



روافد المعرفة

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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 نافذةً 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 لتفانيكم 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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Defect Properties of Nitrogen in ZnO

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المخلص

مادة أكسيد الزنك ZnO لها عدة تطبيقات في الإلكترونيات الضوئية وتستخدم كأشباه موصلات شفافة. ومع ذلك، فقد ثبت أنه من الصعب الحصول على شبه موصل من النوع p-type في مركب أكسيد الزنك عند إضافة شوائب المجموعة الخامسة في الجدول الدوري وعند استبدال ذرة الأكسجين O بشوائب من هذه العناصر والتي فرضت كحل للحصول على شبه موصل النوع الموجب. من خلال برنامج المحاكاة الحاسوبي الإمبرو (AIMPRO) والذي يعتمد على نظرية كثافة دالة البالة (DFT)، تم دراسة بشكل موسع خصائص تطعيم ذرة النيتروجين ((N-doping) في ZnO. وجدنا و بالاتفاق مع الدراسات السابقة الأخرى، أنه عند استبدال ذرة N بذرة Zn (NZn) أن المستويات المانحة هي المهجنة والذي ينتج مادة ZnO من النوع n-type، وأن الشائبة المركبة من NZn مع شواغر و ذلك بإزالة ذرات من Zn تخلق مستويات قابلة، على الرغم من أن هذه المستويات ليست قريبة جدا بالنسبة لحزمات التوصيل و التكافؤ على التوالي. وعند استبدال ذرة أكسجين بالنيتروجين NO تكونت مستويات عميقة من المانحة والقابلة من خلال تكوين رابطة بين ذرة O و ذرة ((N N-O) في الحالة الموجبة. كذلك قمنا بدراسة أيضا خصائص ZnO عند إدخال ذرة O و ذرة N بينيا مع N البديلة والذي يظهر مركب يمكن تشكيله بسهولة، و الذي بدوره عزز الموصلية من النوع n-type على النوع p-type في مادة ZnO. الكلمات المفتاحية: نظرية كثافة الدالة، النيتروجين، أكسيد الزنك.

Abstract

ZnO has applications in optoelectronics and is used as a transparent semiconductor. However, p-type electrical doping of has proved difficult to achieve, with group-V impurities substituting for O being suggested as a solution. Using first-principles local density functional theory, we extensively studied the properties of N doping. In agreement with others, we find that NZn is the dominant donor rendering ZnO n-type, and a complex of NZn with Zn vacancies is an acceptor, although not particularly shallow. NO has deep donor and acceptor levels through the formation of N–O bonds in the positive charge state. We also studied interstitial O and N, which showed that they readily form complexes with substitutional N and can enhance n-type over p-type conductivity in N-doped ZnO.

Keywords: : DFT, Nitrogen, Zinc oxide.





Introduction

Zinc oxide is a transparent semiconductor with a direct, wide band gap of 3.4 eV and a large exciton binding energy of 60 meV. This has led to ZnO being proposed for applications such as optoelectronic devices, lasers, and light-emitting diodes (Bagnall et al., 1997; Tang et al., 1998; Hwang et al., 2005). The most significant impediment to the widespread exploitation of ZnO-related materials in electronic and photonic applications is the difficulty in carrier doping, specifically as it relates to achieving p-type materials. Perhaps the most promising dopants for p-type ZnO are the group-V elements, although theoretical studies have indicated difficulty in explaining the p-type activity for nitrogen at room temperature (Kobayashi et al., 1983; Park et al., 2002). Nevertheless, high hole carrier concentrations from N impurities (10^{17} - 10^{19} [cm]⁻³) have been achieved experimentally (Look et al., 2002; Bian et al., 2004), and p-type samples obtained with other dopants such as P and As (Ryu et al., 2003; Kim et al., 2003). An important characteristic of ZnO is that it exhibits n-type conductivity even without intentional doping, and obtaining p-type conductivity also occurs due to carrier compensation (Zhang et al., 2001). Recent calculations indicate that phosphorous

doping may yield p-type conductivity (Ryu et al., 2003; Kim et al., 2003; Heo et al., 2004). However, experimentally, N-doping tends to enhance the n-type behavior in as-deposited films, indicating the formation of shallow donor states. This is contrary to the simplistic expectation of acceptor-defect formation via substitution on the O site (Heo et al., 2004). In this paper, we investigate the electronic structure of various N defects in ZnO by comparing the formation energies through first-principles density functional pseudopotential calculations and discuss the chemistry that tends to enhance the formation of donors rather than acceptors.

