Electroluminescence of zinc oxide thin-films prepared via polymeric precursor and via sol–gel methods

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Abstract

Zinc oxide (ZnO) is an electroluminescent (EL) material that can emit light in different regions of electromagnetic spectrum when electrically excited. Since ZnO is chemically stable, inexpensive and environmentally friendly material, its EL property can be useful to construct solid-state lamps for illumination or as UV emitter. We present here two wet chemical methods to prepare ZnO thin-films: the Pechini method and the sol–gel method, with both methods resulting in crystalline and transparent films with transmittance >85% at 550 nm. These films were used to make thin-film electroluminescent devices (TFELD) using two different insulator layers: lithium fluoride (LiF) or silica (SiO_2). All the devices exhibit at least two wide emission bands in the visible range centered at 420 nm and at 380 nm attributed to the electronic defects in the ZnO optical band gap. Besides these two bands, the device using SiO_2 and ZnO film obtained via sol–gel exhibits an additional band in the UV range centered at 350 nm which can be attributed to excitonic emission. These emission bands of ZnO can transfer their energy when a proper dopant is present. For the devices produced the voltage–current characteristics were measured in a specific range of applied voltage.
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1. Introduction

Solid-State Lighting (SSL), which is illumination using a semiconductor, has been investigated as an alternative for fluorescent lamps in illumination [1]. SSL has some advantages over fluorescent lamps because it has lower power consumption and higher luminance, and it is environmentally friendly since it is mercury free. As sources of illumination, SSL utilizes light-emitting diodes (LEDs) that can be the traditional semiconductor monocrystals or thin-film electroluminescent devices (TFELDs), which can be divided in three categories: organic light-emitting diodes (OLEDs), polymer light-emitting diodes (POLEDs), and thin-film inorganic compounds [1–8]. Because film deposition is more versatile than crystal growth, TFELDs are preferred over monocrystal LEDs. While OLEDs and POLEDs have the advantage of higher intensity emission compared to TFELDs based on inorganic compounds, the inorganic compounds have the advantage of longer lifespan.

Zinc oxide (ZnO) is an old material facing novel applications due to its optical [8], electrical, and structural properties, especially when it is nanosized. ZnO is a semiconductor with wide bandgap (3.2–3.5 eV) that makes it a promising material for photonics application in the ultra violet (UV) and blue region of the electromagnetic spectrum. The high exciton-binding energy (60 meV) allows efficient excitonic emission even at room temperature [8]. The electroluminescence generates UV and visible light from ZnO. Some electroluminescent devices with different architectures and different preparation methods have been reported in the literature using ZnO as emitter, like varistor type devices [9], heterojunctions [10], homojunctions [11], ZnO/polymer composite [12] and AC-TFELD [13]. These devices were prepared by physical deposition techniques or solid state reaction. Two or three emission bands are observed in these studies, the UV excitonic band emission around 380 nm and in the visible or near infrared range.

In this work we present the results of electroluminescence of ZnO prepared via two different wet chemical routes: the sol–gel and polymeric precursor methods. The devices were constructed following the versatile TFELD architecture using silica (SiO_2) or lithium fluorite (LiF) as insulator layers.

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2. Experimental

The precursor solution via the polymeric precursor method (Pechini method) [14] was synthesized as follows: a solution of citric acid in ethylene glycol was prepared, and then a solution of zinc nitrate in ethanol was added to the system. The molar ratio was fixed in 1.0 Zn^{2+}: 2.5 citric acid: 8.0 ethylene glycol. This solution was maintained at 80 °C and stirred continuously. Viscosity of the resulting precursor solution was around 27 cP (27×10^{-3} Pa s). The sol–gel precursor solution was prepared as follow: 1.10 g of zinc acetate dihydratate was dissolved in 50 mL of anhydrous ethanol. This solution was heated under reflux and stirred with a magnetic bar for 3 h, then it was cooled at about 2 °C and stirred in an ultrasound baths while 0.29 g of lithium hydroxide was added to it [15].

