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Photoluminescence study of *p*-type ZnO:Sb prepared by thermal oxidation of the Zn-Sb starting material

E. Przeździecka,[1] E. Kamińska,[2] I. Pasternak,[2] A. Piotrowska,[2] and J. Kossut[3]
[1]*Institute of Physics, Polish Academy of Sciences, Aleja Lotników 32/46, 02-668 Warsaw, Poland*
[2]*Institute of Electron Technology, Aleja Lotników 32/46, 02-668 Warsaw, Poland*
[3]*Institute of Physics, Polish Academy of Sciences, and ERATO Semiconductor Spintronics Project, Aleja Lotników 32/46, 02-668 Warsaw, Poland*

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We have investigated photoluminescence (PL) from Sb-doped *p*-type ZnO films obtained by thermal oxidation of the Zn-Sb starting material. Very well resolved PL spectra were obtained from samples, with the hole concentration above 1×10^{17} cm^{-3}. Acceptor binding energy is determined to be 137 meV from free electron to acceptor transitions. The binding energy between the acceptor and the exciton obtained from the analysis of the acceptor bound excitonic PL transitions measured as a function of temperature is 12–15 meV.

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Fabrication of *p*-type ZnO represented a challenge for many years because undoped ZnO is usually *n* type, which is associated with the presence of native point defects[1] (oxygen vacancies V_{O} and zinc interstitial Zn$_i$)[1] and hydrogen impurities.[2] Recently, many groups achieved *p*-type ZnO by doping with group V elements such as N,[3–6] As,[7,8] P,[9] and Sb.[10–13] In ZnO matrix, N exists as a simple substitutional acceptor, while As, P, and Sb form more complicated acceptor complexes.[14] As for the nature of the acceptors in *p*-type ZnO:As and ZnO:Sb, it was found theoretically that the acceptor complex of the impurity on Zn site with two zinc vacancies (X_{Zn}-$2V_{\mathrm{Zn}}$, where X denotes As or Sb) has both low formation and ionization energies. Zinc oxide is a II-VI compound semiconductor with a wide direct bang gap of $E_g=3.437$ eV (Ref. 15) and a large exciton binding energy of 60 meV at room temperature.[16] Therefore, optical investigations of *p*-type ZnO are important to understand differences that follow from the different chemical nature of the acceptors and to estimate the activation energy associated with each species. In this Brief Report, we focus on the optical properties of *p*-type Sb-doped ZnO films obtained by thermal oxidation of the Zn-based starting material.[17] We compare the present case of antimony impurity with the previous results on N- and As-related acceptors.[3]

Zn-Sb source material was synthesized by magnetron sputtering on *c*-oriented sapphire substrates. Next, all samples were oxidized by annealing in a flowing O_2 gas at a high temperature (600–900 °C). Room temperature Hall measurement shows that the Sb-doped ZnO obtained in this way has *p*-type conductivity with a carrier concentration of about 10^{17} cm^{-3} and a mobility of $\sim$7 cm^2/V s. The concentration of Sb atoms in the samples, obtained by secondary-ion-mass spectroscopy (SIMS) analysis, is $\sim1\times10^{20}$ cm^{-3}, whereas the concentration of hydrogen impurities is about 1×10^{19} cm^{-3}.

In the photoluminescence measurements, the samples were excited by the 351 nm argon laser line and the emission was collected with a charge coupled device camera. The measurements were performed as a function of the temperature.

Figure 1 shows photoluminescence (PL) spectrum at $T=10$ K for a Sb-doped ZnO film. The spectrum shows dominant emissions at 3.353 eV and at about 3.3 eV. The emission located at 3.353 eV, according to the identification in Ref. 18, corresponds probably to a neutral acceptor-bound exciton (A^0X). Since the sample was intentionally highly doped with Sb atoms, the peak at this energy is likely to be specifically associated with antimony acceptors. However, in the existing literature, there is still a discussion concerning the origin of this peak. For example, Zeng and Ye[19] suggested that this is D^0X emission, while Xiu and Liu[20] suggested an A^0X origin. On the other hand, careful analysis of the temperature dependence of the peak at 3.353 eV clearly shows that it consists of more than one component (see inset in Fig. 2). Thus, we may conclude that, in this region of energy, we observed both the line associated with A^0X (at 3.353 eV) and a line (located at 3.356 eV) probably associated with D^0X or, alternatively, with yet another acceptor A^0X. We observe also a small intensity line (at 3.367 eV) which is associated with D^+X or an excited state of D^0X.

