Observations of nitrogen-related photoluminescence bands from nitrogen-doped ZnO films

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Abstract

We report the synthesis and photoluminescence (PL) properties of nitrogen-doped ZnO films. These films were synthesized by filtered cathodic vacuum arc technique; nitrogen gas was used as a dopant source. X-ray diffraction results indicated that the ZnO films were highly c-axis oriented. The appearance of the nitrogen-related local vibrational Raman scattering peaks showed that nitrogen was incorporated into the films. In the PL spectrum of the undoped films, a near band edge exciton emission peak at 384 nm and a weak visible band related to oxygen interstitial at 660 nm were observed. For nitrogen-doped films, besides the two emission bands observed in the undoped samples, two additional PL bands at around 450 and 890 nm were detected. According to the first-principle total energy calculation, nitrogen-induced acceptor energy level is located at 0.4 eV above the valence band maximum. Therefore the emission band at around 450 nm may originate from the recombination of photo-generated electrons with neutral nitrogen acceptors, and the 890 nm band is attributed to electron transition from oxygen interstitial to this neutral nitrogen acceptors.

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1. Introduction

Zinc oxide is a wide band gap (3.37 eV at room temperature) semiconductor material, and is considered as a potential material for short wavelength optoelectronic devices, such as light-emitting diodes and lasers working in ultraviolet and blue light region [1,2]. Room temperature ultraviolet lasing effects have been realized in ZnO films and ZnO nanowires [2–5]. The realization of high-quality p-type doping is a prerequisite condition for optoelectronic applications of ZnO films, in particular, for light-emitting diodes and lasers. Similar to many other wide band gap semiconductors, ZnO has the “asymmetric doping” limitation, in that n-type doping is easily obtained, but it is
difficult to dope ZnO into p-type [1,6]. Nitrogen is believed to be a promising p-type dopant for ZnO, however no p-type doping was realized until the report by Joseph et al [7], who obtained p-type doping by co-doping of nitrogen and gallium. Many methods such as pulsed laser deposition, molecular beam epitaxy and metal oxide chemical vapor deposition, have been attempted to deposit nitrogen-doped ZnO films [8–11]. At the same time, many investigations have also been carried out to understand the basic properties of nitrogen-doped ZnO. Kaschner et al. [12] observed nitrogen-related local vibration modes in ZnO:N films. Garces et al. [13] detected the signals of neutral nitrogen acceptors using electron paramagnetic resonance (EPR) in single crystal ZnO which was thermally annealed in nitrogen ambient. Photo-luminescence (PL) spectrum is often used to characterize semiconductor materials. It could provide information about the energy level of impurity in the band gap. The PL property of ZnO films has been studied for a long time. The PL spectrum of ZnO is usually composed of two components. One is located at UV range due to excitonic-related emission, and the other is visible emission band whose origin is still controversial [14–16]. However, compared to the large number of studies on undoped ZnO, very few investigations have been reported on the PL properties of nitrogen-doped ZnO films. In this letter, we report the PL spectrum of nitrogen-doped ZnO films growth by filtered cathodic vacuum arc (FCVA). The results show that the good quality and highly (001) oriented ZnO films can be synthesized by FCVA and nitrogen can be incorporated into ZnO films effectively by this technique. Two new PL peaks are observed at around 450 and 890 nm in nitrogen-doped ZnO films.

2. Experimental details

The ZnO thin films were deposited on silicon (001) and quartz glass substrate by FCVA from a zinc target in oxygen/nitrogen atmosphere. The details about the FCVA technique were discussed elsewhere [17]. The chamber was pre-vacuated to \(1 \times 10^{-6}\) Torr by mechanical and cryopump. During deposition, the substrate temperature was maintained at 350°C by resistivity heating, the oxygen flow rate was 50 sccm, the nitrogen flow rate changed from 0 to 10 sccm, the chamber pressure was around \(1 \times 10^{-4}\) Torr during deposition. The arc current was 60 A, and the magnetic field used to steer the plasma was approximately 40 mT. The substrates were cleaned consequently in acetone, methanol, and then de-ionized water for 30 min in ultrasonic bath. Film crystal structure was measured with a Shimadzu X-ray diffractometer (XRD-6000) in \(\theta–2\theta\) model. Raman scattering experiment was carried out in backscattering geometry in Ramanish 1000 system equipped with a charge-coupled detector with resolution of 1 cm\(^{-1}\). The line at 514 nm of Ar ion laser was used as excitation source. PL spectrum was measured at room temperature and excited by the 325 nm line of a He–Cd laser with power of 25 mW, and collected by a grating spectrometer and a photomultiplier tube detector.

