

Supplementary Material

1. Details about ZnO growth and the device fabrication

In this work, a custom-designed MOCVD system was used for the growth of ZnO on commercially available stainless steel foils. Diethylzinc (DEZn) and high purified oxygen were used as Zn and O precursors, respectively. Highly purified argon was applied as the carrier gas of Zn precursors. In the experiments, ZnO were grown at five temperature points (350, 380, 410, 440 and 470 °C), and they were denoted as S1-S5, respectively. During the growth process, the flow rate of Zn source was set as 9.3×10^{-6} mol/min, and that of oxygen source was set as 8.0×10^{-3} mol/min, and the reaction pressure was kept at 80 Pa. The typical growth time was one hour.

The MIS device was based on S4. First, poly(methylmethacrylate) (PMMA) solution (0.25g PMMA powder dissolved in 20 mL toluene) was spin-coated on S4. The spin procedure involves a first low speed spinning at 500r/min for 9 s and the fast speed spinning at 3000r/min for 30 s. Then, the sample was dried at 120 °C under atmosphere ambience for 20 min. After that, The poly(3,4-ethylene-dioxythiophene)-poly(styrene-sulfonate) (PEDOT:PSS) solution (a mixture of PEDOT:PSS original liquid, isopropyl alcohol and water with a volume ratio of 1:2 :1.) was spin coated at the condition involving a first low speed spinning at 500r/min for 9 s and a second fast

spinning at 2000r/min for 30 s. The following drying procedure was taken at 100 °C under atmosphere ambience for 15 min. Finally the top ITO electrode was deposited by a radio-frequency (RF) magnetron sputtering system. Before deposition, the sputtering chamber was evacuated to a base pressure at the order of 3×10^{-3} Pa using a turbo molecular pump, then filled with the working gas (argon) to a pressure of 1.0 Pa. RF power, argon flow rate and temperature of the sample holder were kept constant at 90 W, 40 sccm, and RT, respectively. During deposition, the sample holder was rotated at a speed of 30r/min. The time consumed was 50 min.

2. Discussion about the effects of non-radiative recombinations on the PL intensity

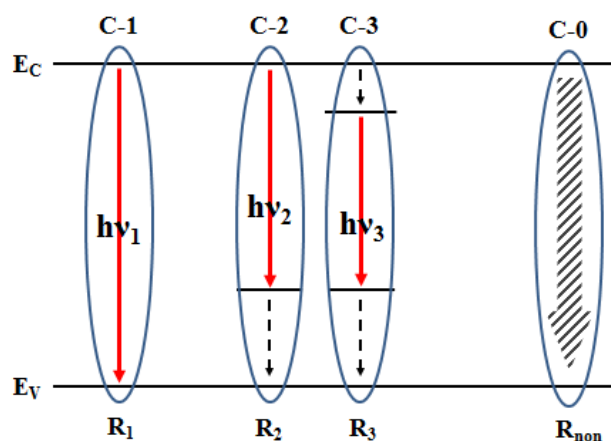


Fig. S1 Schematic diagram of recombination channels considered for the grown ZnO samples.

When a piece of semiconductor (ZnO for our case) is excited by the laser light, excess minor carriers (holes) are generated. In steady state excitation, the minor carrier generation (light excitation) will finally

balance with the recombination of minor carriers. Then, there is the simple relation for minor carriers under dynamic balance:

$$G = R \quad (\text{E} - 1)$$

where G is the generation rate of minor carriers, R is recombination rate of minor carriers. The recombination mechanism usually involves several different processes simultaneously.¹ Here, in order to address this issue easily, we introduce a rough model, which is suitable for our case, as shown in the Figure S1. Four recombination processes are taken into account. Process C-1 represents direct band-band radiative transition (free exciton transition). Processes C-2 and C-3 are mediated by mid-gap levels and involve at least one radiative transition (The DLE relies on processes like C-2 and C-3 as discussed in the manuscript). Process C-0 can also involve several transitions, but none of them is radiative. Processes like C-0 are called non-radiative recombinations, while C-1,2,3 are called radiative recombinations. Each process has its corresponding hole consuming rate: R_1 , R_2 , R_3 and R_{non} . And we have:

$$G = R = R_1 + R_2 + R_3 + R_{\text{non}} \quad (\text{E} - 2)$$

This relation shows that not only non-radiative recombinations compete with radiative recombinations for holes, each radiative recombination also compete with one another. If non-radiative recombinations are strong (large R_{non}), then R_1 , R_2 and R_3 have to be small. In steady state, the light intensity of each emission is proportional to the corresponding transition

rate. And the rates of radiative transition involved in C-1,2,3 equal to R_1 , R_2 and R_3 , respectively. This is because the population of each level remains dynamic constant in steady state. Therefore, if R_{non} is large, the intensity of all emissions will be weak, and vice versa. R_{non} relates to the density of non-radiative recombination centers, which include grain boundaries, dislocations etc..¹ Thus, the improved crystal quality decreases the density of non-radiative recombination centers, hence enhance the intensity of fluorescence.

