An investigation of control mechanisms of the excitonic behavior in reactively sputtered ZnO on (0001) Al$_2$O$_3$

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Above-band-edge absorption spectra of reactively sputtered Zn- and O-rich samples exhibit free exciton and neutral acceptor bound exciton (A^0X) features. It is shown that the residual acceptors which bind excitons with an energy of 75 meV reside about 312 meV above the valence band, according to effective mass theory. An intra-band-gap absorption feature peaking at 2.5 eV shows correlation with the characteristically narrow A-free exciton peak intensity, suggesting a compensation mechanism of the centers involving oxygen vacancy (V_O) related donors. In order to enhance free exciton concentration relative to competing neutral bound exciton density, relevant annealing processes are performed without disturbing the residual shallow acceptor profile which is necessary for at least background p-type conductivity. © *2006 American Institute of Physics.*
[DOI: 10.1063/1.2386926]

I. INTRODUCTION

Wide band gap materials such as GaN with its direct band gap structure have been developed rapidly for applications in short wavelength light emission. ZnO, a II-VI oxide semiconductor, is also promising for various technological applications, especially for optoelectronic light emitting devices in the visible and ultraviolet (UV) range of the electromagnetic spectrum.[1–4] Among several advantages[5] of ZnO with respect to other commonly used wide band gap materials, the most important one is its large exciton binding energy[6] (60 meV), nearly three times higher than in competing semiconductors. The large binding energy insures optically efficient excitonic behavior up to room temperature and even somewhat above. ZnO as naturally grown is n type, so that production of stable and reasonably high p-type conductivity has been the crucial issue in providing short wavelength UV emission from the prepared devices.

The most successful acceptor dopants in ZnO have been the group V elements such as N,[7,8] P,[9] As,[10,11] and Sb.[12] N is known to substitute on the O site but the exact structures of the P, As, and Sb acceptors have not yet been established.[13] Despite success of achieving p-type doping, or even producing p-type conductivity in some reactively sputtered as grown samples,[14] it does not automatically follow that sufficiently stable materials and junctions leading to UV emission can be produced. This makes p-type asymmetry- and stoichiometrically deviated structural Zn-rich and O-rich defects which exhibit some unusual behavior in as-grown and annealed samples still interesting to study. For example, negative U behavior of V_O centers has been reported.[15] Although it was previously predicted that unintentional H impurities are the main source of n-type conductivity,[16] it is now commonly agreed that native Zn-rich defects are rather more important than hydrogen,[17] as previously noted by Vanheusden *et al.*,[18] Studenikin *et al.*,[19] and Tüzemen *et al.*[20]

In this work, we will focus on the samples grown at O-rich and Zn-rich conditions using reactive magnetron sputtering techniques. We have investigated the absorption processes due to free and bound excitons, and also intra-band-gap transitions. We show that postgrowth vacuum annealing enhances the characteristically narrow free exciton line. It is proposed that Zn-rich defects formed by treatments during or after growth may result in high concentrations of free excitons due to the passivation of residual acceptors having a role in the exciton binding mechanism.

II. EXPERIMENT

All the samples were deposited onto the (0001) Al$_2$O$_3$ substrates by reactive sputtering from a Zn (99.99%) metal target in O$_2$ and Ar atmosphere using dc magnetron source (US Gun II) in a turbo molecular pumped stainless steel chamber. The substrate was heated during deposition to 400 or 410 °C, typically. O$_2$/Ar ratios were kept at 1.41 and 0.41 for O-rich and Zn-rich conditions, respectively. Postgrowth annealing processes were performed in a vacuum of 10^{-5} Torr using Edwards' coating unit. The samples were placed into a Mo pipe resistively heated to 400 or 500 °C during the annealing processes. The crystalline structures of the films were determined by x-ray diffraction analysis with a conventional θ-2θ goniometer using 0.7079 Å wavelength Mo $K\alpha_1$ radiation. The wavelength is shorter than commonly used $K\alpha$ of Cu or Cr sources, resulting in a higher resolution.

Absorption measurements of all the samples were performed using a Perkin Elmer UV/vis spectrometer with a wavelength resolution better than 3 nm. The samples were placed on a radiation shielded holder of a closed cycled He

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TABLE I. Growth conditions of ZnO films onto the (0001) sapphire substrate.

Sample	Growth time (min)	O_2 pressure (Torr)	Ar pressure (Torr)	O_2/Ar ratio	Substrate temperature (°C)
452A and 452B	60	0.9×10^{-2}	2.2×10^{-2}	0.41	410
453A and 453B	60	3.1×10^{-2}	2.2×10^{-2}	1.41	400

cryostat with an optical tailpiece fixed into the spectrometer. All absorption measurements were conducted at sample temperatures ranging from 10 to 320 K.

