



روافد المعرفة

مجلة

للعلوم الطبيعية والتطبيقية

تصدر عن كلية العلوم - جامعة زايد - تي هوندت - ليبيا
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الكلمة الافتتاحية،

السلام عليكم ورحمة الله وبركاته،،

عليه نتوكل، وبه نستعين، نحمده سبحانه على كل عمل.

أعزائي القراء والمهتمين بالمعرفة والعلم،

بحمد الله وتوفيقه تم صدور العدد العاشر من مجلة "روافد المعرفة"، الصادرة عن كلية العلوم بجامعة الزيتونة. إن هذا الإصدار الذي نقدمه لكم يعكس التفاني والتميز الذي يتميز به فريق العمل والباحثين الذين ساهموا في إثراء هذا العدد بمقالاتهم وأبحاثهم الرائعة.

مجلة "روافد المعرفة" تعد نافذة مهمة لنشر العلم والبحث العلمي، وهي تسعى جاهدة لتعزيز التواصل العلمي وتبادل المعرفة بين الباحثين والمهتمين بالمجالات العلمية المختلفة. إن تنوع المواضيع المطروحة في هذا العدد يعكس الاهتمام الكبير بمجالات العلوم الطبيعية والتطبيقية، ويعزز الوعي والفهم العلمي للقراء.

في هذا العدد العاشر، ستجدون مقالات متنوعة تتناول العديد من المواضيع المميزة والمفيدة في مجالات العلوم الطبيعية والتطبيقية. ولذلك، نحن واثقون من أن هذا العدد سيثري ثقافتكم ويوسع آفاق المعرفة لديكم.

في ختام كلمتنا، أود أن نعرب عن امتناننا العميق للفريق الذي عمل بجهد واجتهاد لجعل هذا العدد حقيقةً، وأشكر جميع الباحثين الذين شاركوا معنا معرفتهم وخبراتهم. وأتمنى أن يكون هذا العدد بمثابة نقطة انطلاق لمزيد من النجاح والتألق في المستقبل.

نتمنى لكم قراءة ممتعة ومفيدة، ونحن في انتظار ملاحظاتكم وآرائكم القيّمة.

شكراً لتقّنتكم ودعمكم المستمر.

دمتم بخير وعلم نافع.

هيئة التحرير

اشتراطات النشر في مجلة روافد المعرفة

- 1- أن يكون البحث أصيلاً ومبتكراً ولم يسبق نشره في أي جهة أخرى، وتتوفر فيه شروط البحث العلمي المعتمدة على الأصول العلمية والمنهجية المتعارف عليها في كتابة البحوث الأكاديمية.
- 2- أن يكون البحث مكتوباً بلغة سليمة، ومراعياً لقواعد الضبط ودقة الرسوم والاشكال – إن وجدت و مطبوعاً بخط Microsoft Word (Simplified Arabic) بينط (14) للغة العربية، وخط (Times New Roman) بينط (12) للغة الإنجليزية، وألا تزيد صفحات البحث عن (35) صفحة متضمنة المراجع والملاحق (إن وجدت).
- 3- يجب أن يشتمل البحث على العناصر التالية - عنوان البحث باللغتين العربية والإنجليزية - - ملخص تنفيذي باللغتين العربية والإنجليزية في نحو 100 - 125 كلمة والكلمات المفتاحية (keywords) بعد كل ملخص .
- 4- يتم توثيق الهوامش وفق طريقة الجمعية الأمريكية السيكولوجية (APA) بإصدارتها المختلفة.
- 5- يُفضل أن تكون الجداول والاشكال مدرجة في أماكنها الصحيحة، وأن تشمل العناوين والبيانات الإيضاحية الضرورية، ويراعى ألا تتجاوز أبعاد الاشكال والجداول حجم حيز الكتابة في صفحة.
- 6- أن يكون البحث ملتزماً بدقة التوثيق، استخدام المصادر والمراجع، وأن تثبت مصادر ومراجع البحث في نهاية البحث.
- 7- تحتفظ المجلة بحقها في اخراج البحث وإبراز عناوينه بما يتناسب واسلوبها في النشر.
- 8- - ترحب المجلة بنشر ما يصلها من ملخصات الرسائل الجامعية التي تمت مناقشتها وإجازتها على أن يكون الملخص من إعداد صاحب الرسالة نفسه.
- 9 - تُرسل نسخة من البحث مطبوعة على ورق بحجم (A4) إلى مقر المجلة، ونسخة إلكترونية إلى إيميل المجلة : wafedalmarefa@gmail.com او على رقم الواتساب 0921253199 على أن يدون على صفحة الغلاف اسم الباحث لقبه العلمي، مكان عمله، تخصصه، رقم هاتفه وبريده الإلكتروني.
- 10- يخطر الباحث بقرار صلاحية بحثه للنشر من عدمها خلال مدة شهرين من تاريخ استلام البحث.
- 11- في حالة ورود ملاحظات وتعديلات على البحث من المحكم ترسل تلك الملاحظات إلى الباحث لإجراء التعديلات اللازمة بموجبها على أن تعاد للمجلة خلال مدة أقصاها شهر واحد.
- 12- الأبحاث التي لم تتم الموافقة على نشرها لا تعاد إلى الباحثين.
- 13- تؤول جميع حقوق النشر للمجلة.

