Effect of substitution (Al and P) atoms in ZnO nanosheet on structural and electronic properties

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Abstract. We explore the possibility of formation of two different Aln and Pn atoms (n=1-6) are substitute doped of ZnO nanosheet has been investigated based on ab initio density functional theory. We study the effect of Al and P doping on the structural and electronic properties of a ZnO nanosheet. This study explains the effect of several doping on structural and electronic properties. The results indicate that Al and P substituted on the O site. The binding energy of doped system is negative, implying a stable integration of Al and P. We also found that the least energy gap lies in the Al at two atoms either in P at three atoms. These findings demonstrate that ZnO nanosheet doped of Al and P likely to be applied for various applications such as photocatalytic reactions, optoelectronic, solar cells, etc.

1. Introduction
Zinc Oxide (ZnO) is a semiconductor; it has a direct wide band gap 3.37 eV and a large exciton binding energy of 60 meV for the bulk hexagonal wurtzite crystal structure. The wurtzite crystal of ZnO has a normal dipole moment and spontaneous polarization resulting from the positively charged (0001)-Zn and negatively charged (0001)-O polar surfaces. ZnO has continued to attract great attention due to enters into a variety of practical applications such as optoelectronics, piezo-electric devices, solar cells, gas sensors, and biomedical science [1-5]. ZnO has multiple nanoscale structures such as nanosheet, nanorods, nanowire, and nanotubes have been explored in both experimental and theoretical areas. Two-dimensional (2D) materials have attracted great attention in recent times because of their unique properties, such as ultrathin thickness, large lateral size, the electron confinement in two-dimension interlayer interactions, and high optical transparency[6]. In particular, experimental observed the planar sheets of ZnO monolayer has been prepared by deposition on Ag (0001) and predicted theoretically a two-dimensional layer phase of ZnO thin films are less stable than two dimension ZnO sheets[7, 8]. Very recently, nanosheet structures of ZnO have been obtained which prepared on Pd(111) substrate[9]. Previous studies have shown that ZnO nanosheet has distinct properties when compared with thinfilm ZnO due to the effects of quantification. By doping the ZnO nanosheet gives an effective approach to adjust the physical properties...
of the material[6, 10]. ZnO is n-type, in experimental study of P doped ZnO nanorods observed ZnO nanorods transition to p-type[11].

Theoretical studies have shown that substitutional doping is an important and effective strategy for improving chemical activity. This makes two-dimensional materials have a large amount in the fields of sensing and catalysis[12, 13]. The main objective of this study is to understand the effect mechanism of Al and P dopant the stability and electronic properties of the ZnO nanosheet by preforming the first principles calculation based on density functional theory (DFT).

2. Computational approach

All calculations for this work have been implemented by using the Spanish Initiative for Electronic Simulation with Thousands of Atoms (SIESTA)[14] code, in which the density functional theory (DFT)[15]. The electronic calculation was performed using generalized gradient approximation (GGA) with the exchange-correlation potential in the form of Perdew–Burke–Ernzerhof (PBE)[16, 17]. The pseudo-potential standards are built by using Trouiller-Martins schemes that are described as interaction of valence electrons with atomic central. Pseudopotential are used valance electron configurations for Zn 3d10 4s2 and O 2s2 2p4. We note that the electronic arrangement for Al 3s2 3p1 and 3s2 3p3 for P. The initial structure of the ZnO sheet cleaved from a (0001) layer of bulk ZnO. Using the conjugate gradient algorithm, structural improvements were made to ZnO nanosheet so that the remaining forces in the optimization were smaller than 0.001 eV/Å. The Brillouin zone is used by Monkhorst Pack scheme[18]. A plane wave basis set for cut off energy was used as 200eV. We constructed the ZnO nanosheet supercell from a bulk w-ZnO structure with lattice parameters a = 3.29 Å and c = 5.3 Å these values are both experimental and theoretical results[19, 20]. The supercell of ZnO nanosheet consisting of 84 atoms has been used that take hexagonal structures with a vacuum layer 19Å along the perpendicular direction to avoid interlayer interactions.

3. Result and discussion

The structure and electronic properties of doped ZnO nanosheet have been investigated by DFT calculations. First, we have performed a full geometry optimization then the impurities were introduced by substituting Al, and P atoms into the O atoms to create the doping atom (AlO or PO). the bond length of Zn-O has been calculated as 1.9 Å, which agree well with the experimental and theoretical value of 1.92 Å[21, 22]. The Zn-O bond length in bulk ZnO is 2.01 Å is longer than bond length in ZnO nanosheet. In fact, the contraction of bond length ZnO nanosheet due to the atoms has the lowest number of neighbors compared to bulk. As a result, atoms in ZnO nanosheet are closely related, led to a smaller Zn-O bond length compare with bulk. We have done doping of Al atoms in ZnO nanosheet, and in figure 1, shown the ground state structures of Aln-ZnO (n= 1-6). The bond length between the Al and nearest Zn is 2.31 Å, it is clear that the Al-Zn is increased compared of the Zn-O bond of the ZnO nanosheet.

