^{slab} + 2\mu_{Sb}^{slab} = \mu_{Mg_3Sb_2}^{bulk} \quad (3)$$

As we are known, the formation enthalpy is in correlated with the elemental chemical potential in bulk state, and can be expressed as [1-3]:

$$3\mu_{Mg}^{bulk} + 2\mu_{Sb}^{bulk} + \Delta H_f = \mu_{Mg_3Sb_2}^{bulk} \quad (4)$$

Combing the equations (3) and (4),

$$3(\mu_{Mg}^{bulk} - \mu_{Mg}^{slab}) + \Delta H_f = 2(\mu_{Sb}^{slab} - \mu_{Sb}^{bulk}) \quad (5)$$

Because the negative value of the formation enthalpy, the range of Sb chemical potential can be given by:

$$\frac{1}{2}\Delta H_f < \mu_{Sb}^{slab} - \mu_{Sb}^{bulk} < 0 \quad (6)$$

The values of μ_{Sb}^{bulk} and ΔH_f are calculated to be -5.141 eV and -0.4117 eV per atom in our previous work [4]. Based on equation (6), the μ_{Sb}^{slab} value is within in the range of -6.17 eV to -5.14 eV. Therefore, the surface energy of non-stoichiometric (10-11)-Sb surface is within in the range of 2.45 J/m^2 to 2.88 J/m^2. The smaller surface energy

for Mg termination indicates that compared the (10-11)-Sb surface, (10-11)-Mg surface is more stable.

References

[1] Duan Y. Electronic properties and stabilities of bulk and low-index surfaces of SnO in comparison with SnO_2: A first-principles density functional approach with an empirical correction of van der Waals interactions. Phys Rev B 2008;77;045332.

[2] Sun SP, Li XP, Wang HJ, Jiang Y, Yi DQ. Adsorption of oxygen atom on $MoSi_2$ (110) surface. Appl Surf Sci 2016;382;239-248.

[3] Qian G-X. First-principles study of the atomic reconstructions and energies of Ga- and As-stabilized GaAs(100) surfaces. Phys Rev B 1988;38;7649.

[4] Li J, Zhang S, Zheng S, Zhang Z, Wang B, Chen L, Lu G. Defect chemistry for n-type doping of Mg_3Sb_2-based thermoelectric materials. J Phys Chem C 2019;123;20781-20788.