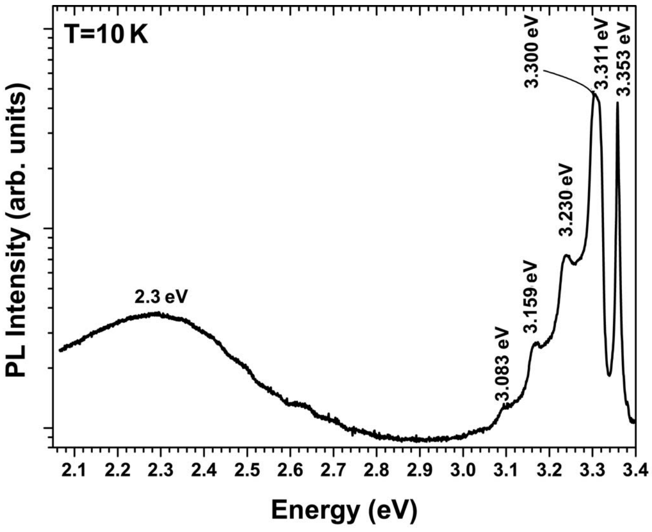

FIG. 1. PL spectrum at 10 K for the Sb-doped *p*-ZnO sample obtained by thermal oxidation of the Zn-Sb starting material (500 °C O_2 for 10 min+800 °C O_2 or N_2 for 2 min).

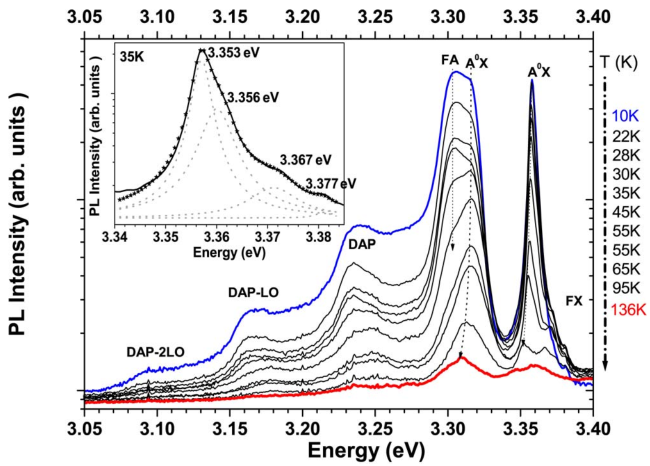

FIG. 2. (Color online) PL spectra of ZnO:Sb sample obtained by thermal oxidation of the Zn-Sb starting material (500 °C O_2 for 10 min+800 °C O_2 or N_2 for 2 min) measured as a function of temperature. FX, free exciton; A^0X, acceptor bound to exciton; FA, free electrons and acceptor transition; and DAP, donor-acceptor pair. Inset: Zoom of excitonic peak at 35 K, with the individual components of excitonic peak clearly showing (solid line, experimental data; dotted lines, Lorentzian multiple peaks).

These excited states are analogous to the rotational states of the H_2 molecule.[21,22] In the temperature dependent PL, we are also able to observe a small peak related to a free exciton (FX) emerging at about 3.377 eV.[23]

The emission located at about 3.3 eV consists of two individual peaks (clearly separated when the temperature is varied) located at 3.311 and 3.300 eV. The emission located at about 3.311 eV may be, again, related to Sb dopants. Equivalent peaks corresponding to nitrogen,[24] arsenic,[25] and phosphorus[26] acceptors in ZnO matrix were previously reported in the same spectral region, therefore it can be supposed that 3.311 eV may also be an A^0X emission. Note, however, that the peak located at 3.311 eV is sometimes ascribed to a free-electron-to-neutral-acceptor (FA) emission, and the one at 3.300 eV to donor-acceptor pair (DAP) emission.[27] A possible way of elucidating this controversy is to study the temperature behavior of these two lines. A characteristic feature of the DAP and FA emissions is a blueshift with the temperature increase. In the PL experiments in the range between 15 and 140 K, we observe that the intensity of the peak located at 3.300 eV transfers to the peak located at 3.311 eV. As a result, at temperatures above 60 K, we observe only the latter peak (see Fig. 2). Therefore, we cannot definitely answer the question in a clear way whether we deal with a blueshift or only with relative changes of the intensities. Nevertheless, in our opinion, the peak located at 3.300 eV is more likely to be associated with FA.[9] In the PL spectrum, we also observe a DAP emission located at 3.230 eV (Ref. 28) and its phonon replicas at 3.159 and 3.083 eV. In the case of the DAP line, we observe a blueshift (see Fig. 3) in the temperature range of 10–50 K, or as Zhang *et al.* suggested,[27] in this region, we have phonon replicas of two peaks observed at 3.311 eV and at 3.300 eV, whose relative intensities change as a function of temperature.

