First-Principles Calculations of Co Impurities and Native Defects in ZnO

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First-principles plane-wave pseudopotential calculations have been conducted to investigate Co impurities and native defects associated with oxygen excess in ZnO. The electronic states and formation energies are evaluated using the total energies of supercells. The electronic states indicate that Co impurities are donor-like, while native defects associated with oxygen excess are acceptor-like. Among the native defects, Zn vacancies are likely to be a dominant species in view of the much lower formation energy than those of the others. Calculations for Co impurity-Zn vacancy complexes imply that Co impurities stabilize Zn vacancies and hence oxygen excess in their vicinities. This is suggested to be a role of Co impurities at grain boundaries in ZnO varistor ceramics.

(Received January 28, 2002; Accepted March 14, 2002)

Keywords: zinc oxide (ZnO), cobalt (Co), native defect, electronic structure, formation energy, first-principles calculation, varistor

1. Introduction

Polycrystalline ZnO with additives such as Bi₂O₃, Pr₆O₁₁ and 3d transition-metal oxides is commercially used as a varistor owing to its highly nonlinear current-voltage characteristic.¹⁻³ The nonlinearity is attributed to the double Schottky barriers that originate from the formation of acceptor-type states at the interfaces between donor-rich grains.^{4,5} Although the interfacial electronic states have been intensively investigated because of the importance in the nonlinear behavior,⁶⁻¹³ the explicit origin still remains open. As an origin, excessive oxygen at the interfaces has been suggested.^{7,13} This is consistent with experimental reports that nonlinear characteristics strongly depend on oxygen partial pressure during heat treatment and sintering processes,^{14,15} and that oxygen accumulation is more abundant at intergranular-fractured surfaces in untreated samples than in electrically degraded samples.^{16,17} The excessive oxygen at interface regions may be regarded as segregation of native defects associated with oxygen excess such as Zn vacancies and O interstitials.

The doped impurities should also have some relations to the appearance of the nonlinearity, although the roles are not necessarily clear. Among the commonly used additives, Co oxides (CoO, Co₂O₃, Co₃O₄) to dope Co impurities are known to improve the nonlinearity greatly in ZnO-Bi₂O₃-based varistors.² For ZnO-Pr₆O₁₁-based systems, these are necessary to obtain nonlinear characteristics.^{3,18} Therefore, Co impurities should play important roles in the formation of the interfacial electronic states as well as excessive oxygen. However, it is not clear whether Co impurities are related to the interface structure at an electronic level. Yano *et al.* have investigated ZnO/PrCoO_x/ZnO thin film varistors doped with various 3d transition-metal impurities and found that the energies of the interface states depend strongly on impurity species.¹⁹ This indicates that the transition-metal impurities make significant contribution to the interfacial electronic states. On the other hand, Tuller and Baek have re-

ported that the energies of the interfacial states seem to be insensitive to species of transition-metal impurities.²⁰

In the present study, two possible origins of the interfacial acceptor states, *i.e.*, native defects associated with oxygen excess and Co impurities, have been investigated using first-principles calculations. The electronic states and formation energies were evaluated for these defects in ZnO bulk supercells, which must be a key step to understand their roles on an atomic/electronic scale at the grain boundaries. A special interest was taken in the interaction between Co impurities and the native defects because it has been suggested that Co impurities play a role to stabilize oxygen adsorption (excess) at surfaces and grain boundaries of ZnO.^{18,21,22} To investigate the interaction, calculations for complexes of a Co impurity and a Zn vacancy, which showed the lowest formation energy and should therefore be dominant among the defects associated with oxygen excess, were conducted. The results imply that Co impurities interact attractively with Zn vacancies, which supports the above suggestion.

2. Computational Procedure

The calculations were conducted using a first-principles plane-wave pseudopotential method²³⁻²⁵ within the generalized gradient approximation (GGA)²⁶ to the density-functional theory.^{27,28} Ultrasoft pseudopotentials²⁹ were employed, where the Zn-3d and Co-3d states were explicitly treated as a part of the valence. 72-atom supercells containing a Co impurity, a native defect, or a Co impurity-Zn vacancy complex were used in the calculations. We have previously conducted calculations of native defects in ZnO using 72- and 128-atom supercells and found that the relative formation energies of an O vacancy and a Zn interstitial differ only by 0.1 eV between the supercells of these sizes.³⁰ Therefore, the defect-defect interactions under three-dimensional periodic conditions are not expected to alter the present discussion based on the results for the 72-atom supercells.

