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P-type conductivity and stability of nitrogen-doped zinc oxide prepared by magnetron sputtering

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Abstract

Nitrogen (N)-doped zinc oxide (ZnO:N) films were deposited on quartz glass substrates at 510 K by reactive radio-frequency magnetron sputtering of a ZnO target with sputtering gas of nitrogen. The as-grown ZnO:N shows insulating at room temperature, but behaves p-type conduction with resistivity of 456 Ω cm, carrier concentration of $1.2\times10^{17}\,\mathrm{cm}^{-3}$ and Hall mobility of $0.1\,\mathrm{cm}^2/\mathrm{V\,s}$ in the dark after annealed at 860 K for 1 h under 10^{-4} Pa. Unfortunately, the p-type conduction is not stable in the dark and transforms into n-type gradually. After irradiated by sunlight for a few of minutes, the n-type ZnO:N reverts to metastable p-type one in the dark and remains p-type conductivity in the brightness. Formation and stability of the p-type ZnO:N are discussed in the present paper.

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Keywords: ZnO; Electric behavior of semiconductor; Photoluminescence; Doping

1. Introduction

Since ZnO has a direct band gap of 3.37 eV at room temperature and large exciton binding energy of 60 meV, it has been considered as promising candidate for ultraviolet (UV) light-emitting diodes (LED) and lasers. However, this material has largely failed to live up to its potential, because LEDs require both n-type and p-type ZnO with high crystal quality, and it has proven very difficult to produce high conductive and stable p-type ZnO. In the past years, many sources containing N atoms, such as N_2, NO, N_2O, and NH_3 etc., were used to prepare p-type ZnO by N doping. However, the results are controversial. Some groups reported only observing n-type conductivity in the N-doped ZnO (denoted as ZnO:N) [1], while some groups reported obtaining p-type ZnO:N [2,3]. According to previous reports, however, most of the p-type ZnO:N usually has low mobility and are unstable even. For example, it was found that a p-type ZnO:N reverted to n-type ZnO:N in a period of several days after deposition [4]. Therefore, it is necessary to investigate formation mechanism and stability of p-type ZnO.

2. Experimental procedures

A ZnO:N film was deposited on quartz glass substrates by radio-frequency (rf) magnetron sputtering technique. 99.99% pure ZnO is used as target, sputtering gas is 99.999% pure N_2, and substrate temperature is 510 K. The quartz substrate was cleaned in an ultrasonic bath with acetone for 15 min at room temperature, and then washed using deionized water. The growth chamber was pumped down to a base pressure of about 4×10^{-4} Pa firstly, and then filled with N_2 up to 0.3 Pa. The sputtering power and time are 100 W and 2 h, respectively. The as-grown film thickness is about 600 nm. The as-grown ZnO:N film was

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annealed for 1 h at 860 K under $\sim 10^{-4}$ Pa and in O_2 flow, respectively, in a tube furnace. In order to prevent pollution, a quartz tube was inserted into the furnace and the films were placed in a quartz boat.

Structures of the samples were characterized by X-ray diffraction (XRD) with Cu $K_{\alpha 1}$ radiation ($\lambda = 0.15406$ nm). Photoluminescence measurement was performed at room temperature by the excitation from 325 nm He–Cd laser. Compositions and chemical state of elements in the ZnO:N were detected by X-ray photoelectron spectroscopy (XPS) using an Al K_α X-ray source. Electrical properties were measured in the van der Pauw configuration by a Hall effect measurement system.

3. Experimental results and discussions

A deep-yellow and transparent ZnO:N film was deposited at 510 K on quartz glass substrates by reactive rf magnetron sputtering technique. XRD results reveal that the as-grown ZnO:N film is preferentially oriented in the (0 0 2) and (1 1 0) direction, as shown in Fig. 1a. The lattice constants were $a = 0.3311$ nm and $c = 0.5274$ nm, respectively, much larger than those of pure ZnO given in literature [5]. That may be attributed to internal stress and N atom incorporation. In order to understand effect of N incorporation on the lattice constants, an undoped ZnO film (denoted as ZnO:Ar) was grown on a quartz glass substrate by sputtering of the ZnO target with argon (Ar) plasma under the same experimental condition as ZnO:N used. Being different from the ZnO:N, the ZnO:Ar film is preferentially oriented in the (0 0 2) and (1 0 3) directions, as shown in Fig. 1b, and is colorless and transparent. The lattice constants were measured by XRD to be $a = 0.3276$ nm and $c = 0.5249$ nm, respectively, larger than those of pure ZnO, indicating that the internal stress in the ZnO:Ar is tensile but not compressive stress. It is also noted that the lattice constants of the ZnO:Ar is smaller than those of the ZnO:N. The differences in the a and c between ZnO:N and ZnO:Ar are $\Delta a = 0.0017$ nm and $\Delta c = 0.0005$ nm, respectively, which are due to incorporation of N atom into ZnO.

