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A model bismuth oxide intergranular thin film in a ZnO twist grain boundary

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Abstract

The electronic properties of a model bismuth oxide intergranular film in ZnO were investigated using density functional plane wave calculations. It was found that oxygen excess plays a fundamental role in the appearance of electrical activity. The introduction by oxygen interstitials or zinc vacancies results in depletion of the charge in deep gap states introduced by the bismuth impurities. This makes the boundary less metallic and promotes the formation of acceptor states localized to the boundary core, resulting in Schottky barrier enhancement. The results indicate that the origin of electrical activity in thin intergranular bismuth oxide films is probably not distinct from that in decorated ZnO boundaries.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Zinc oxide is an n-type direct bandgap semiconductor with a broad range of applications, from gas sensors to solar cells, catalysts and light-emitting devices [1–3]. In the polycrystalline form it is widely used as a varistor material [4]. While the engineering of varistors has been commonplace for a number of years, the detailed microscopic processes involved are not fully understood.

The varistor effect is known to be related to the formation of a double Schottky barrier (DSB) in the grain boundary region. This barrier, in pristine and decorated boundaries, originates from a mixture of direct charge accumulation in the atoms in the boundary core [5] and impurity and interface states localized to the core [6–9]. Also, intrinsic defects like Zn vacancies and O interstitials are thought to directly promote varistor function and to control the optical properties of ZnO [1]. Intergranular phases may play an important role, as general boundaries tend to saturate with Bi and form barriers to the electronic flow. The intergranular phases (IGPs) that have been observed are composed of spinel [10], pyrochlore [11] or amorphous [12–14] non-stoichiometric Bi₂O₃ and thin intergranular films can be electrically active. The Bi-doped grain boundaries often exhibit intergranular bismuth oxide films of 0.6–1.5 nm thickness and with a composition of ZnO:Bi₂O₃ molar ratio between 2.3 and 3.3 [12, 13]. These values are intermediary between the molar ratios of spinel and pyrochlore phases involving Bi and Sb and the highest

nonlinearity coefficients are known to result from the largest Bi content [15]. This study aims at gaining further insight into the mechanisms that control the functionality of thin intergranular phases of bismuth oxide, which can form in the boundary regions [12, 14, 16, 17]. In particular, it is important to determine when these thin phases can exhibit electrical activity, the origin of interface states and elucidate DSB formation mechanisms that may be identical to other thin amorphous films.

We have studied the behavior of an experimentally observed $\Sigma = 7(\theta = 21.79^\circ)[0001]$ boundary in ZnO [18], using plane wave *ab initio* calculations with the computer code CASTEP [19], and then systems containing 14 Bi doping impurities in the boundary core, substituting Zn atoms and corresponding to two Bi layers. This system was then depleted of one and two Zn atoms in the boundary core region, simulating a situation of increasing oxygen concentration. This corresponds to a simple model system of a bismuth oxide IGP in ZnO. In particular, it is important to obtain indications as to which boundaries produce more pronounced nonlinear behavior and the origin of this. Although the model system considered here does not strictly correspond to observed compositions in IGPs, it illustrates features and processes that are identical to previously studied boundaries and appear to be general characteristics.

In this work the stability and segregation properties of the optimized structures are described first, along with the Mulliken and overlap bonding populations. The connection to barrier formation mechanisms is established and the electronic

density of states (DOS) is then interpreted. Finally, a relation to chemical composition is established.

These systems may be relevant to a number of different problems. The understanding of the detailed mechanisms that originate the varistor properties may enable the investigation of novel devices in the same material. For example: ZnO nanorods have an electronic structure that is similar to ZnO bulk plus surface states that are shallow. If two nanorods are to make contact it is then conceivable that the defects can have the same effect at the nanocontact that they have in an extended defect. This would yield a novel device with nonlinear I – V characteristics but with a much higher density of nonlinear elements. Thus, the optimization of the varistor device may, at least conceivably, be taken onto a new level of miniaturization. Another area where the understanding of defects in ZnO can be of importance is TMR and GMR. In this case ZnO:(Mn,Co) is known to be a ferromagnet at room temperature with half-metal properties. Mn, Co, Bi and Sb are dopants that are involved in varistor formation. The concept of a tunnel barrier with spin-polarized interface states is attractive since it is known that tunneling can be assisted by states of special symmetry. Thus, the co doping of ZnO with these known varistor-forming dopants can be of great interest in the investigation of TMR. Also, the p-type doping of ZnO is relevant to the realization of UV laser diodes. The combination of defects that can generate p-type behavior and the conditions under which this happens deserve extensive investigation. Therefore, the thorough understanding of interfacial properties in this material yields a broad interest.

