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Full Length Article

The effect of doping with rare earth elements (Sc, Y, and La) on the stability, structural, electronic and photocatalytic properties of the O-termintaed ZnO surface; a first-principles study

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ABSTRACT

The effect of doping with rare earth atoms (Sc, Y, and La) on the stability, structural, electronic, and photocatalytic properties of the O-terminated ZnO surface was investigated by using the first-principles method. The obtained results show that all these elements have negative formation energies for all possible values of the oxygen chemical potential, and this means that the doping process with RE atoms (RE = Sc, Y, and La) enhances the stability of this surface. Our results show also that, among all considered elements, the Sc atoms have the lowest formation energy followed by Y and La, respectively. We have also investigated the effect of the formation of a RE-V_O complex on the properties of the ZnO(0 0 0 $\bar{1}$) surfaces. We find that the formation of a RE-V_O complex is energetically more favored than the formation of isolated RE_{Zn} defect under Zn-rich conditions. The effect of the formation of both RE_{Zn} and RE-V_O defects on the electronic and photocatalytic properties of the O-terminated ZnO surface was studied in details and the obtained results show that the RE-V_O complex may be the origin of the photocatalytic properties enhancement of the doped surfaces. Moreover, we found that the Sc-doped surface prepared under Zn rich conditions may have the best photocatalytic properties followed by Y- and La-doped surfaces, respectively.

1. Introduction

Zinc oxide is an important member of the II-VI semiconductors family [1]. It has a direct band gap of 3.3 eV at room temperature which means that it is a wide-band-gap semiconductor. Because of its very interesting properties, this material has attracted much attention in the last two decades and it is considered as a promising material for many application fields such as; gas sensing, photonic, photovoltaic, energy conversion, water splitting, photocatalysis, and transparent devices [2–4]. Among the proposed applications, the use of ZnO as a catalyst has attracted a lot of interest in the scientific community and many researchers have claimed that this material can be a promising material for photocatlytics and environmental safety applications [5–6]. The photodegradation of many pollution agents by ZnO based phtotcatalysts was studied in details [6–7].

From structural point of view, ZnO crystallize under ambient conditions in the well-known wurtzite structure. Because of the symmetry and the stacking sequence of atomic plane of the WZ structure, ZnO films and crystals can have both polar and nonpolar surface terminations [8–9]. The (0 0 0 $\bar{1}$) polar surface which terminates with oxygen atoms, known also as the O-terminated surface, has attracted a lot of attention and many studies have focused on the stability, electronic structure and properties of this surface [10–16].

Because of its termination with oxygen atoms, the ZnO(0 0 0 $\bar{1}$) polar surface can reacts with many molecules and chemical species, and consequently it can be very suitable for photocatalytic and gas sensing applications.

On the other hand, the performances of the as grown ZnO material are somewhat very weak. Therefore, for better performances, the doping step is very necessary. However, the choice of the dopant element is crucial and depends on the desired application [17–25]. For photocatalytic applications, the rare earth elements appear as suitable dopants. Many studies have showed that the doping of semiconductor materials like ZnO, TiO_2, SnO_2 and others with the RE atoms can improve greatly the photocatalytic performances of these materials [26–29]. However, the mechanism behind this improvement is not understood completely.

In this paper, we have used the first-principles method to study the effect of doping with rare earth atoms (X = Sc, Y, and La) on the stability, electronic and phtotcatalytic properties of the O-terminated ZnO polar surface.

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2. Computational details

In this study, the DFT + U method as implemented in the version 4.1 of the SIESTA package [30–31] was used. The Hubbard parameters values are the same as in Ref.[32]. The exchange-correlation effect was treated by the PBE exchange-correlation functional, as parametrized by Wang, Perdew and Ernzerhof [33]. The used pseudopotentials are norm-conserving (NC) and they are constructed by the Troullier-Martins scheme [34]. The atomic configurations used to generate the NC pseudopotentials involve 12, 6, and 3 valence electrons for Zn($3d^{10}4s^2$), O($2s^22p^4$) and Al($3s^23p^1$), respectively. In the case of the rare earth metals, the used pseudopotentials include semicore states and the used atomic configurations are ($3s^23p^63d^14s^2$), ($4s^24p^64d^15s^2$), ($5s^25p^64d^16s^2$) for Sc, Y, and La, respectively. The double-ζ plus polarization basis sets are chosen for all atoms and a value of 350Ry was used for the real space mesh cut-off. The real space mesh cut-off defines the plane wave cutoff for the used grid. The conjugate gradient method was used for the relaxation of all studied structures until the Hellman–Feynman force on each atom becomes smaller than 0.05 eV/Å.

The Gamma centered grid of (4 × 4 × 1) k points was used for the Brillouin zone integration during the structural relaxation and a higher grid of (6 × 6 × 1) k points was used to calculate the final properties of the investigated surfaces.

In this work, a (3 × 3) surface slab model consisting of 10 layers and a vacuum layer of 15 Å separating the slabs in the z-direction were used to model the ZnO(0 0 0 $\bar{1}$) surface (Fig. 1). The atoms in the top seven layers are allowed to fully relax while the atoms of the bottom three layers are fixed at their bulk positions to mimic the bulk substrate. Pseudo hydrogen atoms with single-ζ basis and a nuclear charge of 1.5e are used to saturate the Zn dangling bonds in the bottom layer. We note here that the use of the pseudo-hydrogen atoms to passivate the dangling bonds is usual in DFT calculations and it was done previously in many ZnO polar surfaces studies [11,35–38].

