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ZnO thin films produced by magnetron sputtering

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Abstract

ZnO thin films were deposited onto glass substrates with direct current (dc) or radio frequency (rf) magnetron sputtering using Zn or ZnO target. SEM and XRD analysis demonstrated that the type of deposition mode, plasma excitation, working pressure and oxygen partial pressure, bias, working distance, and doping could significantly change the quality and microstructure of the films. The electrical conductivity of ZnO films is strongly affected by the deposition mode (dc or rf), crystal structure, chemical composition and microstructure. Photoluminescence of these films were also studied, and the relationships of processing parameters, microstructure, and properties were explored.

Keywords: B. Microstructure; D. ZnO; Thin films; Magnetron sputtering deposition; Conductivity; Photoluminescence

1. Introduction

Zinc oxide, one of the most important binary II–VI compounds, is a direct semiconductor of wurtzite structure. Its minimum energy gap is 3.2 eV at room temperature and 3.44 eV at 4 K [1]. ZnO thin films present many remarkable characteristics due to their large bond strength, good optical quality, extreme stability of excitons, and excellent piezoelectric properties, therefore, they have been studying actively in various fields, and have many potential applications in various technological domains, such as transparent conducting films/electrodes in display devices and solar energy cells, surface and bulk acoustic wave devices (SAW) and acoustic-optical devices, and light-emitting diodes (LEDs) and laser diodes (LDs) [2–5]. Another advantage of zinc oxide relative to other materials is its low price, placing it as a highly potential candidate for industrial applications.

A number of techniques have been used for fabrication of ZnO thin films, including chemical vapour deposition, sol–gel, spray-pyrolysis, molecular beam epitaxy, pulsed laser deposition, vacuum arc deposition, and magnetron sputtering [6–12]. In the present project, we used magnetron sputtering deposition to prepare ZnO thin films. The influences of processing parameters on the structural, electrical and optical properties of thin films were studied and discussed briefly.

2. Experimental

The substrate selected for the deposition was glass slide. The slides with a typical size of ∼12 mm × 10 mm × 1 mm were ultrasonically cleaned in acetone, rinsed in alcohol and then dried in hot air. When the working chamber was pumped down to $\sim 2 \times 10^{-6}$ Torr, a radio frequency (rf) plasma cleaning was conducted for 1.5 h. After that, argon or a mixture of argon and oxygen was introduced. Sputtering was performed with a dc power of 0.25 A, or an rf power of 125/250 W for direct deposition from a ZnO target or reactive sputtering deposition from a Zn target. During deposition, the substrates were rotating with a speed of 3 rpm.

The surface and fractured cross-section morphologies of the thin films were observed with an FEG-SEM (Philips XL-30S); and phase characterisation was carried out with an X-ray diffractometer (Bruker D8) using Cu Kα radiation. Electrical conductivity was measured with a typical four-point electrical resistance probe or by a Hall automatic measuring system using the Van Der Pauw technique. For PL measurements, a continuous wave He–Cd laser (325 nm) with a power density of 1 W/cm^2 was used. The spectra were dispersed by a 0.5 m single grating monochromator

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(SpectraPro-500i) and detected by an air-cooled GaAs photomultiplier.

3. Results and discussions

3.1. Microstructure

3.1.1. Sputtering deposition from a ZnO target

For the direct sputtering deposition from a ZnO target with dc power, the surface morphology showed that with a low Ar working pressure (2.0 mTorr) the surface of the film was not flat, showing the formation of oxide islands among smaller clusters. As the number of oxide islands decreased with increasing pressure, the size of the clusters increased. With an Ar working pressure of 10.0 mTorr, the surface became flat without islands. As the Ar pressure increased further, the grain size did not changed much, but the edge of the grains became less sharp (Fig. 1a and b). ZnO thin films with rf sputtering demonstrated similar features; higher working pressure led to a flatter top surface. In comparison with dc sputtering, rf sputtering resulted in larger clusters but smaller grains inside (Fig. 1c).