2. Methods

First-principles density functional theory (DFT) calculations using the PW-91 GGA exchange–correlation functional [20] were carried out. A plane wave basis set with an energy cutoff of 340 eV was used and ultrasoft pseudopotentials [21] utilized. The coincidence site lattice model (CSL) for obtaining periodic boundary conditions was used and the models contained 112, 111 and 110 atoms, corresponding to the complete Bi coverage and subsequent consideration of one and two Zn vacancies respectively.

The Brillouin zone sampling was done using the Monkhorst–Pack scheme [22] and two k -points were considered. An electronic smearing factor of 0.01 eV was used to enhance convergence and the atomic relaxation was performed using the BFGS algorithm until the forces on the atoms were less than $0.05 \text{ eV } \text{Å}^{-1}$. The projected density of states (PDOS) and Mulliken population analysis were calculated by projecting the wavefunctions on the pseudopotential pseudo-atomic orbitals [23]. The population analysis carried out on the systems showed a spilling parameter of 0.1–0.17%, values considered adequate to our purposes.

The segregation energy E_{seg} was calculated according to

$$E_{\text{seg}} = (E^{\text{GB}}[\text{ZnO}:n\text{Bi}] - E^{\text{GB}}[\text{ZnO}]) - (E^{\text{bulk}}[\text{ZnO}:n\text{Bi}] - E^{\text{bulk}}[\text{ZnO}]), \quad (1)$$

where n is the number of Bi atoms and $E^{\text{bulk}}[\text{ZnO}:n\text{Bi}]$ is approximated by $nE^{\text{bulk}}[\text{ZnO}:\text{Bi}]$, assuming non-interacting bulk defects.

3. Results and discussion

The $\Sigma = 7[0001]$ twist grain boundary has been previously studied [24, 5], it has been shown not to introduce deep levels in the bandgap and therefore no electrical activity is assigned to the pristine boundary [18]. This boundary is obtained by a 21.79° rotation of the crystal around the $[0001]$ direction, cutting through the polar bonds of ZnO and forming a CSL supercell. The model is periodically repeated in 3D. The pure twist does not produce dangling bonds or interface states. The pristine boundary is totally re-bonded and expands only very slightly. No new states are introduced by this crystal rotation. It can, in terms of band structure, be thought of as a distortion of the bulk structure. The inclusion of dopants in the grain boundary core, Bi and Sb, has shown that the dopants alone do not produce the desired acceptor states and instead result in donor levels. We have taken the pristine twist grain boundary and doped the core with 14 Bi atoms, substituted at the Zn sites. This system is a model for the study of an amorphous IGP, more than a stoichiometrically correct phase. The subsequent inclusion of one and then two Zn vacancies tends to increase the $\text{Bi}_2\text{O}_3:\text{Bi}$ ratio. This approach is based on taking the intergranular phase as being the 1 nm wide region centered around the totally doped twist boundary, corresponding to two zinc planes, two bismuth planes and four oxygen planes. Upon doping, this phase comprises a ZnO:BiO molar ratio of 1:1 or $\text{ZnO}:\text{Bi}_2\text{O}_3 = 2.978:1$ with 4.6 Bi surplus, in comparison with $\text{ZnO}:\text{Bi}_2\text{O}_3 \approx [2.3, 3.3]:1$ measured stoichiometric ratios [12]. Our main emphasis has been on the amorphous character of the phase and the relative importance of Bi- and O-induced states and not on the stoichiometric equilibrium, but the stoichiometry is within the right parameters. The accurate determination of the equilibrium composition is a problem involving the value of the thickness equilibrium of the film and is beyond the scope of our study.

In figure 1 the relaxed geometry of the thin IGP is depicted along with the positions where the vacancies were included. The first notorious feature is the expansion of the intergranular phase region, resulting in a lower density than the grains. In the IGP there is an average of 3.43 Bi–O bonds per Bi atom, whereas in the bulk the Bi atom is tetrahedrally coordinated. The relaxation leads to a stabilized core structure with a total segregation energy of -0.73 eV for the bismuth layers or -0.05 eV per Bi atom. The negative values indicate slight favoring of the Bi impurities in the IGP relative to the bulk and, consequently, the stability of the model.

