Carrier concentration dependence of acceptor activation energy in *p*-type ZnO

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The characteristics of an acceptor level in Sb-doped, *p*-type ZnO were studied using cathodoluminescence (CL) spectroscopy as a function of hole concentration. Variable-temperature CL measurements allowed us to estimate the activation energy of an Sb-related acceptor from temperature-induced decay of CL intensity. The values of activation energy of about 212 ± 28, 175 ± 20, 158 ± 22, and 135 ± 15 meV were obtained for samples with carrier concentrations of 1.3×10^{17}, 6.0×10^{17}, 8.2×10^{17}, and 1.3×10^{18} cm^{-3}, respectively. The involvement of acceptor levels is supported by the temperature-dependent hole concentration measurements. The possible origins of the strong temperature dependence are discussed. © *2006 American Institute of Physics*.
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Although nitrogen has long been considered the substitutional acceptor of choice for obtaining *p*-type conductivity in ZnO, the possibility of *p*-type doping with larger radii group V atoms, such as phosphorus,[1–3] arsenic,[4,5] and antimony,[6,7] has also been explored. The studies demonstrated that despite the large size mismatch, which, in principle, should inhibit the substitution of these impurities on the oxygen site, effective *p*-type doping with hole concentrations up to 10^{20} cm^{-3} can be achieved.[7] These findings prompted the first-principles investigation by Limpijumnong *et al.*, who suggested that the role of acceptors in size-mismatched impurity doped ZnO is performed by a complex of the impurity with two zinc vacancies ($X_{Zn}-2V_{Zn}$, where X denotes As or Sb), the ionization energy of which is several-fold lower than that of a substitutional configuration and is consistent with the independent experimental observations.[8] In this letter, we explore the nature of the Sb-related acceptor level by studying the luminescence properties as a function of carrier concentration.

The experiments were performed on ZnO:Sb layers grown on Si (100) substrates by an electron cyclotron resonance (ECR)-assisted molecular beam epitaxy (MBE). The detailed growth procedures are available in Ref. 6. Hall effect measurements revealed a strong *p*-type conductivity, with hole concentrations up to 1.3×10^{18} cm^{-3} and mobility up to 28.0 cm^2/V s at room temperature (Table I).

Cathodoluminescence (CL) measurements were conducted *in situ* in the Philips XL30 scanning electron microscope (SEM) integrated with Gatan MonoCL cathodoluminescence system. The SEM is also fitted with a hot stage and an external temperature controller (Gatan) allowing for temperature-dependent experiments. The decay of near-band-edge (NBE) luminescence intensity was monitored as a function of temperature in the range of 25–175 °C. Accelerating voltage of 10 kV was used. Note that each measurement was taken in a previously unexposed area to avoid the potential influence of electron irradiation.[9,10]

The investigation of the luminescence properties of Sb-doped ZnO was started with the acquisition of room-temperature cathodoluminescence spectra shown in Fig. 1. The inset of Fig. 1 reveals that the CL spectra of all four samples are dominated by the NBE band, which generally contains the band-to-band transition as well as the transition from the conduction band to a deep, neutral acceptor level (e,A^0).[10,11] Since acceptor levels form a band in the forbidden gap, the redshift of the NBE peak with increasing carrier concentration (i.e., higher doping levels) is consistent with the (e,A^0) emission and may indicate the broadening of the Sb-related acceptor band.[12,13] Another observation that can be made from Fig. 1 is the systematic decay in intensity of the NBE luminescence with increasing doping level. This decrease may be attributed to the reduction in radiative recombination rates as more disorder is introduced into the ZnO lattice by large-radius Sb atoms. The increasing trend in the values of the full width at half maximum (FWHM) of the NBE spectra provides further evidence for the impact of the size-mismatched dopant—FWHM values were determined to

TABLE I. Room-temperature electronic properties of Sb-doped *p*-type ZnO films.

Sample No.	Hole concentration (cm^{-3})	Carrier mobility (cm^2/V s)
1	1.3×10^{17}	28.0
2	6.0×10^{17}	25.9
3	8.2×10^{17}	23.3
4	1.3×10^{18}	20.0

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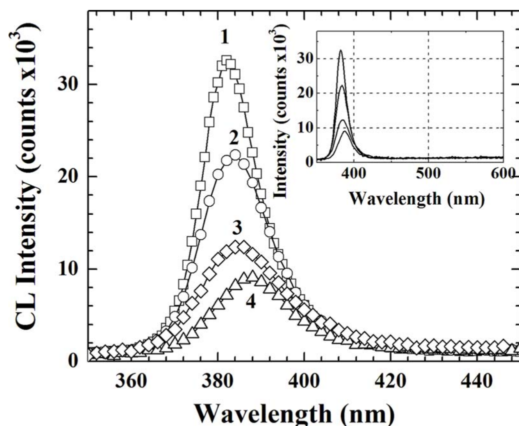

FIG. 1. NBE cathodoluminescence spectra of samples 1–4 taken at room temperature. The peaks are at 382, 384, 385, and 387 nm, respectively. Inset: broad-range CL spectra of the same samples.

be about 16.1, 19.4, 23.5, and 21.7 nm (corresponding to 136, 163, 196, and 178 meV) for samples 1, 2, 3, and 4, respectively.

