First-principles Study of Structural and Electronic Properties of Ag_n and Au_n (n=3-4) Clusters Adsorbed on $ZnO(000\bar{1})$ Surface

Benkrima Yamina[1*], Achouri Abderrahim[1], Benmebrouk Lazhar[1], Mohammedi Lazhar[1], Bentouila Omar[2], Ouahab Abdelouahab[3]

[1]*University of Ouargla, Faculty of Mathematics and Sciences of Matter, Laboratory Development of New and Renewable Energies in Arid and Saharan Areas, Ouargla-30000, Algeria*
[2]*Department of Matter Sciences, Faculty of Mathematics and Matter Sciences, LENREZA Laboratory, Optoelectronics Team, Kasdi Merbah, Ouargla University, Ouargla-30000, Algeria*
[3]*LPCMA, Thin Film Laboratory and Interfaces, University of Biskra-07000, Algeria*

ABSTRACT

We perform first-principles calculations to investigate various surface structures of adsorbed Ag_n and Au_n (n=3-4) clusters on a wurtzite ZnO $(000\bar{1})$ surface. The results show that both Ag_3 and Au_3 clusters prefer to be adsorbed on the T4 (hcp-hollow) and Top sites of the surface while Ag_4 and Au_4 clusters prefer to be adsorbed on the T4 (hcp-hollow sites) of the ZnO $(000\bar{1})$ surface. Ag_n/ZnO $(000\bar{1})$ system is more stable than Au_n/ZnO $(000\bar{1})$ system due to a stronger binding energy. The calculated electron structure shows that the Ag_n and Au_n clusters adsorbed on ZnO $(000\bar{1})$ surfaces exhibit metallic characteristics. We calculated and discussed the functions of Ag_n and Au_n clusters adsorbed on ZnO $(000\bar{1})$ surfaces for the first time in the present work.

Keywords: Surface, Clusters, Adsorbed, Atomic structure, DOS, Catalysts

INTRODUCTION

Zinc Oxide ZnO is a direct wide band gap ($\Delta E = 3.37$ eV) semiconductor with a large excitation binding energy of 60 meV, which makes ZnO a relation versatile material applied in field effect transistors, solar cells, gas sensors, photodetectors and photocatalysts [1-5]. To expand more its application range, scientists apply various methods to modify the electronic structures of ZnO, for example depositing or doping various atoms into ZnO bulk materials both experimentally and theoretically.

Wurtzite ZnO is the most stable among all the structures of ZnO. Its surfaces have been extensively used as active catalysts and catalyst supports and, because of their opposite polarity (0001) and (000$\bar{1}$) surfaces, have become the subject of intensive work in past years [6-9]. Noble metal/oxide systems have become an interesting field of investigation in the last years [10-12]. In these model systems, the interaction between the metal clusters and the oxides has a big role in the geometric and electronic structure of the resulting cluster/oxide interface, which in turn has a strong influence on the catalytic activity [13-15].

From late studies it is clear that ZnO supported Cu catalysts are important and become a fascinating subject of widespread investigations in recent years due to the practical applications. In deed surface properties become a little bit different from those of bulk copper [16]. From the theoretical side semi-empirical and accurate Density Function Theory (DFT) methods have been applied to study structures and electronic properties of atom or molecule deposition surfaces of ZnO [17-19].

There are theoretical and experimental studies for the surface structures and electronic properties of other noble metal clusters deposition on ZnO, such Ag_n and Au_n [20]. For clarity noble metal adsorbed on the ZnO surface, we study in this paper the structures and electronic properties of Ag_n and Au_n clusters deposition on wurtzite ZnO-O terminated (000$\bar{1}$) surface by *ab-initio* calculations (DFT). In this work we concentrate on the size effect of supported metal clusters. The results allow us to make a direct comparison of these two metals clusters on ZnO (000$\bar{1}$) surfaces. In this paper some useful information for future investigations on supported metal catalysts are provided.

Computational details

Our calculations are performed by using the first principles pseudo potential method based on DFT [21], the electronic exchange-correlation

interactions were treated by the Generalized Gradient Approximation (GGA) with the (PBE) functional [22] as implemented in the SIESTA code [23]. The energy cutoff of the plane wave basis was chosen as 200 eV. The Brillouin Zones were sampled by very dense Monkhorst Pack K points grids of $(6 \times 6 \times 1)$ for bulk ZnO, and $(3 \times 3 \times 1)$ for ZnO $(000\bar{1})$ surface and M/ZnO $(000\bar{1})$ systems. Our self-consist-field (scf) calculation of total energy was carried out with a convergence criterion of 5×10^{-4} eV, and the maximum ionic movement tolerance within the cluster and atoms were set to 0.05 Å. The structure relaxation was done using the conjugated gradient method, when the atomic forces were smaller than 0.005 eV/Å.