III. RESULTS AND DISCUSSION

We have grown two sets of samples by a radio frequency reactive sputtering (rfRS) method: The first set of samples are O rich, grown at O_2/Ar ratios of about 1.41 and the second set have the ratio of 0.41 and therefore Zn rich. The two samples are expected to contain high concentrations of O-rich defects such as V_{Zn} and O_i and of Zn-rich defects such as V_O and Zn_i. The growth conditions of these samples are shown in Table I. X-ray diffraction measurements on the reference single crystal provided by Eagle Picher Technologies and on the rfRS grown films are shown in Figures 1(a)–1(d). It is seen that the rfRS grown films are c-axis oriented nearly as well as the single crystal. The peak at around $2\theta=18$ which is observed in all the films corresponding to the (0006) surface of the Al_2O_3 substrate, according to the Joint Committee on Powder Diffraction Standards (JCPDS) database, as also observed elsewhere.[21]

A. As-deposited samples

Optical absorption spectra of both Zn-rich (O_2/Ar =0.41) and O-rich (O_2/Ar=1.41) as-deposited samples are shown in Fig. 2 at sample temperatures of 30 K. In order to convert the original absorbance data to absorption coefficient
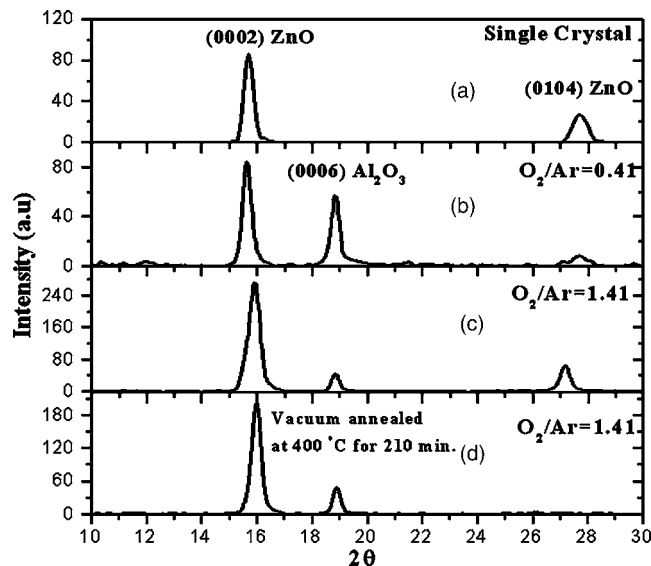

FIG. 1. XRD plots of the ZnO samples; (a) reference single crystal, (b) as-deposited Zn-rich sample (O_2/Ar=0.41), (c) as-deposited O-rich (O_2/Ar=1.41), (d) 210 min vacuum annealed at 400 °C, O_2/Ar=1.41

values, we made use of the following equations which were previously proposed for nominal incidence of light on III-V compounds;[22–24]

$$T = \frac{(1-R)^2 \exp(-\alpha t)}{1 - R^2 \exp(-2\alpha t)} = \exp(-A), \qquad (1)$$

where R, T, and A are the reflectivity, transmittance, and absorbance, respectively, α the absorption coefficient, and t the film thickness. We observe that the absorbance as a function of wavelength (or energy) is nearly flat and achieves its lowest level at around 1100 nm (or 1.127 eV). Therefore we assume that the optical absorption due to the deep levels within the band gap is zero at this wavelength, and Eq. (1) reduces to

$$T = \frac{(1-R)^2}{1 - R^2} = \exp(-A) \quad \text{at 1100 nm.} \qquad (2)$$

From this equation we determine the reflectivity R for ZnO to be around 15%–20% for each sample which is quite consistent with the previous $T=80\%-90\%$ measurements of Ciobanu *et al.*[25] Having determined R, we are able to determine the absorption coefficient spectra for each sample using Eq. (1).

As can be seen in Fig. 2, the free and bound exciton peaks are clearly observed in the sample that is grown at Zn-rich conditions, and the free exciton peak intensity is high in comparison to the competing bound ones. On the other hand, the free exciton in O-rich material can barely be observed as a shoulder of the bound exciton absorption in O-rich material. As the temperature of Zn-rich samples is increased, the free exciton peak intensity decreases, and the differences between the free and bound exciton peak energies remain nearly constant at a value of 75 meV. We therefore assume that exciton binding centers are dependent on the valance band rather than the conduction band.