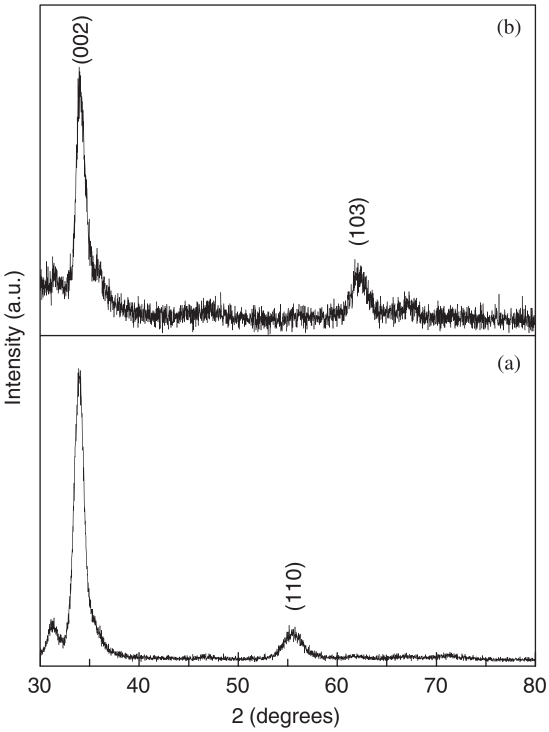

Fig. 1. XRD patterns of (a) the as-grown ZnO:N and (b) ZnO:Ar.

XPS measurement was used to estimate N concentration in the ZnO:N. Two N_{1s} peaks were observed at binding energy of 396.6 and 404.9 eV, respectively. The low binding energy peak corresponds to substitution of atomic N for O sublattice $(N)_o$, and the high binding energy peak is due to substitution of molecular N for O sublattice $(N_2)_o$. The concentrations of $(N)_o$ and $(N_2)_o$ are estimated to be 1.8 and 0.7 at%, respectively. Since Zn–N bond length is somewhat smaller than Zn–O one [6], the substitution of atomic N for O sublattice should result in decrease of the lattice constants, as reported by Barnes.[4] However, radius of N_2 is much larger than that of atomic O, therefore, the increase of lattice constants induced by N doping should be attributed to substitution of N_2 for O in the as-grown ZnO:N.

Upon annealing the as-grown ZnO:N for 1 h at a temperature of 860 K under about 10^{-4} Pa, the lattice constants decrease to $a = 0.3248$ nm and $c = 0.5214$ nm, respectively, close to the literature values of pure ZnO, and the color also changes from deep yellow to light yellow, implying that the N concentration in the ZnO:N decreases with increasing annealing temperature [7] and N_o is a dominant substitutional form in the 860 K annealed ZnO:N.

Electrical measurement shows that the as-grown ZnO:N behaves insulting, while the 860 K annealed ZnO:N shows semiconducting conductivity. Hall measurement for the 860 K annealed ZnO:N was performed in the dark at room temperature in a magnetic field range of 0–15 kGauss, indicating that it behaved p-type conduction with resistivity of 456 Ω cm, carrier concentration of 1.2×10^{17}/cm^3 and Hall mobility of 0.1 cm^2/Vs. Unfortunately, the p-type conductivity is not stable, and transforms into n-type gradually in the dark. Interestingly, the n-type ZnO:N could revert into p-type one in the dark after irradiated by sunlight for several minutes and remained the p-type conductivity under a bright condition. That is very different from a previous result [8], which indicates that a p-type P-doped ZnO reverts to n-type at room temperature after impinged by ultraviolet light, and attributes this change to excessive electrons resulted from UV irradiation and electron mobility much higher than hole mobility.

It is well known that the $(N_2)_o$ forms shallow double donors, while $(N)_o$ forms a shallow acceptor. Based on XPS results mentioned above, the net acceptor concentrations due to N doping alone are estimated to be about 0.4 at% for the as-grown ZnO:N but 0.87 at% for the

860 K annealed ZnO:N, that is attributed to that $(N_2)_o$ concentration decreases faster than N_o concentration with increasing annealing temperature. However, XPS measurement shows that the atomic ratio of Zn to O is 54.5:45.5 in the 860 K annealed ZnO:N, implying that there are many O vacancies (V_o) and Zn interstitial atoms (Zn_i) in the annealed ZnO:N. Obviously, the net acceptors cannot compensate the V_o and Zn_i shallow donors. Therefore, the p-type conductivity of the 860 K annealed ZnO:N cannot be due to N doping completely, but both N-doping and some p-type intrinsic defects, such as, Zn vacancy.