For the bulk ZnO, the calculated lattice constants are a=b=3.284 Å and c=5.330 Å, which are in reasonable agreement with the corresponding experimental values of 3.25 Å and 5.207 Å [24]. We periodically repeated the slab supercell including four Zn-O double layers of ZnO. The slab possesses the same lattice spacing's as those of the bulk in the x and y directions, but the atoms in z direction are relaxed.

The top two ZnO bilayers as well as the ad atom layer of the slab are allowed to be fully relaxed in the geometric optimization, while the two bottom ZnO bilayers are fixed. In addition, the dangling bonds on the bottom layer are saturated with pseudohydrogens in order to prevent unphysical charge transfer between the top and bottom slabs.

RESULTS AND DISCUSSION

Structure and stability of the surface

The models of clean ZnO $(000\bar{1})$ surface and M/ZnO $(000\bar{1})$ system are simulated from the optimized bulk wurtzite ZnO unit cell. The optimized lattice constants by the (GGA) method are a=b=3.284 Å and c=5.33 Å, which are close to the experimental values of a=b=3.258 Å and c=5.22 Å [25]. We first optimized the clean wurtzite ZnO $(000\bar{1})$ surface before investigating different structures of Ag_n or Au_n adsorbed surfaces. The calculated results for the surface are listed in Table 1. The relaxed results of the distance between the uppermost four layers (R12, R23 and R34) are given by means of the difference from the un-relaxed ideal interlayer distance.

The Zn-O monolayer spacing's for the first, second, and third bilayers are -0.309 Å, 0.082 Å, -0.104 Å respectively, in good, agreement with the theoretical results of -0.301 Å, 0.112 Å and -0.083 Å [26]. We can see that polar surface ZnO $(000\bar{1})$ tend to relax inward, because surface relaxation is mainly affected by Coulomb force and hybrid quantum effect. The energy of the surface relaxation is greater than the energy of the unrelaxation surface, so the surface relaxation of ZnO $(000\bar{1})$ is most stable. For the study of Ag_n and Au_n (n=3-4) clusters adsorbed on the ZnO $(000\bar{1})$ surfaces, a slab model with 3×3 surface periodic supercell consisted of four Zn-O double layers (Figure 1).
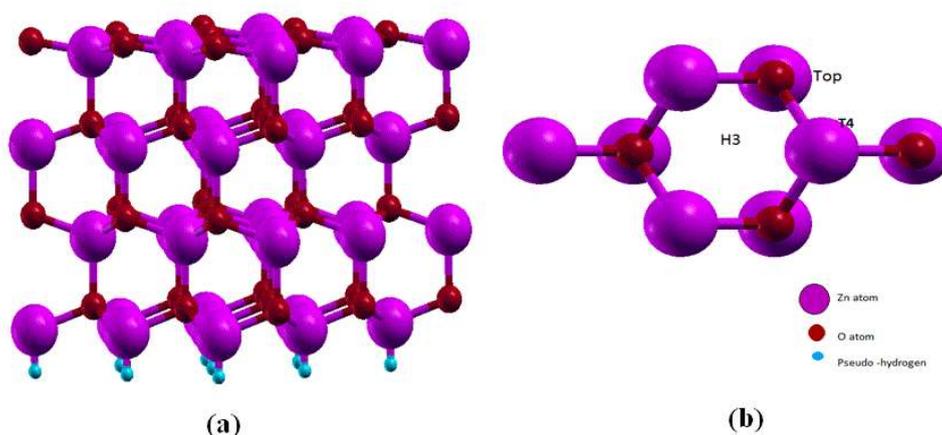

Figure 1: (a) Side view of the slab supercell 3×3 for ZnO $(000\bar{1})$ surface, (b) Top view of the slab supercell 2×2 for ZnO $(000\bar{1})$ surface. The T4 (hcp-hollow site), H3 (fcc-hollow site) and Top (top site) are the considered adsorption sites

Table 1: Relaxation of the distance between the uppermost four layers

Relaxation interlayer	Difference between the relaxed distance and the initial distance	
	This work	**Ref [26]**
R12 (Å)	-0.309	–0.301
R23 (Å)	0.082	0.112
R34 (Å)	-0.104	–0.083