3.1.2. Reactive sputtering deposition from a Zn target

Reactive magnetron sputtering deposition was firstly performed using dc power. At the lowest pressure, the film was not uniform; large islands (∼150–250 nm) were presented among smaller clusters (∼70 nm). These islands and clusters consisted of smaller grains (∼10–25 nm), which form a porous columnar structure as observed from the fracture cross-section. As the oxygen partial pressure (pO_2) increased to 1 mTorr, the average grain size increased to ∼29 nm, and the large islands disappeared. When the total and oxygen pressure increased further, a film composed of grains of ∼53 nm was developed. Fracture cross-section morphology showed a more distinct columnar structure, in which voids were still presented. The negative bias appeared to have certain effects on the film morphology. In comparison with the deposition using −50 V, the deposition with a bias of −150 V

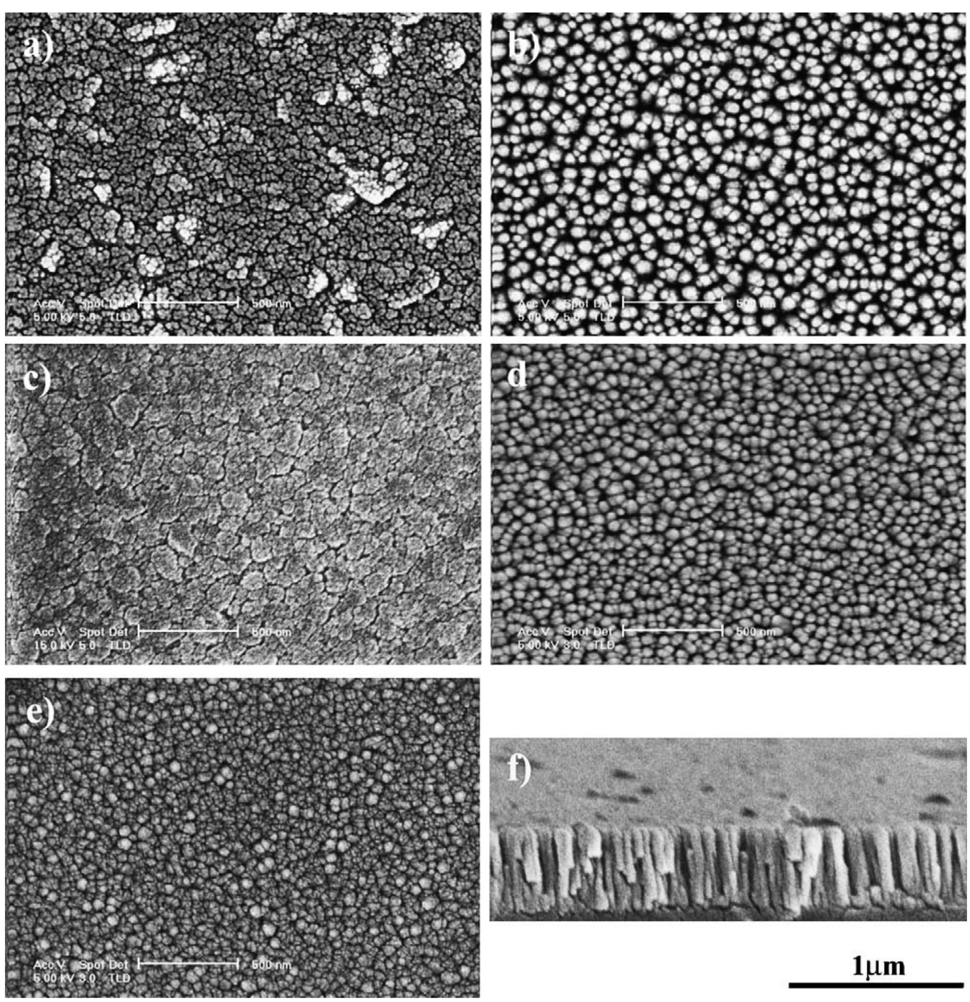

Fig. 1. ZnO thin films produced by magnetron sputtering deposition: (a) ZnO target, dc power, $p\text{Ar} = 2$ mTorr; (b) ZnO target, dc power, $p\text{Ar} = 20$ mTorr; (c) ZnO target, rf power, $p\text{Ar} = 20$ mTorr; (d) Zn + Al target, reactive sputtering, dc power, $P = 5$ mTorr; (e and f) Zn + Al target, reactive sputtering, rf power, $P = 10$ mTorr.