The intensity of NBE luminescence was also monitored as a function of temperature. It was observed that the intensity decays with sample temperature T, in agreement with the following expression:[14]

$$I = \frac{A}{1 + B\exp(-E_A/kT)}, \tag{1}$$

where A and B are scaling factors, E_A is activation energy, and k is Boltzmann's constant. From Eq. (1), it can be deduced that the inverse intensity, $1/I$, should exhibit an exponential dependence on $1/kT$. This is shown in the inset of Fig. 2 on the example of sample 1. Note that the intensity in this and subsequent figures was normalized with respect to its room-temperature value for each of the samples. The activation energies E_A were obtained from the slopes of Arrhenius plot shown in Fig. 2. In case of a (e,A^0) transition, E_A is related to the ionization energy of acceptors: the lower the value of the activation energy, the more likely is the ionization of the acceptor by a valence band electron $(A^0 + e \rightarrow A^-)$; since an ionized level does not participate in recombination via the (e,A^0) route, the rate of these transitions (i.e., the intensity of the luminescence) decreases with E_A at any given temperature. Conversely, for a constant E_A, the intensity decays with increasing temperature as more and more acceptors are ionized.

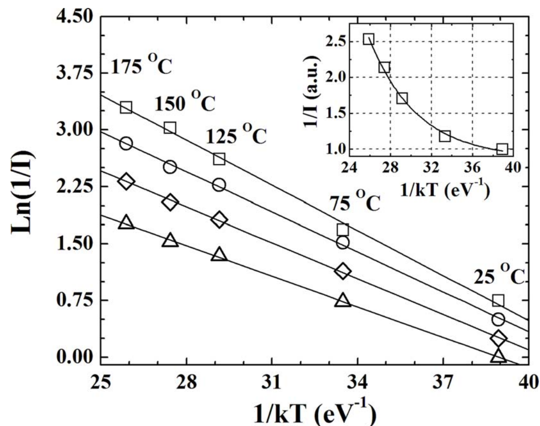

FIG. 2. Arrhenius plot showing the decay of normalized NBE luminescence intensity with increasing temperature for sample 1 (open squares), sample 2 (open circles), sample 3 (open diamonds), and sample 4 (open triangles). The linear fits (solid lines) yielded activation energies of 212±28, 175±20, 158±22, and 135±15 meV for samples 1, 2, 3, and 4, respectively. The data were vertically offset for clarity. Inset: Exponential decrease of CL intensity for sample 1 (open squares) and the fit (solid line).

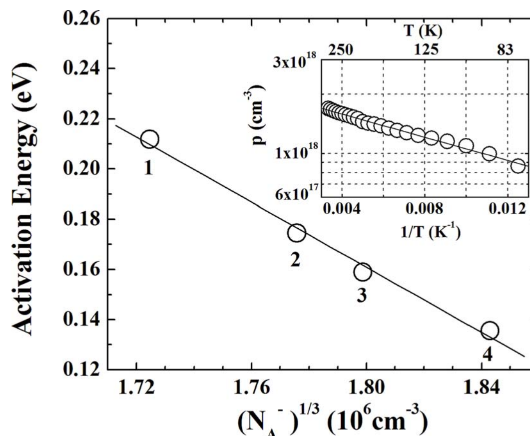

FIG. 3. Decrease of activation energy as a function of ionized acceptor concentration. Inset: Temperature dependence of hole concentration in sample 4.

It is apparent from Fig. 2 that the activation energy shows a systematic dependence on the carrier concentration. The values of E_A are 212±28, 175±20, 158±22, and 135±15 meV for samples 1, 2, 3, and 4, respectively. These values are in reasonable agreement with the ionization energy of an $Sb_{Zn}-2V_{Zn}$ complex predicted by Limpijumnong *et al.* to have a value of about 160 meV.[8] Furthermore, the decay of activation energy with carrier density, p, follows a common pattern observed previously in other semiconductors[13,16,17] and is described by an equation of the type

$$E_A(N_A^-) = E_A(0) - \alpha (N_A^-)^{1/3}, \tag{2}$$

where N_A^- is the concentration of ionized acceptors, $E_A(0)$ is the ionization energy at very low doping levels, and α is a constant accounting for geometrical factors as well as for the properties of the material. Figure 3 demonstrates that Eq. (2) provides a reasonable fit to the experimentally obtained activation energies under the approximation that $N_A^- - N_D^+ = p$, where N_D^+ is the density of ionized shallow donors (due to compensation, the p-type conductivity is determined by the difference between the concentrations of ionized donors and acceptors). The value of α was found to be equal to 6.4×10^{-7}, which is comparable to that in p-GaN and p-Si.[13,17] N_D^+ can be roughly estimated from the electron concentration in undoped, n-type ZnO samples grown by the same method and is about 5×10^{18} cm^{-3}.[6]

It should be noted that earlier PL measurements performed on sample 4 showed a consistent activation energy of 140 meV.[15] Furthermore, temperature-dependent measurements of hole concentration in sample 4 shown in the inset of Fig. 3 also support the involvement of acceptor levels (see Ref. 6 for more details).

Although the existence of other Sb-related acceptors cannot be categorically excluded, their involvement in the temperature-induced CL intensity decay is highly unlikely.[8]

The phenomenon of variation of the dopant activation energy with carrier concentration in semiconductors has been

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attributed to a number of causes. Among these are the formation of the band-tail states that extend into the forbidden gap, the broadening of the acceptor band in the gap, and the reduction of binding energy due to Coulomb interaction between the holes in the valence band and the ionized acceptor states.[12,13,16]

In summary, the variable-temperature cathodoluminescence studies of Sb-doped *p*-type ZnO allowed us to estimate the activation energy of the Sb-related acceptor in the range of 135–212 meV. The activation energy was found to be strongly dependent upon the hole concentration. While the nature of the acceptor cannot be determined conclusively, evidence suggests that it is an $Sb_{Zn}-2V_{Zn}$ complex proposed by Limpijumnong *et al.*

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