A control on the photoluminescence properties in P-passivated nanocrystalline ZnO films

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Abstract

P-passivated nanocrystalline ZnO films on InP substrates were prepared by thermal oxidation of Zn films. By a simple thermal annealing cycle process, uniform photoluminescence (PL) samples with controllable visible emission and intense UV emission were obtained at different annealing conditions. Through a detailed study of the photoluminescence spectra of P-passivated nano-ZnO films vs the annealing-temperature and annealing-time, it is shown that applying different annealing time or temperatures provides a very practical technique to control the deep-level defect emission. A core-shell structure model of the surface passivation was helpfully used to discuss the P-passivation mechanism.

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Recent investigations of ZnO have resulted in many remarkable achievements, e.g., quantum effect in superlattices [1], laser emission [2–4], and a heterojunction light-emitting diode [5]. However, the mechanism of defect-related electron–hole recombination in ZnO is still unclear, and control of defect states remains the most important issue for improvement of emission efficiency. In previous reports [6–8], the exact mechanism for deep-level emission is still controversial; intrinsic defects such as oxygen vacancies, oxygen interstitial, zinc vacancies and interface/surface-related defect states have all been considered as the origin. However, there was seldom report about the realization of controlling defect states so as to control the PL properties in ZnO. In our previous report [9], the P ions diffusing from InP substrates were appropriate for passivation of radiative recombination centers giving visible (VIS) emission. However, the details of this passivation mechanism are unclear. This work reports results of modifying the structure of the nanocrystalline ZnO films and the concentration of P ions in the films by further annealing processes. Here, we firstly report the effect of such changes on the photoluminescence properties and apply a very practical technique to control it.

The ZnO films were prepared on InP (001) substrates by thermal oxidation of Zn films. The thickness of the as-deposited films was approximately 600 nm. Details of preparation procedure are given by Chen et al. [9]. After deposition, the films were oxidized in a thermal oxidation furnace. Thermal oxidation procedure was carried out in three steps. In an initial study, several different annealing-temperatures between 300 and 700 °C for one hour were investigated, with all
samples characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and photoluminescence (PL). Subsequently, films oxidized at 500 °C were subjected to further annealing at 500 °C for 1 to 2.5 total annealing time, with PL and XPS measurements every 30 min. Finally, the same samples were annealed at 300 °C for additional 1–3 h, with PL and XPS measurements again every 30 min. The spectra of the XRD and XPS were recorded by using a D/ max-RA X-ray spectrometer (Rigaku) with Cu Kα line of 1.54056 Å and a VG ESCALAB MK II X-ray photoemission spectrometer, respectively. Micro-PL measurements were conducted with a J-Y UV-lamb micro-Raman spectrometer using the 325 nm line of a He–Cd laser as the excitation source.

XRD results by measuring annealed at different temperatures were investigated from He–Cd laser as the excitation source. Presence of the Zn 3P2 peak indicates that the P ions diffused into Zn films and chemically combined with Zn ions to form Zn3P2. As the annealing temperature increases, peak intensities for ZnO (101) and Zn3P2O7 increased markedly, and decrease for InP substrate. According to the XRD and XPS results and considering the experimental processes, the core layer, the interfacial layer and the shell regions. According to the XRD and XPS results and considering the experimental processes, the core layer, the interfacial layer and the shell region.