ملاحظة.

البحوث المنشورة في هذه المجلة تعبر عن رأي أصحابها ولا تعبر بالضرورة عن رأي المجلة أو الكلية أو الجامعة.

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Theoretical Study of Phosphorus Impurity Incorporation in ZnO

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المخلص

أكسيد الزنك (ZnO) هو مادة شبه موصلة شفافة و يمكن أن تستخدم في تطبيقات الالكتروضوئية. على الرغم من أن شوائب المجموعة الخامسة التي تحل محل ذرة الأكسجين O قد اقترح أن تكون الحل لمشكلة صعوبة انجاز مادة مطعممة من النوع **p-type** ذو خصائص كهربية. تم استخدام نظرية كثافة دالة الدالة المحلية لدراسة خصائص تطعيم ذرة الفوسفور P في ZnO من نوع **p-type** باستفاضة. و قد وجدت أن النتائج كانت متفقة مع الدراسات السابقة الأخرى. وهذا يعني أن المستوى المانح هو المستوى المهين متحصلا على ZnO من النوع **n-type** عندما يتم استبدال ذرة الزنك Zn بذرة الفوسفور (PZn) ، وكذلك يمكن إنشاء المستوى القابل عندما يتم تشكيل المركب ((Pzn-2Vzn) عند إدخال P وإزالة ذرتين Zn شاغرتين-2 (V)، لكن هذه المستويات لم تكن قريبة جدا من حزمة التوصيل و حزمة التكافؤ على التوالي. من خلال استبدال ذرة الأكسجين O بذرة P في الحالة الموجبة، الرابطة بين الذرتين O و (P-O) يمكن أن تتشكل مؤديا إلى خلق مستويات عميقة من المانحين والمستقبلين. بالإضافة إلى ذلك، تمت دراسة P المدخل بينيا في ZnO و أظهرت الدراسة أنه يمكن تشكيل بسهولة مع P المدخلة تبادليا والتي يمكن أن تعزز الموصلية من النوع **n-type** على الموصلية من النوع **p-type** في ZnO المطعم بذرة P.

الكلمات المفتاحية: نظرية كثافة الدالة، الفسفور، أكسيد الزنك.

Abstract

ZnO is a transparent semiconductor that can be used in optoelectronic applications. However, substitution of O with group-V impurities has been suggested as a solution for achieving p-type electrical doping. First-principles local density functional theory has been used extensively to study the properties of P-doping in ZnO. These results were in agreement with those of previous studies. This means that the donor level is the dominant yielding n-type ZnO when the Zn atom is replaced with a phosphor atom (PZn), and the acceptor level can be created when a PZn complex with two Zn atoms (two vacancies) is formed, but they are not particularly shallow. By substituting P atoms with O atoms in the positively charged state, a P-O bond was formed, yielding deep donor and acceptor levels. In addition, interstitial P has been studied, and it has been shown that it can be easily formed with substitutional P and can enhance the n-type over p-type conductivity in P-doped ZnO.