There has always been conflict concerning the bound exciton lines, as to whether they arise from neutral donor bound excitons (D^0X) or neutral acceptor bound excitons (A^0X). It has been reported by Gutowski *et al.*[26] that, in general, the binding energies of neutral-donor-exciton complexes are smaller than those of excitons bound to neutral acceptors in II-VI semiconductors. A comprehensive study on the excitonic structures in ZnO has been reported by Teke *et al.*[27] supporting the Gutowski *et al.* findings.[26] According to the PL measurements by Teke *et al.*,[27] the main neutral-donor-bound exciton peak ($D_2^0X_A$) differs only 17 meV from that of the *A*-free exciton line, indicating that binding energies to donors are quite low in comparison to the defect binding energies of about 75 meV observed in the present
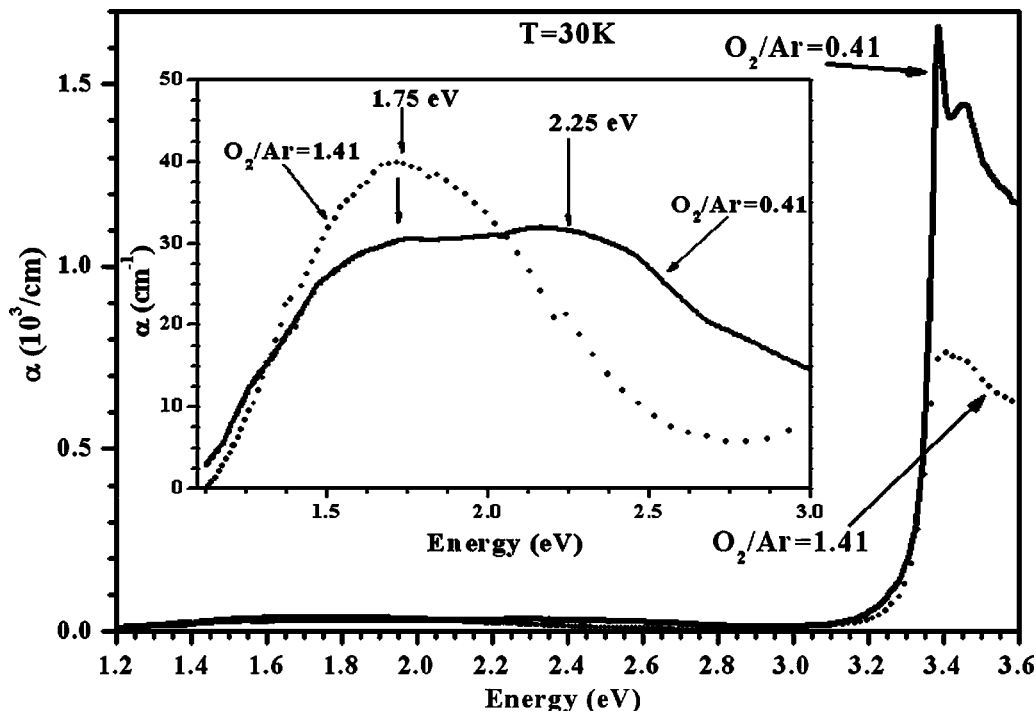
FIG. 2. Absorption coefficient spectra of both as-deposited Zn-rich and O-rich samples. The insert shows magnified intra-band-gap absorption for both samples. Subtracting the 1.75 eV peak from the other peak in Zn-rich sample results in a shift towards 2.5 eV.

work. Thereby we propose that the broader peak observed at 3.464 eV with a full width at half maximum (FWHM) of about 189 meV is an acceptor bound complex rather than a donor bound one in our absorption measurements. Look *et al.* have also suggested that impurity binding energies of this kind (59 meV in their case) should be acceptor-bound-exciton complexes such as an exciton bound to N substituted for O (N_O).[28] Our experimental evidence arising from further vacuum annealing experiments indicates that the acceptor(s) binding excitons are native O-rich defects rather than chemical impurities.

Although these shallow acceptor binding energies are observed at 79,[26] 21–29,[27] 59,[28] and 75 meV (present work), the actual level of these defects are, in general, considered to be deeper due to the fact that the most shallow effective mass acceptor in ZnO is expected to be at 100–150 meV. From a Haynes factor of 0.24 suggested by Gutowski et al,[26] these acceptor ground levels having a role in the exciton binding mechanism are situated at respectively 329,[26] 87,[27] 246,[28] and 312 meV (present work), resolving the conflict between the effective mass theory and experiments. On the other hand, we propose that the effective binding energies of these levels should be considered as the former ones because any kind of flaw incorporated as physical or chemical impurities in semiconductors has a ground state binding energy E_d or E_a, which is different than the value calculable from effective mass theory. The origin of this shift is usually attributed to the difference between the mean macroscopic dielectric constant of the material as a whole and the microscopic dielectric constant around the particular defect center attracting electrons or holes.[29]

Returning to the absorption measurements, it has been observed that the band-edge absorption tails of all the samples have the spectral dependence only of the quadratic joint density of states, as