Table 1 as a function of annealing temperature. When the annealing temperature increased from 300 to 500 °C, P3- concentration decreased from 7.4% to 4.9%, and P5+ concentration increased from 8.4% to 19.6%. The total concentration of P ions, including P3- and P5+ ions, increased from 15.8% to 24.5%, indicating a higher diffusing velocity of P ions from InP substrates, accompanied by a higher oxidizing velocity at annealing temperature of 500 °C. It should be noted that the concentration of the P3- increased further, from 4.9% to 6.7%, when the samples were annealed at 300 °C for 3 h in the third annealing process. It showed a higher diffusing velocity of P ions and a lower oxidizing velocity at a lower annealing temperature of 300 °C. No any detectable peak of In ions was observed in XPS spectra. It indicated that the concentration of In in the film was too low to detect. To understand this fact, it must be considered that a few In ions can be thermally diffuse into film. This is because the surface vapor pressure of In is much lower than that of P, as a result of this, the In ions with a low diffusion combine with oxygen in the thermal process conducted in oxygen ambience to form In2O3 easily in the surface of InP. Also, In2O3 further prevents the In ions to diffuse into ZnO films. By contraries, the inner nuclear emission of P ions can be fairly detected, indicating a high P content in the film resulting from the high surface vapor pressure of P.

When the Zn films were annealed in O2 ambience, many ZnO nano-clusters embedded in Zn matrix would be formed at first, and large number of P3- ions simultaneously diffused into Zn film. The P3- ions diffused into the Zn films should be divided into two parts. Most of the P3- ions combined with Zn to form Zn3P2 enveloped the ZnO nanoclusters since the ZnO nanoclusters were previously embedded in Zn matrix. Another part of P3- ions diffused into ZnO clusters to form P doped ZnO. At the same time, Zn3P2 would be partly oxidized into Zn3P2O7 in O2 ambience as the annealing temperature increased, and this oxide layer would be easier to form on the surface of Zn3P2. XRD and XPS results have confirmed coexistence of crystallized ZnO, Zn3P2 and Zn3P2O7. According to these results a schematic view of P-passivation ZnO nanocrystallite was suggested, which was shown in Fig. 2. The passivated ZnO nanocrystallite consists of three regions: the core, interfacial, and shell regions. According to the XRD and XPS results and considering the experimental processes, the core layer, the interfacial layer and the shell region.

![Fig. 1](image-url) (a) XRD spectra of ZnO thin films grown on InP at different annealing temperatures for an hour (b) XPS spectra in the region of the P 2p core levels of P-passivated nanocrystalline ZnO thin film.
layer would be created by ZnO:P, Zn3P2 and Zn2 P2O7, respectively.

Fig. 3 shows PL spectra acquired at room temperature. In Fig. 3a, intense UV emission peaks with negligibly weak deep level emissions are observed for the samples annealed at different temperatures from 300 to 700 °C for 1 h. These spectra are normalized so that the strongest peaks are of the same intensity with enhancement factors given in the figure. The UV emission intensity is greatest at 500 °C annealing temperature. Values of the full-width of half-maximum (FWHM) of the UV peaks are in the range of 90–140 meV, as shown in the Fig. 4a. FWHM decreases to a minimum when the temperature reaches 500 °C, and then increases quickly. The room temperature FWHMs are comparable with those of ZnO films grown on CaF2 (98 meV) [11], on sapphire (117 meV) [12], on GaN/SiC (129 meV) [13] and on bulk ZnO (115 meV) [14]. The typical intensity ratio of the UV emission to the VLS emission (IRUV) is 560 for the sample annealed at 500 °C. This high intensity ratio manifests low defect concentration by introducing P ions into ZnO films. The annealing temperature dependent behavior of the FWHM and PL intensity indicates that the film annealed at 500 °C has better crystal quality and fewer defects than films prepared at other temperatures.

To investigate the P-passivation effect on the PL properties in ZnO films, the annealing-time-dependent PL properties at different annealing temperatures were also studied as shown in Fig. 3b. For samples annealed at 500 °C, PL spectra show two distinct features: an obvious increase in intensity of the VIS emission and a widening of the FWHM of the UV emission peak with increasing annealing time. When the sample was subsequently annealed at 300 °C, the intensity of the VIS emission decreases remarkably again and the FWHM of the UV emission peak has a narrowing trend with increasing annealing time. After the sample was annealed for 3 h at 300 °C, the VIS emission was almost completely re-quenched.

