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Structure and energetics of small size noble metal clusters on Zno(000$\bar{1}$) ultra-thin layers: A DFT study

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ABSTRACT

Clusters of Noble metals (Ag, Au, Cu, and Pt) with number of atoms of 3, 5 and 7 atoms deposited on ultra-thin polar oxygen terminated layer of ZnO corresponding to the surface (000$\bar{1}$) are studied within the context of density functional theory (DFT). The slab thickness is varied from 1 to 3 double-monolayers. The calculated adsorption energies of these clusters show significant negative values indicating good adhesion to the semi-conductor surface. In general, the adhesion energy decreases with the cluster size. The effect of oxygen surface defect inserted directly under the metallic cluster in some chosen systems is studied. The adhesion energy of the metallic clusters still adhered to the surface is constant in this case but the interaction energy varies in non-regular form.

KEYWORDS

Semi-conductor;
ZnO;
Polar surface;
Metallic cluster;
Nobel metals;
Surface defect;
Adhesion energy;
DFT.

INTRODUCTION

Metal nanoclusters are commonly used in numerous areas of technology applications. Noble metals nanoclusters and especially their supported nanoclusters on semiconducting surfaces are known for their catalytic and photo-catalytic activities[1-3] and low temperature carbon monoxide catalysis[4]. Supported nanocluster semiconducting oxide surfaces are often used to develop new photo-catalytic systems[5,6]. Experimental and theoretical studies are abundant in this field. Many DFT studies and experimental results of metal clusters deposited on semiconducting oxide surfaces such as titanium dioxide and zinc oxide are available[3,7-11]. The available experimental works provide a lot of details about the atomic structure of the interface and features of small size palladium and gold clusters deposited in high vacuum conditions on clean and defected surfaces. The STM and AFM images show clearly that this metal clusters adhere strongly onto these surfaces. Many of these strudels are completed by DFT calculations to emphasize some properties of the deposited clusters such as the effect of steps or the presence of vacancies at the surface. The effect of the oxide ultrathin layers surface on the structure and adhesion of the metallic clusters at atomic scale is less available in literature. In contrast to the case of single metal atoms, there are few theoretical and experimental studies deal-

ing with the effect of the cluster size and the thickness of the polar oxygen terminated ZnO substrate on the energetics and the structural properties of the metal clusters, which affect naturally the electronic properties; and thus the their activity. In order to have a more complete picture about noble metal clusters adsorbed on this particular ZnO surface, we present in this paper a DFT based theoretical study on the deposition of small size Ag, Au, Cu and Pt clusters on clean and defect ZnO($000\bar{1}$) surfaces with a thickness ranging between 2 and 4 double monolayers of ZnO atomic planes.

COMPUTATIONAL DETAILS

The study is performed using density functional theory based on pseudo-potential approximation and using numeric atomic orbital pseudo-potentials based on Siesta code. The ground state valence electronic configurations of Zn, O, Ag, Au, Cu, and Pt are $4s^2$ $3d^{10}$, $2s^2$ $2p^4$, $5s^1$ $4d^{10}$, $6s^1$ $5d^{10}$, $4s^1$ $3d^{10}$ and $5d^{10}$ respectively. The GGA pseudo- potential functional type is used in all calculations. The mesh cu-off used for all calculation was 200 Rh and the reciprocal space was sampled for all structures with a mesh of 3x3x1 k points. The generalized gradient approximation (GGA) has been utilized in all calculations, based on the specific functional of Perdew, Burke and Ernzerhof (PBE)[12]. Core electrons are represented by norm-conserving pseudo-potentials of the form proposed by Troullier-Martins[13].