$$\alpha^2 = A(E - E_h), \quad \hbar\omega \geqslant E_g, \tag{3}$$

where extrapolation of α^2 vs E ($\hbar\omega$; incident photon energy) to zero would result in $E = E_g$. The band gap energy values, E_g, as a function of temperature for both Zn- and O-rich samples determined from the α^2 vs E plots are shown in Fig. 3. As can be seen, band gap energies of Zn-rich material are in general greater than those of O-rich samples and they are parabolic as a function of temperature, as observed by some
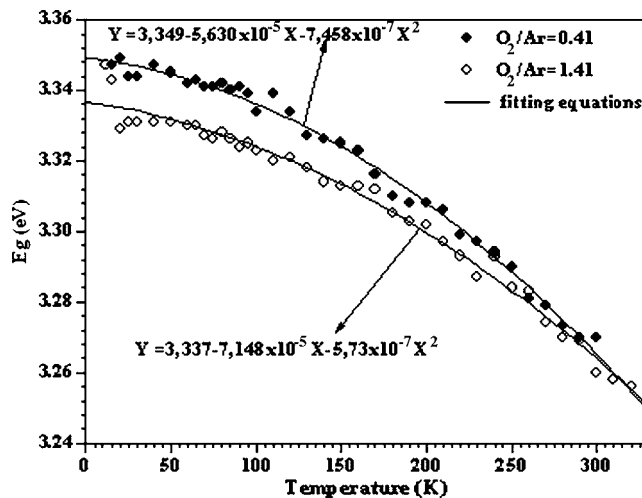

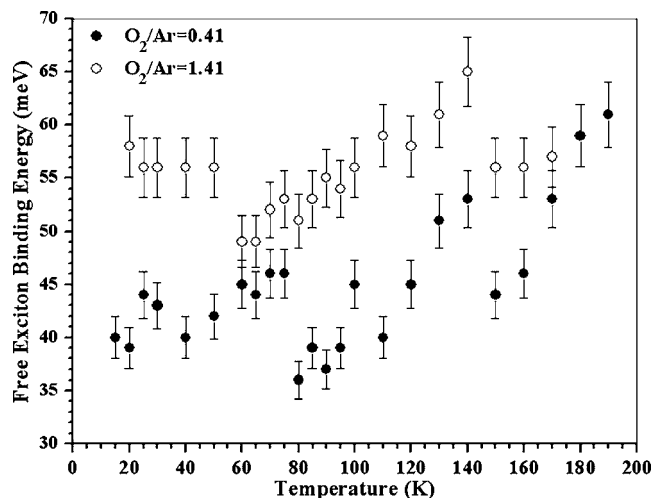FIG. 3. Variation of E_g as functions of temperature for Zn- and O-rich samples.

FIG. 4. Free exciton binding energies vs temperature for Zn-rich and O-rich samples.

others in the literature.[30] The smaller E_g values in O-rich samples usually attributed to O content on the surface of the films,[31] unless it is due to the Moss-Burstein shift. However, our previous Hall measurements[14] show that while the Zn-rich sample is moderately n type having free electron concentrations of about 8×10^{17} cm^{-3}, the O-rich sample has a low density of holes around 8×10^{14} cm^{-3}, which is unlikely to cause such a shift. Free exciton binding energies illustrated in Fig. 4 are evaluated from the difference between the A-free exciton peak and E_g at a sample temperature T. Although free exciton binding energies are in general higher for O-rich sample, they became identical to the free exciton value of about 60 meV at temperatures over 180 K, which is usually reported in the literature.[6,32]

B. Effect of vacuum annealing

It is so far observed that in as-deposited samples, increasing Zn-rich conditions results in an increase in characteristicly narrow A-free exciton behavior. The A-free exciton intensity is reduced by O-rich conditions having high concentrations of structural acceptors that, we assume, play an important role in the exciton binding mechanism in sputtered thin films of ZnO. However O-rich conditions are necessary for at least establishing the background p-type conductivity by compensating the residual shallow donors, i.e., while the material for optoelectronic applications should have a sharp, high quality A-free exciton profile, it should also have certain concentrations of shallow acceptors in order to compensate the residual donors and therefore have the least p-type conditions. Since the first experiments on as-deposited samples show that Zn-rich conditions are relevant for A-free exciton behavior but also O-rich conditions are necessary for background p-type characteristic of the material, we decided to anneal the O-rich samples in vacuum. It is expected that the O vapor pressure is very much higher than that of Zn, so that the reaction
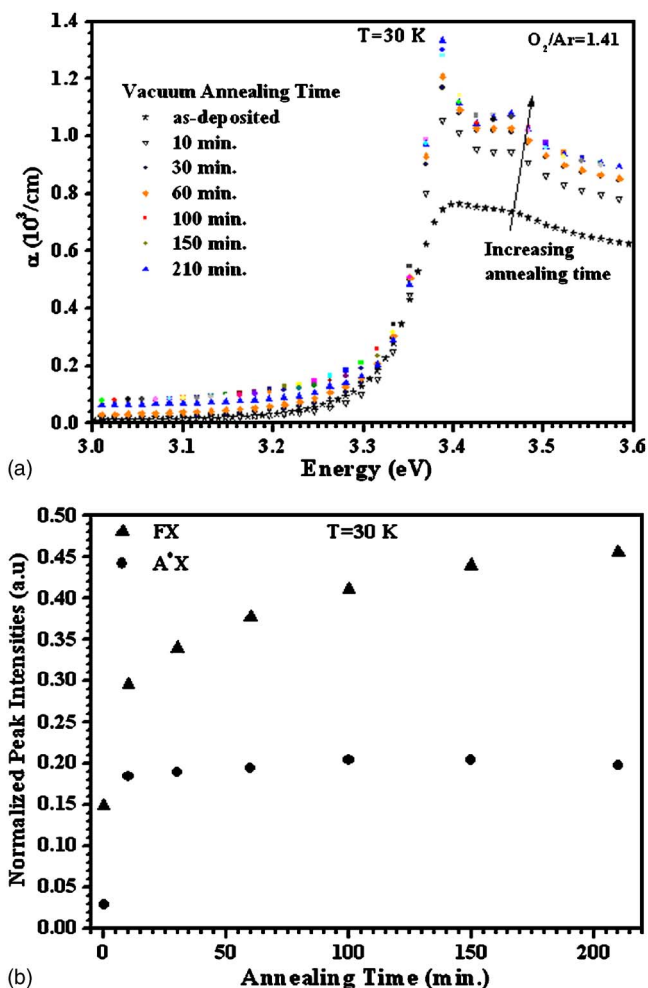