To further investigate the influence of the adsorption sites to the stability of Ag_n and Au_n (n=3-4) clusters on the ZnO $(000\bar{1})$ system, four relative stable structures have been selected. The optimized structures are shown in Figure 2. Clusters used in the adsorption process in this study were calculated using the simulated annealing process' method, where heating to a high temperature around 1000 K was performed in 1000 steps. Then, they were equilibrated at this temperature in another 1000 steps, and slowly cooled down to 0 K in 500 steps. Finally, the clusters were allowed to relax at 0 K. We find that both Ag_3 and Au_3 clusters prefer to be adsorbed on the T4 (hcp-hollow sites) and the Top sites of the ZnO $(000\bar{1})$ surface while Ag_4 and Au_4 clusters prefer to be adsorbed on T4 (hcp-hollow sites) of the ZnO $(000\bar{1})$ surface.

The adsorbed Ag_n or Au_n clusters not only bond with surface O atoms, but also bond with each other. The Ag-Ag or Au-Au bond that leads has the lowest energy and is the most stable adsorption structure. So in the process of adsorption on the ZnO surface Ag_n and Au_n clusters are preferred to connect with Zn atoms with very few bonds with O atoms.
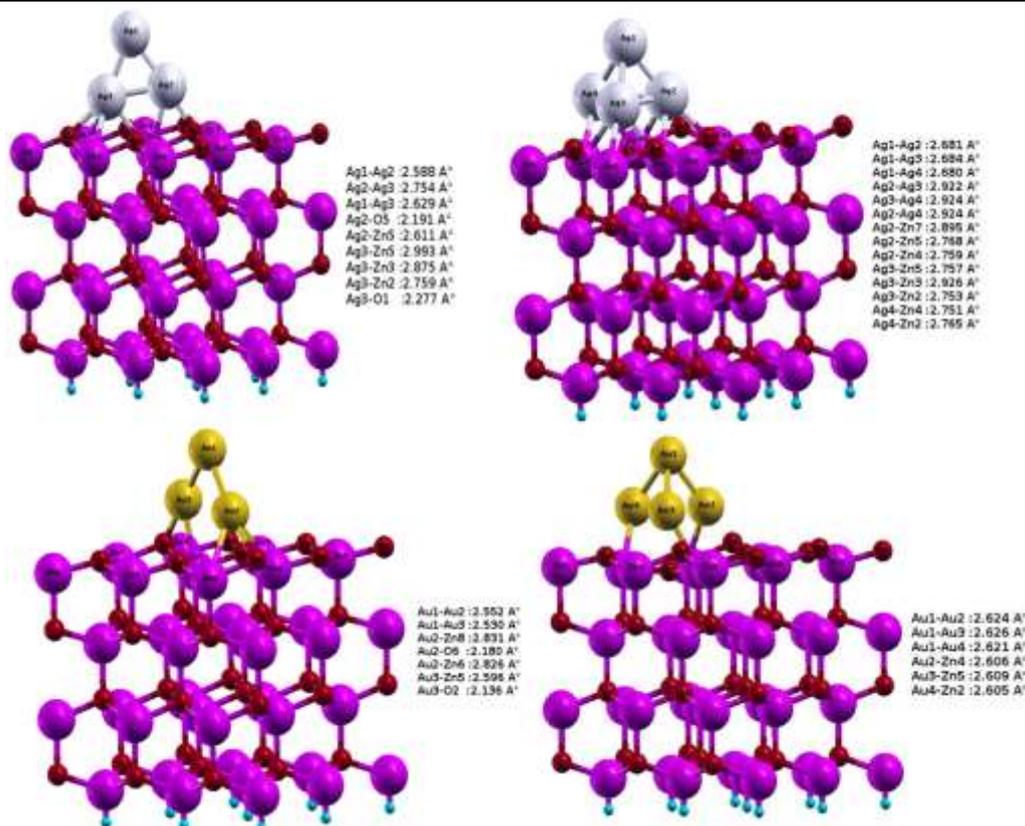
Figure 2: Side view of the selected optimized structures with a part of bond lengths of Ag$_n$ and Au$_n$ (n=3-4) clusters adsorbed ZnO ($000\bar{1}$) surfaces respectively

The calculated energies for different interaction modes of Ag$_n$ and Au$_n$ clusters with the surface are listed in Table 2. In Table 2 one can see that the adsorption of Ag$_3$ on the surface ZnO ($000\bar{1}$) is energetically more favorable than the cluster Au$_3$. It's the same observation for Ag$_4$ and Au$_4$.