For more accuracy and to confirm the obtained results, additional calculations with the GGA-PBE functional have been carried out.

In surface science studies, a key quantity which determines the stability of any surface termination is the surface energy γ. In DFT calculations, this quantity can be calculated according to [11]:

$$\gamma = \frac{1}{A}(E_{slab} - \sum N_i\mu_i) \tag{1}$$

where E_{slab} is the total energy of the clean ZnO(0 0 0 $\bar{1}$) slab. N_i and μ_i are the number of atoms of type i in the slab and their chemical potential, respectively. A is the surface area of the slab.

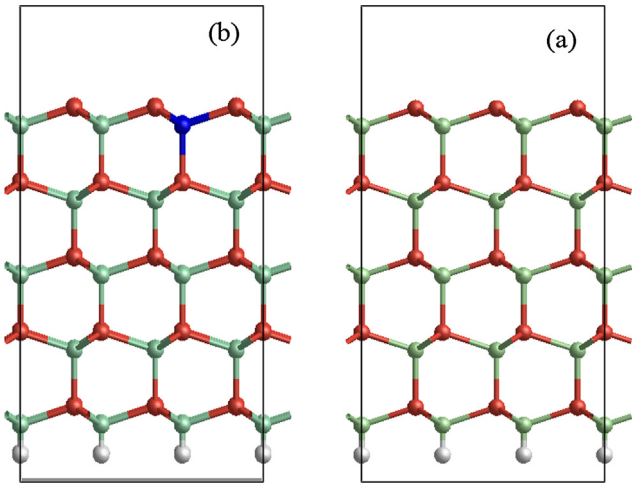

Fig. 1. The (3 × 3) ZnO(0 0 0 $\bar{1}$) surface slab model used in this study; (a) the undoped and (b) the RE-doped slab. The Zn, O, RE, and pseudo H atoms are given by green, red, blue, and white color, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The doping of the surface was done by replacing a Zn atom with a rare earth metal one. The surface energy change Δγ after doping or defect creation can be calculated by the following formula:

$$\Delta\gamma = \frac{1}{A}(E_{Tot}(\text{Slab + D}) - E_{Tot}(\text{perfect}) + \sum n_i\mu_i) \tag{2}$$

where E_{Tot}(Slab + D) is the total energy of the slab with a defect D. E_{Tot}(perfect) is the total energy of the defect-free slab. n_i is the number of added (n_i < 0) or removed (n_i>0) atoms.

We note here that a negative value of Δγ means that the stability of the surface was enhanced after the doping or the defect creation while a positive value means an opposite effect.

The chemical potential of each element X (X = Zn or O) depends on the experimental conditions, and therefore it can vary from the X-poor conditions to the X-rich conditions.

In our case, we have calculated these quantities as next:

$$\mu_{Zn} = \mu_{Zn}^{Bulk} + \Delta\mu_{Zn} \tag{3}$$

$$\mu_O = \frac{1}{2}E(O_2) + \Delta\mu_O \tag{4}$$

where μ_{Zn}^{Bulk} is the chemical potentials of Zn and it is set to half of the total energy of the Zn(hcp) unit cell. $E(O_2)$ is the total energy of the oxygen molecule.

Since the surface termination is in thermodynamic equilibrium with the bulk, the chemical potentials of the different atoms are constrained by the formation enthalpy of bulk ZnO (ΔH_f^{ZnO}) in order to maintain its stability.

$$\Delta\mu_{Zn} + \Delta\mu_O = \Delta H_f^{ZnO} \tag{5}$$

The SIESTA calculated lattice parameters and properties of ZnO as obtained by GGA and GGA + U methods are listed in Table 1. These values are in good agreement with experimental [39] and theoretical [40–42] values found in literature.

The chemical potential of the RE dopant atoms was calculated with the same manner as for Zn. For this reason, we have firstly optimized the lattice parameters of Sc, Y, and La metals and the obtained results are listed in Table 2.

Another important quantity in surface studies is the surface work function which is by definition the energy needed to transport an electron from the bulk material to vacuum through the selected surface. In our case, the work function (Φ) values of the investigated surfaces are calculated according to:

$$\Phi = E_{Vac} - E_F \tag{6}$$

where E_{Vac} is the averaged value of the electrostatic potential energy in the vacuum region of the slab and E_F is the Fermi level energy as calculated in the same slab.

The surface work function change (ΔΦ) caused by the formation of a given defect (dopant) is calculated according to:

$$\Delta\Phi = \Phi - \Phi_c \tag{7}$$

where Φ_c and Φ are the work function values of the defect-free and defective surfaces, respectively.

Table 1
The optimized lattice parameters of the w-ZnO as obtained by GGA and GGA + U calculations.

Quantity	GGA	GGA + U	Exp
a	3.298	3.301	3.248
c	5.298	5.299	5.208
c/a	1.606	1.605	1.602
ΔH_f	−3.80	−4.15	−3.60