Method

Calculations are based on density functional theory using the AIMPRO package (Briddon & Jones, 2000; Rayson & Park, 2008). Defects are simulated using large supercells and periodic boundary conditions. The cells are repeats of the primitive hexagonal unit cell containing four atoms (Zn₂O₂) with lattice vectors $a[1000]$, $a[0100]$, and $c[0001]$. The calculated values for a and c are 6.18 and 9.81 Å, respectively. We analyzed P-centers in supercells containing 72 or 192 atoms, comprised from $(3 \times 3 \times 2)$ and $4 \times 4 \times 3$ primitive cells, respectively.

The Brillouin-zone is sampled using the Monkhorst-Pack (Monkhorst & Park, 1976) scheme generally with a mesh of $2 \times 2 \times 2$ k-points. Structures are optimized via a conjugate gradient scheme until the change in energy between iterations is less than 10^{-5} Ha.

Atoms are simulated using ab initial pseudopotentials (Troullier & Martins, 1991) and the total energies and forces are obtained with a local density approximation for the exchange-correlation (Perdew & Wang, 1992). The wave functions and charge density are expanded in terms of Gaussian orbitals and plane-waves, respectively (Shaw & Briddon, 2007). For Zn, O and N, we includes s, p and d functions, with a total of 28, 28 and 32 functions per atom, respectively. Plane waves up to 150 Ha are used to expand the charge density. We calculate the formation energy of 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 species (i =Zn, O and N), $E_v(X, q)$ is the Fermi energy at the valence-band top, 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 $E(\text{ZnO}) = \mu_O + \mu_{Zn}$ where $E(\text{ZnO})$ is the energy per bulk 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 its decomposition into its elemental constituents, so that the zinc-rich limit is taken from zinc-metal, and the oxygen-rich limit μ_O is taken from the O_2 molecule. The heat of reaction for ZnO in this way is calculated to be 3.9 eV, whereas experimentally it is 3.61 eV (Lide, 2004). The chemical potential for N is the N_2 molecule.

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

RESULTS

1. N on the Zn site, and related centers.

First, we examine N substituting for Zn (NZn). Since N has three more valence electrons than Zn, it is expected that NZn may be a triple donor, potentially able to exist in a range of positive charge states. However, some care has to be taken in such an interpretation. Examination of the relaxed structure, shown schematically in Fig. 1 indicates that the nitrogen atom

bounded with two oxygen in the horizontal plane to make NO₂-1 nitrate ion molecule in the negative charge state.

It is more realistic to describe the system not as NZn but as the NO₂-1 molecular group (a nitrate anion) inside a cavity. The combination with the native double-donor V₂O may be expected to result in a single donor (Gsiea et al., 2014), so that in effect the nitrogen group in ZnO is a single donor. The (0/1+) transition level lies above the conduction-band minimum, becoming a shallow donor.

By calculating the formation energy as a function of charge state and $[\mu]_e$, we can estimate the electrical levels of NZn. The results are summarized in Fig. 2. We find that the NZn is thermodynamically stable only in the +1 charge state, and can

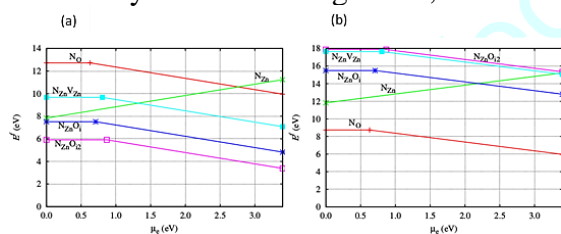


Fig. 2: Plot of E_f vs. μ_e for key N-containing defects in ZnO calculated using the 192 atom supercell. (a) Oxygen-rich conditions and (b) zinc-rich conditions.

be therefore viewed as a highly effective n-type dopant.

We have also examined the possibility for NZn to form pairs. One may expect a strong Coulomb repulsion between these centers, and indeed by increasing the distance between two NZn in the same simulation cell, the energy is reduced.

Although NZn is a single donor, it may be converted into an acceptor by formation of a complex with components with sufficient acceptor activity. One model is a complex with vacant Zn (VZn). This is possible because VZn is a double

acceptor (Gsiea et al., 2014; Limpijumnong et al., 2004), and the stability of the complex will be favorably influenced by the attractive Coulomb interaction.

There are many possible NZn VZn orientations determined by the VZn positions relative to NZn, all of which are at least metastable. The most stable structure we find is shown in Fig. 3. The energies of the various orientations where the vacancies are in the nearest shell of Zn-neighbors to the N-site vary by just 100s of meV.

The binding energy of the complex relative separate NZn and VZn centers is 3.9 eV.