Fig. 1 shows the structure of the devices assembled in this work. Commercial glass covered with indium-thin oxide (ITO) was used as substrate. Then, a film of insulator, silica (SiO_2) or lithium fluorite (LiF) was deposited. The silica layer was grown over the ITO substrate by rf-magnetron sputtering achieving a final thickness of 90 nm. LiF layer was deposited by using electron beam technique with a final thickness of 50 nm confirmed by profilometer measurements. The precursor solutions were then spun over the substrate for 60 s at 7000 rpm for Pechini or 3500 rpm for sol–gel precursors, followed by a thermal treatment at 500 °C or 300 °C for Pechini or sol–gel precursors, respectively, during 30 min. Just one layer of the Pechini precursor was deposited achieving a final ZnO film thickness of 500 nm, measured after annealing. For the sol–gel precursor it was necessary to deposit 20 layers to achieve a final ZnO film thickness of 300 nm, measured after annealing. Over the ZnO films, a second layer of insulator was deposited as described above. Finally, the aluminum electrode (150 nm of thickness) was deposited by electron evaporation. The effective area of the device is about 25 mm^2. A DC power supplier was used to apply different voltages to the devices, while their electroluminescence spectra were recorded by a spectrofluorimeter PTI 1469 equipped with a photomultiplier tube.

3. Results and discussion

The crystalline structure of the films was investigated by X-ray diffraction. Fig. 2(a) shows the diffractogram of the ZnO film prepared via Pechini method, and Fig. 2(b) shows the diffractogram of ZnO film prepared via sol–gel method. It is possible to identify the characteristic peaks of the wurtzite ZnO structure in both cases, according to the JCPDS-ICDD 36-1451
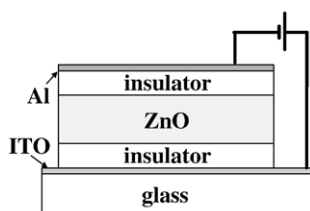

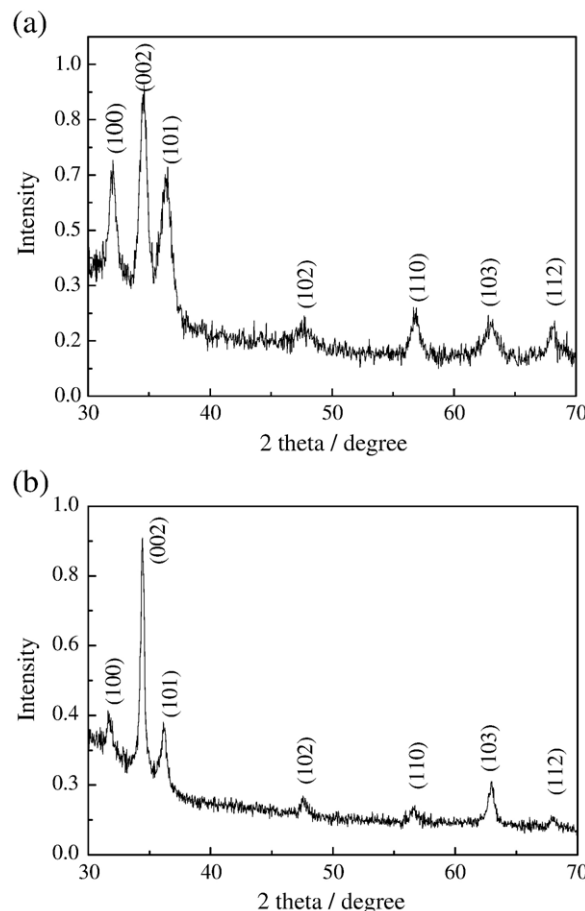Fig. 1. Schematic structure of the TFEL device.

Fig. 2. X-ray diffractogram of the ZnO film obtained (a) via the Pechini method, and (b) via the sol–gel method.

data base, indicating that after the thermal treatment the precursor solutions were turned into crystalline ZnO. The results show that the peak (002) is bigger than the others especially in the sol–gel case, indicating a preferential growth along the c-axis. This is probably due to the way as the sol–gel film is grown. In fact, this film is constituted by 20 layers each one thermally treated before the deposition of the subsequent, increasing the orientation effect.

Both films are highly transparent at the visible range with transmittance >85% at 550 nm, and they show intense energy absorption for wavelengths less than 380 nm, as shown in Fig. 3. The optical band gap for the two films was calculated by the Tauc method [16,17], and the values found were 3.27 eV and 3.26 eV for the ZnO film obtained via Pechini method and sol–gel method respectively. Absorption spectra and calculated optical gap of the two films do not show considerable difference indicating that they are optically similar.