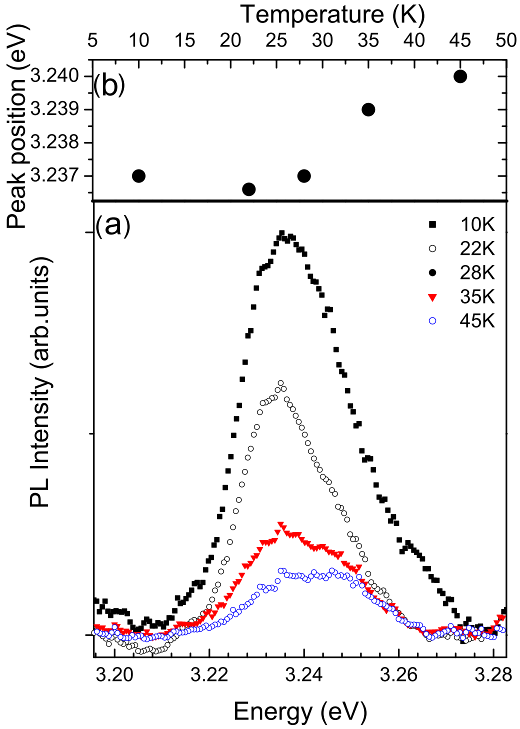

FIG. 3. (Color online) (a) DAP line energy position as a function of temperature and (b) the temperature dependence of the maximum of the DAP line.

Yet another feature observed in the PL spectrum is a broad line centered at about 2.3 eV. Usually, this green defect emission is centered at about 2.4 eV and attributed to oxygen vacancies, but in our sample, we observe it at 2.3 eV. This may be related to the fact that we have obtained the sample by thermal annealing in an oxygen flow,[29] and probably, we have a low concentration of oxygen vacancies.

In the PL spectrum, we see no band located at 3.050 eV, observed by Xiu *et al.*,[30] who associated it with zinc vacancies V_{Zn}. In the Sb-doped ZnO, the zinc vacancies are usually joined with Sb atoms and produce an acceptor complex Sb_{Zn}-$2V_{Zn}$. The energy level of this complex is located 160 meV above the valence band. Consequently, in the antimony-doped samples, we probably have no free zinc vacancies. Of course, this effect may be due to growth conditions of the ZnO such as the oxidation temperature.

The binding energy of an acceptor E_A can be calculated from the equation

$$E_A = E_g - E_{FA} + kT/2, \tag{1}$$

where E_g is the ZnO energy gap at low temperature (E_g =3.437 eV),[15] and E_{FA} is the FA energy peak position at 10 K. In this way, we determine the binding energy of the acceptors to be 137 meV.

As mentioned, the two peaks (3.353 and 3.311 eV), observed in the low temperature PL, are probably both associated with A^0X emissions. Figure 4 shows the integrated intensities of these two emissions peaks as functions of the temperature. The temperature dependence of the integrated PL intensity can be described by

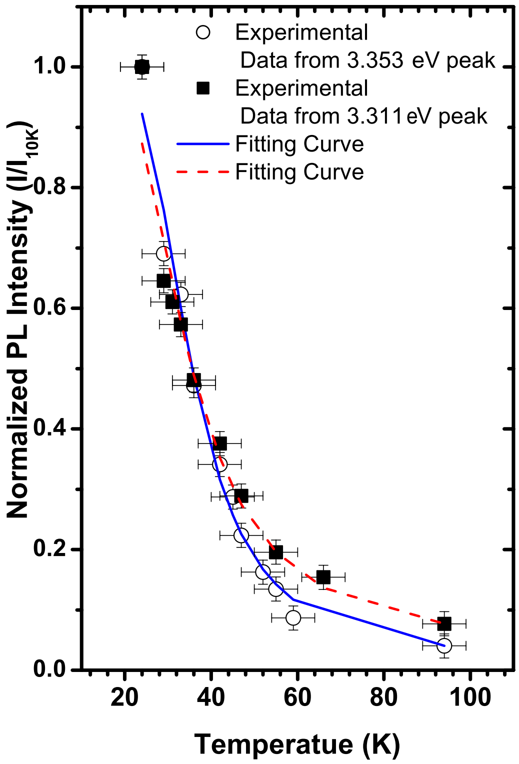

FIG. 4. (Color online) The integrated intensity of the A^0X emission as a function of temperature. The black squares and the open circles represent the experimental data, and the solid line is the fitting of Eq. (2).