3. Results and discussion

Fig. 1 shows the XRD patterns obtained from ZnO films grown with different nitrogen flow rates. Sample A is undoped ZnO film, samples B and C are nitrogen-doped ZnO films obtained with nitrogen flow rates of 5 and 10 sccm, respectively. Only the (0 0 2) diffraction peak is observed in the three spectra, which indicates the c-axis preferred texture growth of the ZnO films. With the increasing of nitrogen gas flow rate, the peak intensities decrease greatly and its full-width at half-maximum (FWHM) increases from 0.15° for sample A to 0.31° for sample C. The FWHM values were corrected for instrumental broadening. The estimated grain sizes of samples A, B and C is 58, 45 and 28 nm, respectively, using the Scherrer formula. With the increasing of nitrogen gas flow rate, the crystal quality degrades and the grain size becomes smaller, which is consistent with the results of others researchers [10,18]. The peak position of sample C shifts slightly to lower angle. It may be attributed to the change in grain size and strain in the film.
The Raman spectra of the three samples are shown in Fig. 2. Three peaks appear in these Raman spectra, are 273, 437 and 580 cm\(^{-1}\). ZnO has a hexagonal wurtzite structure and belongs to the \(C_{6v}\) symmetry group. The 437 cm\(^{-1}\) peak is the high frequency \(E_2\) mode of ZnO, the low frequency \(E_2\) mode is out of the detecting range of our system. The 273 and 580 cm\(^{-1}\) peaks have been observed in nitrogen-doped ZnO films; however, they are explained as electric field-induced \(A_1\) (LO) and \(B\) modes, respectively [9,19]. Recently, Kaschner et al. [12] found that there is a proportional relationship between the intensity of the two peaks and the nitrogen concentration in nitrogen-doped ZnO films, and attributed them to the nitrogen-related local vibrational modes (LVM). They suggested that the relative intensity of the LVMs to the 437 cm\(^{-1}\) peak could be used to evaluate the relative nitrogen doping concentrations in ZnO films. In Fig. 2(a) of undoped sample, no nitrogen-related LVM peaks are detected; with the increase of nitrogen gas flow rate, the intensities of the two LVMs increase, as can be seen from Figs. 2(b) and (c). The observation of the nitrogen-related LVM indicates the effective incorporation of nitrogen into ZnO films using the FCVA technique.

The room temperature PL spectra obtained from samples deposited with different nitrogen gas flow rates are shown in Figs. 3(a)–(c). Spectrum (a) of undoped ZnO film is composed of a UV emission peak and a broad deep level visible emission band. The UV peak at 384 nm originates from near band edge (NBE) free exciton emission with FWHM of 93 meV, this value is comparable to ZnO films deposited by other methods [4,16]. The inset in Fig. 3(a) shows the enlarged deep level emission band at around 660 nm. The intensity ratio of NBE peak to deep level emission band is \(\sim 50\). The small FWHM and high-intensity ratio of NBE to deep level emission indicate the high crystal quality of the ZnO films deposited by FCVA. The position of the deep level emission band is different from the normally observed green band at 550 nm [15]. This band was observed in oxygen-rich ZnO films prepared by spray pyrolysis [20] or pulsed laser deposition [21]. Figs. 3(b) and (c) show the PL spectra of nitrogen-doped ZnO film with nitrogen gas flow rate of 5 sccm (sample B) and 10 sccm (sample C), respectively. It can be seen clearly that the peak positions and intensities changed greatly by nitrogen doping. The intensity of the NBE peak in samples B and C is only 1.6% and 0.4%, respectively, of that of undoped films. The intensities of NBE emission peak decrease with the increase of nitrogen gas flow rate; the oxygen interstitial-related visible band can still
be observed, its position shifts slightly to lower energy (~690 nm). In addition to these, two additional broad emission bands are also observed, as shown in Figs. 3(b) and (c). The centers of the two new peaks are around 450 and 890 nm, and their FWHMs are about 100 and 200 nm, respectively. These two bands are not observed in the undoped sample; this enables us to exclude the possibility that the two bands are originated from impurities. If the bands are due to unintentionally incorporated impurities from the chamber, they should also present in the undoped sample. Another possible origins for the two additional deep level emission bands are intrinsic defects or surface states. However, we have checked the PL of undoped ZnO films from a wide range of deposition conditions such as O2 flow rates, substrate temperature or by thermal annealing of zinc thin films in oxygen ambient, no broad deep level emission bands are detected at around 450 and 890 nm. The intrinsic defects and surface states possibilities can also be excluded. Therefore, we can conclude that the two new broad emission bands are due to nitrogen doping.