The formation energies for the various charge states of the most stable acceptor system are also plot- ted in Fig. 2. We find that the acceptor level is quite deep at around $E_v+0.4$ eV, and would therefore may not be a good candidate for p-type doping. Although we have analysed many other configura- tions including NZn-VO, N₂ complexed substituting for Zn and O site, and many other configura- tions including NZn complex with interstitial oxygen, which are considered the very stable structure for p-type doping. Fig. 2 illustrates the formation energies for most stable structure for p-type doping.

2. N on the O site, and related centers

Secondly, we examined nitrogen on the O-site (NO). The structure obtained from neutral NO is showed in Fig. 4

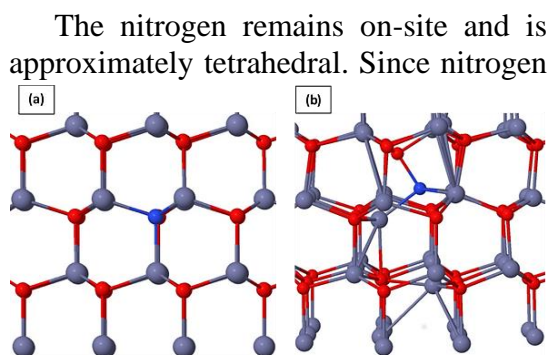


Fig. 4: Schematics of N_O in (a) the neutral charge state and (b) the positive charge state, AX structure. Colors and axes are as in Fig. 1.

The nitrogen remains on-site and is approximately tetrahedral. Since nitrogen has one fewer valence electron than the oxygen atom it replaces, it is expected that NO will be an acceptor, and indeed this is what we found. The charge-dependent formation energies in Fig. 2 indicate an acceptor level around $E_v + 0.6$ eV, far too deep for p-type doping. In addition, one can form a donor state with NO as it can undergo a chemical reaction with a next-nearest-neighbor oxygen atom, forming the structure shown schematically in Fig. 4, the so-called AX center (Park et al., 2002). Indeed, in this form our calculations suggest that NO may donate two electrons. 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 0.32 eV, higher in energy. The substantial structural rearrangement can be viewed as the formation of an N=O molecular fragment within the ZnO lattice, and the band-gap levels are highly characteristic of π^* -interactions between the two atoms.

This picture is extended when we examine the possibility of (NO)₂ forming pairs. In this case we can view the formation of (NO)₂ as the insertion of a

N₂-molecular fragment. This significantly reduces the formation energy for substitution onto the oxygen lattice, but (NO)₂ only has donor properties. In equilibrium, therefore, the formation of NO acceptors will have to compete with the formation of (NO)₂ donors, further reducing the probability of successfully producing p-type ZnO via such a route.

The (NO)₂ defect behaves as a double donor. The (0/+), and (+/++) transition levels which is occupied by four electrons is located in the middle band-gap, associated to the wave function exhibits the occupied levels are derived from anti-bonding combination between N atom and O atoms which surround, and the AX+1 structure is proven that.

Discussion

Four of the N-related defects discussed here are acceptors. The notable exceptions are the possible AX behavior of NO, and the shallow donor properties of NZn. 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 growth conditions, Fig. 2, substitution onto the Zn-lattice with oxygen interstitial is highly favorable, and potentially yields p-type material. Perhaps surprisingly, NZnO₂ is very low in formation energy in comparison with the other structures examined, so we conclude this is likely to form.



For Zn-rich material (i.e., that grown in oxygen lean conditions) the NO structure is most favorable. Up to now, it has been almost uniformly assumed that this is the dominant defect in N-doped ZnO. Our calculations show, however, that NO is an effective sink for mobile interstitial species, which generally convert it into donors. Such complexes are thought to be important compensation centers in the production of real p-type material.

We note that both in O-rich and Zn-rich conditions, there is a strong trend towards the formation of N-O bonds. This is energetically favoured as such bonding includes a much greater degree of covalence than Zn-O and Zn-N. Thus, reactions that produce either N-O or N-N covalent bonds generally stabilize N-defect configurations which are donors, with the notable exception of NZn-O_i type centers which are acceptors.

In summary, the overwhelming trend is for N to adopt defect structures bonding with oxygen. Indeed, this trend is extended over all group-V elements, and similar result which we obtained for nitrogen are found for the other elements. Where differences arise, it is because nitrogen is much smaller than other group-V elements such as P, As and Sb,

and can form different bonding configurations such as N-O double bonds. However, in general, we conclude that group V-doping is effective for n-type material, and may generate p-type material under favorable conditions.

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