Table 1 shows the bond lengths and overlap populations of the Zn–Zn, Bi–Bi and Bi–O bonds in the systems. For the overlap populations the most prominent feature is the formation of two Bi–Bi bonds, depicted in figure 1, of a strong covalent character and overlap populations of 1.26 and 2.29 (e), which are remarkably high values for metal–metal overlap. These types of bonds have been previously encountered [6] and their energies can be located within the bandgap of ZnO. This is considered to be an indication that the density of these bonds can be related to varistor function and that they may be more common in a situation where the bismuth oxide IGP is disordered.

Table 1. The relevant bonding information for the three systems is shown. The units are electrons for the bond orders and ångströms for the lengths. There are new metal–metal bonds in the IGP systems that introduce gap states which are absent in bulk or pristine grain boundary environments. The average Bi–O bonding characteristics are also shown, where a modest increase of overlap relative to ZnO:Bi can be noted.

Bond	IGP		IGP: V_{Zn}		IGP: $2V_{Zn}$		ZnO:Bi	
	(e)	(Å)	(e)	(Å)	(e)	(Å)	(e)	(Å)
Bi–Bi (1–2)	1.26	2.87	1.62	1.95	1.17	2.94	—	—
Bi–Bi (1–3)	2.29	2.98	1.51	2.96	1.96	2.96	—	—
Zn–Zn (X – Y)	0.82	2.84	0.69	2.85	0.60	2.84	—	—
Zn–Zn (Z – T)	0.56	2.98	1.17	2.95	1.47	2.95	—	—
Bi–O	0.29	2.22	0.27	2.11	0.30	2.17	0.20	2.17

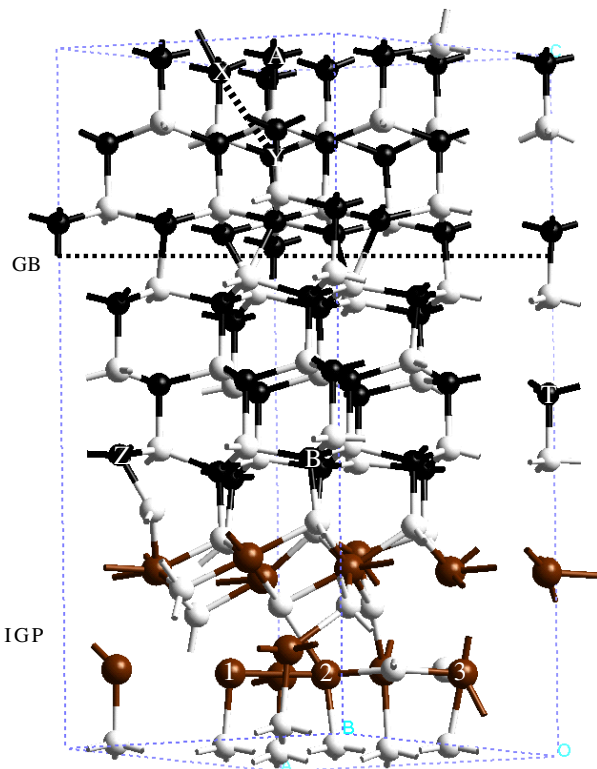


Figure 1. The relaxed geometry for the thin intergranular film. The C axis is the [0001] direction. The black atoms are Zn, the white ones O and the gray ones Bi. The Bi–Bi bonds are between atoms 1 and 2, and 1 and 3, across the periodically repeated unit cell. The Zn–Zn bonding effects between X and Y , Z and T . The sites A and B were the ones chosen for V_{Zn} . The intergranular thin film region is denoted IGP and GB stands for the pristine grain boundary region.

In a pristine grain boundary a limiting segregation behavior for Bi may be observed [5]. The systems considered here do not strictly correspond to a doped grain boundary, since it simulates a grain boundary doped beyond its limit. Therefore, it bears a greater resemblance to a stable thin IGP interface. The remarkable bonding aspects of the amorphous layer are similar to the doped grain boundary properties, including the formation of metal–metal bonds. In figure 2 we can see the average charge gain of each layer in comparison to its average pristine boundary charge and position. From this figure it is clear that there is potential barrier formation and charge accumulation in the boundary core, with an average gain of 0.64 (e) per Bi impurity for the IGP. This corresponds to a much larger gain than in a singly doped twist boundary,