Keywords: DFT, phosphorus, zinc oxide.





Introduction

Zinc oxide is an ionic material composed of Zn^{+2} and O^{-2} and it has a wide direct band gap with an energy of 3.4 eV and a large binding energy of 60 meV. This makes the material an exciting material for many applications such as optoelectronic devices, lasers, and light-emitting diodes (Bagnall et al., 1997; Tang et al., 1998; Hwang et al., 2005), where it is a transparent semiconductor for a wide range of wavelengths. The difficulty in carrier doping of ZnO-related materials to achieve p-type materials is the greatest obstacle to using the material in electronic and photonic applications.

The most interesting p-type ZnO is group-V elements, such as nitrogen, phosphorus, and As. Theoretical studies have shown that it is difficult to explain the p-type activity of nitrogen at room temperature (Kobayashi et al. 1983; Park et al. 2002). In addition, a high concentration of hole carriers of nitrogen impurities (10^{17} – 10^{19} cm⁻³) has been shown experimentally (Look et al., 2002; Bian et al., 2004), and other dopant phosphors and As have been incorporated to obtain p-type samples (Ryu et al., 2003; Kim et al., 2003).

ZnO exhibits n-type conductivity even without intentional doping, and it is also difficult to obtain p-type conductivity because of carrier compensation (Zhang et al., 2001). Recent calculations have shown that incorporating phosphors into ZnO may result in a p-type conductivity (Kim et al., 2003; Ryu et al., 2003; Heo et al., 2004).

However, experimentally, P-doping tends to enhance n-type behavior in as-deposited films, indicating the formation of shallow donor states. This is contrary to the simple expectation of acceptor defect formation via substitution at the O site (Heo et al., 2004).

The P on the Zn and O sites, interstitial phosphors, and related defects in ZnO were modeled to investigate the electronic structures. That has been obtained by comparing the formation energies using density functional pseudopotential calculations implemented in the AIMPRO program. The results are discussed in terms of chemistry to explain the formation of donors, rather than acceptors.

Method

AIMPRO package, which is based on density functional theory, has been used in these calculations (Briddon & Jones, 2000; Rayson & Briddon, 2008). Defects were simulated using large supercells and periodic boundary conditions. The cells are repeats of a primitive hexagonal unit cell containing two Zn and two O atoms with lattice vectors $a[1000]$, $a[0100]$, and $c[0001]$. The lattice constants of the unit cell were calculated as $a=6.18 \text{ \AA}$ and $c=9.81 \text{ \AA}$. P-centers are modelled in supercells composed of 72 or 192 atoms formed from (3 3 2) and (4 4 3) primitive cells, respectively.

The Brillouin zone was sampled using the Monkhorst-Pack (Monkhorst and Pack, 1976) scheme with a mesh of 2





2 2 k-points. A conjugate-gradient scheme was used to optimize the structures, with the force on atoms of optimized structures having 10⁻³ au, and the total energy of optimized structures was reduced to less than 10⁻⁵ Ha.

Atoms were simulated using ab initio pseudopotentials (Troullier & Martins, 1991), and the total energies and forces were obtained with a local density approximation for the exchange-correlation (Perdew and Wang, 1992). The wave functions and charge density were expanded in terms of Gaussian and plane waves, respectively (Shaw & Briddon, 2007). The s, p, and d functions for Zn, O, and P were included, with 28, 28, and 32 functions per atom, respectively. Plane waves of up to 150 Ha were used to expand the charge density.