The electroluminescence spectra as function of applied DC-voltage of devices using ZnO obtained via Pechini method are shown in Fig. 4. Fig. 4(a) refers to the device using LiF while Fig. 4(b) refers to device using SiO_2, as insulator layers. The electroluminescence intensity increases with the applied voltage for both devices achieving a maximum with a voltage of 23.3 V and 17.3 V for LiF and SiO_2, respectively. In both
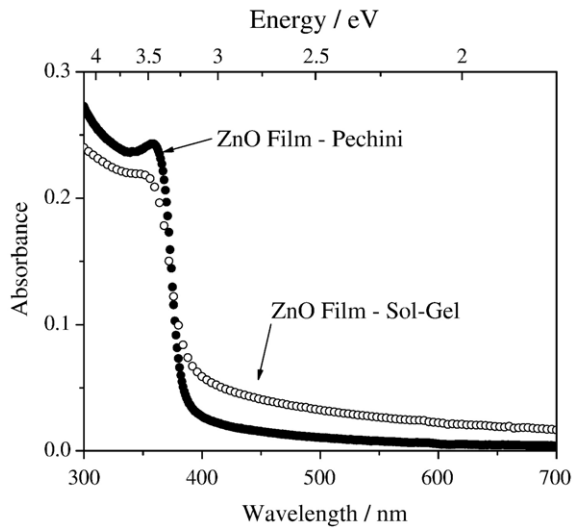
Fig. 3. UV–Vis absorption spectrum of the ZnO film obtained via (a) the Pechini method, and (b) the sol–gel method.
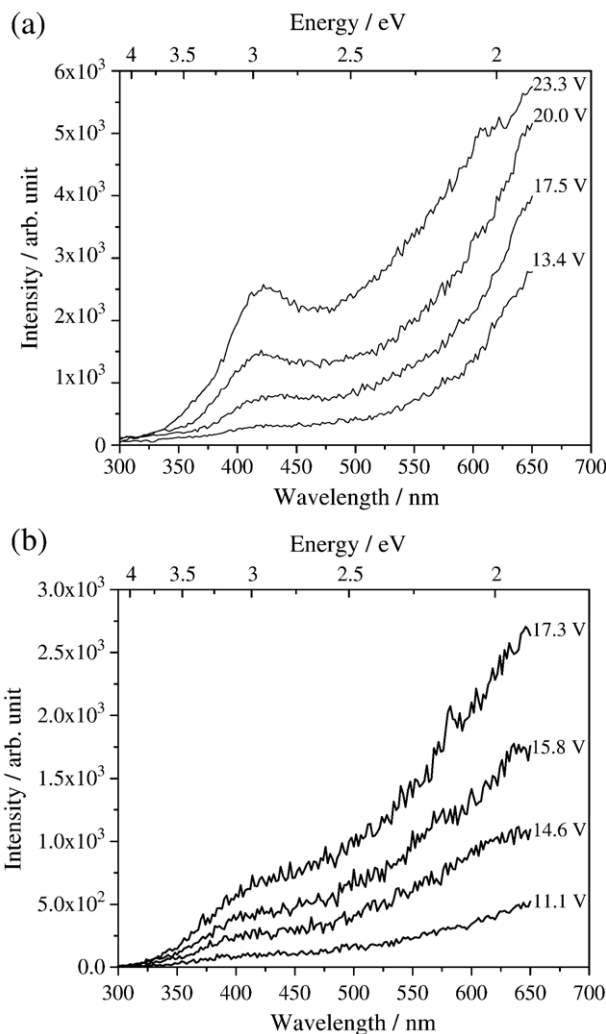

Fig. 4. Electroluminescence spectra of ZnO films at different applied voltage. ZnO films obtained via the Pechini method using (a) LiF as insulator layer, and (b) SiO$_2$ as insulator layers.