$$I(T) = I_0/[1 + P\exp(-E_b^{A_0X}/kT)], \qquad (2)$$

where P is a free fitting parameter, I_0 is the integrated PL intensity at $T=0$, taken to be approximately the same as experimentally measured at $T=10$ K, and $E_b^{A^0X}$ is the binding energy between the acceptor and the exciton. From the fit of Eq. (2) to the data, we obtain the values of $E_b^{A^0X} \sim 15$ and ~ 12 meV corresponding to the 3.353 and 3.311 eV peaks, respectively. In order to calculate the acceptor binding energy E_A from the temperature dependent PL, we apply the Haynes rule.[31] The rule postulates a linear dependence between $E_b^{A^0X}$ and E_A: $E_b^{A^0X} = a + bE_A$.[32] In the case of acceptors in Si (for which the Haynes rule was originally proposed), the corresponding relation is $E_b^{A^0X}/E_A \sim 0.1$ ($a=0$ and $b=0.1$). In some publications, the authors applied these values also to ZnO.[30,33] However, a very comprehensive study of acceptors in ZnO performed in Ref. 34, indicated that more appropriate is a linear dependence $E_b^{A^0X} = 0.24E_A - 0.02$, with both $E_b^{A^0X}$ and E_A given in meV. On the other hand, other values of b, in the range 0.07–0.24, were also reported.[28,35,36] Using $b=0.24$ from Ref. 34, we estimate the acceptor binding energies E_A, for the 3.353 and 3.311 eV emissions, to be about 65 and 50 meV, respectively. From our data, we have not obtained any clear information about the range of possible values for b in p-type ZnO. Using $b=0.07$, we obtain E_A of about 214 and 171 meV, respectively. The determination of E_A using Eq. (1) is within the range of E_A's derived using the Haynes rule from Eq. (2).

To conclude, we observe a well-resolved PL from p-type Sb-doped ZnO. In particular, in the region of about 3.3 eV, we observe two peaks at 3.311 and 3.300 eV corresponding probably to A^0X and FA transitions. From the position of the FA peak, we obtain an acceptor binding energy $E_A = 137$ meV. This corresponds well to theoretical predictions for $\mathrm{Sb_{Zn}}-2V_{\mathrm{Zn}}$ acceptor complex, where E_A is 160 meV.[14] From the temperature dependence of various PL peaks, we obtain the binding energy between the acceptor and the exciton to be 12–15 meV and, further, by applying Haynes rule for ZnO system, we estimate the acceptor binding energy to be in rough agreement with that mentioned above.

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[1] S. B. Zhang, S. H. Wei, and A. Zunger, Phys. Rev. B **63**, 075205 (2001).

[2] C. G. Van de Walle, Phys. Rev. Lett. **85**, 1012 (2000).

[3] E. Przezdziecka, E. Kamiska, K. P. Korona, E. Dynowska, W. Dobrowolski, R. Jakiela, L. Klopotowski, and J. Kossut, Semicond. Sci. Technol. **22**, 10 (2007).

[4] E. Kaminska, A. Piotrowska, J. Kossut, A. Barcz, R. Butkute, W. Dobrowolski, E. Dynowska, R. Jakiela, E. Przezdziecka, R. Lukasiewicz, M. Aleszkiewicz, P. Wojnar, and E. Kowalczyk, Solid State Commun. **135**, 11 (2005).

[5] A. Zeuner, H. Alves, D. M. Hofmann, B. K. Meyer, A. Hoffmann, U. Haboeck, M. Strassburg, and M. Dworzak, Phys. Status Solidi B **234**, R7 (2002).

[6] J. F. Rommeluere, L. Svob, F. Jomard, A. J. Mimila, A. Lusson, V. Sallet, and Y. Marfaing, Appl. Phys. Lett. **83**, 287 (2003).

[7] Y. R. Ryu, S. Zhu, D. C. Look, J. M. Wrobel, H. M. Jeong, and H. W. White, J. Cryst. Growth **216**, 330 (2000).

[8] H. S. Kang, G. H. Kim, D. L. Kim, H. W. Chang, B. D. Ahn, and S. Y. Lee, Appl. Phys. Lett. **89**, 181103 (2006).

[9] F. X. Xiu, Z. Yang, L. J. Mandalapu, and J. L. Liu, Appl. Phys. Lett. **88**, 152116 (2006).