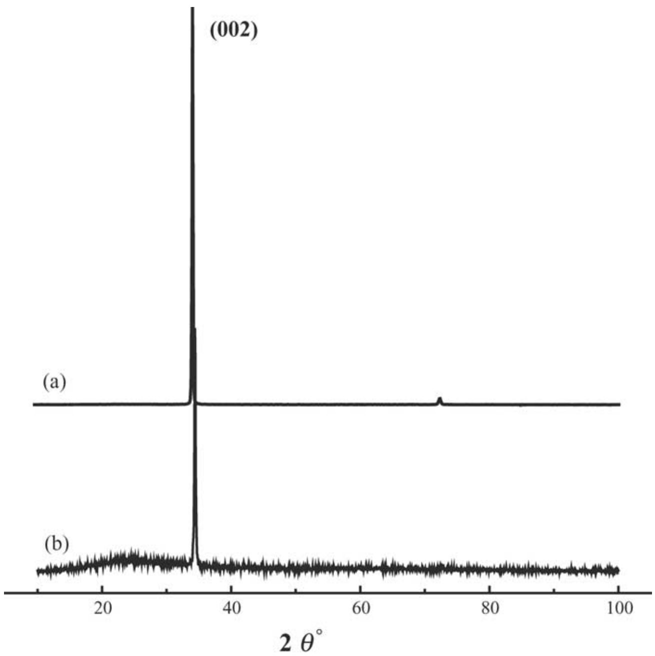

Fig. 2. X-ray diffraction spectra of magnetron-sputtered ZnO thin films: (a) ZnO target, dc sputtered, $p\mathrm{Ar} = 5\,\mathrm{mTorr}$ and (b) Zn + Al target, dc reactive sputtering, $P = 10.0\,\mathrm{mTorr}$.

demonstrated more uniform and denser films, composed of grains with an average size of ∼24 nm.

A small Al sheet was attached onto the Zn target for the deposition of Al-doped ZnO thin films (∼2 at.% Al). In comparison with the undoped films, the Al-doped films were more uniform with smaller grains. In general, the fracture cross-section showed that these fine grains formed a less distinct columnar structure in comparison with the ZnO without Al-doping (Fig. 1d–f).

All films exhibited (0 0 2) preferential orientation with clear peak shape and high intensity, and Al-doping decreased the intensity of (0 0 2) to a certain degree (Fig. 2).

With reactive magnetron sputtering using rf, it was observed that the negative bias applied had certain influence on the uniformity and compactness of the films. The film with a bias of −50 V was more uniform than the other two, while the film with −100 V bias showed the densest structure among these three samples. It was known that an increase in bias voltage could increase the average energy of the bombarding ions to the growing film, therefore, enhancing the adatom mobility on the surface. Undoped ZnO films showed regular grain shape, indicating that Al dopant might have negative influence on the crystal growth. Decreasing the distance between substrate and target did not change the grain size significantly, but led to the formation of small clusters, which were composed of smaller grains. Its fracture cross-section showed this film had distinct columnar structure with significantly reduced number of pores/voids. With rf excitation, strong (0 0 2) preferential orientation was also achieved on all the samples.

3.1.3. Processing and microstructure

Obviously, direct sputtering deposition from oxide target using dc or rf power was significantly influenced by the working pressure in the chamber. Higher Ar pressure led to flatter film surface and more regular grain shape. It is supposed that at a low working pressure, sputtering yields of ZnO was low; film growth on the substrate mainly depends on the further development of the relatively large and stable clusters since the nucleation rate is limited due to the short supply of particles. This leads to the generation of large oxide islands. At a high pressure, the plasma intensity is high enough to strike out a large amount of particles from the target, thus nucleation and growth of film will be fully guaranteed, leading to a smooth and uniform surface.

Reactive sputtering deposition from a metal target is a complex process in comparison with direct deposition. It highly relies on the generation, absorption and reaction of the reactive species (atoms or ions). The depositing material must react rapidly or it will be buried by the subsequent depositing material. Therefore, the reaction rate is an important factor, and is determined by the reactivity of the species, their supply, and the substrate temperature.

In this study, it was observable that the quality and microstructure of the films changed with the total and oxygen pressure. It is believed that, at a low $p\mathrm{O}_2$, the amount of Zn arrival on the substrate surface is sufficiently high. High nucleation rate and low growth rate of the existing particles led to a film with fine grains. The supply of oxygen may not be sufficient. Formation of zinc oxide with good stoichiometry requires continuous transport of oxygen from the gas phase and the complete reaction between Zn and O. Thus, a stable growth of ZnO grains with perfect crystallinity may not be able to realise. With an increased $p\mathrm{O}_2$, the generation of Zn species would be inhibited, whereas output of oxygen ions might be increased, larger grains could therefore be formed. While further increasing $p\mathrm{O}_2$ and total pressure increases the generation of film components, a lower nucleation rate and higher growth rate would occur, resulting in larger grain size in the film. Due to the sufficient supply of oxygen, grains will be able to grow stably; the number of oxygen vacancies could also be reduced; and films with better crystallinity would form.

