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Temperature-dependent photoluminescence of ZnO films codoped with tellurium and nitrogen

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The photoluminescence spectra as well as their temperature dependence of the tellurium and nitrogen (Te-N) codoped ZnO films have been investigated in detail. Explicit evidences of the emissions related to two acceptors [A1: the NO-Zn-Te subunits and A2: the conventional N ions substituting on oxygen sites (N0)] have been found. The acceptor activation energy level of the A1 (∼118–124 meV) is much shallower than that of the A2 (∼224–225 meV) indicating that the A1 should be mainly responsible for the room-temperature p-type nature of the codoped samples. Meanwhile, the acceptor activation energy level of A1 shows a slight decrease (∼6 meV) as the Te atomic concentration increases in the codoped samples implying that the actual form of the A1 may be a mixture of the NO-Zn-nTe (n = 1, 2, 3, 4). More incorporation of the Te ions into N-doped ZnO films not only makes the acceptor energy level shallower but also improves the crystalline quality and results in the efficiently suppressed native donorlike defects. The optical properties accord well with the crystalline and electrical ones indicating that the Te-N codoping technique is a potentially feasible route to get controllable p-type ZnO materials.

I. INTRODUCTION

The controversy over whether nitrogen (N) can achieve effective p-type conductivity has accompanied the research and development of ZnO materials all along. Some theoretical investigations inclined to the view that N ions alone were deep acceptors. However, tangible evidences of p-type N-doped ZnO films were reported not long ago. Consequent questions were naturally revolved around how N contributed and antimony (Sb), the vacancy-antisite complex acceptors potential p-type dopants from group-V, i.e., phosphorus (P) and antimony (Sb), the vacancy-antisite complex acceptors with shallow energy levels have been well acknowledged. However, prior literatures which are focused on the mechanism of realizing p-type conductivity in N-doped ZnO are rare. Until recently, a theoretical work has demonstrated that the p-type conductivity of N-doped ZnO originates from the dual-acceptor complex NO-VZn which evolves from another dual-donor complex NZn-VO. The conclusion explains some inconsistency between theoretical prediction and experimental results on the p-type nature of N-doped ZnO to a certain extent. Anyhow, the hope of realizing high-efficiency and reproducible p-type ZnO via N doping is and will be alive.

Apart from the N monodoping, a few codoping paths of N plus another element are also extensively studied for the p-type realization. The codoped element could be a donor, an acceptor or an isoelectronic one leading to plenty of combinations. Researchers have utilized theoretical calculations for investigating the band-structure, density of states, and total energy of the codoped lattice, and given various possible mechanisms that are beneficial to the enhancement of the p-type conductivity. However, except for several III-V (Ga-N, Al-N, In-N) codoping mechanisms, most of the rest ones lack convincing experimental verifications, including the tellurium-nitrogen (Te-N) codoping. At early 2006, Porter et al. had explored the properties of ZnO films codoped with Te and N and suggested a feasible route to realize intrinsic, even p-type ZnO. Since then, Park et al. and our research team had successively attempted the Te-N codoping in ZnO, and reported the findings of p-type characters measured on the codoped samples. Some possible mechanisms being responsible for the origin of the free hole carriers had also been proposed. Among them, the enhanced solid solubility of the N dopants, the improved crystalline quality, and the suppressed donorlike impurities had been experimentally proven then. However, the lowered acceptor energy level, which is sufficiently important to the effective activation of the acceptors at room temperature, still requires further investigation.

Previously, two chemical environments of N ions, i.e., the NO-Zn-O and the NO-Zn-Te, had been proposed in the Te-N codoped ZnO films. The NO acceptors with Te ion(s) as the second nearest neighbor(s) were deemed to be the origin of the measured p-type conductivity. At that time, the lowered activation energy level was just an implication or inference from the behaviors of N acceptors in similar ZnTe and ZnSe compounds, hence not conclusive then. The research group of Park et al. had also pointed out that the co-incorporation of Te might help lower the energy level of the N acceptors according to the analysis of the low-temperature (LT) photoluminescence (PL). However, the discussions there were just brief and not detailed. In this article, a comprehensive and systematic investigation on the temperature-dependent (TD) PL of the Te-N codoped ZnO films is presented. The lowered energy level and the two...
chemical states of N$_{O}$ acceptors in the Te-N codoped films are confirmed.