[10] F. X. Xiu, Z. Yang, L. J. Mandalapu, D. T. Zhao, J. L. Liu, and W. P. Beyermann, Appl. Phys. Lett. **87**, 152101 (2005).

[11] T. David, S. Goldsmith, and R. L. Boxman, Thin Solid Films **447-448**, 61 (2004).

[12] T. Aoki, Y. Shimizu, A. Miyake, A. Nakamura, Y. Nakanishi, and Y. Hatanaka, Phys. Status Solidi B **229**, 911 (2002).

[13] L. J. Mandalapu, Z. Yang, F. X. Xiu, D. T. Zhao, and J. L. Liu,

Appl. Phys. Lett. **88**, 092103 (2006).

[14] S. Limpijumnong, S. B. Zhang, Su Huai Wei, and C. H. Park, Phys. Rev. Lett. **92**, 155504 (2004).

[15] B. K. Meyer, H. Alves, D. M. Hofmann, W. Kriegseis, D. Forster, F. Bertram, J. Christen, A. Hoffmann, M. Strabburg, M. Dworzak, and U. Haboeck, Phys. Status Solidi B **241**, 231 (2004).

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

[17] E. Kaminska, E. Przezdziecka, A. Piotrowska, J. Kossut, P. Boguslawski, I. Pasternak, R. Jakiela, and E. Dynowska, in *Zinc Oxide and Related Materials*, edited by J. Christen, C. Jagadish, D. C. Look, T. Yao, and F. Bertram, MRS Symposia Proceedings No. 957 (Materials Research Society, Pittsburgh, 2007), Paper No. 0957-K08-04.

[18] A. Teke, U. Ozgur, S. Dogan, X. Gu, H. Morkoc, B. Nemeth, J. Nause, and H. O. Everitt, Phys. Rev. B **70**, 195207 (2004).

[19] Y. J. Zeng and Z. Z. Ye, Appl. Phys. Lett. **90**, 116102 (2007).

[20] F. X. Xiu and J. L. Liu, Appl. Phys. Lett. **90**, 116103 (2007).

[21] J. Rorison, D. C. Herbert, P. J. Dean, and M. S. Skolnick, J. Phys. C **17**, 6435 (1984).

[22] D. C. Reynolds, D. C. Look, B. Jogai, C. W. Litton, T. C. Collins, W. Harsch, and G. Cantwell, Phys. Rev. B **57**, 12151 (1998).

[23] U. Ozgur, Y. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Dogan, V. Avrutin, S. J. Cho, and H. Morkoc, J. Appl. Phys. **98**, 041301 (2005).

[24] D. C. Look, C. Coskun, B. Claflin, and G. C. Farlow, Physica B **340-342**, 32 (2003).

[25] D. C. Look, G. Renlund, R. Burgner, and J. R. Sizelove, Appl. Phys. Lett. **85**, 5269 (2004).

[26] D. K. Hwang, H. S. Kim, J. H. Lim, J. Y. Oh, J. H. Yang, S. J. Park, K. K. Kim, D. C. Look, and Y. S. Park, Appl. Phys. Lett. **86**, 151917 (2005).

[27] B. P. Zhang, N. T. Binh, Y. Segawa, K. Wakatsuki, and N. Usami, Appl. Phys. Lett. **83**, 1635 (2003).

[28] Y. R. Ryu, T. S. Lee, and H. W. White, Appl. Phys. Lett. **83**, 87 (2003).

[29] Y. G. Wang, S. P. Lau, X. H. Zhang, H. W. Lee, S. F. Yu, B. K. Tay, and H. H. Hng, Chem. Phys. Lett. **375**, 113 (2003).

[30] F. X. Xiu, Z. Yang, L. J. Mandalapu, D. T. Zhao, and J. L. Liu, Appl. Phys. Lett. **87**, 252102 (2005).

[31] J. R. Haynes, Phys. Rev. Lett. **4**, 361 (1960).

[32] R. E. Halsted and M. Aven, Phys. Rev. Lett. **14**, 64 (1965).

[33] D. C. Look, D. C. Reynolds, C. W. Litton, R. L. Jones, D. B. Eason, and G. Cantwell, Appl. Phys. Lett. **81**, 1830 (2002).

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

[35] D. C. Look and B. Claflin, Phys. Status Solidi C **241**, 624 (2004).

[36] J. G. Lu, Q. Liang, Y. Zhang, Z. Ye, and S. Fujita, J. Phys. D **40**, 3177 (2007).