FIG. 5. (Color online) Increase in excitonic behavior as the subsequent vacuum annealing processes at 400 °C are performed in O-rich sample; (a) (color online) spectral change of free (FX) and neutral acceptor bound exciton (A^0X) lines and (b) FX and (A^0X) peak intensities as a function of annealing time.

$$ZnO \rightarrow Zn_i + V_O \quad \text{(evaporation of O)} \quad (4)$$

is quite possible at annealing temperatures. Therefore the concentration of Zn-rich defects, which are thought to act as donors, increases. Annealing experiments by Chen *et al.*[33] prove this assumption. Here, the relevant annealing process should result in an increase in free exciton concentrations without changing the native shallow acceptor profile that plays an important role in compensating residual shallow donors.

In fact, as can be seen in Fig. 5, when the duration of vacuum annealing at 400 °C is increased for the O-rich sample, the free exciton (FX) peak intensity is dramatically increased [Figs. 5(a) and 5(b)] and the neutral acceptor bound exciton (A^0X) peak intensity remains nearly unchanged after an initial increase [Fig. 5(b)]. It means that, while the vacuum annealing process did not make too much difference in the native shallow acceptor profile which is necessary for background p-type conductivity, the high quality free exciton peak intensity can be increased in O-rich sample.
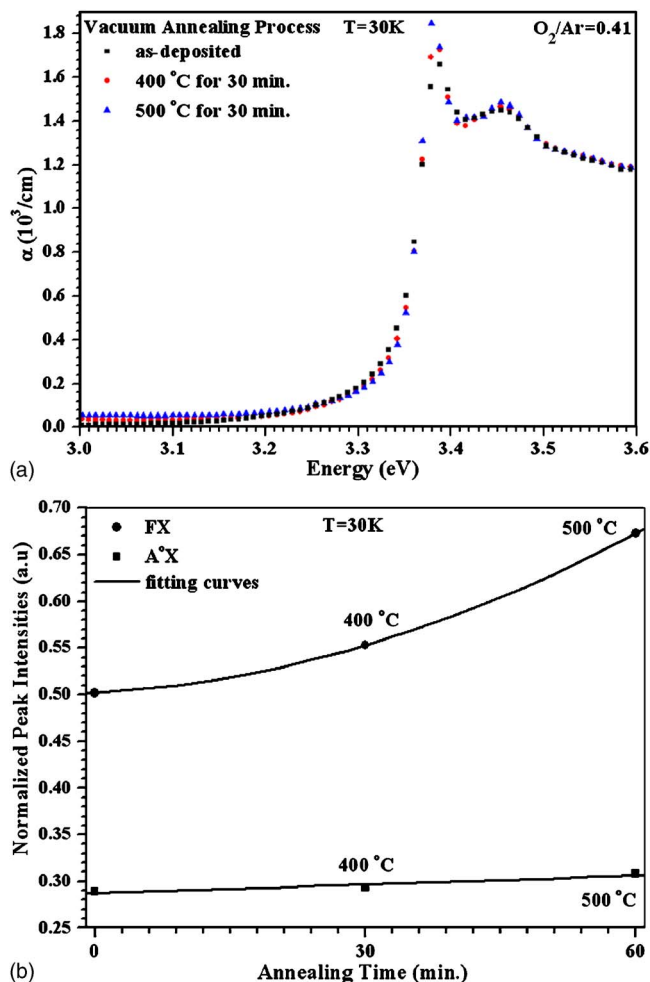
FIG. 6. (Color online) Increase in exciton peaks as the vacuum annealing processes at 400 °C and subsequently at 500 °C are performed in Zn-rich sample; (a) (color online) spectral change of free (FX) and neutral acceptor bound exciton (A^0X) lines and (b) FX and (A^0X) lines and (b) FX and (A^0X) lines and (b) FX and (A^0X) peak intensities as a function of annealing time.
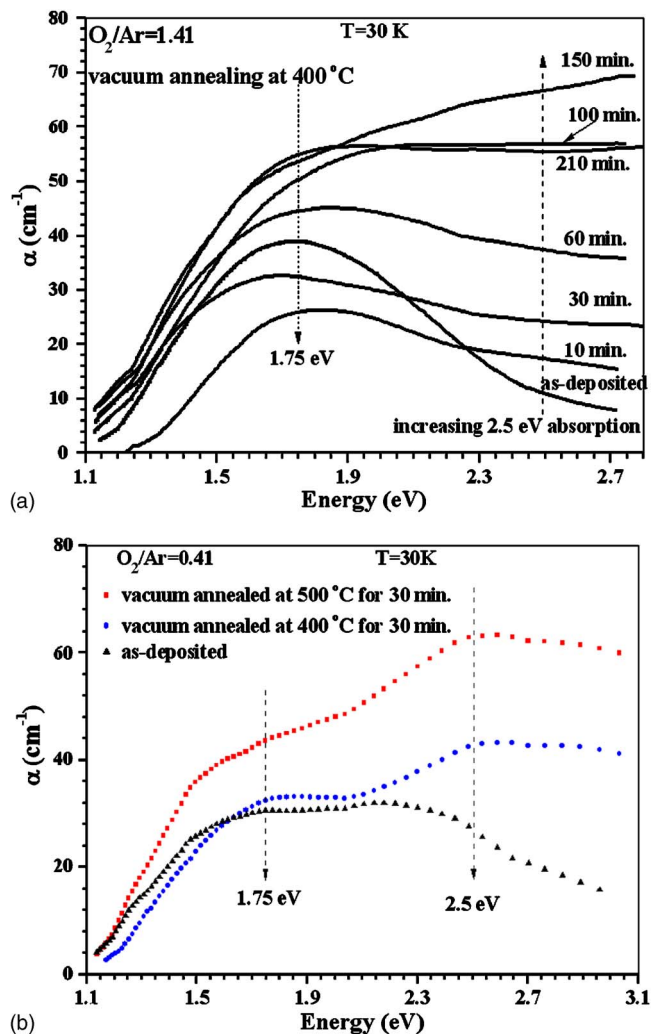