cases the maximum electrical field which can be applied is of the order of 4×10^5 V/cm. Any attempt to increase the voltage over these values results in a decrease in the electroluminescence intensity. The effect is associated to the degradation of the aluminum electrode due to the high electric field applied. The difference between the maximum applied voltage in each case is related to the dielectric constant of the two insulator materials ($\varepsilon_{LiF} \sim 9.0$, $\varepsilon_{SiO_2} \sim 3.8$), but also related to the inhomogeneity of the layer. In all spectra there are two emission bands, one centered at 420 nm (2.95 eV) and the other at longer wavelength with maximum around 680 nm (1.82 eV). Unfortunately due to a limitation of the equipment, it was not possible to detect the entire band in the IR region. The photoluminescence spectrum of a Pechini ZnO film, presented in Fig. 5, which was recorded with a different equipment, shows a wide band covering part of near infrared region when the sample is excited with $\lambda = 370$ nm. Fig. 5 shows that a band centered at 435 nm (2.85 eV) is also present, and the origin of the electroluminescence band centered at 420 nm and observed in Fig. 4 must be the same. The origin of photo- and electroluminescence in ZnO is a result of the recombination of the electron-hole pair. In electroluminescence this pair is generated by the impact of hot electrons injected in the semiconductor layer. When the electron in the valence band is excited to the conduction band it can be trapped in a shallow level and then recombine with the hole left in the valence band, this process give rise to the band centered at 420 nm. This band is more evident in the device using LiF than in the device using SiO$_2$ as insulator layers. The less energetic band is a result of the recombination of the excited electrons trapped in deep levels to the valence band or electrons trapped in shallow level to deep levels. The presence of deep levels is dependent on structural defects and how the sample was prepared [18].

Fig. 6 shows the electroluminescence spectra of the devices using ZnO obtained via sol–gel method. The emission spectra of the device using LiF are shown in Fig. 6(a) and although this device has the lower emission intensity, it exhibits the same wide band feature with no defined maximum. The spectra of the
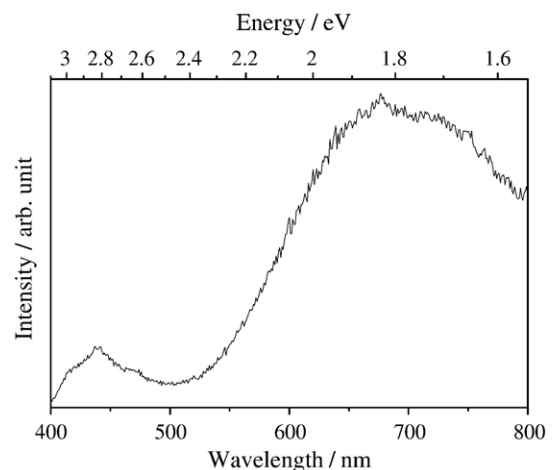

Fig. 5. Photoluminescence of ZnO powder obtained via the Pechini method excited at 370 nm (band-gap).
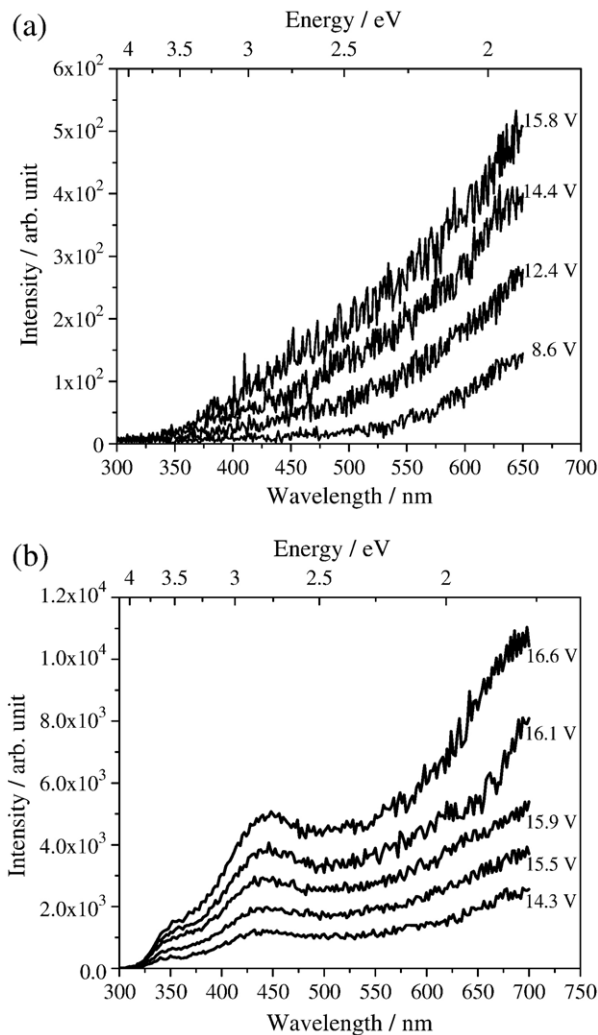
(a)