The results also showed that the rf films had better quality than dc films. It is believed that rf excitation has a higher degree of ionisation/dissociation, which leads to a higher oxidation rate at the substrate surface due to the larger ratio of O to Zn that arrive at the substrate. rf discharge also leads to a more intensive ion bombardment of the growing film, both by higher ion densities and energy [13]. This additional energy input into the film causes increased surface mobility of the adatoms, which improves the film perfection.

ZnO films showed porous to a relatively dense columnar structure, especially for those with reactive sputtering deposition. This might be partially caused by the low homologous temperature, T/T_m [14]. Since the substrate was not intentionally heated, only the energy flow from the sputtered

Table 1
Resistivity of ZnO thin films deposited by magnetron sputtering

Number	P (mTorr)	Power	Target	Resistivity (Ω cm)
1	5.0/Ar	dc	ZnO	3.7×10^5
2	10.0/Ar	dc	ZnO	1.0×10^6
3	10.0/Ar	rf/125 W	ZnO	0.0306
4	20.0/Ar	rf/125 W	ZnO	1.06
5	10.0/Ar	rf/250 W	ZnO	0.009
6	2.0/Ar:O_2 = 6:4	dc	Zn, reactive	2.0×10^6
7	10.0/Ar:O_2 = 9:1	rf/250 W	Zn + Al, reactive	0.137

particles and the heat of formation of the oxide could contribute to the substrate heating up. The accurate temperature of the substrate was not measured, however, according to the previous studies, it should be lower than 100–150 °C. This gives $T/T_m = 0.04$–0.06, and a dense structure may not be achieved easily.

However, the results showed that a decrease of the substrate to target distance promoted the formation of dense columnar structure. This is hard to explain [15]. The films by dc sputtering from ZnO target showed a denser columnar structure according to our studies. It was reported that ion current (density) increased with decreasing substrate-to-target distance. Thus, it is supposed that with a high ion current drawn at the substrate, the reaction between Zn and O could well complete. Additionally, high ion bombardment could lead to the densification of the film, and transfer more energy to the substrate, which could increase the temperature of the substrate and improve the density of the film.

3.2. Electrical property

The measured conductivity of a number of ZnO films is shown in Table 1. In general, some phenomena could be observed:

Firstly, the ZnO thin films with good conductivity show that the (0 0 2) *d*-space is close to that of the standard power sample, while film with poor conductivity has a large *d*-space value. It was revealed that the *d*-space and log ρ has a good linear relationship (Fig. 3). The change of *d*-space for (0 0 2) peak suggests that the unit cell might be elongated along the *c*-axis, and stress existed in the plane. The stress in the film was then derived and plotted against log ρ, yielding a similar linear relation [16]. This indicated that the stress generated in the film during deposition had certain influence on the electrical properties.

Secondly, almost all films prepared by dc sputtering from the Zn or ZnO target have high resistivity, while the films with rf sputtering have low resistivity to the level of 10^{-3} Ω cm. In rf sputtering, breakdown ionisation occurs by heating electrons in gas plasma with a fluctuating field, an effect that is not present with a constant dc field. In comparison with dc discharge, rf excitation leads to a self-sustained and stable sputtering process, suitable for poor conducting materials. A homogeneous distribution of grains with a good crystalline quality results in a higher carrier mobility, and therefore a higher conductivity [16].

Thirdly, SEM observations suggest that the conductivity of the films may be affected by their microstructure. From the cross-sectional micrographs, it can be seen that the oxide grains in the dc films grow mainly along the *c*-axis to form a good columnar structure, while the rf films grow also along *c*-axis, but the grains grew with less columnar structure and much diverse orientations. The surface morphology shows that the rf films have denser feature (smaller gaps between clusters) than the dc films. Dense microstructure with diverse growth direction seems helpful to electron conduction.