The atomic structure of bulk ZnO was optimized with some of other calculation parameters such as the mesh cut-off, the K points mesh and split norm. The obtained results were used to optimize the C parameter of a ZnO slab of few double monolayers. This set of crystallographic and calculation parameters are used to perform the determination of atomic structures and system energies of the deposited clusters on the ZnO polar surface. The structures are made of slabs of ZnO of few atomic monolayer where the z axis is parallel to the crystallographic [$000\bar{1}$] direction. The monolayers are taken in pair number to ensure the presence of zinc and oxygen atomic planes in the structure, where the thickness is varied from 2 to 4 double monolayers. The atomic clusters are first put at a height above the surface of about 2 Å. At this distance, the interactions can drive the cluster towards its equilibrium location according to how the relaxation process is performed. If the height is much bigger, the relaxation may take more calculation time. The atoms in the clusters are positioned randomly with inter-atomic nearest neighbor distances ranging between 1.8 and 2.5 Å. The horizontal atomic positions of the 'first' atomic plane are chosen so that some atoms are located above Zn atoms while others are above O atoms. Some atoms may locate above the hollow sites on the surface. This ensures the cluster to have all type of inter-atomic interaction with the surface so that the relaxation can lead to a realistic equilibrium location on the surface. The distance between the cluster and its image is about 10 Å, enough to ensure the non interaction between the given cluster and its images. The surface effect is simulated by a thick vacuum layer of about 4 double atomic bilayers. This is an enough thickness for such calculations as reported by other works on polar ZnO surface [Zhang Yufei et al; 2010]. The conjugate gradient relaxation algorithm is adopted for all calculations[14]. All atoms of both the surface and the cluster are allowed to move according to the forces exerted by the surrounding atoms. The number of steps needed to the full relaxation varies from one structure to another. The relaxation is undertaken when the applied force on each atom is less than 5.10^{-3} eV/Å. For the defected surface, one or two oxygen atoms are removed from the surface oxygen atomic monolayer. The clusters are positioned as given in the clean surface configuration where the defected sites of the surface layer are directly under the cluster.

RESULTS AND DISCUSSION

Bulk and surface ZnO structure optimization

In this section we present the optimization of the structure of the bulk ZnO in its wurtzite phase using the SIESTA code. This includes the test of pseudo-potentials, the optimization of calculation parameters and the mesh cut-off energy, the Eshift and Norm split parameters to be used later in this study. Experimental unit cell parameters for bulk ZnO were used for this purpose. The obtained values are 150 Ry for the mesh cut-off (starting from this value), 0.15 meV for the Eshift parameter for both the bulk and surface respectively.

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The Norm split parameters are 0.30, and 0.14 meV for bulk and surface respectively. The SZP (Single Zeta Polarization) and DZP (Double Zeta Polarization) for atomic orbitals were also tested and the results give more accuracy when DZP is as mentioned in the SIESTA manual. The obtained parameters' set is then used to relax the Bulk wurtzite ZnO unit cell. The obtained unit cell parameters a, b, and c are 3.272, 3.281 and 5.293 Å respectively. This is very close to experimental and theoretical values found in the literature[15,16].

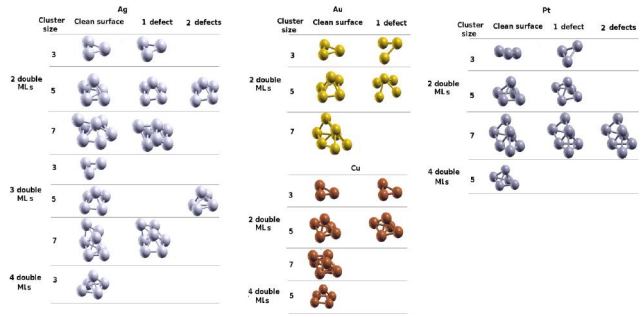

Figure 1 : Cluster deposited on the clean and oxygen defected polar oxygen terminated ZnO (000 $\bar{1}$) surface with variable thickness

Metal clusters adsorption on ZnO polar surface

The structures were built as mentioned in the previous section. The total energy E*tot* is computed for the last obtained configuration. The total energies for separated surface and cluster E*ZnO* and E*Clust* are also calculated conserving their relaxed structures and vacuum conditions. The distances ensuring the loss of interaction between the considered system and its images to zero are conserved for the separated systems calculations. The adsorption energy per atom of the cluster is estimated using the following formula:

$$E_{ads} = \frac{1}{Nat}(E_{tot} - E_{ZnO} - E_{Clust}) \qquad (1)$$

Where Nat is the number of atoms in the cluster or the cluster size.