3. Blue shift effect of DLE caused by the decrease in portion of DAP emissions with increase of temperature

As mentioned in the manuscript, the green or red band involves transitions from conduction band to the deep levels, which is also called free to bound transitions (FA). Besides, transitions from shallow donor levels to deep levels, which are known as donor-acceptor recombinations (DAP), are also taken into consideration. Considering a certain deep level, its related FA emission will show a higher energy than that of its related DAP emission, because the common donor level is below the conduction band. When the FA and DAP emissions co-contribute to the spectrum, the combined emission will probably peak in between. If the DAP emission decreases, the position of the combined spectrum will show blue shift. With the increase of temperature, the DAP emissions decreases in relative intensity due to the ionization of donors. This causes the blue shift effect

of the DLE. In fact, the successively blue shift of green band with increase of temperature has been reported in literature.²

3. Discussion on the decaying behaviors of the NBE and DLE emission with increase of temperature

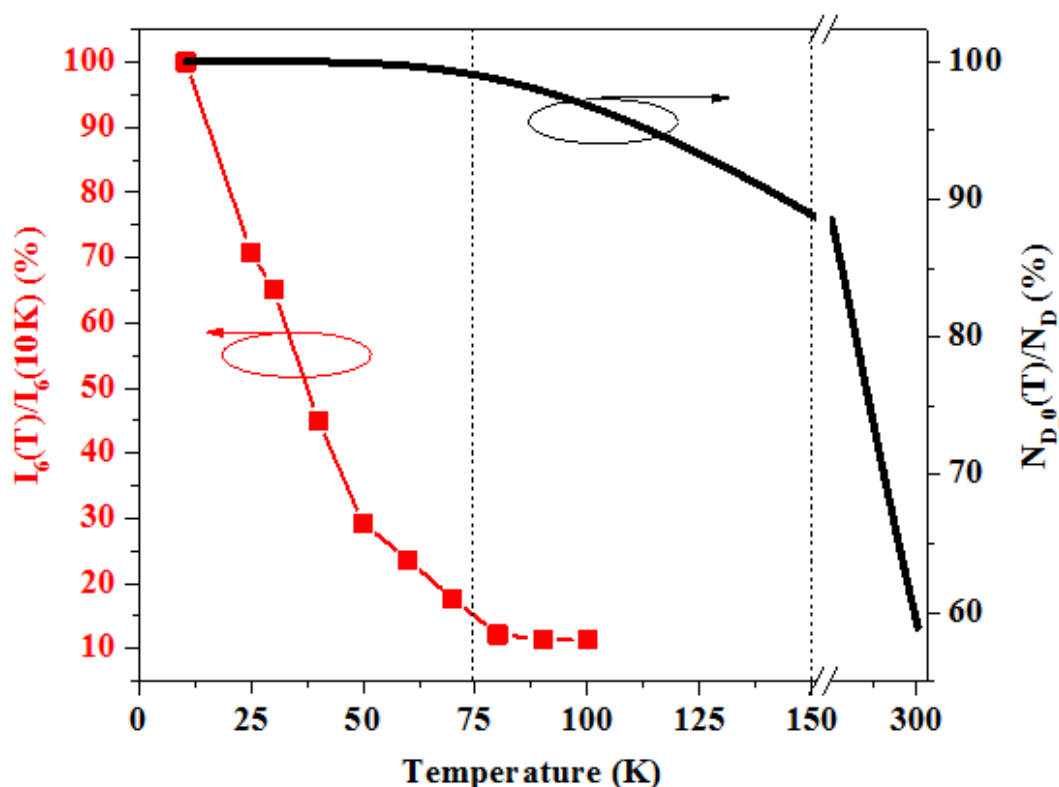


Fig. S2 Red line connected squares: temperature dependent integrated intensity of I_6 normalized to its intensity at 10 K; black line: simulated temperature dependent density of neutral Al donor, which is normalized to the density of Al impurity.

As mentioned in the manuscript, the Al donors affect the NBE through its neutral donor bound exciton (D_0X) emissions (mainly I_6 line) at low temperature. And they also affect the DLE emissions through their shallow donor levels. For Al donor, its donor ionization energy is ~ 51 meV, and its related D_0X only has a small thermal activation energy of ~ 15 meV.³ This leads to that as temperature increases, the density of D_0X decays much

faster than that of neutral donor. Figure S2 gives the temperature dependent intensity of the I_6 line of a ZnO sample grown on sapphire. The intensity values are normalized to the value at 10 K. This sample was grown at the same condition as that of S4. Note that only PL spectrum at 66 K rather than 10 K of S4 is given in the manuscript is because that ZnO samples grown on stainless steel foils can not be lowered to 10 K with our cryostat. This is probably attributed to the fact that the thermal conductivity of stainless steel material is small at low temperature.⁴

As can be seen, the intensity of I_6 line decreases very fast below 75 K. This can explain the rapid decrease of the intensity of NBE below 78 K for the case of S4. On the contrast, the intensity of DLE shows increases with escalation of temperature below 78 K. This can be explained by the thermal de-trapping effect of electrons from surface states,⁵ which leads to the increase of electron density in the conduction band, and which in turn can enhance the DLE related FA recombination. Figure S2 also gives the temperature dependent normalized density of neutral Al donor. This curve is obtained by solving charge balance equation assuming that Al is the only donor with a donor ionization energy of 51 meV. One can note that the

density of neutral Al donor remains almost invariant below 75 K, which means that the ionization of Al donor can be neglected during this temperature range. When the temperature is above 75 K, the ionization of Al donor becomes prominent, which can lead to the weakening of the DLE related DAP emissions. This may partially explain the much faster decay rate of the intensity of DLE between 75 and 150 K. Other reasons probably include the enhancement of phonon replicas of FX during this temperature range. When the temperature is above 150 K, the successively ionization of Al donor keep increasing the electron concentration in conduction band, which can compensate the decaying of DLE. Besides, the rapid thermal quenching of the phonon replicas of FX together leads to a slower decaying rate of DLE between 150 and 300 K.

References

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