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Influence of deposition temperature (T_s), air flow rate (f) and precursors on cathodoluminescence properties of ZnO thin films prepared by spray pyrolysis

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Abstract

Semiconducting metal oxide such as ZnO films were prepared by the spray pyrolysis technique on glass substrates. The cathodoluminescence properties of these films were investigated with respect to deposition temperature (T_s) and air flow rate (f). The luminescent films had a polycrystalline hexagonal wurtzite-type structure. Cathodoluminescence intensity was critically dependent on substrate temperature and spray rate. The best films had three emissions: near ultra-violet (UV) band gap peak at 382 nm, a blue-green emission at 520 nm and a red emission at 672 nm. These films were deposited at optimum condition: $T_s = 450\,°C$ and $f = 5$ ml/min.

Keywords: Spray pyrolysis; Cathodoluminescence

1. Introduction

A^{II}–B^{VI} compounds, such as transparent and conducting oxides films, have been attracting ample attention as starting material for electro-luminescent devices because of their high visible transmittance and low electrical resistivity in the visible region. Zinc oxide (ZnO) is one of the few metal oxides, which can be used as a transparent conducting material. It has some advantages over other possible materials such as In_2O_3–Sn, $CdSnO_4$, or SnO_2, due to its unique combination of interesting properties: non-toxicity, good electrical, optical and piezoelectric behaviour, high stability in a hydrogen plasma atmosphere and its low price [1–3]. So, ZnO is a good candidate to

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substitute indium tin oxide (In_2O_3:Sn) and tin oxide (SnO_2), in conductive electrodes of amorphous silicon solar cells. Furthermore, ZnO has the same crystal structure as GaN: wurtzite crystal structure and direct wide band gap. It is closely lattice matched to GaN. ZnO therefore offers potential as a substrate material on which high-quality GaN may be grown. The room temperature band gap of ZnO is 3.3 eV with emission in ultra-violet (UV) region. An outstanding feature of ZnO is its large excitonic binding energy of 60 meV leading to the existence and extreme stability of excitons at room temperature and/or even higher temperatures [4–7]. These characteristics have generated a wide series of applications for example, as gaz sensors [8], surface acoustic devices [9], transparent electrodes [10] and solar cells [3] among others. The preparation of zinc oxide thin films has been the subject of continuous research. Many techniques are used for preparing this transparent conductive ZnO such as: RF sputtering [11], evaporation [12], chemical vapour deposition [13], ion beam sputtering [14] and spray pyrolysis [15–18]. Among these methods spray pyrolysis has attracted considerable attention due to its simplicity and large scale with low-cost fabrication. Additionally, by using this technique one can produce large area coatings without the need of ultra high vacuum.

Some papers dealing with the influence of different process parameters of the intrinsic and doped ZnO films by spray technique have been published [19–22]. The investigation on their luminescence remains very limited, especially the cathodoluminescence. However, band-edge photoluminescence in polycrystalline ZnO has not received as much attention as the bulk material because the band-edge photoluminescence is usually weaker and lacks the fine structure of the bulk crystals [23,24]. Nevertheless, a study of the photoluminescence structure of this material is interesting, because it can provide valuable information on the quality and purity of the material [25]. Polycrystalline films may also have different photoluminescence mechanisms as compared to the bulk material.

In this paper, we describe the effects of different process parameters such as substrate temperature, air flow rate and precursors of undoped ZnO films prepared by spray pyrolysis on glass substrate. Several cathodoluminescence bands and the corresponding emission processes are identified. It is also shown that SP is an adapted technique to achieve ZnO films with a quality comparable with that of transparent conducting oxide thin films prepared by other techniques.

2. Experimental details

The spray pyrolysis experimental set-up and the details on the procedure applied for the deposition of the investigated ZnO thin films has been described elsewhere [21]. It can be briefly reminded that the spraying bath consists of a 0.05 M aqueous solution of Fluka $ZnCl_2$ product. This bath is always buffered by a small amount of hydrochloric acid. The nozzle is directed towards a substrate (distance nozzle–substrate = 0.45 m) and the air flow rate was varied from 2.5 to 7.5 ml/min. The substrate made of soda lime glass was heated to different temperatures. The same film thickness of 0.5 μm, estimated from the deposition time, is retained. A good agreement is obtained with the value deduced from the cross-sectional images obtained by scanning electron microscopy. The structural aspect was investigated by X-ray diffraction (XRD) using Cu ($K\alpha$) radiation. The cathodoluminescence set-up was a home-made system developed for performing near-field cathodoluminescence microscopy [26]. This one combines a scanning force microscope (SFM) with a field emission scanning electron microscope (FES-EM GEMINI 982 from LEO), the related mechanical details being already reported in Ref. [26]. Since the cathodoluminescence intensity in the near-field regime was under the minimum acceptable level of signal-to-noise ratio, to minimize the noise of the images, we have preferred to collect the photons in the far field mode with a multimode optical fibre (numerical aperture = 0.48) placed close to the sample surface ($\approx$50 μm) [27], by using a stepper piezomotor (Z-movement). Our cathodoluminescence system, in association with a spectrometer (Triax 190 from JOBIN YVON), allows monochromatic cathodoluminescence