II. EXPERIMENTS

The N monodoped and Te-N codoped ZnO films discussed here were grown by a home-built metal-organic chemical vapor deposition (MOCVD) system. Details of the machine and the growth/process conditions were described and could be found in a previous paper.21 By tuning the temperature of the Te metal-organic (MO) precursor bubbler, three specific samples with different Te concentrations were fabricated on $c$-plane sapphire substrates. Based on extensive previous research papers by others22–25 and us,26,27 the incorporation of neutral N-H complexes followed by an annealing to drive out the H atoms (i.e., the de-hydrogen process) has been well-established to be a feasible path to the realization of p-type ZnO. Consequently, a post-growth thermal treatment in oxygen atmosphere for 10 min was employed for all the samples to activate the acceptors,28 and also to repair the damaged host lattice caused by large quantities of Te and H atoms incorporated as grown.29–31 Table I shows several parameters of the samples. The atomic concentration percentages (a.c. %) of Te were derived from the 20 angular shifts of an x-ray diffraction $\theta$–$2\theta$ scan by assuming a linear Vegard’s law. The N concentrations were deduced indirectly from the integrated intensity ratio of the x-ray photoelectron spectra (XPS) of N and Zn (i.e., fitted area ratio of the N $1s$ and the Zn $2p$ peaks). A conspicuous increase of the N concentrations was noticed in the Te-N codoped samples indicative of an enhancement of the N solid solubility by an addition of Te.21 The electrical properties were obtained from a Hall-effect measurement done under the van der Pauw’s configuration and double-checked by the dependence of Hall voltages upon applied magnetic fields. According to the results listed in Table I, the N monodoped sample shows an n-type conductivity possibly due to (I) a small amount of the N dopants, (II) a relatively deep energy level of the N$_{O}$ acceptors, and (III) compensations from the intrinsic and unintentionally doped impurities.21 However, the Te-N codoped samples show p-type conductivities with hole carrier concentrations in the range of $10^{17}$ ~ $10^{18}$ cm$^{-3}$. As introduced in Sec. I, our previous paper proposed that the p-type characters originated from the mutual effects of improving the abovementioned three aspects by the assistance of the Te incorporation. In Sec. III, the TD-PL spectra of all the samples are analyzed to further elucidate the intrinsic mechanisms of the radiative recombination of the carriers/excitons and the conductive characters in Te-N codoped ZnO films. The PL spectra were excited by a 325-nm helium-cadmium laser with a power density of $\sim$ 40 mW cm$^{-2}$. A helium cryo-system and a Lakeshore Model 331 temperature controller guaranteed the TD measurement from 10 K to 300 K. The resolution of the spectra is 0.1 nm.

III. RESULTS AND DISCUSSIONS

An obvious distinction can be seen even in the room-temperature (RT) PL spectra between the N monodoped sample and the Te-N codoped samples as plotted in Fig. 1. For the N monodoped sample A, the near band edge (NBE) emission is dominated by a transition line centering 3.282 eV as well as a tail toward the lower energy side. However, for the Te-N codoped samples B and C, the NBE peak positions centers 3.226 eV and the line at around 3.282 eV becomes a shoulder peak. It is unreasonable to assign them only according to the RT PL spectra. But after observing the temperature evolutionary trends of the lines (to be shown and discussed later) and considering the p-type conductivity of the codoped samples, the peak at 3.226 eV is assigned to a transition of an electron from the conduction band to an acceptor energy level (FA) while the one at 3.282 eV to a recombination of an electron-hole pair from a free exciton (FX). Besides, the band tail of sample A is more likely to be the 1st order longitudinal phonon (LO) line of the FX also based on an inference from the temperature evolution of the peak. Admitting the above assignments and utilizing the energy relation between the FA and the FX transitions