Reaction paths and energies were obtained using a climbing nudged elastic band (NEB) model (Henkelman et al., 2000; Henkelman & Jonsson, 2000). We calculate the formation energy of a defect X using

$$E^f(X, q) = E^{tot}(X, q) - \sum_i \mu_i + q(E_v(X, q) + \mu_e) + \zeta(X, q) \quad (1)$$

where E^{tot}(X,q) is the total energy calculated for system X containing the defect in charge state q, μ_i denotes the chemical potential of the species (i =Zn, O, and P), E_v(X,q) is the Fermi energy at the top of the valence band, and μ_e is the electron chemical potential, which is

defined as zero at the top of the valence band. In ZnO, the chemical potentials of components μ_O and μ_{OZn} are related by E(ZnO)=μ_O+μ_{Zn} where E(ZnO) is the energy per bulk of pair in ZnO. The range of possible values for μ_O and μ_{Zn} is related to the requirement for ZnO to be stable relative to decomposition into its elemental constituents; thus, the zinc-rich limit is taken from zinc metal and the oxygen-rich limit μ_O is taken from the O₂ molecule. The heat of formation for ZnO in this way is calculated to be 3.9 eV, while experimentally is 3.61 eV (Lide, 2004)[20]. The chemical potential for P was obtained by assuming that ZnO is in equilibrium with either P₄O₆ or Zn₃P₂.

For the electrical characteristics of the defect centers, we calculated the transition levels, E(q,q'), defined as the electron chemical potential, where the formation energies for the two charge states, q and q', are equal. For example, the donor level is the value of μ_e for which E^f(X,0)=E^f(X,+1) and E^f(X,0)=E^f(X,-1) for the acceptor level.

RESULTS

1- P on the Zn site, and related centers

First, we examined the substitution of P for Zn (PZn). Because P has three more valence electrons than Zn, it is expected that PZn may be a triple donor, potentially able to exist in a range of positive charge states. However, care must be taken in





such an interpretation. Examination of the relaxed structure, shown schematically in Fig. 1 indicates the dramatic dilation of some of the surrounding Zn-O bonds, and it is more realistic to describe the system not as PZn but as the PO₄ molecular group (a phosphate anion) inside a cavity made up immediately by 12 Zn sites. The phosphate group normally exists in the 3 oxidation state, and the twelve Zn atoms surrounding PO₄ provided these electrons. However, since each Zn atom has an excess of 1/2 an electron, there are a further three electrons to be accounted for. In our calculations, these go to the host conduction band so that the phosphate group in ZnO is a triple donor.

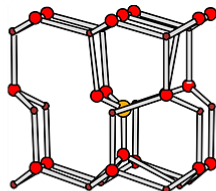


Fig. 1: Schematic of the structure of P_{Zn} in ZnO. Brown, red and yellow atoms are Zn, O and P respectively. Vertical and horizontal axes are approximately [0001], and [0110].

By calculating the formation energy as a function of the charge state and μ_e , the electrical levels of PZn can be estimated. The results are shown in Figure 2. We found that PZn is thermodynamically stable only in the +3 charge state, and can therefore be viewed as a highly effective n-type dopant. We also examined the possibility for PZn of PZn-forming pairs. One may expect a strong Coulomb repulsion between these centres; indeed, by increasing the distance between two

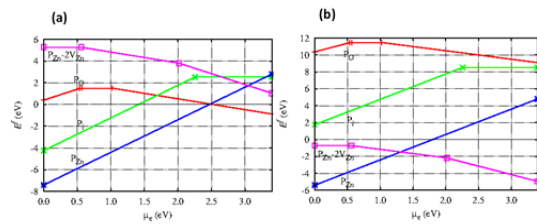


Fig. 2: Plot of E_f vs. μ_e for key P-containing defects in ZnO calculated using the 192 atom supercell. (a) Oxygen-rich conditions and (b) zinc-rich conditions.

PZn atoms in the same simulation cell, the energy is reduced.