Concerning defects species associated with oxygen excess, Zn vacancies, O interstitials at the tetrahedral and octahedral

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interstitial sites, and O antisites were considered. Numerical integration over the Brillouin zone was carried out at the Γ point. Since the valence and conduction band edges are located at the Γ point in ZnO, the use of only the Γ point and a large supercell should be a good strategy to simulate dilute solution of defects, as described in Ref. 31). The plane-wave cutoff energy was chosen to be 380 eV. Test calculations using 16-atom supercells for two samples, a neutral Co impurity and a neutral zinc vacancy, showed that this cutoff energy gives the convergence of the formation energies within 0.02 eV for cutoff energies up to 700 eV. Spin polarization was considered for supercells with Co impurities. The atomic positions of the first and second nearest neighbors of the defects were relaxed under the condition that the cell volume was fixed to be the value optimized for the ZnO perfect crystal: lattice constants a , c , and internal parameter u were calculated to be 100.5%, 100.3%, and 99.8% of experimental values,³²⁾ respectively. The optimization procedure was truncated when the residual forces for the relaxed atoms were less than 4.0 eV/nm and the root mean squares of the forces were less than 1.5 eV/nm.

The formation energies of the defects were calculated using the total energies of the supercells. For compound systems, the formation energies depend on atomic chemical potentials. In addition, those of charged defects also vary with the Fermi energy. The atomic chemical potentials describe equilibrium conditions under which materials are treated. The Fermi energy depends on concentrations of native defects and impurities.

For a defect in a charge state q , the formation energy is given by,^{33,34)}

$$E_{\text{formation}}(q) = E_{\text{T}}(q) - n_{\text{Zn}}\mu_{\text{Zn}} - n_{\text{O}}\mu_{\text{O}} - n_{\text{Co}}\mu_{\text{Co}} + qE_{\text{F}}, \quad (1)$$

where E_{T} is the total energy of a supercell with a defect or a defect complex in a charge state q . n_{Zn} , n_{O} and n_{Co} are the number of Zn, O and Co atoms in the supercell. μ_{Zn} , μ_{O} , and μ_{Co} are the atomic chemical potentials, and E_{F} is the Fermi energy. For charged defects ($q \neq 0$), the total charge of supercells was neutralized using jellium background. Energy shifts associated with the jellium neutralization were estimated by the total energy difference between the neutral (normal) and charged supercells of the perfect crystal; *e.g.*, for the positively charged perfect crystals, electrons were removed from the valence band maximum and the jellium neutralization was included. Correcting this energy shift should correspond to setting the valence band maximum to be the reference of the Fermi energy, and thus the total energies of the supercells with positively charged defects, $E_{\text{T}}(q)$ for $q > 0$, were evaluated with this reference. Negatively charged systems were dealt with in the same manner, except that the conduction band minimum was used as the reference.

Assuming thermal equilibrium conditions, μ_{Zn} and μ_{O} are variables correlated as,

$$\mu_{\text{Zn}} + \mu_{\text{O}} = \mu_{\text{ZnO(bulk)}}, \quad (2)$$

where $\mu_{\text{ZnO(bulk)}}$, the chemical potential of the bulk ZnO, is a constant value calculated as a total energy per ZnO unit formula. Total energies per atom for the bulk Zn and O were chosen as the upper limits of μ_{Zn} and μ_{O} , respectively. μ_{Zn} and μ_{O} therefore vary over a range given by the heat of for-

mation of ZnO, which was calculated to be -3.06 eV. This value is close to an experimental value reported, -3.63 eV (298.15 K).³⁵⁾

The formation energy of Co impurities depends on μ_{Co} as well as μ_{Zn} and μ_{O} . In the present study, μ_{Co} was chosen to be a value at the solubility limit. Assuming the equilibrium condition between ZnCo_2O_4 and ZnO doped with Co, μ_{Co} was obtained by subtracting μ_{Zn} and μ_{O} from the calculated total energy of ZnCo_2O_4 .