$$E_A = E_{FX}(T) + 60 \text{meV} - E_{FA}(T) + \frac{1}{2} k_B T,$$

TABLE I. Concentrations of Te and N ions and electrical properties of the Te-N codoped ZnO films.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Te a.c. % from XRD (%)</th>
<th>Integrated intensity ratio of N/Zn from XPS</th>
<th>Conduction type</th>
<th>Resistivity ($\Omega$ cm)</th>
<th>Mobility (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>Carrier concentration (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>0.027</td>
<td>n</td>
<td>4.0</td>
<td>6.0</td>
<td>3.9 x 10$^{17}$</td>
</tr>
<tr>
<td>B</td>
<td>0.687</td>
<td>0.148</td>
<td>p</td>
<td>1.3</td>
<td>4.8</td>
<td>4.4 x 10$^{17}$</td>
</tr>
<tr>
<td>C</td>
<td>0.898</td>
<td>0.130</td>
<td>p</td>
<td>1.1</td>
<td>1.9</td>
<td>3.0 x 10$^{18}$</td>
</tr>
</tbody>
</table>
the energy level of the acceptors $E_A$ is estimated to be $\sim 129$ meV. This value is much shallower than the well accepted one ($\sim 200$ meV) for the NO acceptors in ZnO materials, but comparable to some reported $E_A$ values for codoped ZnO, inferring that the form of acceptors in the Te-N codoped ZnO samples is not the simple NO substituting defect. The value of $E_A$ signifies a $\sim 0.7\%$ activation rate of acceptors. Park et al. reported the N atomic concentration could be as high as $10^{20}$–$10^{21}$ cm$^{-3}$ in Te-N codoped ZnO films. Moreover, for our N-doped ZnO films with a similar growth condition of sample A, the N concentration can easily reach $10^{19}$ cm$^{-3}$. Therefore, the RT hole carrier concentrations of $10^{17}$–$10^{18}$ cm$^{-3}$ for the Te-N codoped samples (as listed in Table I) are reasonable and achievable.

In order to confirm the nature of the shallow acceptors and to further investigate the energy levels of defects brought by the Te and N co-incorporation, the TD-PL spectra of all the samples from 15 K to 300 K were recorded and are shown in Fig. 2. The peaks with highest intensities are located at 3.362 eV for sample A and 3.360 eV for samples B and C. The values are within the typical range of the bound exciton recombination lines. The origin of the line at 3.362 eV, namely, $I_4$ in literatures, is not clearly identified, but it is commonly ascribed to the recombination of excitons bound to some extrinsic donors (D$^0_X$). The line at 3.360 eV, namely, $I_6$ or $I_7$, is also related to a D$^0_X$. However, several prior works assigned the transition lines at 3.355–3.360 eV to the recombination of excitons bound to acceptors (A$^0_X$), especially in the papers discussing codoping techniques in ZnO. The exact energy position for an A$^0_X$ is linked to its localization energy, and based on the Haynes rule for acceptors in ZnO, the localization energy is in direct proportion to the binding energy for a specific acceptor. As a result, the energy position for the recombination of an exciton bound to a shallow acceptor should be higher than that to a deep one. This might be a partial reason why researchers sometimes assign the transition line in the energy range of a D$^0_X$ to an A$^0_X$ for p-type ZnO samples with shallow acceptor energy levels. For our case, assuming the Haynes factor as $\sim 0.1$, the localization energy of the A$^0_X$ is estimated to be 12.9 meV, and by considering the energy position for a FX at low temperature to be approximately 3.375 eV, it is possible that the line at 3.360 eV is an A$^0_X$ transition. Park et al. had once assigned the emission peak at 3.359 eV to an A$^0_X$ in the LT-PL spectrum of a p-type Te-N codoped ZnO film. Furthermore, if the line at 3.360 eV is a D$^0_X$, it is related to a donor with a binding energy of 51–54 meV, which will definitely make the samples into heavily n-type conductivities. It is contradictory to the p-type conductivities of samples B and C. By taking RT conduction types of the samples into account, the peaks at 3.360 eV in Figs. 2(b) and 2(c) are consequently ascribed to an A$^0_X$ transition, while the one at 3.362 eV for sample A to a D$^0_X$.

On the higher energy side of the D$^0_X$ in Fig. 2(a), another peak begins to emerge at 20 K and can be clearly resolved from 35 K to 300 K. From the temperature evolutionary trends of the D$^0_X$ and this peak, it is certainly related to the thermal dissociation from a D$^0_X$ to a FX. However, no obvious FX-related peaks can be resolved in the spectra of the codoped samples, which could be attributed to two possible reasons. One is the spectral broadening caused by the ionized impurity scattering, the discrepancy of the binding energies between acceptor impurities and excitons, and/or the film strains. The other is the thermal quenching of FXs into free electrons and holes caused by potential fluctuations of the band edges, i.e., the band tailing effect. In this case, the permitted energy of electrons/holes is lower than that in the undoped/lightly doped material. Hence, the energy that is required to break a FX into an electron and a hole is
smaller. From the above discussion, it can be concluded that both proposals, whichever is dominant, require high concentration of dopants suggesting that high Te and N concentrations have been achieved. Similar phenomena frequently occurred in the TD-PL spectra of ZnO materials with various dopants, such as antimony, phosphorus, sodium, arsenic, and nominally undoped samples.

