§11. Study on Electronic Transitions in Cs-metal Surface Using First Principles Density Functional Theory

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Work function is a fundamental property that is important in different applications. A desirable low value of work function surface is aimed for producing high yield of negative ions.[1] Negative ions are used as sources of accelerators in laboratories. They are also used as heating sources in fusion reactors.

The adsorption of alkali metal atoms on metal surfaces has been studied previously as a method to induce low work function on metallic surfaces.[2] The large difference between the electronegativity of the adsorbed alkali metal atom with that of the surface induces surface dipole that lowers the work function of the surface. Fig. 1 shows the mechanism lowering work function by Cs adsorption on W(110) surface. The presence of spilled out charges near the vacuum region creates the surface dipole in a clean W(110) surface (Fig. 1a). Adsorbed Cs produces charge polarization that lowers work function (Fig. 1b). However, a minimum work function should induce large amount of dipole but maintaining weak Cs-Cs repulsion (Fig. 1c-d). Thus, theoretical investigation on the surface electronic properties that affects work function was conducted.[3]
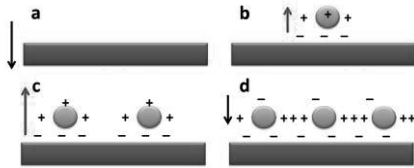

Fig.1. Mechanism of lowering work function through induced surface dipole by Cs adsorption.

The variation of work function for adsorbed alkali metals (Li, Na, K, Rb and Cs) on W(110) at different coverages was analyzed. From the analyzed systems, the minimum work function occurs at an optimum coverage of 0.22 ML for Cs, Rb and K, and 0.33 ML for Na and Li. Among the alkali metal considered in this study, Cs gives the lowest work function (1.42 eV). It was attributed to the largest change in the surface dipole induced by Cs being the most electropositive and readily allowing its charge to redistribute to the surface. It was also verified through calculating the surface dipole density using[4]:

$$\Delta\mu_z = \int_{z_o}^{c/2} z\Delta\rho_z(z)dz$$

where $\Delta\rho_z(z)$ is the planar average of the difference in charge density as a function of the surface normal (z axis). The calculated surface dipole density corresponding to the minimum work function are 1.43×10^{-2}, 1.61×10^{-2},

1.82×10^{-2}, 1.83×10^{-2}, and 1.87×10^{-2} $e/\text{Å}$ for Li, Na, K, Rb, and Cs, respectively.

As alkali metal surface coverage affects the minimization of the work function to a particular minimum through induced surface dipole, work function increase at higher coverages is attributed to depolarization. Depolarization occurs when the orbital of the adsorbed atom start to interact and form chemical bond. Fig. 2 shows the correlation between the electronic property of the alkali metal and the change in the work function
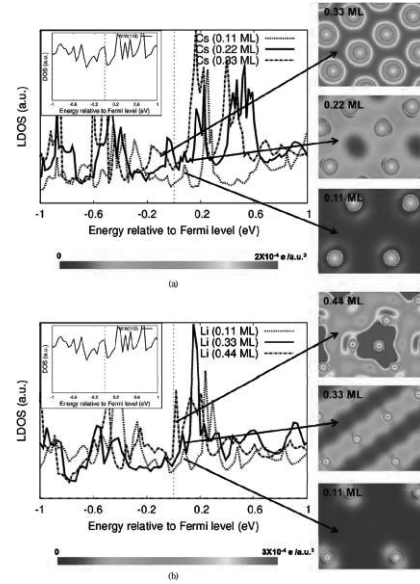

Fig.2. Local density of states projected onto the s orbital of adsorbed (a) Cs and (b) Li on W(110) at different coverages. *Inset:* density of states projected onto the surface W atom of the clean W(110)

It is observed that in general, the states of the alkali metal hybridize with the states of the surface W atom. Furthermore, at low coverages, an unoccupied state just above the Fermi level could be observed and it shifts towards the Fermi level as the coverage increases. Charge density distribution along these peak identify that these states correspond to the span of the orbital of the adsorbed alkali metal. At higher coverages, the initially unoccupied states shift towards the occupied region suggesting higher adsorbate-adsorbate interaction. This shift towards the occupied region depicts orbital overlap which is an indication of depolarization. It is also observed that for Li, the state is partially occupied in contrast to the fully occupied state of Cs. This could be attributed to the smaller atomic radius of Li.

These results clearly depict that changes in the work function can be completely resolved by investigating the electronic structure through the density of states profiles.

1) Wada, M. et al.: AIP Conf. Proc. **1515** (2013) 41.
2) Papageorgopoulos, C. A. et al.: Phys. Rev. B **40** (1989) 1546.
3) Padama, A.A. et al.: J. Vac. Soc. Jpn. **57** (2014) 27.
4) Leung, T.C. et al.: Phys. Rev. B **68** (2003) 195408.