(b)

Fig. 6. Electroluminescence spectra of ZnO films at different applied voltage. ZnO films obtained via the sol–gel method using (a) LiF as insulator layer, and (b) SiO_2 as insulator layers.
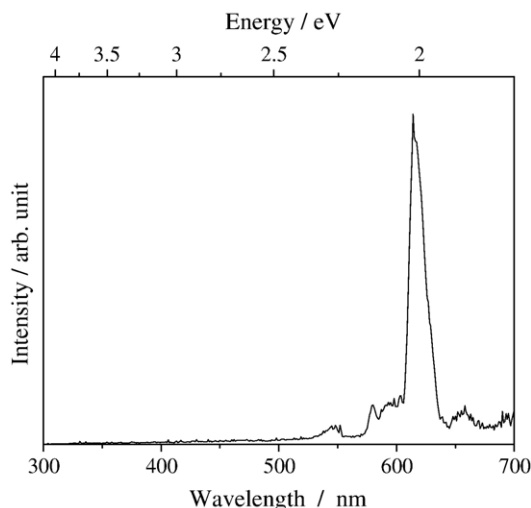

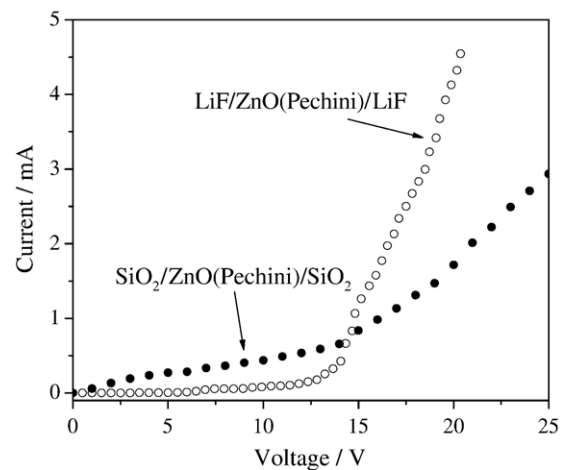Fig. 7. Electroluminescence of thin-film ZnO:Eu (5 at.%) at 19.9 V [19].

Fig. 8. Voltage–current curves of the devices. ZnO films obtained via the Pechini method using LiF and SiO_2 as insulator layers.

device using SiO_2 are shown in Fig. 6(b). Here, besides the two emission bands previously discussed, there is one more band in the UV region, with maximum around 350 nm (3.54 eV). It is generally accepted that this near-edge-band (NBE) UV emission is of excitonic nature and is a result of the radiative annihilation of free and bound excitons [11]. This could be related to the smaller particle size of the ZnO obtained via sol–gel method compared to the particle size of ZnO obtained via Pechini method [14,15]. Fig. 7 shows an electroluminescent spectrum of europium doped ZnO device obtained via Pechini method indicating that when properly doped, the energy of the emission bands of ZnO can be efficiently transferred to the dopand, which will then emit [19].

The voltage–current (I–V) curves for the device based on ZnO obtained via the Pechini precursor solution are shown in Fig. 8. These I–V curves indicate the diode behavior of the devices, and they do not differ considerably from the behavior of those devices based on ZnO obtained via sol–gel method. From the curves is possible to see that the threshold voltage is about 13 V for devices using either LiF or SiO_2.

4. Conclusions

ZnO thin films produced by wet chemical processes were used to fabricate electroluminescent devices. After the thermal treatment, the ZnO films obtained by both methods are crystalline and they show high transmittance in the visible range ($T > 85\%$ at 550 nm). These films were used as active layer in a TFELD architecture that used two different insulator layers: LiF and SiO_2. All four electroluminescent devices showed at least two wide emission bands covering the visible and near IR-region, which are attributed to ZnO recombination of the pair electron-hole. The device (ITO/SiO_2/ZnO(sol–gel)/SiO_2/Al) exhibited an additional band in the UV region around 350 nm (3.54 eV). This near-edge band could be attributed to excitonic emission and is probably related to the smaller particle size of ZnO obtained via the sol–gel method. The energy of these emission bands can be transferred to a proper dopand like europium. In conclusion, this work demonstrates that the two

wet chemical methods for preparation of precursor solutions for ZnO, the Pechini method and the sol–gel method, can be suitable to obtain transparent ZnO thin-films. This films have been used to make TFEL-type devices.

Acknowledgments

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