FIG. 7. (Color online) Spectral change of intra-band-gap absorption as the subsequent vacuum annealing processes are conducted; (a) O-rich sample and (b) (color online) Zn-rich sample.

The same effect is also valid for the Zn-rich sample, as seen in Fig. 6. While the FX peak intensity can be increased up to 70% by 400 °C and subsequent 500 °C vacuum annealing for 30 min [Figs. 6(a) and 6(b)], the neutral acceptor bound exciton (A^0X) peak intensity remained at nearly the same level [Fig. 6(b)].

C. Possible role of intra-band-gap absorption

As seen in Fig. 2, intra-band-gap absorption extending from 1.1 to 3.0 eV exhibits two broad characteristic features peaking respectively at ~1.75 and ~2.5 eV, indicating that they are most probably both intracenter transitions rather than band-to-defect or defect-to-band ones. Although the higher energy peak is seen at around 2.25 eV in as-deposited samples, one can see that it is actually peaking at around 2.5 eV by extracting the effect of the 1.75 eV band from the peak in the as-deposited O-rich sample. The 1.75 eV peak is less effective in annealed samples so that it cannot cause such a redshift.

As seen in Fig. 7, the 2.5 eV broad band can be observed only in the Zn-rich sample and vacuum annealing increases the concentration of these defects [Fig. 7(a)], indicating that

this is most probably due to the Zn-rich defects such as V_O or Zn_i. In fact, the calculations by Van de Walle[15] show that this peak belongs to $\epsilon(2+/0)$ state of V_O centers which is usually attributed to green emission in photoluminescence (PL).[13] The 1.75 eV broad band is more difficult to interpret whether it is due to O-rich or Zn-rich defects because the feature can be observed in both samples. On the other hand, while the 2.5 eV peak is remarkably increased in Zn-rich sample by vacuum annealing at 400 °C and subsequent 500 °C for 30 min [Fig. 7(a)], the 1.75 eV peak slightly increases in Zn-rich samples [Fig. 7(a)] and can hardly be observed in as-deposited O-rich samples [Fig. 7(b)]. In fact, according to first principles calculations by Kohan et al,[34] O-rich defects such as V_{Zn} and O_{Zn} have still low formation energies around 1.5 eV even at low Zn-partial pressure when the Fermi level is close to the top of the valance band (p type). Therefore, as seen in Fig. 7(b), O-rich defects such as V_{Zn} and O_{Zn} can also be produced by vacuum annealing process having Zn-rich conditions because the O-rich samples are originally observed as p type.[14] Hence, we propose that the 1.75 eV feature might be related to O-rich defects such as V_{Zn} or O_{Zn} although further investigation has to be continued.
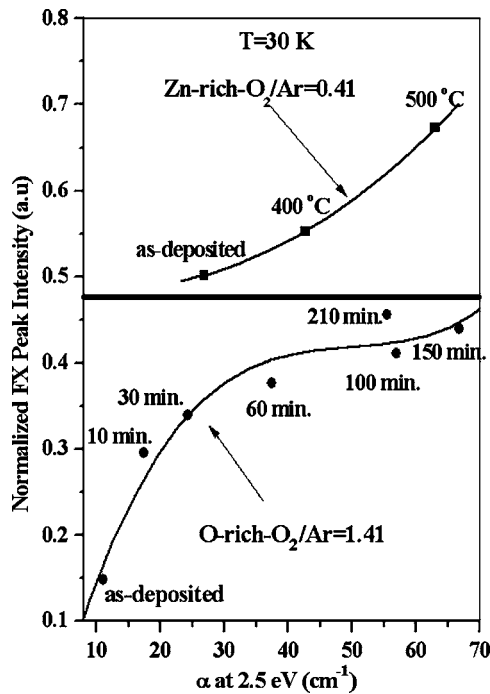
FIG. 8. Increase in FX peak intensity as the absorption coefficient at 2.5 eV is increased by vacuum annealing of both Zn- and O-rich samples.