The electrical properties of the nitrogen-doped ZnO films are investigated by Hall effect measurement using van der Pauw method at room temperature. The resistivity increases from $6.5 \times 10^{-2} \Omega \text{cm}$ of sample A to $4.3 \times 10^{3} \Omega \text{cm}$ of sample C, however, the carrier is still $n$-type. The increase of resistivity is caused by the decrease of carrier concentration and mobility with the increase of nitrogen gas flow rate. Garces et al. studied the property of nitrogen-doped ZnO using photo-induced EPR, and they observed that the signals of uncompensated neutral nitrogen acceptors [13]. Park et al. calculated the nitrogen doping in ZnO by first-principle total energy calculations, the energy level of substitutional $N_0$ is 0.40 eV above the valence band maximum [22]. The two newly observed emission bands at around 450 and 890 nm could be attributed to the recombination of photo-excited electrons with nitrogen acceptors. In n-type semiconductor, the acceptor should be in negative state and filled with electrons; however they can be photo-ionized by exciting photons in the process of PL that is similar to the process of photo-induced EPR. The electrons at high-energy levels can transfer to the acceptor level and then emit light correspondingly. This type of photon radiation involving acceptor has been observed in ZnO, for example, zinc vacancy and arsenic acceptor [21,23]. In Figs. 3(b) and (c), the position of oxygen interstitial-related emission is located at 690 nm (1.8 eV), while the position of the low-energy band is 890 nm (1.39 eV), the energy difference between them is 0.41 eV which is in good agreement with the nitrogen acceptor energy level calculated by Park et al. [22]. Therefore, the low-energy emission band can be attributed to the transition between oxygen interstitial and nitrogen acceptors. For the emission band at around

![Fig. 3. PL spectra of the three samples, A (a), B (b), and C (c).](Image)
450 nm (2.76 eV), which is higher than the often-observed green band of 2.4 eV, the emission band may originate from the recombination of the electron in the conduction band or in shallow donors (such as Zn interstitial) with the nitrogen acceptors (0.4 eV). The actual mechanism responsible for the deep level emission bands is still controversial [2,15,20,21,23]. More experiments are needed to confirm the above-proposed mechanism for the two nitrogen-related bands.

In the FCVA system, a special designed long distance off-plane double bend magnetic filter is used to remove macroparticles [17], the growth species are immersed in plasma for a distance of about 80 cm before arriving at the growing surface. This improves the ionization ratio of reactive gases (O₂ and N₂) and favors sufficient reaction between zinc and reactive gases. This can explain why the often-observed oxygen vacancy-related green PL band could not be observed in the ZnO films deposition by the FCVA. On the other hand, the ions in the vacuum arc plasma has a high ion energy, this high ion deposition energy provides a kind of pseudo-temperature to the growing film that in turn provides surface atom mobility and enables deposition of high-quality films at low substrate temperature. We have shown that high-quality ZnO films can be deposited at 350°C, which is much lower than that used by other methods. Low temperature and non-equilibrium growth can increase the incorporation of nitrogen in ZnO [22]. This work demonstrates the possibility and advantages of deposition of nitrogen-doped ZnO film by the FCVA technique.

4. Conclusions

In conclusion, nitrogen-doped ZnO films can be prepared by the FCVA technique. The Raman scattering showed that nitrogen could be incorporated in the ZnO effectively using the nitrogen-related local vibrational mode at 580 cm⁻¹. Two new emission bands at around 450 and 890 nm are observed from the nitrogen-doped ZnO films. The former one is attributed to the recombination of photo-generated electrons with neutral nitrogen acceptors, which is consistent with the theoretical calculations. The latter one could be due to the electron transition from oxygen interstitial to nitrogen acceptor.

References