In TABLE 1 we present the adsorption energy per atom as a function of the cluster size and the ZnO slab thickness. These energies are plotted in figure 3. The interaction energies are plotted for oxygen defected surfaces. The adsorption energy ranges from -0.879 eV/Å for 7 atoms copper clusters to -3.57 eV/Å for platinum clusters deposited on one oxygen defected surface of 2 double monolayers. Our calculations are limited to 4 bilayers thicknesses which is the limit of surface effects as reported in literature[17]. It is clear from the figures that, in general, the adsorption energy decreases with increasing cluster size. The Ag, Au, and Cu have quite comparable values while the Pt clusters adhere stronger on the ZnO polar surface. These results were reported for similar systems[18-21]. Other studies reported opposite behavior of the formation energy of noble metal deposited on the Zn terminated ZnO surface. The adhesion energy increases in this case with the surface for low coverage which is assumed to small size cluster deposition[10,17].

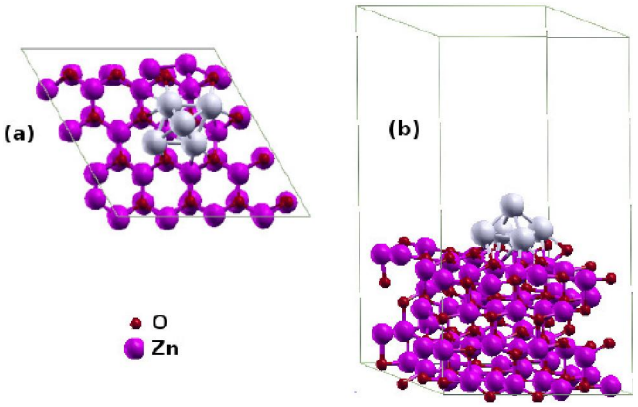

Figure 2 : Atoms silver cluster deposited on 4 double monolayers thickness ZnO(000 $\bar{1}$) surface: (a) Top view, (b): 3D view

In figure 1, a sample of the suited systems after relaxation is shown. In figure 2, the studied clusters are presented in 3D view. As we can see, the shape of the clusters is non regular, and it depends on the cluster size, the slab thickness and the existence of oxygen vacancies on the ZnO surface. To have a quantitative description width (W), length (l), height (H), and Mean negators distance (d) within the cluster, the calculated values are plotted in 4. As the figure shows, the general geometrical features for Ag (and for the other studied metals) clusters varies consistently with the adhesion energies. The clusters width (and length) increases with the cluster size. This is directly related to the decrease of the adhesion energy per atom. The weaker the adhesion is, the more the horizontal size of cluster is bigger. In one hand, the additional interactions from the surface strengths the interatomic forces and hence compacts the cluster, and in the other hand, the cluster get more vertical structure as we can see from the increase