When we look at the lower energy side of the A0X and D0X from 3.300 eV to 3.340 eV in Figs. 2(a)–2(c), the shapes of the spectra are quite distinctive for each sample. Two shoulder peaks are observed for sample C yet not well resolved, which is also owing to the relatively high concentration of the dopants in that sample. For sample B, two peaks with different thermal quenching rate are resolved while only one peak centering 3.332 eV at 15 K is found for sample A. Many possible origins can be assigned to the transition lines within this energy range, like A0X, two-electron satellite (TES), free electrons to an acceptor (FA), donor-acceptor pair, phonon replicas of FX, etc. Correct assignments require a comprehensive consideration of the temperature evolutionary trends of the peak positions and the peak intensities. Accordingly, how to get accurate values of the peak positions and intensities is needed to be figured out.

The commonly used method to deal with the spectra which are not well resolved is to do a peak fitting or deconvolution. The advantage is that after peak fitting, all parameters of the peaks are fully obtained which is convenient for further analysis. However, the deconvolution process itself is generally arbitrary, subjective, and complicated. It frequently occurs that not only one solution can be applicable to a specific curve. Since the change trends of the peak intensities are not so important in the assignment of the abovementioned possible origins, another easy-to-use method is exploited for the determination of the peak positions. Figures 3(a) and 3(b) depict the differentiated curves of Figs. 2(b) and 2(c), respectively. It is a common sense that for a well resolved peak, the peak position is determined at dl/dE = 0. However, for a peak which is not well resolved, the value of dl/dE will never reach zero. For this kind of peaks, it is not difficult to understand that the peak position should be within the range between the maximum and the minimum of the dl/dE. The change trends of the photon energies at (dl/dE)max and (dl/dE)min with temperature can be utilized to represent the one of the actual peak positions. Since that to perform a differentiation to a couple of curves is absolutely easier than do the fitting, and the persuasion is even stronger, this method is adopted consequently. Moreover, the values of all the peak positions for the well resolved peaks are also picked via this way. The dashed lines in Figs. 3(a) and 3(b) mark the evolutionary tendencies of the two shoulder peaks of sample C (denoted by peak-I and peak-II) and one peak with lower photon energy of sample B (denoted by peak-III) at the energy range of 3.290–3.330 eV. The peak with higher photon energy of sample B (denoted by peak-IV) is not shown as the position of this peak can be directly ascertained by the condition of dl/dE = 0 from 25 K to 150 K. The solid bold lines are the averages of the (dl/dE)max and (dl/dE)min, and the values along these lines are treated as the position for each peak.

The values for the peaks at different measuring temperatures discussed in the above paragraphs are extracted and plotted in Fig. 4. The following task is to explore the origins for each emission. The continuous redshifts of the A0X for the codoped samples are owing to the bandgap shrinkage with increasing the measuring temperature, which could be well fitted by the Varshni’s equation as well as the Bose-Einstein (BE) model. The solid lines along the experimental A0X data points shown in Figs. 4(a) and 4(b) are the fitting curves by the Varshni’s equation as the fitting quality is better to a small extent (the coefficient of determination R2 ~ 0.9991) over the one by the BE model (R2 ~ 0.9976). The important fitting parameters are the two temperature values of β and θE in each model, respectively. The β is proportional to the Debye temperature θD, while the θE denotes the Einstein temperature which represents the average phonon frequency. The values of the β and θE are fitted to be 768 K and 274 K for sample C, and 707 K and 252 K for sample B, respectively. The ratio of θE/β is ~0.35 for both samples which accords well with the reported value of 0.33 for p-type ZnO.