Although PZn is a multiple donor, it can be converted into an acceptor by the formation of a complex with components with sufficient acceptor activity. One model was a complex with two vacant Zn (VZn) sites (Limpijumnong et al., 2004; Lee et al., 2006). This is possible because VZn is a double acceptor (Limpijumnong et al., 2004), and the stability of the complex is favourably influenced by attractive Coulomb interactions.

Many possible PZn–2VZn orientations are determined by the VZn positions relative to PZn, all of which are metastable. The most stable structure is shown in Fig. 3. The energies of the various orientations where the vacancies are in the nearest shell of the Zn neighbours to the P site vary by just 100s of meV, and the most stable is 35 meV, which is lower than that previously suggested using smaller simulation cells (Lee et al., 2006).

The binding energy of the complex with relatively separate PZn and two VZn centres is 3.9 eV. The formation energies for various charge states of the most stable acceptor system are shown in Fig. 2. We





find that the acceptor level is quite deep at approximately $E_v+0.5$ eV, and would therefore not be a good candidate for p-type doping.

2- P on the O site, and related centres

Second, we examined the P at the O-site (PO). The structure obtained for neutral PO is shown in Fig. 4(a). The P remains on-site and is approximately tetrahedral. Since P has one fewer valence electrons than the oxygen atom it replaces, it is expected that PO will be an acceptor, and indeed this is what we find.

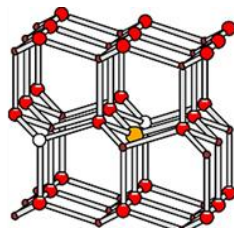


Fig. 3: Plot of atomic structure of phosphorus substitutional ZnO at a Zn site with two Zn vacancy, where brown, red, and yellow atoms are zinc, oxygen, and phosphorus, respectively. The vertical and horizontal axes are [0001], and [0110]

The charge-dependent formation energies (Fig. 2) indicate an acceptor level around $E_v+1.0$ eV, which is too deep for p-type doping. This result is in agreement with previous theory (Park et al., 2002). In addition, one can form a donor state with PO, as it can undergo a chemical reaction with a next-nearest-neighbor oxygen atom, forming the structure shown schematically in Fig. 4(b), the so-called AX center (Park et al., 2002). Indeed, our calculations suggest that PO may donate two electrons in this form. The AX+1 structure which we find to be lowest in energy is more stable than the previously

suggested orientation (Park et al., 2002), which we find is meta-stable and 0.5 eV, higher in energy. In addition, there is a meta-stable, on-site form in the positive charge state which is around 1.0 eV higher in energy than AX+1.

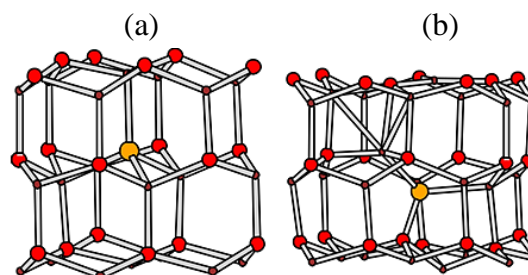


Fig. 4: Schematics of P_o in (a) the neutral charge state and (b) the positive charge state, AX structure. Structure colors and axes are as in Fig. 3.

The substantial structural rearrangement can be viewed as the formation of a P=O molecular fragment within the ZnO lattice, and the band gap levels are highly characteristic of - interactions between the two atoms.

This picture is extended when examining the possibility of PO-forming pairs. In this case, we can view the formation of (PO)₂ as the insertion of a P₂-molecular fragment. This significantly reduces the formation energy for substitution onto the oxygen lattice; however, (PO)₂ only has donor properties. Therefore, at equilibrium, the formation of PO acceptors will have to compete with the formation of (PO)₂ donors, further reducing the probability of successfully producing p-type ZnO via such a route.

The PO defect behaved as a double donor. The (0/+) and (+/++) transition levels, which are occupied by four electrons, are located in the middle band



gap, and the wave function shows that the occupied levels are derived from the anti-bonding combination between the surrounding P atom and O atoms, and the AX+1 structure is proven to be.