It seems that Zn-rich defects cause an increase in the characteristically narrow FX peak intensity because the Zn-rich sample has high concentrations of Zn-rich defects to start with, and vacuum annealing processes increase the FX peak intensity as the Zn-rich 2.5 eV absorption increases in both samples (Fig. 7). As seen in Fig. 8, there exists a remarkable increase in the FX absorption coefficient at the peak as the 2.5 eV feature is increased in both samples. Therefore the prediction below is quite possible.

We propose the following mechanism for the role of Zn-rich defects on the enhancement of FX peak intensity: The acceptor ground state A^0 is a state which tends to capture an electron from the valance band to go to deeper A^- state. We consider the lowest state of the neutral acceptor bound exciton A^0X consisting of two holes on the acceptor level and one electron in the conduction band, similar to the description for neutral donor bound excitons (D^0X) given by Wang *et al.*[35] The transition from A^0X to the ground state of A^0 is called the "principal transition" and results in the A^0X bound exciton peak in the absorption spectra. As previously shown, if the 2.5 eV feature belongs to V_O centers, they play an important role in the compensation mechanism. According to Van de Walle's calculations[15] the V_O centers are normally in the inactive metastable negative-U deep state of $V_O^{0/++}$ and cannot directly compensate acceptors.[20] However, with the effect of incident light in the absorption measurements, it is possible that they are excited to $V_O^{+/++}$ shallow state resulting in 2.5 eV intracenter transition at which they can well play a role in compensating acceptors. Therefore, in the situations which involve high concentrations of structural donors such as V_O (as in the case of Zn-rich conditions) resulting in an intensive passivaiton of acceptors due to compensation, we suppose that most of the acceptors would be initially in the deeper negative charge state of A^- which is unable to bind

excitons. Therefore the absorption spectra just over the band edge would involve high concentrations of characteristically narrow free exciton transitions. Although the proposed $V_O^{0/++} \rightarrow V^{+/++}$ transition happens with the assistance of the incident light in low temperature absorption measurements, it has been shown that the most of the V_O centers are in the compensating $V^{+/++}$ shallow state at room temperature (RT) conditions so that the level might have important role in devices which are supposed to be working at RT.

As a result, it has been observed that optically important A-free exciton peak intensity can be enhanced by the production of Zn-rich V_O centers having role in pasivation of exciton binding structural acceptors. Fortunately, the structural acceptor profile remains unchanged during the vacuum annealing process because these structural acceptors are relevant for p-type conduction

IV. CONCLUSION

A-free and neutral acceptor bound excitons are, respectively, measured at 3.389 and 3.464 eV for Zn-rich and at 3.387 and 3.464 eV for O-rich samples. It is found that residual acceptors bind the exciton with about 75 meV energy, which corresponds to the acceptor level about 312 meV above the valence band according to effective mass theory. The absorption feature at about 2.5 eV seems to play an important role in improving high quality, characteristically narrow free exciton line, which is probably the Zn-rich V_O centers, resulting in passivation of exciton binding shallow acceptors. A model for this mechanism involving the passivation of shallow acceptors is also proposed. We have shown that we can enhance the free exciton line in O-rich material, compared to its diminished value in the as-deposited sample. Vacuum annealing at around 400 °C for up to approximately 2.5 h can increase the free exciton line without disturbing the structural acceptor profile, which is relevant to background p-type conductivity. It is of great importance that the p-type side of optoelectronic devices such as p-n light emitting diodes (LEDs) have characteristically narrow excitonic behavior while also preserving the p-type conductivity.