In Al2-ZnO having Al-Al bond length is 2.28 Å in ZnONS. In the same way, we doped the P atoms the relaxed structures of Pn-ZnO (n= 1-6) are presented in figure 2.

The bond length of P-Zn in relaxed structure is 2.18 Å this value agrees well with the theoretical value in case (6×6) is 2.18 Å[23]. In both cases it is found that the complexes doping ZnO are stable up to n=1-6. To demonstrate the relative stability of Al and P atoms doping ZnO nanosheet, the binding energy can be expressed as

$$E_b(ZnO:M) = E_{tot}(ZnOM_n) - nE_{Zn} - nE_O - nE_M/N$$

(1)
Figure 1. ZnO nanosheet, the red and purple spheres refer to O and Zn, atoms respectively. The blue sphere refers to the dopants Al atoms. (a) pristine and (b-g) optimized structure of Al doped in the ZnO nanosheet respectively.
Figure 2. (a-f) Optimize structure of P doped ZnO nanosheet, the gold spheres refer to P atoms.

Where $E_{\text{tot}}(\text{ZnOM}_n), E_{\text{Zn}}, E_{\text{O}},$ and $E_{\text{M}}$ are the total energies one atom of Zn, O, and dopant $n$ representing the number of atoms of each Zn, O, and dopant respectively, and $N$ are the total number of atoms. The negative value of binding energy corresponds the system is a stable, and observed the system is metastable when add the dopant. This makes the system in a state of relaxation in relation to all degrees of freedom. In figure 3, it was observed that binding energy will increase when the doping one atom, then decreases gradually with increasing doping dose of Al and P atoms in nanosheet. This is due to the association of both Al and P atoms with Zn atoms will weaken Zn-O bonds.

![Graph of binding energy vs number of dopant atoms](image)

**Figure 3.** The variation binding energy for Al$_n$-ZnO and P$_n$-ZnO ($n=1-6$).

The ionization process for Vertical Ionization Potential (VIP) and Vertical Electron Affinity (VEA) is an instantaneous process occurs when removing or adding an electron in addition does not relax of
molecular geometry. The Vertical Ionization Potential of ZnO nanosheet doping Al and P atoms is shown in fig. 4. In the case of Al we observed that there is a slight stability with the increase of doping and then get a sharp decrease in Al$_n$-ZnO and then returns in increase. The decrease in the ionization potential due to the fact that the Al contains one electron in the secondary casing p, which facilitates the loss of this electron. In the case of p the potential of ionization was found to vary between 3.5eV and 4.1eV and take a form oscillatory. The ionization potential for p higher of ionization potential for Al, this is due to the secondary casing for P is saturated with more than that in the Al. Figure 5 shows our calculated electron affinity of doped ZnO nanosheet for different Al and P atoms. We observed that the electron affinity for Al dopant takes a form of oscillator and shows the similar trend for P dopants. The lowest value of electron affinity at Al$_1$-ZnO and P$_1$-ZnO while highest value Al$_6$-ZnO and P$_6$-ZnO, in general the behavior is oscillatory. The high electron affinity for Al and P dopants is found to very 3.0eV and 3.28eV; this indicates that ZnO nanosheet is likely to be a good electron acceptor. So it can be used in applications such as photovoltaics as well as charge mobility and re-regulation energy.

Figure 4. The variation ionization potential for Al$_n$-ZnO and P$_n$-ZnO (n= 1-6).
The energy band gap of nanosheet can be determined by the difference between highest occupied molecular orbital and lowest unoccupied molecular orbital (HOMO-LUMO gap), and energy gap is also considered one of chemical stability indicators for nanosheet. A plot of the variation of energy with number of atoms is shown in Fig. 6. The energy gap has been calculated at the GGA-PBE level that shows the lowest energy gap has 0.03 eV and 0.012 eV for Al and P doped. It is less than the energy gap in pure ZnO nanosheet. This is due to the fact that the electrons reside in the conduction band of a semiconductor and get full saturation. While we get the highest energy gap 0.10 eV at Al atom and 0.11 eV for P atoms this leads to higher stability kinetic.

**Figure 5.** The variation electron affinity for Alₙ-ZnO and Pₙ-ZnO (n= 1-6).
4. Conclusions
In summary, we investigated the electronic structure, and structural stability of ZnO nanosheet doped by Al, and P using the ab initio calculation in generalized gradient approximation (GGA). Our results show that the lowest energy gap in Al$_n$-ZnO, and P$_n$-ZnO are smaller than the of ZnO nanosheet. This refers to the kinetic reactive of these complexes. Also we observed that the P doped ZnO nanosheet is slightly more reactive compared to Al because it has the highest value of a vertical electron affinity and ionization potential.

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