It has to be emphasized that several prior papers have reported similar shapes and evolutionary trends of the two peaks from 3.300 to 3.330 eV as shown in Figs. 2(b) and 2(c). Although the viewpoints regarding the attribution are varied, most of the researchers prefer that these two...
peaks are related to a FA emission accompanied by a DAP one with the same acceptor. By taking the thermal quenching rate into account, there exists an apparent conversion from a peak-III to the peak-IV as well as the peak-I to the peak-II, which really resembles a DAP to FA conversion. Moreover, there is always thermally ionized from donors and consequently convert a rate into account, there exists an apparent conversion from a peak-III to the peak-IV as well as the peak-I to the peak-II, which really resembles a DAP to FA conversion. During the increase of the measuring temperature, electrons are thermally ionized from donors and consequently convert a DAP emission to a FA one. Furthermore, there is always thermally ionized from donors and consequently convert a rate into account, there exists an apparent conversion from a peak-III to the peak-IV as well as the peak-I to the peak-II, which really resembles a DAP to FA conversion. Therefore, the peak-II and -IV are both assigned to the FA transitions.

However, after a careful comparison, it is noted that the energy positions of the FA emission lines are not exactly same for the two Te-N codoped samples, which indicates the acceptors have slightly different activation energy levels \(E_A\). Applying Eq. (1) for every temperature point in Figs. 4(a) and 4(b) and averaging the obtained values, the acceptor energy \(E_A\) is estimated to be 124 meV for sample B and 118 meV for sample C meaning that the acceptor level of sample C is \(\sim 6\) meV shallower than that of sample B. In the Be-N and Mg-N codoped ZnO materials, a first-principle calculation based on density functional theory has demonstrated that the energy level of an NO acceptor can be decreased by incorporating more Be or Mg ions by forming the complex \(n\)Be\(_{2}\)Zn\(_{m}\)N\(_{O}\) or \(n\)Mg\(_{2}\)Zn\(_{m}\)N\(_{O}\). \((n = 1, 2, 3, 4)\). However, the formation of this kind of complexes is nearly impossible because both the incorporation of N and Be/Mg would induce a contraction to the wurtzite lattice. Taking Be as an example, in order to release the stress, the Be-N bond along the \(c\)-axis must be unexpectedly long (0.288 nm) compared to a regular Be-N bond (0.182 nm), which makes the Be\(_{2}\)Zn\(_{m}\)N\(_{O}\) be impossible to be bonded along the \(c\)-axis. In this case, the formation energy of the \(n\)Be\(_{2}\)Zn\(_{m}\)N\(_{O}\) should really high. However, in case of a Te-N codoping, since a Zn-Te bond length is 0.263 nm inferring that the incorporation of Te would cause a lattice expansion, the codoping of Te can just compensate the contraction induced by N doping and thus the incorporation of N with a minimum lattice stress. As a result, the formation of \(n\)N\(_{O}\)-Zn\(_{m}\)-nTe \((n = 1, 2, 3, 4)\) subunits should be possible and the formation energy of such complexes may not increase with \(n\). Moreover, a recent first-principle calculation on a Te-N codoped ZnO system has proven that the acceptor level is narrow and deep for N acceptors related to the FA transitions of the Te-N codoped ZnO samples (marked as A in all figures). The specific form of \(E_A\) should be a mixture of the \(n\)N\(_{O}\)-Zn-1Te, \(n\)N\(_{O}\)-Zn-2Te, \(n\)N\(_{O}\)-Zn-3Te, and \(n\)O\(_{2}\)-Zn-4Te. By noticing that the concentration of Te in sample C is higher than that of sample B as

\[
E_{A'X}(T) = E_{FA}(T) - E_{A'X},
\]

and Eq. (1), we have

\[
E_{A'X}(T) = E_{FA}(T) + (E_A - E_{A'X} - 60\text{ meV}) - \frac{1}{2} k_B T, \tag{4}
\]

where the \(E_{A'X}\) denotes the localization energy of A\(_{0}\)X. From the Eq. (4), the \(1/2k_B T\) offset also exists between \(E_{A'X}(T)\) and \(E_{FA}(T)\). Figures 4(a) and 4(b) clearly show that after subtracting \(1/2k_B T\) from \(E_{FA}(T)\), the curves can just match the trends of the A\(_{0}\)X. Therefore, the peak-II and -IV are both assigned to the FA transitions.