3. Results

Figure 1 shows formation energies of Co impurities in relevant charge states at Zn sites (Co_{Zn}). The energies were evaluated at the solubility limit under the extreme oxygen-rich condition ($\mu_{\text{Zn}} = \mu_{\text{ZnO(bulk)}} - \mu_{\text{O(bulk)}}$ and $\mu_{\text{O}} = \mu_{\text{O(bulk)}}$). The slope corresponds to the charge state q as used in eq. (1). The bold lines highlight the charge states that give the lowest formation energy with respect to the Fermi energy; change in the slope indicates transition in the charge state. The Fermi energy where the transition takes place corresponds to the defect electronic state. This energy is independent of the atomic chemical potentials, whereas absolute formation energies change with the chemical potentials; *e.g.*, when the other extreme case at the solubility limit of Co, the zinc-rich limit ($\mu_{\text{Zn}} = \mu_{\text{Zn(bulk)}}$ and $\mu_{\text{O}} = \mu_{\text{ZnO(bulk)}} - \mu_{\text{Zn(bulk)}}$), is considered, the formation energies for respective charge states are rigidly shifted to the lower energy side by 1.5 eV. The Fermi energy is measured from the valence band maximum, and the conduction band minimum is shown at 0.96 eV. This energy, *i.e.*, the band gap, was calculated as $\{E^{(1)} - E^{(0)}\} - \{E^{(0)} - E^{(-1)}\}$, where $E^{(N)}$ indicates the total energy of a perfect lattice supercell with additional N electrons. The same value was obtained from the difference of the one-electron energies. The calculated band gap of 0.96 eV is considerably

Fig. 1 Formation energies of Co impurities in relevant charge states. The energies are calculated at the solubility limit under the extreme oxygen-rich condition (See text). The broken lines show the formation energies for respective charge states. The bold lines highlight the charge states that give the lowest formation energies with respect to the Fermi energy. The change in the slope of the bold lines indicates transition in the charge state, which is denoted by open circles. The valence band maximum is chosen as the zero of the Fermi energy, and the vertical line at 0.96 eV indicates the conduction band minimum. The superscripts denote the charge states defined relative to Zn^{2+} , which correspond to the valences of Co shown in the parentheses.

smaller than a reported experimental gap of 3.30 eV.³⁶⁾ We have also made a calculation using the local-density approximation (LDA) and obtained a band gap of 0.79 eV, which is within LDA values reported: 0.23–0.88 eV.^{37–39)} These underestimations have been attributed to the GGA/LDA.⁴⁰⁾ Although this may cause some systematic errors in absolute energy, the electronic structure and formation energies of Co impurities and native defects can be discussed relatively.

As recognized in Fig. 1, the Co impurities show electronic states of $2+/1+$ and $1+/0$ in the band gap. The one-electron structure suggested that these states are associated with Co-3d. The presence of the electronic states in the band gap indicates that Co impurities show transition in charge state from $2+$ to 0 with the Fermi energy. The charge states are defined relative to Zn^{2+} and hence the transitions correspond to the changes in the valence of Co from quadrivalence to divalence. When the Fermi energy is close to the conduction band minimum, neutral charge state, *i.e.*, divalence, is the most favorable. As the Fermi energy is decreased, $1+$ or $2+$ charge state, *i.e.*, trivalence or quadrivalence, become preferable. Negative charge states were not considered in the calculations because it was expected to form electronic states above the conduction band minimum; for the neutral charge state, occupied states associated with Co-3d already showed resonance with the conduction band in the one-electron structure. Thus, Co impurities are likely to exhibit only positive and neutral charge states. This implies that Co impurities are donor-like and therefore cannot accept electrons. Some experimental works have shown that the *n*-type conductivity of ZnO is enhanced or unaffected by doping of Co impurities,^{21,41,42)} which also indicate Co impurities are donor-like.

Figure 2 shows the formation energies of native defects associated with oxygen excess at the oxygen-rich limit ($\mu_{\text{Zn}} = \mu_{\text{ZnO(bulk)}} - \mu_{\text{O(bulk)}}$ and $\mu_{\text{O}} = \mu_{\text{O(bulk)}}$). Only the charge states that give the lowest formation energy with respect to the Fermi energy are highlighted, which correspond to the bold lines in Fig. 1.

Fig. 2 Formation energies of native defects associated with oxygen excess at the oxygen-rich limit. For respective defect species, only the charge states that give the lowest formation energies with respect to the Fermi energy are shown. Change in the slope indicates transition in the charge state, which is indicated with symbols. The valence band maximum is chosen as the zero of the Fermi energy, and the vertical line at 0.96 eV corresponds to the conduction band minimum. Subscripts indicate defect sites, *e.g.*, Zn and i(oct) denote the Zn lattice and octahedral interstitial sites, respectively.

