Effect on nitrogen acceptor as Mg is alloyed into ZnO

Y. Q. Gai, B. Yao, Z. P. Wei, Y. F. Li, Y. M. Lu et al.

Citation: Appl. Phys. Lett. 92, 062110 (2008); doi: 10.1063/1.2857496
View online: http://dx.doi.org/10.1063/1.2857496
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v92/i6
Published by the American Institute of Physics.

Related Articles
Donor behavior of Sb in ZnO

Transition levels of defects in ZnO: Total energy and Janak's theorem methods

Ab-initio studies on Li doping, Li-pairs, and complexes between Li and intrinsic defects in ZnO

Intrinsic and extrinsic defect relaxation behavior of ZnO ceramics

Dual roles of doping and trapping of semiconductor defect levels and their ramification to thin film photovoltaics

Additional information on Appl. Phys. Lett.
Journal Homepage: http://apl.aip.org/
Journal Information: http://apl.aip.org/about/about_the_journal
Top downloads: http://apl.aip.org/features/most_downloaded
Information for Authors: http://apl.aip.org/authors

ADVERTISEMENT

HAVE YOU HEARD?

Employers hiring scientists and engineers trust

http://careers.physicstoday.org/post.cfm
Effect on nitrogen acceptor as Mg is alloyed into ZnO

Y. Q. Gai,1,2 B. Yao,3,a) Z. P. Wei,3 Y. F. Li,3 Y. M. Lu,3 D. Z. Shen,3 J. Y. Zhang,3
D. X. Zhao,3 X. W. Fan,3 Jingbo Li,1,8 and Jian-Bai Xia1

1Key Laboratory of Excited State Processes, Chinese Academy of Sciences, Changchun Institute of Optics,
Fine Mechanics and Physics, Chinese Academy of Sciences, 16-Dongnanhu Road, Changchun 130033,
People's Republic of China
2Graduate School of Chinese Academy of Sciences, Beijing 100039, People's Republic of China
3State Key Laboratory for Superlattice and Microstructures, Institute of Semiconductors,
Chinese Academy of Science, P.O. Box 912, Beijing 10083, People's Republic of China

(Received 13 January 2008; accepted 25 January 2008; published online 14 February 2008)

Our Raman measurement indicates that the intensity of the peaks (510 and 645 cm⁻¹) related to nitrogen concentration is enhanced in MgZnO compared with that in ZnO. Using first-principles band structure methods, we calculated the formation energy and transition energy level for nitrogen acceptor in ZnO and random Mg,Zn₁₋ₓO (with x=0.25) alloy. Our calculations show that the incorporation of nitrogen can be enhanced as Mg is alloyed into ZnO, which agrees with our experiments. The acceptor energy level deeper in the alloy ascribes to the downward shift of the valence-band maximum edge in the presence of magnesium. © 2008 American Institute of Physics.

[DOI: 10.1063/1.2857496]
is, for substitutional nitrogen in oxygen site, the formation energy of NO will decrease if the chemical potential of N increases or if the chemical potential of O decreases. To keep ZnO thermodynamically stable, it is required that \( \mu_{\text{O}} + \mu_{\text{Zn}} = \Delta H_f(\text{ZnO}) \) and to avoid the phase separation, i.e., the formation of MgO, \( \mu_{\text{O}} \) is limited by \( \mu_{\text{O}} + \mu_{\text{Mg}} = \Delta H_f(\text{MgO}) \), where \( \Delta H_f(\text{ZnO}) \) and \( \Delta H_f(\text{MgO}) \) are the formation energy of solid ZnO and MgO. Our calculated \( \Delta H_f(\text{MgO}) = -5.946 \text{ eV} \) and \( \Delta H_f(\text{ZnO}) = -3.458 \text{ eV} \) is in good agreement with the experimental value of \(-3.6 \text{ eV}\).

The calculated formation energies for NO as the function of \( -\mu_{\text{N}} + \mu_{\text{O}} \) and the ionization energy \( \varepsilon(0/-) \) for NO in ZnO and the random Mg\(_{x}\)Zn\(_{1-x}\)O\(_{2}\) alloys are shown in Table I. For N in the alloy, we have calculated the NO at different sites. The nNN denotes that there are \( n \) Mg atoms in the tetrahedral nearest neighboring sites centered on the dopant N atom. It can be noticed from these results that the change of formation energy for the NO defect in Mg\(_{0.25}\)Zn\(_{0.75}\)O strongly depends on the number of Mg atoms that are nearest neighbors to nitrogen. For example, the formation energy of NO increased for nitrogen at an oxygen site with zero, one, two, and three Mg atoms as the nearest neighbors. These results suggested that N is easier to bind with Zn than Mg. This is because the Zn–N bond is stronger than Mg–N and our calculation shows that Mg–N bonds are longer than that of Zn–N. Figure I is the Raman spectra for samples ZnO, N doped ZnO, and N doped MgZnO alloy with Mg content at about 20 at. % prepared by plasma-assisted molecular beam epitaxy. Peaks at 510 and 645 cm\(^{-1}\) are attributed to nitrogen related defect.\(^\text{21}\) We could see the obvious increase of N incorporation into MgZnO alloy. This might be related to the reduction of chemical potential of oxygen in the presence of Mg. Experimentally, we can obtain the Zn\(_{1-x}\)Mg\(_x\)O films with different Mg contents by changing the oxygen flow rate and keeping the other conditions unchanged and the Mg content is decreased with the increase of oxygen flow rate.\(^\text{22}\) Therefore, on the contrary, we could control the \( \mu_{\text{O}} \) in Mg–ZnO smaller than that in ZnO by controlling the temperature of Mg source. From Table I, the formation energy of NO in Mg\(_{0.25}\)Zn\(_{0.75}\)O\(_{2}\) will be lower than that in ZnO if \( -\mu_{\text{N}} + \mu_{\text{O}} \) in the alloy is about 0.2 eV smaller than that in ZnO, which becomes possible as Mg is alloyed into ZnO for fear of forming MgO.