\[
E_{A'X}(T) = E_{FA}(T) + (E_A - E_{A'X} - 60\text{ meV}) - \frac{1}{2} k_B T, \tag{4}
\]

and Eq. (1), we have

\[
E_{A'X}(T) = E_{FA}(T) + (E_A - E_{A'X} - 60\text{ meV}) - \frac{1}{2} k_B T, \tag{4}
\]

and thus the acceptor level should become shallower when more Te ions are doped. Therefore, it is believed that the N\(_{O}\) acceptors in N\(_{O}\)-Zn-nTe environment are ascribed to the acceptors related to the FA transitions of the Te-N codoped ZnO samples (marked as A\(_1\) in all figures). The specific form of A\(_1\) should be a mixture of the N\(_{O}\)-Zn-1Te, N\(_{O}\)-Zn-2Te, N\(_{O}\)-Zn-3Te, and O\(_{2}\)-Zn-4Te. By noticing that the concentration of Te in sample C is higher than that of sample B as
shown in Table I, the average number of \( n \) of sample C should be slightly larger than that of sample B, leading to a \( \sim 6 \text{ meV} \) difference of the acceptor activation energy value \( (E_A) \).

For the peak-I and –III, we have assigned both of them as the accompanied DAP emission lines. The energy positions just follow the trends of their respective \( A^0X \) as observed in Figs. 4(a) and 4(b). For a DAP transition, the temperature dependence of the energy is usually expressed as:

\[
E_{\text{DAP}}(T) = E_g(T) - E_D - E_A + e^2/4\pi r_{\text{DA}},
\]

where \( r_{\text{DA}} \) denotes the averaged distance between donors and acceptors and can be roughly estimated by the major carrier concentration \( n \) as

\[
r_{\text{DA}} = (3/4\pi n)^{1/3},
\]

When the sample is not heavily doped (>10\(^{19} \text{ cm}^{-3}\)), most of the major carriers are frozen at a LT range resulting in a low carrier concentration, and the change of the Coulomb energy \((e^2/4\pi r_{\text{DA}})\) should be negligible. For this reason, it is rational that the DAP energy positions match that of \( A^0X \), i.e., the bandgap \( E_g(T) \), at relatively low temperatures. However, the energy interval between the DAP and the FA of sample C is obviously larger than that of sample B. If the \( E_D \) values are same for both samples, in virtue of a smaller \( E_A \) value for sample C, even smaller value of the Coulomb item is required. However, the hole carrier concentration of sample C is higher than that of sample B, and the Coulomb energy is in direct proportion to \( n^{1/3} \), which means the Coulomb energy should be larger in sample C. This contradiction implies that the \( E_D \) values are different. By utilizing Eqs. (6) and (7), the \( E_D \) values are calculated as \( \sim 27 \text{ meV} \) and \( \sim 55 \text{ meV} \) for samples B and C, respectively.

TD-PL spectra reported by Park et al. also show that the energy of the DAP transition is lowered by Te-N codoping in ZnO films, but they did not find and investigate it in depth. The donor with \( \sim 27 \text{ meV} \) activation energy is really shallow which matches the value of some native donorlike defects, e.g., interstitial Zn. The formation of this kind of intrinsic defects is possible because the formation energy of donorlike defects in p-type ZnO is always very low. The donor with \( \sim 55 \text{ meV} \) activation energy is commonly ascribed to some unintentionally incorporated impurities, like Al. Park et al. have conscientiously demonstrated that the codoping of Te in N-doped ZnO shows definite effect on the suppression of the native donor-type defects and the improvement of the crystalline quality. The mechanism there is ascribed to the surfactant effect of Te on the growing surface which favors two-dimensional growth by the reduction in surface energy. In our case, it is believed that a similar mechanism can explain the suppression of native defects in sample C as well as the difference of the donor activation energies in the Te-N codoped ZnO samples with different Te concentrations. Furthermore, since the donor energy level of sample C is deeper compared with that of sample B, the compensation effect from the donors in sample C is much weaker than that of sample B, resulting in a stronger p-type conduction in sample C.