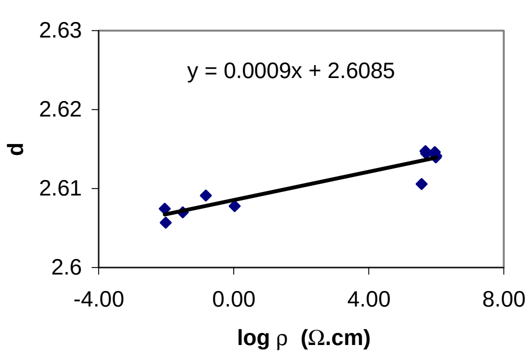

Fig. 3. The relation between (0 0 2) *d*-spacing and conductivity of ZnO films.

3.3. Photoluminescence (PL) property

Fig. 4 shows a typical PL spectrum of the ZnO films deposited on glass substrate under different conditions. Normally, rf films showed better stimulated emission properties than the dc films. A sharp emission peak dominating at the

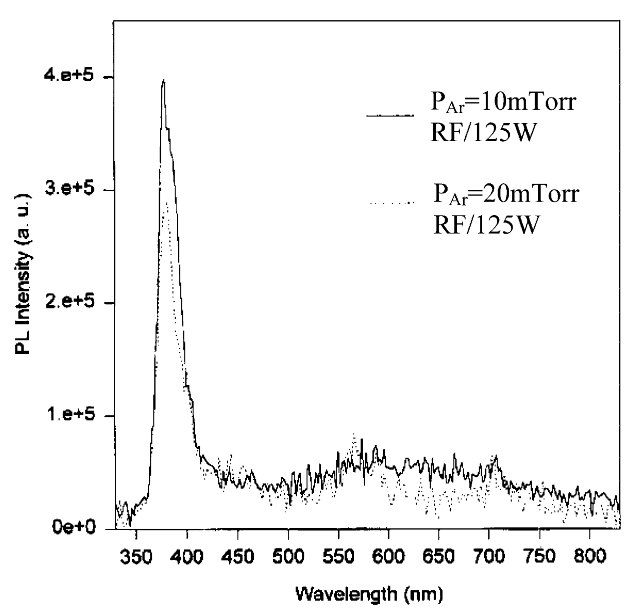

Fig. 4. Typical PL spectra of ZnO films deposited on glass substrates.

wavelength around 380 nm was observed, corresponding to the UV near-band edge emission. A relatively broad emission of 510–700 nm was also found, and showed certain relation with processing conditions. These results are quite close to those indicated in the earlier reports [17,18]. It was reported that the blue/green emission from ZnO is associated with defect-related states, located in the band gap of ZnO, involving oxygen vacancies [19], oxygen interstitials [20], Zn vacancies [21], Zn interstitials [22] and/or antisite defect O_{Zn} [23]. The stronger UV emission from the rf-sputtered films then indicates that the stoichiometry and quality of the ZnO films, critical to its optical properties, could be controlled by the deposition conditions. The relation between processing and property will contribute to a better understanding of the origin of luminescence from ZnO.

4. Conclusions

ZnO thin films were deposited onto glass substrate with direct or reactive sputtering process using dc or rf power. Direct sputtering deposition from oxide target was highly influenced by the pressure level in the working chamber. A high pressure produced films with smooth and regular morphological features. Reactive sputtering deposition was dependent on the oxygen partial pressure and total pressure. A high pressure led to the formation of films with large grain size and good crystal quality. ZnO films deposited with rf power were generally better than the films with dc deposition. It is believed that with a good control of processing conditions, such as the total and oxygen partial pressure, type of plasma excitation, bias voltage, target to substrate distance, and doping, thin films with optimised microstructure and high conductivity could be obtained.