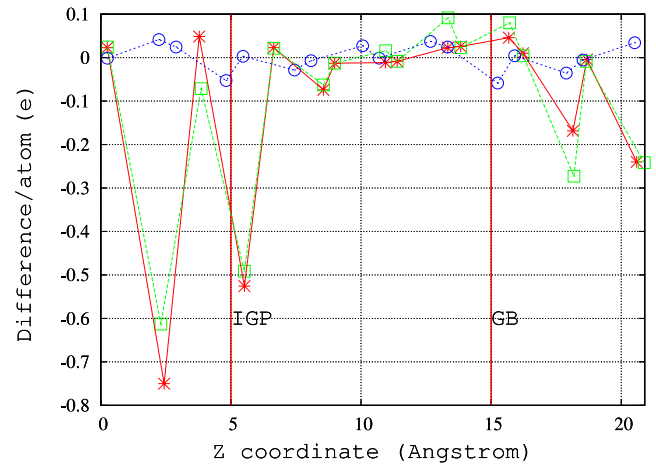


Figure 2. The picture shows the comparison between the pristine boundary (circles), thin bismuth oxide phase (star) and the IGP: V_{Zn} (square). The charges refer to the average difference per atom between the systems and the isolated atoms in bulk ZnO, starting with an O layer and alternating with metal/oxygen. The abscissa is the average position for that plane. Note the charge accumulation in the metal layers adjacent to the IGP, in contrast to the bulk-like behavior of the pristine grain boundary.

where the charge increase is 0.11 (e). In this case the charge accumulation in the boundary is promoted by the impurities through direct charge gain and also by the formation of metal–metal bonds and interface states. The pristine grain boundary shows no signs of a large barrier and so the potential barrier is generated, in this case, mostly by dopant segregation and not crystallographic mismatch.

The Bi–Bi bonds appear to be altered by the introduction of vacancies in the system and there may be depletion of this charge in some cases. In the IGP boundary system there are two Bi–Bi bonds, one of them (bond 1–3, see table 1) with a population of 2.29 (e). This bond is depleted in the IGP: V_{Zn} system to 1.51 (e). Such charge removal may correspond, as discussed later, to the removal of electrons from states in the bandgap region.

The bandgap of ZnO is typically underestimated in density functional calculations [25], in this case yielding a bandgap of only 1 eV. The electronic density of states in figure 3 shows states in the bandgap region of ZnO that correspond to the Bi–Bi bonds in the IGP- and Bi-induced donor states. The chemical potential is lowered with respect to the rest of the band structure as a consequence of the inclusion of the Zn vacancies and can result in the depletion of previously

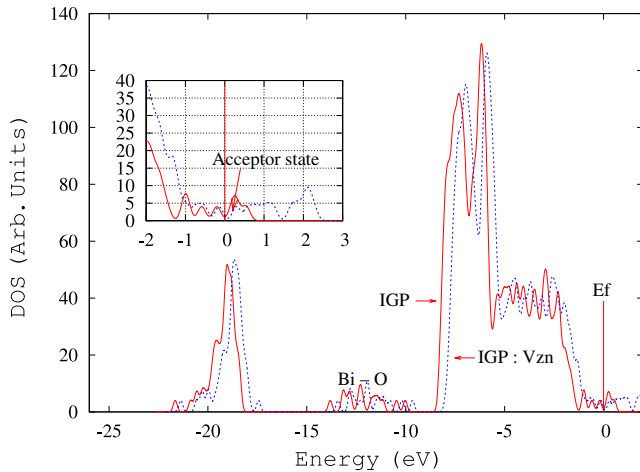


Figure 3. The total DOS for the IGP and IGP: V_{Zn} systems at $k = (0, 0.5, 0)$. The graphs are aligned to the Fermi level. It is clear that the V_{Zn} tends to lower the Fermi level with respect to the rest of the DOS and this can deplete the occupied interface states. This is evident from the graphs. The main effect of the inclusion of another V_{Zn} is to lower the Fermi level further and potentiate further depletion of occupied states. The inset shows the bandgap region.

occupied gap states or bonds, activating the Bi deep levels. The effect demonstrates some degree of control of the population of the interface states through the stoichiometry of the system and is a consequence of the creation of extra shallow acceptor states by the Zn vacancies in the interface, which are located very close to the valence band edge in the 1 eV calculated bandgap. The occupied states, located higher in the bandgap, will be preferentially depleted of charge. The figure shows the DOS for the $(0, 0.5, 0)$ k -point so that the depletion of charge in gap states can be fully noticeable.