For the ionization energy of NO in ZnO, the calculated level \( \varepsilon(0/-) \) locates at 0.42 eV. This agrees well with previous first-principles calculations.\(^\text{23,24}\) For that in Mg\(_{0.25}\)Zn\(_{0.75}\)O\(_{2}\) alloy, we find that the relative position of NO(/0) depends on the location of nitrogen in the alloy. It decreases from 0.468 eV when N has zero nearest neighboring Mg atoms to 0.385 eV with three Mg nearest neighbors. This is related to the decrease of p–d coupling that lowered the acceptor level relative to the VBM in the same alloy. Li et al.\(^\text{25}\) have proposed that the acceptor transition energy could be reduced by replacing the surrounding Zn with isovalent Mg. Combined with the formation energy shown in Table I, which showed that N preferred to locate at the position with no NN Mg surrounding it, we see that the N acceptor is about 50 meV deeper in the random alloy with \( x=0.25 \), which is consistent in our experimental observation from the study of the photoluminescence of nitrogen-doped MgZnO films.\(^\text{26}\) To account for the above observed trends, we have plotted in Fig. 2 the valence-band offsets between MgO, ZnO, and Mg\(_{0.25}\)Zn\(_{0.75}\)O alloy and the nitrogen acceptor energy level in them. The conduction-band offsets are obtained from our calculated valence-band offsets by adding the difference of measured gaps \( E_g = 3.34 + 2.0x \).\(^\text{27}\) From the calculated results, we see that the valence-band offset for MgO/ZnO is about 1.74 eV, which is in contrast with the “common-anion rule”\(^\text{28,29}\) that the valence-band offset between two semiconductors having the same anion will be small. This is because the VBM is composed of the anion \( p \) states and the interaction between cation \( d \) states and anion \( p \) states will strongly affect the position of VBM.\(^\text{30}\) Our calculated valence-band

<table>
<thead>
<tr>
<th>( \Delta H_f(\text{N}_0, 0) )</th>
<th>( \varepsilon(0/-) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3NN 2.50 - ( \mu_{\text{N}} + \mu_{\text{O}} )</td>
<td>0.385</td>
</tr>
<tr>
<td>2NN 2.054 - ( \mu_{\text{N}} + \mu_{\text{O}} )</td>
<td>0.404</td>
</tr>
<tr>
<td>1NN 1.623 - ( \mu_{\text{N}} + \mu_{\text{O}} )</td>
<td>0.436</td>
</tr>
<tr>
<td>0NN 1.215 - ( \mu_{\text{N}} + \mu_{\text{O}} )</td>
<td>0.468</td>
</tr>
<tr>
<td>ZnO 1.113 - ( \mu_{\text{N}} + \mu_{\text{O}} )</td>
<td>0.420</td>
</tr>
</tbody>
</table>

FIG. 1. (Color online) Raman spectra of ZnO, N doped ZnO, and Mg\(_{0.25}\)Zn\(_{0.75}\)O with \( x=20 \) at. %.
offset between Mg$_x$Zn$_{1-x}$O and ZnO is about 0.134 and 0.336 eV, consequently, the $\Delta E_F/\Delta E_v$ is 0.87/1 and 0.49/1 for $x=12.5\%$ and $25.5\%$, respectively, suggesting that the band alignment between ZnO and Mg$_x$Zn$_{1-x}$O depends obviously on the Mg concentration and the valence-band offset is non-negligible. The experiment from the analyses of exciton binding energy also revealed that the offset of valence band was large enough to be neglected.\textsuperscript{31} Using this band alignment, we find that for acceptors, the absolute transition energy level with respect to vacuum increased with the addition of Mg due to the downward shift of the VBM edge as the Mg incorporation.

In summary, our first principles total energy calculations indicate that the formation energy for nitrogen on the O site decreases with the addition of Mg. Our Raman spectra clearly show that the solubility of nitrogen is enhanced as Mg is alloyed into ZnO. The calculated N$_{\text{O}}$ acceptor energy level in Mg$_x$Zn$_{24}$O$_{32}$ is significantly deeper than that in ZnO as the result of the downward shift of the VBM edge in the presence of magnesium. Our general understanding of substitutional acceptor N in Mg$_x$Zn$_{1-x}$O alloys at relative high Mg content is expected to be applicable to other substitutional acceptor, such as P, As, Li, and Na. Qiu et al.\textsuperscript{32} has proved that the acceptor Li$_{\text{Zn}}$ in Mg$_x$Zn$_{1-x}$O was deepened by the increase of Mg content.

This work is supported by the Key Project of National Natural Science Foundation of China under Grant Nos. 60336020 and 50532050, the “973” program under Grant No. 2006CB604906, the Innovation Project of Chinese Academy of Sciences, the National Natural Science Foundation of China under Grant Nos. 60429403, 60506014, 50402016, 10674133, and 60776011.

\textsuperscript{19}C.-Y. Yeh, S.-H. Wei, and A. Zunger, Phys. Rev. B \textbf{50}, 2715 (1994).