Response to "Comment on 'Photoluminescence study of Sb-doped *p*-type ZnO films by molecular-beam epitaxy'" [Appl. Phys. Lett. 90, 116102 (2007)]

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In the comment[1] on our recent letter,[2] Zeng and Ye argued that the *p*-type conductivity of Sb-doped ZnO is questionable and the assignments of neutral acceptor-bound exciton (A ^{0}X) and free-to-neutral-acceptor (FA) emission are incorrect. We disagree with their comments.

For the Sb-doped ZnO growth in our experiments, we used a highly resistive *n*-type Si with a resistivity value of 30–40 Ω cm. This resistivity contributes to an electron carrier concentration of about $(1-2)\times10^{14}$ cm^{-3}. From hole concentrations that we obtained (10^{16}–10^{18} cm^{-3}), the depletion goes deeply into the Si substrates. In addition, our Al/Ti contacts used for Hall effect measurements were annealed, and metal atoms diffuse only into the ZnO films by secondary-ion-mass spectroscopy measurements (not shown here), suggesting that the Hall effects came from the ZnO films only. If, however, carriers below ZnO/Si junctions would contribute the Hall voltage suspected by the comment, then the contacts have penetrated through the depletion layer into the Si substrates. Since the *n*-type Si wafer is orders of magnitude thicker than the *p*-type ZnO film on top, the resultant conductivity would only be *n* type, which is not the case. Therefore the Sb-doped ZnO films undoubtedly possess *p*-type conductivities. Another possibility could be that the Si near the ZnO/Si interface is completely inverted, where holes are accumulated. However, this is only possible when ZnO films exhibit strong *p*-type behavior.

Based on the report of donor binding energies with respect to different emission lines,[3] Zeng and Ye asserted that, if the 3.358 eV emission is an A ^{0}X, it should have an acceptor level located at about 60 meV above the valence-band maximum. However, Zeng and Ye have completely misinterpreted the data of Table II from Meyer *et al.*,[3] giving an incorrect estimation of the acceptor activation energy. In this table, the donor binding energies were obtained based on the Haynes rule with a Haynes factor of 0.3, i.e., the ratio between the energy required to free the bound exciton from a defect and the energy required to free the bound carrier from the same defect. This factor indeed works quite well to estimate some donor binding energies, such as H, Al, Ga, and In. However, in terms of A ^{0}X, a certain factor has not been identified as different values of 0.07–0.24 were reported so far.[4–7] Therefore Zeng and Ye mistakenly used the Haynes factor of 0.3, which only applies to some D ^{0}X, to infer the acceptor activation energy of 60 meV. Obviously, this methodology is not logical and incorrect. In our opinion, if the 3.358 eV emission line is a D ^{0}X, suggested by Zeng and Ye, the donor level will be about 60 meV below the conduction band edge. Such a shallow donor will inevitably provide electrons to make ZnO heavily *n* type. However, from the Hall effect measurements, the Sb-doped ZnO films present positive Hall coefficients, meaning that the majority carriers in the films are holes. Thus the 3.358 eV emission line is unlikely a D ^{0}X, but possibly an A ^{0}X. Although the Haynes factor was not well established for A ^{0}X in ZnO, a factor of ~0.1 suggested by Ryu *et al.*[6] and Jeong *et al.*[7] would give a rough estimation of ~190 meV for the acceptor activation energy, instead of 60 meV by Zeng and Ye.[1] As a matter of fact, many researchers assigned A ^{0}X for emissions in the same range of 3.355–3.358 eV,[6–10] including Zeng and Ye themselves.[11,12]

Zeng and Ye then adopted Varshni's equation to calculate the shift of FA transition in the temperature range of 8.5–50 K. A blueshift with a value of 1–2 meV was calculated; however, the parameters of α and β were not provided, which are extremely critical for the final calculation results. From the literature survey, we found that α and β have not been accurately determined, but have certain ranges, for instance, Ref. 13, $\alpha=(1.1\pm0.09)\times10^{-3}$ eV/K, $\beta=377\pm51$ K; Ref. 14, $\alpha=9.00\times10^{-4}$ eV/K, $\beta=2230$ K; Ref. 15, $\beta=305$ K; Ref. 16, $\beta=(416-477)\pm65$ K; and Ref. 17, $\alpha=(8.2\pm0.3)\times10^{-4}$ eV/K, $\beta=700\pm30$ K. Considering all these values, in the temperature range of 8.5–50 K the shift of FA transition was recalculated to be 0.9–6 meV, instead of 1–2 meV in Zeng and Ye's calculation.[1] From the temperature-dependent photoluminescence (PL) spectra (Fig. 3 in Ref. 2), the shift of the FA transition in this temperature range is about 7 meV with a measurement resolution of about 1.5 meV[2]. Therefore this method presents a significant difficulty to judge the FA emission. Here, we present more experimental evidence to prove that our original assignments are correct, i.e., the 3.296 emission is not a donor-acceptor pair (DAP) transition, but a FA transition. As shown in Fig. 1, the excitation-power-dependent PL measurements were carried out at 8.5 K for sample G (Ref. 2). It is well known that as the excitation power increases, more photoexcited donor-acceptor pairs are created, resulting in a smaller donor-acceptor pair distance.[18] Therefore, a DAP luminescence line shows a typical blueshift as the excitation power increases. This technique has long been believed to be one of the most powerful techniques to determine DAP transitions. As clearly seen from Fig. 1, the emission line at 3.222 eV

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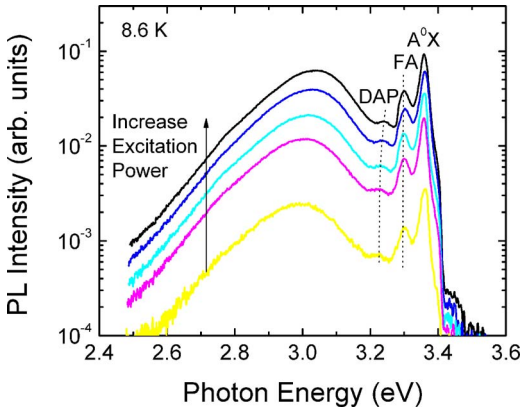

FIG. 1. (Color online) Excitation-power-dependent PL spectra for the Sb-doped *p*-type ZnO film at 8.6 K.

shows an obvious blueshift with higher excitation power. Combining the previously observed blueshift in the temperature-dependent PL in Ref. 2 (due to thermal ionization of donor at higher temperatures), it is believed that this emission is indeed a DAP transition. For the 3.296 emission, however, there is no evident blueshift, as shown in Fig. 1.

Zeng and Ye agreed that the 3.353 eV emission line in our undoped ZnO film is a D ^{0}X with a donor binding energy of 72.6 meV. In fact, this statement makes our assignments even stronger. The distance between 3.296 (FA) and 3.222 (DAP) in Fig. 1 is 74 meV, which is reasonably close to the donor activation energy of 72.6 meV considering our spectrum resolution. Similar observations were also reported in Refs. 6 and 9. In addition, when the temperature increases, the DAP emission line at 3.222 eV progressively merges into FA emission line at 3.396 eV, showing the feature of the thermal ionization of donors.[2] Therefore, from both temperature-dependent and excitation-power-dependent PL measurements, we confirmed that our assignments of FA and DAP transitions are correct. The approach of identifying FA emission in Ref. 1 is problematic.

In summary, the *p*-type conductivity of Sb-doped ZnO is not questionable at all and the original assignments of A ^{0}X, FA, and DAP emissions are correct.

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