Table 2: The calculated energies of M/ZnO($000\bar{1}$) (M = Ag$_n$ and Au$_n$ clusters) surfaces

Clusters	Energies (eV)
Ag$_3$	-72947.3155
Ag$_4$	-73931.7662
Au$_3$	-72690.0802
Au$_4$	-73587.9086

Binding energy

The mean interaction (binding) energy per atom of the cluster to the surface is calculated including those atoms which are not in direct contact with the surface for two reasons: (1) The non-bonded atoms interact with the bonded ones and can be considered as interacting indirectly with the surface, and (2) This is the only way to compare with the interaction energy for clusters of different size. The binding energy per atom, E$_B$ can be estimated by the following Equation:

$$E_B = \left[E(M/ZnO) - \left(E(slab) + E(M)\right)\right]/n \quad (1)$$

Where, n is the number of Ag or Au atoms, $E(M/ZnO)$ is the total energie of Ag$_n$ or Au$_n$ adsorbed on the surface, and $E(M)$ are energies of Ag$_n$ or Au$_n$ clusters respectively. The more negative value of E_B, the more stable the M/ZnO($000\bar{1}$) system. The calculated binding energies of Ag$_n$ and Au$_n$/ZnO ($000\bar{1}$) system are listed in Table 3.

Table 3: The calculated binding energies of Ag$_n$ and Au$_n$ on ZnO($000\bar{1}$) surfaces

System	Binding energies (eV)
Ag$_3$/ZnO ($000\bar{1}$)	-2.255
Ag$_4$/ZnO ($000\bar{1}$)	-2.083
Au$_3$/ZnO ($000\bar{1}$)	-1.997
Au$_4$/ZnO ($000\bar{1}$)	-1.753

The tabulated binding energies show clearly that, for the polar surface ZnO ($000\bar{1}$), the binding energy of the Ag$_3$/ZnO system is greater than for the Ag$_4$/ZnO system, and Au$_4$/ZnO system is less active in binding than the cluster Au$_3$ adsorbed of the ZnO ($000\bar{1}$) surface. Comparing the binding energies of Ag$_n$/ZnO and Au$_n$/ZnO, it is found that the binding of Ag$_3$/ZnO is stronger with the binding energy greater by -0.26 eV than that in Au$_3$/ZnO, and the same result of Ag$_4$/ZnO is stronger with the binding energy greater by -0.33 eV than that in Au$_4$/ZnO system. M/ZnO ($000\bar{1}$) system with adsorbed Ag$_n$ clusters is more stable than with adsorbed Au$_n$ clusters. This reveals that the chemical activities of

Ag_n clusters adsorbed on ZnO $(000\bar{1})$ are more than Au_n clusters adsorbed on the same surface.

Electronic properties

We calculate the electron structure for the bulk wurtzite ZnO after the structure optimization by using the same method. Our calculated results show that the band gap of the bulk is 0.45 eV, in good agreement with the theoretical results [27], which is lower than the experimental value. This is regarded as a spread problem of DFT calculations (Figure 3). The bulk ZnO calculation imply semiconductor characteristics as it is found in the literature [27].'
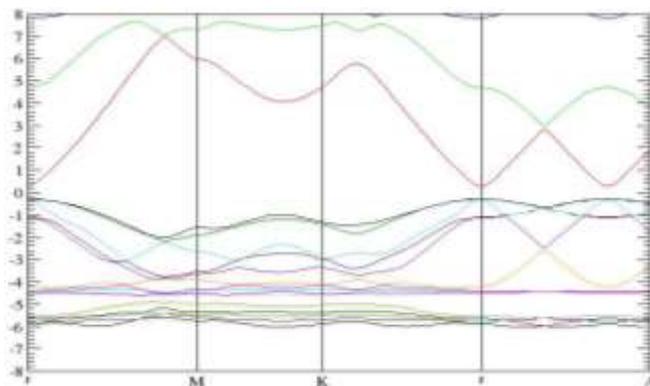