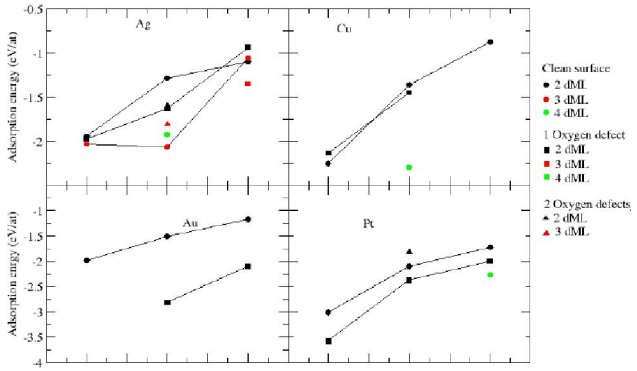

Figure 3 : Calculated adsorption energies per atom of noble metal clusters deposited on the clean and oxygen defected polar oxygen terminated ZnO(000 $\bar{1}$) surface with variable thickness and for clean and defect surfaces.3 Calculated adsorption energies per atom of noble metal clusters deposited on the clean and oxygen defected polar oxygen terminated ZnO(000 $\bar{1}$) surface with variable thickness and for clean and defect surfaces

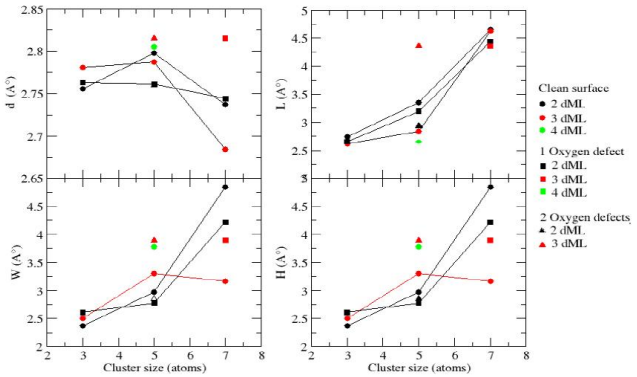

Figure 4 : Geometrical features of the Ag clusters deposited on the clean and oxygen defected polar oxygen terminated ZnO(000 $\bar{1}$) surface with variable thickness and for clean and defect surfaces

of the height of the clusters as a function of their size. The ratio width/height returns to its value for isolated clusters. Nevertheless, the mean nearest neighbor distance varies in small range (2.682 to 2.844 Å), its value for the floating clusters is naturally that for the isolated ones for the same size. The small variations of inter-atomic distances show that, in general, there is small changes in the coordination number of the atoms and thus the main bonding mechanism within the cluster. The effect of the adsorption remains in the rearrangement of the shape of the atomic aggregates. The interaction energy increases with the layer thickness. Adding more double monolayers enhances the metal clusters adhesion, thus acting as stabilization factor. The oxygen defects on the surface of the ultrathin layers behave as strengthening agent for Au and Ag clusters. For copper and platinum clusters, the adhesion is weaker for studied cases.

TABLE 1 : Calculated adsorption energy of metallic clusters on the oxygen terminated ZnO(000 $\bar{1}$) surface

		0 Ox.defect			1 Ox. defect		2 Ox. defects	
		Slab	Thickness	(double ML)				
	2	3	4	2	3	2	3	
	Clsuter size (atoms)	Eads (eV/at)						
	3	-1.940	-2.035		-1.977			
Ag	5	-1.287	-2.062	-1.926	-1.633		-1.595	-1.804
	7	-1.100	-1.062		-0.941	-1.353		
	3	-1.985						
Au	5	-1.507			-2.812			
	7	-1.172			-2.097			
	3	-2.251		-2.295	-2.137			
Cu	5	-1.359			-1.451			
	7	-0.879						
	3	-3.011			-3.575			
Pt	5	-2.101		-1.813	-2.373			
	7	-1.719			-1.997		-2.265	

CONCLUSION

We presented the results of the structural properties and the energies of adhesion of small size noble metal clusters deposited on the polar oxygen terminated ZnO ultra-thin layers using pseudo potential DFT method. The calculated energies indicate the strong adhesion of the clusters on the clean and oxygen defected zinc oxide polar surfaces. We showed also that the adhesion energy decreases with the clusters size. The shape of the clusters is controlled by its size and the interactions from the adjacent surface. The presence of oxygen defects at the surface of the ultrathin layers acts as strengthening agent for some metals while is the contrary for the others. A detailed study of the exact oxygen defect effects is desirable.

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