Other features of the DOS have been previously documented [24] and include the Bi–O bonding states and further down the characteristic oxygen s states (see figure 3). We note that, in this case, the Bi–O density is high and a corresponding band is formed, but this does not interfere with the conduction process. The oxygen atoms can decrease the metallicity of both doped boundaries and thin films, resulting in the creation of acceptor states localized to the boundary core. These states are in the origin of p-type material in between the grains and contribute to DSB formation [8, 9].

This model shows that it is possible to create an electrically active boundary from an inactive metallic one by the inclusion of Zn vacancies. This process is considered to be identical in Bi-decorated GBs and thin intergranular films. There is considerable experimental evidence of the important role of oxygen in the promotion of varistor behavior and in recovering the nonlinear conductive behavior of a degraded boundary [4]. We have, for the first time, shown an interplay of defects capable of producing this behavior for intergranular films in ZnO.

The stoichiometry of the boundary can then be related to the electronic properties in the following way: the number of ZnO molecules in half the model (i.e. the 1 nm thick boundary core) is 14, as is the number of BiO molecules. This results in $ZnO:BiO = 1:1$ and $ZnO:Bi_2O_3 = 14/4.7 = 2.978$ plus

4.6Bi, as mentioned earlier. Alternatively, we can consider that there is oxygen deficiency in our model. In this case we get $ZnO:Bi_2O_3 = 2$ minus 7O. When one vacancy is introduced we get $ZnO:Bi_2O_3 = 2.6$ with a surplus of 2Bi or, alternatively, considering the situation as a result of oxygen deficiency, $Bi_2O_3 = 2$ minus 6O. When two Zn vacancies are introduced we then get $ZnO:Bi_2O_3 = 1.87$ plus 1.6Bi or, alternatively, $ZnO:Bi_2O_3 = 2$ minus 5O. Hence, we get that models where the Bi_2O_3 molecule to Bi excess atom ratio is smaller than or equal to 2 are metals and if more than or equal to 2.25 can show acceptor states. Conversely we can formulate the relation in terms of oxygen deficiency; for an oxygen deficiency of more than or equal to one O atom per Bi_2O_3 molecule we get a conductive interface and for an oxygen deficiency of less than or equal to 0.85 O atoms per Bi_2O_3 molecule we can get acceptor states. This limiting behavior does not have to do with the strict stoichiometry of the model interface, but results from the relative influence of the oxygen acceptor states versus the metallic states that must be compensated. Therefore, amorphous Bi_2O_3 IGPs with the approximately correct stoichiometric composition and no oxygen deficiency, as was defined above, are to yield electrical activity. Our results strongly suggest that the function degradation in Bi-doped ZnO varistors is related to oxygen deficiency in the grain boundary core, with metallization of the grains.

4. Conclusions

We have studied substitutional Bi dopant segregation at a twist grain boundary in ZnO in the extreme case of total doping of the grain boundary core, using pseudopotential plane wave density functional theory. The resulting intergranular films had some of the desired characteristics of a varistor material. Impurity states can be identified localized to the intergranular phase and the occupancy of these deep levels was modified by including a Zn vacancy in the core structure. Deep acceptor states can result, localized to the core, and these have been previously identified to influence transport. Single and double vacancy doping were considered in the intergranular layer system and the principal effect was shown to be a decrease in the chemical potential of the systems, producing depletion of previously occupied states in the bandgap, as the result of the introduction of lower lying oxygen states.

The Mulliken population analysis indicated an overall charge accumulation in the core region, showing potential barrier enhancement and an average charge accumulation of 0.64 (e) per Bi atom with respect to ZnO:Bi. The overlap demonstrated that Bi–Bi bonds can form and the corresponding states fall in the bandgap region. The results indicate that the nature and character of the potential barrier formation mechanisms and interface states in thin intergranular films are likely to be not distinct from those in decorated ZnO boundaries and that in this case the metal–metal interactions are candidate contributors to DSB formation and varistor function. The oxygen appears to be of critical importance in producing and maintaining the varistor action, through the lowering of the chemical potential and the introduction of

shallow states. The amorphous character of the layers will tend to enhance oxygen diffusion and augment the effect.

Finally, we have related the stoichiometry of the interface to the electronic structure to conclude that amorphous Bi_2O_3 interfaces without oxygen deficiency are likely to display nonlinear conduction properties. We have concluded that for our system more than one O atom missing per Bi_2O_3 molecule results in a metallic interface and less than 0.85 in an electrically active film.

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