3- Interstitial phosphorus

Finally, we examined the possibility of phosphorus lying at an interstitial site (Pi). A significant number of metastable Pi structures are separated by small energy differences. They are characterized by P coordinated with either one or two host oxygen atoms, and the most stable structure is illustrated in Fig. 5.

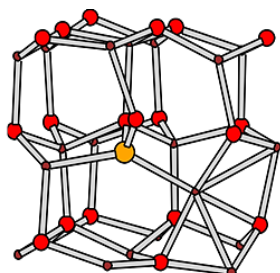


Fig. 5: Schematic of the most stable Pi structure. Colors and axes are as in Fig. 3.

As can be seen in Fig. 2, Pi behaves as a triple donor, with a (0/+3) transition around $E_v+2.3$ eV (the +1 and +2 charge states are thermodynamically metastable). As with PZn behaving as a phosphate ion, the band gap levels of Pi suggest that Pi can be characterized as a PO₂ ion fragment.

More importantly, for Pi, we examined the energy barrier for migration. The profile is shown in Fig. 6, which includes many stages such as bond rotations and interconversion between PO₂ and P=O

molecular fragments. The path details are less important than the rate-limiting barrier, which is approximately 1 eV. At growth temperatures, such a barrier would be easily overcome, so we interpret this as Pi being a relatively mobile species.

In addition, during the simulations of Pi, under favourable conditions, we observed spontaneous reactions of the type $P_i \rightarrow P_{Zn} + Z_{(n_i)}$. Both products were donors, further supporting the role of P as an n-type dopant. We estimate the reaction to be exothermic by 0.44 eV in the neutral charge state.

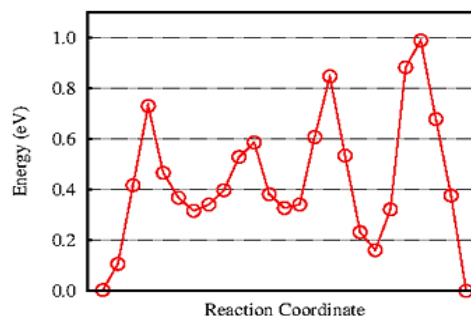


Fig. 6: NEB calculated migration barrier for interstitial phosphorus in ZnO.

Discussion

Table 1 lists the different formation energies of different structures as a function of the supercell size. The relatively large differences between PZn and PZn-2VZn illustrate that the smaller cells commonly used in previous studies (Lee et al., 2006; Kim et al., 2003) are insufficient.



Tab.1: The difference in formation energies of different structures, $E^f(192) - E^f(72)$.

Defect	P _O	P _{Zn}	P _{Zn} -2V _{Zn}	P _i
E ^f (eV)	-0.23	0.69	-0.63	-0.02

Most of the P-related defects discussed here are donors, with the possible exception of PZn-(VZn)₂. However, in order to predict which species are most likely to form under real conditions, we must compare their total formation energies.

In the limit of O-rich condition, Fig. 2(a), substitution onto the Zn-lattice is highly favorable and the possible acceptor species PZn-(VZn)₂ is favored for n-type material. However in p-type material, PZn is favored, so in equilibrium a combination of the two species would form and a highly electrically compensated material is the most probable result. Under O-rich conditions, unsurprisingly PO is very high in energy and unlikely to form at all. Similarly, P_i has a high formation energy and is therefore at most likely to be a minority species.

For Zn-rich material the PZn-(VZn)₂ is much less favorable than PO, but for most values of e , it is still PZn which is favored.

The trend for the stabilization of PZn can be traced to the same driving force for the formation of the AX-form of PO: the P-O bonds formed in these configurations

include a much greater degree of covalence than Zn-O or P-Zn bonds, and this generally stabilizes P-defect configurations where P-O bonding is possible.

In summary, the overwhelming trend is for phosphorus to adopt forms with P-O bonds which are consistently donor in character. We conclude that P-doping is most effective for n-type material.

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