In contrast to the Co impurities, only neutral and negative charge states are recognized for all the defects, indicating that these defects are acceptor-like. On the other hand, our previous study has shown that defects associated with zinc excess, *i.e.*, O vacancies, Zn interstitials and Zn antisites, are all donor-like.³⁰⁾ Thus, the defects associated with oxygen excess can be sources of interfacial acceptor states when they are enriched at interfaces. Among these defects, Zn vacancies are much lower in the formation energy than the others in all the range of the Fermi energy. This tendency is not altered when the other conditions of the chemical potentials are considered; under more zinc-rich conditions, relative formation energies of Zn vacancies and O interstitials remain unchanged, while O antisites become much higher in energy relative to the others. The lowest formation energy of Zn vacancies among the defects associated with oxygen excess is consistent with other theoretical results recently reported.^{43,44)} Zn vacancies are expected to act as single- or doubly-ionized acceptors since the defect electronic state of $1-/2-$ is located close to the valence band maximum as recognized in Fig. 2.

We have previously conducted lattice statics calculations for Zn vacancies and O interstitials at a $\Sigma = 7$ tilt boundary of ZnO using empirical interatomic potentials and found that Zn vacancies have lower formation energies than O interstitials.⁴⁵⁾ In addition, molecular orbital calculations showed that Zn vacancies form acceptor-type states close to the valence band maximum. Thus, Zn vacancies are likely to be dominant among the acceptor-like defects and form shallow acceptor states at grain boundaries as well as in the bulk.

To investigate interactions between Co impurities and the defects associated with oxygen excess, calculations for supercells containing a Co impurity-Zn vacancy complex ($\text{Co}_{\text{Zn}} - \text{V}_{\text{Zn}}$) were performed. The Zn vacancy was chosen as a representative of the defects associated with oxygen excess because it is expected to be dominant as discussed above. Two configurations of $\text{Co}_{\text{Zn}} - \text{V}_{\text{Zn}}$ were considered: a Zn vacancy was located at the second or fourth nearest neighbor site of a Co impurity, which corresponds to an interatomic distance of 0.322 or 0.523 nm in the geometry before the atomic relaxation. Concerning the charge state, Co impurities show 0 or $1+$ in most of the range of the Fermi energy, while Zn vacancies are present in the $2-$ charge state as recognized in Figs. 1 and 2. The charge state of the complexes was therefore chosen to be $1-$ or $2-$, which can be regarded as $(\text{Co}_{\text{Zn}}^0 + \text{V}_{\text{Zn}}^{2-})^{2-}$ or $(\text{Co}_{\text{Zn}}^{1+} + \text{V}_{\text{Zn}}^{2-})^{1-}$.

The energy differences between the two configurations were listed in Table 1. The negative values indicate that the second nearest neighboring (2NN) configurations are energetically preferable. A possible reason is that strains associated with substitutional Co impurities are released more by Zn va-

Table 1 Energy differences between the two configurations of $\text{Co}_{\text{Zn}} - \text{V}_{\text{Zn}}$ complexes, the second and fourth nearest neighboring (2NN and 4NN) arrangements.

Energy difference [2NN-4NN], $\Delta E/\text{eV}$	
$(\text{Co}_{\text{Zn}}^0 - \text{V}_{\text{Zn}}^{2-})^{2-}$	-0.2
$(\text{Co}_{\text{Zn}}^{1+} - \text{V}_{\text{Zn}}^{2-})^{1-}$	-0.3

cancies. This result implies that Co impurities interact with Zn vacancies attractively. For $\text{Co}_{\text{Zn}}^{1+}$, *i.e.*, Co is trivalent, the energy gain is larger by 0.1 eV, suggesting that the attractive interaction is enhanced. This may be attributed to increase in electrostatic interaction owing to the higher charge state of Co.