[1] T. Aoki, Y. Hatanaka, and D. C. Look, Appl. Phys. Lett. **76**, 3257 (2000).
[2] X.-L. Guo, J.-H. Choi, H. Tabata, and T. Kawai, Jpn. J. Appl. Phys., Part 2 **40**, L177 (2001).
[3] H. Ohta, M. Orita, M. Hirano, and H. Hosono, J. Appl. Phys. **89**, 5720 (2001).
[4] Ya. I. Alivov, J. E. Van Nostrand, D. C. Look, M. V. Chukichev, and B. M. Ataev, Appl. Phys. Lett. **83**, 2943 (2003).
[5] D. C. Look, Mater. Sci. Eng., B **80**, 383 (2001).
[6] W. Y. Liang and A. D. Yoffe, Phys. Rev. Lett. **20**, 59 (1968).
[7] D. C. Look, D. C. Reynolds, C. W. Litton, R. L. Jones, D. B. Eason, and G. Cantwel, Appl. Phys. Lett. **81**, 1830 (2002).
[8] W. Xu, Z. Ye, T. Zhou, B. Zhao, L. Zhu, and J. Huang, J. Cryst. Growth **265**, 133 (2004).
[9] K.-K. Kim, H.-S. Kim, D.-K. Hwang, J.-H. Lim, and S.-J. Park, Appl. Phys. Lett. **83**, 63 (2003).
[10] D. C. Look, G. M. Renlund, R. H. Burgener II, and J. R. Sizelove, Appl. Phys. Lett. **85**, 5269 (2004).
[11] D.-K. Hwang, K.-H. Bang, M.-C. Jeong, and J.-M. Myoung, J. Cryst. Growth **254**, 449 (2003).
[12] T. Aoki, Y. Shimizu, A. Miyake, A. Nakamura, Y. Nakanishi, and Y. Hatanaka, Phys. Status Solidi B **229**, 911 (2002).
[13] D. C. Look, Semicond. Sci. Technol. **20**, S55 (2005).
[14] G. Xiong, J. Wilkinson, B. Mischuck, S. Tüzemen, K. B. Ucer, and R. T.

Williams, Appl. Phys. Lett. **80**, 1195 (2002).

[15]C. G. Van de Walle, Physica B **308–310,** 899 (2001).

[16]D. H. Hofmann *et al.*, Phys. Rev. Lett. **88**, 045504 (2002).

[17]D. C. Look, C. Coşkun, B. Claaffin, and G. C. Farlow, Physica B **340–342,** 32 (2003).

[18]K. Vanheusden, C. H. Seager, W. L. Warren, D. R. Tallant, and J. A. Voigt, Appl. Phys. Lett. **68**, 403 (1996).

[19]S. A. Studenikin, N. Golego, and M. Cocivera, J. Appl. Phys. **87**, 2413 (2000).

[20]S. Tüzemen, S. Doğan, A. Ateş, M. Yıldırım, G. Xiong, J. Wilkinson, and R. T. Williams, Phys. Status Solidi A **195**, 165 (2003).

[21]H. L. Porter, C. Mion, A. L. Cai, X. Zhang, and J. Muth, Mater. Sci. Eng., B **119**, 210 (2005).

[22]P. Dobrilla and J. S. Blakemore, J. Appl. Phys. **58**, 208 (1985).

[23]R. Fornari and J. Kumar, Appl. Phys. Lett. **56**, 638 (1990).

[24]S. Doğan, S. Tüzemen, B. Gürbulak, A. Ateş, and M. Yıldırım, J. Appl. Phys. **85**, 6777 (1999).

[25]G. Ciobanu, G. Carja, G. Apostolescu, and I. Taraboanta, Superlattices Microstruct. **39**, 328 (2006).

[26]J. Gutowski, N. Presser, and I. Broser, Phys. Rev. B **38**, 9746 (1988).

[27]A. Teke, Ü. Özgür, S. Doğan, X. Gu, H. Morkoç, B. Nemeth, J. Nause, and H. O. Everitt, Phys. Rev. B **70**, 195207 (2004).

[28]D. C. Look, R. L. Jones, J. R. Sizelove, N. Y. Garces, N. C. Giles, and L. E. Halliburton, Phys. Status Solidi A **195**, 171 (2003).

[29]J. S. Blakemore, *Solid State Physics* (Cambridge University Press, Cambridge, 1985), p. 314.

[30]K. J. Hong, and T. S. Jeong, J. Cryst. Growth **280**, 545 (2005).

[31]R. Hong, J. Shao, H. He, and Z. Fan, J. Cryst. Growth **284**, 347 (2005).

[32]D. G. Thomas, J. Phys. Chem. Solids **15**, 86 (1960).

[33]Z. Q. Chen, S. Yamamoto, M. Maekawa, A. Kawasuso, X. L. Yuan, and T. Sekiguchi, J. Appl. Phys. **94**, 4807 (2003).

[34]A. F. Kohan, G. Ceder, D. Morgan, and C. G. Van de Walle, Phys. Rev. B **61**, 15019 (2000).

[35]Available online at http://www.physics.uconn.edu/~syelin/publication.htm