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References

[1] L.I. Berger, Semiconductor Materials, CRC Press, Boca Raton, 1997.
[2] F.R. Blom, F.C.M. Van de Pol, G. Bauhuis, T.J.A. Popma, R.F. planar magnetron sputtered ZnO films: II. Electrical properties, Thin Solid Films 204 (1991) 365.
[3] W.E. Devaney, W.S. Chen, J.M. Stewart, R.A. Mickelsen, Structure and properties of high efficiency ZnO/CdZnS/CuInGaSe_2 solar cells, IEEE Trans. Electron Devices 37 (1990) 428.
[4] F.S. Mahmood, R.D. Gould, M.H. Salih, D.C. properties of ZnO thin films prepared by R.F. magnetron sputtering, Thin Solid Films 270 (1995) 376.
[5] C.R. Gorla, N.W. Emanetoglu, S. Liang, W.E. Mayo, Y. Lu, M. Wraback, H. Shen, Structural, optical, and surface acoustic wave properties of epitaxial ZnO films grown on (0112) sapphire by metalorganic chemical vapor deposition, J. Appl. Phys. 85 (1999) 2595.
[6] B.S. Li, Y.C. Liu, Z.S. Chu, D.Z. Shen, Y.M. Lu, J.Y. Zhang, X.W. Fan, High quality ZnO thin films grown by plasma enhanced chemical vapor deposition, J. Appl. Phys. 91 (2002) 501.
[7] M.J. Alam, D.C. Cameron, Preparation and properties of transparent conductive aluminum-doped zinc oxide thin films by sol–gel process, J. Vac. Sci. Technol. A19 (2001) 1642.
[8] A.J.C. Fiddes, K. Durose, A.W. Brinkman, J. Woods, P.D. Coates, A.J. Banister, Preparation of ZnO films by spray pyrolysis, J. Cryst. Growth 159 (1996) 210.
[9] T. Ohgaki, N. Ohashi, H. Kakemoto, S. Wada, Y. Adachi, H. Haneda, T. Tsurumi, Growth condition dependence of morphology and electric properties of ZnO films on sapphire substrates prepared by molecular beam epitaxy, J. Appl. Phys. 93 (2003) 1961.
[10] Y.R. Ryu, S. Zhu, J.D. Budai, H.R. Chandrasekhar, P.F. Miceli, H.W. White, Optical and structural properties of ZnO films deposited on GaAs by pulsed laser deposition, J. Appl. Phys. 88 (2000) 201.
[11] T. Minami, S. Ida, T. Miyata, High rate deposition of transparent conducting oxide thin films by vacuum arc plasma evaporation, Thin Solid Films 416 (2002) 92.
[12] K.H. Kim, K.C. Park, D.Y. Ma, Structural, electrical and optical properties of aluminum doped zinc oxide films prepared by radio frequency magnetron sputtering, J. Appl. Phys. 81 (1997) 7764.
[13] D.M. Mattox, Handbook of Physical Vapor Deposition (PVD) Processing: Film Formation, Adhesion, Surface Preparation and Contamination Control, Westwood, Noyes Publications, New Jersey, 1998.
[14] B.A. Movchan, A.V. Demchishin, Structure and properties of thick vacuum-condensates of nickel, titanium, tungsten, aluminum oxide, and zirconium dioxide, Phys. Met. Metallogr. 28 (1969) 653.
[15] P.J. Kelly, R.D. Arnell, Development of a novel structure zone model relating to the closed-field unbalanced magnetron sputtering system, J. Vac. Sci. Technol. A16 (1998) 2858.
[16] R. Cebulla, R. Wendt, K. Ellmer, Al-doped zinc oxide films deposited by simultaneous rf and dc excitation of a magnetron plasma: relationships between plasma parameters and structural and electrical film properties, J. Appl. Phys. 83 (1998) 1087.
[17] S. Im, B.J. Jin, S. Yi, Ultraviolet emission and microstructural evolution in pulsed-laser-deposited ZnO films, J. Appl. Phys. 87 (2000) 4558.
[18] W. Gao, Z.W. Li, R. Harikisun, S.S. Chang, Zinc oxide films formed by oxidation of zinc under low partial pressure of oxygen, Mater. Lett. 57 (2003) 1435.
[19] I.Y. Prosanov, A.A. Politov, Intrinsic defects and luminescence of zinc oxide, Inorg. Mater. 31 (1995) 663.
[20] M. Liu, A.H. Kitai, P. Mascher, Point defects and luminescence centers in zinc oxide and zinc oxide doped with manganese, J. Lumin. 54 (1992) 35.
[21] A. Ortiz, C. Falcony, J. Hernandez, M. Garcia, J.C. Alonso, Photoluminescent characteristics of lithium-doped zinc oxide films deposited by spray pyrolysis, Thin Solid Films 293 (1997) 103.
[22] E.G. Bylander, Surface effects on the low-energy cathodoluminescence of zinc oxide, J. Appl. Phys. 49 (1978) 1188.
[23] B.X. Lin, Z.X. Fu, Y.B. Jia, G.H. Liao, Defect photoluminescence of undoping ZnO films and its dependence on annealing conditions, J. Electrochem. Soc. 148 (2001) G110.