In fact, the changes of PL properties with the annealing-temperature and annealing-time are clearly revealed in Fig. 4 by investigating the FWHM values of the UV emission peak and IRUV as a function of the annealing temperature and annealing time. As shown in Fig. 4a, FWHM at first decreases obviously to a minimum of 90 meV, when the temperature reaches 500 °C for 1 h; then FWHM widens remarkably with increasing annealing time to 128 meV for 2.5 h annealing, as shown in Fig. 4b; and finally, FWHM decreases slightly to 119 meV for 3 h 300 °C annealing, as shown in Fig. 4c. The IRUV first decreases obviously with the annealing time for the sample annealed at 500 °C, then increases during 300 °C annealing, reaching a value of 510 at 3 h, which could be comparable with the maximum 560 in the ZnO film annealed at 500 °C for 1 h. These results show that the already-poor optical quality of the ZnO film sample was improved by using lower annealing temperature and longer annealing time. Significant variation in PL properties observed here indicates that the optical properties of P-passivation ZnO films can be controlled by changing the annealing temperature and time.

The aforementioned three-region model suggests that P3− ions diffusing from the substrate may play two important roles. One is that P3− ions diffusing into the core layer act as scavengers of oxygen vacancy,
significantly decreasing the number of oxygen vacancies. The other is that Zn$_3$P$_2$ in the interfacial layer covering the ZnO particle passivates Zn dangling bonds and eliminates surface trappers. If the roles of P$^{3-}$ are known, it is not surprising that the optical properties change with the annealing temperature and time in our P-passivation nanocrystalline ZnO films. When the samples were annealed at temperatures from 300 to 700 °C, many P$^{3-}$ ions diffused into ZnO films and occupied the lattice of O to form ZnO:P, which remarkable decreases the number of oxygen vacancies in the core layer. Moreover the Zn$_3$P$_2$ in the interfacial layer covering the ZnO particle passivates the Zn dangling bonds and eliminates the surface trappers; and the passivated layer has a potential energy large enough to prevent surface states from trapping photogenerated electrons or holes, so the pathway to form the V$_{O}^{+}$ centers which are responsible for VIS emission [15] is blocked. The visible emission can be quenched, as shown in Fig. 3 a. But at the same time the formation of Zn$_2$P$_2$O$_7$ was not suppressed because the P ions were also reactive to O when the films were annealed in O$_2$ ambient and the P$^{5+}$ ions cannot act as scavengers of oxygen vacancies and surface trappers because it competes for O with Zn$^{2+}$. Based on the above analysis, it is not difficult to draw the conclusion that further increase of annealing temperature beyond 500 °C or increase of annealing time at 500 °C would lead to the decrease of P$^{3-}$ concentration in the films due to the higher velocity of P$^{3-}$ oxidizing than that of its diffusing at such temperatures. As a result, the IRUV would decrease because of the decrease of the concentration of P$^{3-}$ resulting in less quenching of the VIS emission (Fig. 4b). Whereas, when the sample was annealed at 300 °C again, many new P$^{3-}$ ions diffuse into the films from InP substrates. In this case, the diffusing velocity is higher than the oxidizing velocity, so the newly generated oxygen vacancies are passivated by the redundant P$^{3-}$, resulting in an increase of the IRUV, as shown in Fig. 4c. In addition, UV emission from P-passivated ZnO films annealed at 500 °C for one hour shows the narrowest FHWM. This suggests that P substitutes for O homogeneously enough to suppress inhomogeneity-induced broadening effect at this temperature.

In conclusion, optical properties of ZnO films grown on InP substrates from thermal oxidization of metallic Zn films were investigated. From the results of XRD, XPS, and the annealing temperature and time dependences of PL characteristics, the P passivation effect on the PL properties of the nanocrystalline ZnO and its mechanism were investigated in detail. It is shown that applying different conditions of annealing time or temperatures provides a highly practical technique for controlling the PL properties of nanocrystalline ZnO films.

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