For sample A, the peak centering 3.332 eV at 15 K follows the tendency of its \( D^0X \) as shown in Fig. 4(c), and the energy position is a bit higher than that of the FA emission in the Te-N codoped samples. Considering its n-type conduction, the peak is thus ascribed to a TES emission of the \( D^0X \). Since the energy separation of the \( D^0X \) and its TES equals the difference between the donor energies in the 1s and 2p states, which is \( 3/4 \) of the \( E_D \) value in the hydrogenic effective-mass-approach, i.e.,

\[
E_D = 4/3(E_{D^0X} - E_{\text{TES}}),
\]

the donor activation energy is estimated to be \( \sim 40 \text{ meV} \). Meanwhile, the localization energy of \( D^0X \) can be obtained by

\[
E_{D^0X}(T) = E_{\text{FX}}(T) - E_L,
\]

where the \( E_L \) denotes the localization energy of the \( D^0X \) and is estimated to be \( \sim 12.4 \text{ meV} \). The ratio of \( E_L/E_D \) of sample A equals 0.31 which is in perfect agreement with the Haynes factor of \( \sim 0.3 \) for donors in ZnO. From previous literatures, the donors are more likely to be H or Al atoms. However, neither of them should be fully responsible for this dominant recombination. First, the line was observed in sample A, i.e., the annealed N monodoped sample. As shown in Sec. II, during the annealing process, the H atoms were driven out in a large amount, so the excitons bound to the residual H may not be the dominant radiative recombination path; Second, high temperature annealing would cause Al atoms from a sapphire substrate to diffuse into the epilayer and make the nominally undoped sample show a considerable electron concentration. However, the Al atoms need a long time to reach the film surface region, which has been revealed in our previous paper. Considering the wavelength of the laser (325 nm) used in this TD-PL measurement, the penetration depth (the depth that the intensity of the laser is attenuated to its 1/e) into the ZnO samples is only \( \sim 60 \text{ nm} \). A large number of Al atoms definitely cannot be accumulated with the penetration depth by the 10-min annealing. As a result, the diffused Al atoms should also not be the main contributor to the transition at 3.362 eV. Moreover, by considering that the calculated activation energy (40 meV) for the \( D^0X \) is slightly smaller than the reported values for H (46–57 meV) and Al (51–55 meV), it is not inclined to assign this line to H or Al. In fact, the chemical origins of most of the DBE lines, including this \( I_4 \) line, are not exactly known currently and the common sense we know is that the \( D^0X \) line should be related to the dominant donors in the sample. Therefore, in our opinion, the \( I_4 \) line here could be related to a few intrinsic donors generated during annealing process or some carbon/nitrogen related donor-type complexes which are very common in N monodoped ZnO films grown by nitride oxide. The donor activation energies of these complexes are as low as the intrinsic donors. One of our prior works has demonstrated that the co-incorporation of Te shows remarkable suppression effect on the C and N related donorlike complexes, such an annoying compensation to holes is accordingly fully
removed in the Te-N codoped samples making the p-type nature more efficient.

After completing the analysis on the major parts of the NBE emissions with relatively high intensities, we move to the deeper side (3.150 eV–3.280 eV). The relevant range of Fig. 2 is zoomed in and shown in Fig. 5 in order to see the details more clearly. There is nothing special in this energy range for the N monodoped sample A apart from the LO replicas of the FX, D0X, and TES. More attractions originate from the codoped samples. Only one peak centering 3.219 eV at 15 K is observed for the sample C. Noticing that the position of this peak is not close to any of the possible phonon replicas of the well resolved transitions at higher energy side, it is hence a new transition. By plotting the temperature dependence of the energy position of this peak, the trend is just along the FA1 in Fig. 4(a). As a result, it is ascribed to another FA transition, denoted as FA2. The activation energy is calculated as \( \sim 224 \text{meV} \) above the valence band using Eq. (1). For the sample B, except for the 1st and 2nd LO emissions of FA1 and DA1P, it is obviously seen in Fig. 5(b) that a shoulder exists aside of the 1LO-DA1P. When the energy positions are separated from the broad band and depicted in Fig. 4(b), the trend is almost the same as the FA2 in Fig. 4(a) which also copies the temperature dependence of its FA1. Moreover, the position at 15 K (3.218 eV) only shows a below 1 meV difference to that of FA2 of the sample C. Therefore, this shoulder peak of sample B is also assigned to the FA2 emission with its acceptor activation energy of \( \sim 225 \text{meV} \). Although the Zn-vacancies have similar energy levels, they can be easily refuted because of their high formation energy in a p-type ZnO film.\(^9^4\) Since our prior paper has demonstrates that the NO acceptors exist in two kinds of chemical environment, i.e., the NO-Zn-O and the NO-Zn-Te, by XPS, and the energy positions, which are close to the reported value of the NO acceptors in ZnO,\(^9^5\) show little change, it would be reasonable that the acceptor A2 is the basic N substituting defects in a ZnO lattice. From the overview of Figs. 2(b) and 2(c), the intensity of FA2 is much lower than that of FA1 and the RT activation rate of A1 is around 100 times A2, indicating that the NO in the NO-Zn-Te chemical states should dominate the electrical properties of the codoped films and make them exhibit p-type conduction at room temperature.