Figure 3: The calculated band energy structure of the ZnO wurtzite

Density of states

As we know, Ag and Au are inactive in bulk, but they turn into more active catalysts for ZnO nanostructures when small clusters of Ag_n or Au_n are deposited on the ZnO $(000\bar{1})$ surface. To make clear the way for this change in properties, we performed a comparative study of the electronic structure of the metal/oxide interface and the free surface. To find the electronic properties of Ag_n and Au_n clusters adsorbed on ZnO $(000\bar{1})$ surfaces, the density of states DOS of the system with a 3×3 surface cell for Ag_n and Au_n clusters adsorbed on ZnO $(000\bar{1})$ surfaces are presented in Figure 4.
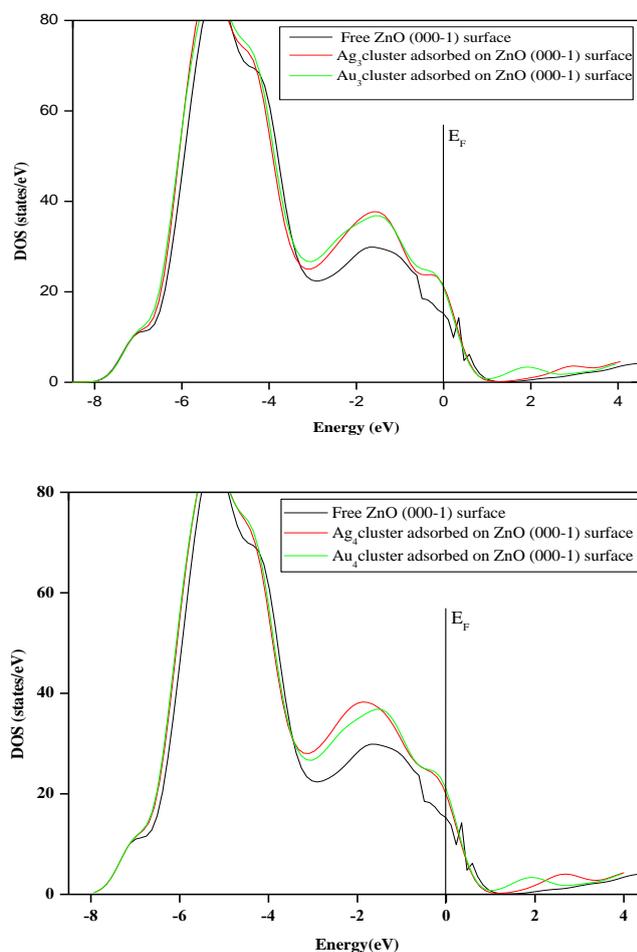

Figure 4: Density of states for Ag_n and Au_n (n=3-4) clusters adsorbed on ZnO$(000\bar{1})$ surfaces

The energy Zero (marked by a vertical line) is aligned at the Fermi level. The M/ ZnO ($000\bar{1}$) system is quite different from the surface ZnO (000-1). The density of states gives important information about the 'available' charge (electron or fraction of it) for a given energy. For example, chemical activity of a metal/oxide is proportional to the electron density near the Fermi level. The higher the density in this region, the higher the chemical activity. In Figure 4, we present the plot of the DOS variation for the M/ZnO ($000\bar{1}$) system. As we can see, the highest DOS near Fermi level is present for Ag_3, Ag_4, Au_3 and Au_4, while the free ZnO surface has little DOS in this region.

Two interesting features are observed immediately from Figure 4; First, the electronic structures of Ag_n and Au_n clusters adsorbed by ZnO ($000\bar{1}$) surfaces are the same. Second, the DOS shows that these surfaces exhibit metallic characteristics. This property is similar to the results obtained from adsorption of Ag and Au atoms on wurtzite ZnO (0001) surface [28]. Through this analysis, we can predict that Ag_n clusters can be the most chemically active with a 'selective' activation energy due to the energy distance variation from the Fermi level which is a very important property for catalysis. This notable energy of E_F for the M/ZnO compared to that of the free ZnO surface contributes in the enhanced catalytic activity of M/ZnO system.

CONCLUSION

In this paper, we investigate the structures, stabilities and electronic properties of Ag_n and Au_n clusters adsorbed on ZnO ($000\bar{1}$) surfaces are systematically investigated. We find that both Ag_4 and Au_4 clusters prefer to be adsorbed on T4 (hcp-hollow sites) of the ZnO ($000\bar{1}$) surface, and Ag_3 and Au_3 clusters prefer to be adsorbed on the T4 (hcp-hollow) and the Top sites of the ZnO ($000\bar{1}$) surface. In DOS analysis we find that the Ag_n and Au_n clusters adsorbed on ZnO ($000\bar{1}$) surfaces exhibit metallic characteristics. These conclusions were obtained using first-principles density functional theory calculations. Finally, the work function of Ag_n and Au_n clusters adsorbed on ZnO ($000\bar{1}$) surfaces are calculated and discussed for the first time in the paper. We wish the present work provided useful information about noble metal clusters adsorbed on ZnO surfaces.

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