4. Discussion

The calculated electronic structure indicates that Co impurities are donor-like defects, while the defects associated with oxygen excess are all acceptor-like. Therefore, Co impurities themselves should not be a source of interfacial acceptor states. In ZnO varistors, grains exhibit *n*-type conductivity associated with donors such as native defects and doped impurities. The Fermi energy should therefore be close to the conduction band minimum. Under such conditions, Co impurities are likely to be divalent, as suggested by the present calculations. Although Co impurities are known to be dissolvable in grains and clear boundary segregation has not so far been reported, they should be somewhat enriched in the vicinity of grain boundaries due to a size mismatch. This may result in oxygen excess at boundary regions since Co impurities are expected to attract Zn vacancies. Likewise, easier mass transportation at boundary regions should facilitate such a work of Co impurities to form Zn vacancies in their vicinities, which may again result in more abundant Zn vacancies at boundaries than in grains. Since the defects associated with oxygen excess such as Zn vacancies are acceptor-like, the enrichment should correspond to the formation of interfacial acceptor states that can trap carrier electrons and hence form the double Schottky barriers.

In addition, Co impurities may be oxidized to be trivalent in the vicinity of boundaries since effective Fermi energy should be lowered as the double Schottky barriers grow. Such oxidation of Co impurities has been suggested by Yodogawa *et al.* through differential thermal and thermal gravimetric analyses.¹⁸⁾ In this case, the attractive interaction is likely to be enhanced, as suggested by the calculations for the $\text{Co}_{\text{Zn}} - \text{V}_{\text{Zn}}$ complexes. The present result supports the previous suggestion that Co impurities work to stabilize oxygen adsorption (excess) at surfaces and grain boundaries of ZnO.^{18, 21, 22)}

Regarding the energies of electronic states, the unoccupied parts of interfacial states have been experimentally observed at 0.6–1.0 eV below the conduction band minimum.^{6–11)} Considering an experimental band gap of 3.30 eV, these should correspond to 2.3–2.7 eV above the valence band maximum. In the present results, the acceptor-type states associated with Zn vacancies are located close to the valence band maximum. Our previous calculations on a ZnO tilt boundary indicated that Zn vacancies form shallow acceptor states at grain boundaries as well.⁴⁵⁾

As the band gap was underestimated, GGA may have caused some errors in the calculated energies of defect electronic states. Stampfl *et al.* have made calculations for native defects and impurities in InN including self-interaction and electronic relaxation corrections.⁴⁶⁾ These corrections increased the band gap by about 1.3 eV and this resulted in a good agreement with experimental values. However, the energies of acceptor-type states associated with In vacancies were

increased only by 0.02 eV. This has been attributed to the orbital character: shallow acceptor-type states should have a character similar to that of the valence band and hence remain close to the valence band even if the corrections are included.^{34, 46)} Considering this result, the acceptor-type states of Zn vacancies are likely to keep close to the valence band maximum even if more elaborate approximations are used in the calculations. Therefore, the electronic structure of Zn vacancies cannot solely explain the deep interfacial states experimentally observed.

A possible origin of such deep states is electronic states associated with 3*d* transition-metal impurities. For Co impurities, the present calculations show that there are no unoccupied electronic states in the band gap when Co is divalent. However, when it is oxidized to be trivalent or quadrivalent, the unoccupied parts appear in the band gap. These unoccupied states may correspond to the deep states experimentally observed. It has been reported that the energies of the interfacial states depend strongly on the species of doped 3*d* transition-metal impurities in ZnO/PrCoO_x/ZnO thin film varistors, indicating that the 3*d* transition-metal impurities make significant contributions to the electronic structure.¹⁹⁾ On the other hand, another report imply that the energies of interfacial states are insensitive to species of doped transition-metal impurities.²⁰⁾ Further experimental/theoretical approaches to the local electronic structure should be required to clarify the details of the interfacial states in ZnO varistor ceramics.

5. Summary

The electronic states and formation energies of Co impurities and native defects associated with oxygen excess in ZnO have been investigated using first-principles plane-wave pseudopotential calculations. The electronic states indicate that Co impurities are donor-like. On the other hand, native defects associated with oxygen excess are acceptor-like, which can be sources of interfacial acceptors. Among these acceptor-like defects, Zn vacancies should be a dominant species because they are much lower in the formation energy than the others. Calculations for Co impurity-Zn vacancy complexes are conducted to investigate the interaction between these defects. The results imply that Co impurities stabilize Zn vacancies and hence oxygen excess in their vicinities. This is suggested to be a role of Co impurities at grain boundaries in ZnO varistor ceramics.

Acknowledgments

This study was supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 751) and for JSPS Fellows from the Ministry of Education, Culture, Sports, Science and Technology of Japan, and Ceramic Integration Project through the Science and Technology Agency in Japan.

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