Another way to estimate the activation energy of acceptors is to fit the temperature dependence of the integrated intensity of the \( \text{A}^0X \) by the following equation:\(^9^6\)

\[
I(T)/I_0 = 1/[1 + C \exp(-E^b_{\text{A}^0X}/k_BT)],
\]

where \( C \) and \( E^b_{\text{A}^0X} \) are the fitting parameters, and \( I_0 \) is the integrated intensity of \( \text{A}^0X \) at 0 K. Since 0 K is not achievable experimentally, the common way to do the fitting is to treat the integrated intensity at the lowest temperature point \( I_{15\text{K}} \) as \( I_0 \), and normalize other \( I(T) \) values to the \( I_{15\text{K}} \).\(^7^2\) Figures 6(a) and 6(b) show the temperature dependence of the integrated intensities of the \( \text{A}^0X \) as well as the fitting curves of samples C and B. The \( R^2 \) statistics are 0.9985 for both the fittings indicative of high fitting qualities. The localization energies \( (E^c_{\text{A}^0X}) \) deriving from the curves are deduced to be 10.65 \( \pm \) 0.28 meV and 11.24 \( \pm \) 0.32 meV for sample C and sample B, respectively. In order to deduce the activation energies of the acceptors, the Haynes rule for p-type ZnO films has to be used. The Haynes factor \( (E^c_{\text{A}^0X}/E^c_{\text{NO}}) \) for n-type materials has been well defined, however, it is not established yet for p-type ZnO.\(^9^7\) Although many prior works

![Fig. 5. Zooming in of the TD-PL spectra of (a) sample C from 3.17 eV to 3.28 eV and (b) sample B from 3.12 eV to 3.28 eV.](image1)

![Fig. 6. The normalized integrated intensity of \( \text{A}^0\text{X} \) (normalized to the value at 15 K) as a function of temperature for (a) sample C and (b) sample B and their respective fitting curves by Eq. (10).](image2)
have adopted the empirical value of ~ 0.1 to estimate the \( E_A \) value from the \( E' = 0.1x \), there are still other reported values of Haynes factor ranging from 0.07 to 0.25. Using the above-derived \( E_A \) values of the codoped samples (118 meV for sample C and 124 meV for sample B), the Haynes factor in the Te-N codoped ZnO films is determined to be ~ 0.09. This value is very close to the Haynes factor in a N-doped ZnSe (~0.09), and also consistent with those reported for some N-doped and As-doped ZnO films with shallow acceptor energy levels. (~0.07–0.09).

IV. SUMMARY AND CONCLUSIONS

The TD-PL spectra of one N monodoped and two Te-N codoped ZnO thin films have been comparatively and comprehensively studied. Two forms of the NO acceptors, i.e., the NO\(_Z\)-O and the NO\(_Z\)-Te proposed previously, have been demonstrated. The activation energy of the NO\(_Z\)-Te acceptors is defined as 118 – 124 meV, while the one of the traditional NO\(_Z\)-O acceptors is much deeper (~224–225 meV). The ~ 6 meV difference of the activation energy of the NO\(_Z\)-Te acceptors in the two codoped samples corresponds to the achievement of a shallower acceptor energy level brought by more incorporation of the Te ions. Moreover, the suppression of native donor-type defects is proven by the DAP emissions related to different donors and ascribed to the improved crystalline quality induced by the Te codoping. Finally, the Haynes factor is proposed to be ~ 0.09 for the Te-N codoped ZnO films. To sum up, the optical properties of the monodoped and codoped samples are in good agreement with their electrical and crystalline properties. In consequence, the Te-N codoping technique should be a feasible path to realizing p-type ZnO materials with controllable hole carrier concentration.

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