Fig. 2a shows photoluminescence spectrum of the 860 K annealed ZnO:N at room temperature, revealing a weak and broad ultraviolet emission at 3.25 eV and three strong visible light emissions at about 3.05, 2.29 and 2.06 eV, respectively, The 3.05 eV band is attributed to electron transition from conduction band to single ionized Zn vacancy (V_{Zn}^-) [9]. The 2.29 eV are assigned to be single ionized O vacancy (V_o^+) [10]. The origination of orange emission band at 2.06 eV has been an argumentative problem, it is usually due to Zn_i [11], or single ionized O interstitial (O_i^-) [10] or Zn_i-related defects (or called Zn_i complex) [12] in the previous literatures. When the as-grown ZnO:N is annealed at 860 K under oxygen ambient, PL measurement shows that ultraviolet emission at 3.29 eV is very strong while visible emissions become very weak, as shown in Fig. 2b, indicating that crystal quality is improved greatly and the amount of intrinsic defects decreases. Hall measurement shows that the ZnO:N annealed under O_2 ambient behaves stable n-type conduction with resistivity of $7.14 \times 10^3\,\Omega$ cm, carrier concentration of $5.30 \times 10^{14}/\text{cm}^3$ and Hall mobility of $4.87\,\text{cm}^2/\text{V s}$, and its conductivity was not affected by light illumination. Above results indicate that the p-type conduction induced by irradiation of sunlight is related to crystal quality and the amount of the intrinsic defects.

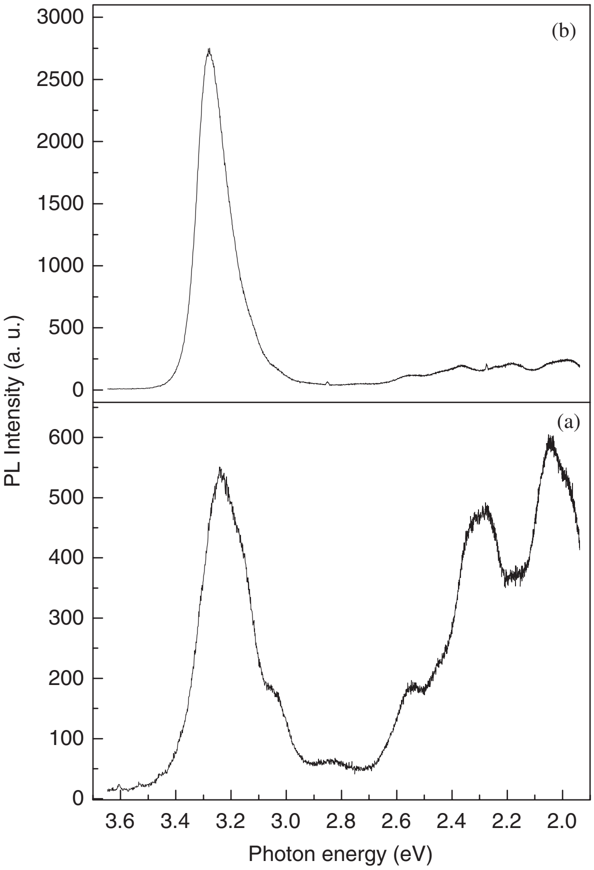

Fig. 2. Photoluminescence spectra of the ZnO:N annealed at 860 K (a) under 10^{-4} Pa and (b) O_2 ambient.

Based on above discussions, it is suggested that p-type conduction of the 860 K annealed ZnO:N is attributed to both N_o and some p-type intrinsic defects, such as V_{Zn}^{-1}, and its stability is related to crystal quality. While influence of illumination on conduction behavior of 860 K annealed ZnO:N is related to the intrinsic defects V_{Zn}, V_0^+ and defect responsible to orange emission. The electrons in valence band may transit to the deep level of the defects and localize around the defects metastably when the annealed ZnO:N is irradiated by sunlight, generating holes in the valence band. These holes may be enough to compensate electrons cased by shallow donors, resulting in p-type conductivity of the ZnO.

4. Conclusions

The ZnO:N films were deposited on quartz glass substrates at 510 K by reactive rf magnetron sputtering of a ZnO target with N plasma. The as-grown ZnO:N shows insulating at room temperature, but behaves p-type semiconducting conductivity with resistivity of $456\,\Omega$ cm, carrier concentration of $1.2 \times 10^{17}\,\text{cm}^{-3}$ and mobility of $0.1\,\text{cm}^2/\text{Vs}$ in the dark after annealed at 860 K for 1 h under 10^{-4} Pa. However, the p-type conduction is not stable in the dark and transforms into n-type gradually. As the n-type ZnO:N was irradiated by sunlight for a few of minutes, it reverted to p-type in the dark and remained p-type conductivity in the brightness. P-type conduction of the 860 K-annealed ZnO:N is due to both N_o and some p-type intrinsic defects, such as V_{Zn}^{-1}, and its stability is related to crystal quality. Effect of illumination on conductivity of the 860 K annealed ZnO:N is related to crystal quality and the intrinsic defects V_{Zn}, V_0^+ and defect responsible to orange emission.

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