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High efficiency white luminescence of alumina doped ZnO

Alban A. Letailleur^{a,b,c,*}, Sergey Yu Grachev^a, Etienne Barthel^a, Elin Søndergård^a, Komla Nomenyo^b, Christophe Couteau^b, Stefan Mc Murtry^b, Gilles Léron del^b, Emilie Charlet^d, Emmanuelle Peter^d

^a Surface du Verre et Interfaces, UMR 125 CNRS/Saint-Gobain, 39 quai Lucien Lefranc, BP 135, 93303 Aubervilliers Cedex, France

^b Laboratoire de Nanotechnologie et d'Instrumentation Optique, Institut Charles Delaunay, CNRS UMR 6279, Université de Technologie de Troyes, 12 rue Marie Curie, BP 2060, 10010 Troyes Cedex, France

^c Laboratoire de Chimie de la Matière Condensée de Paris, UMR CNRS 7574, UPMC—Université Paris VI, Collège de France, 11 place Marcelin Berthelot, 75231 Paris, France

^d Thin Films Division, Saint-Gobain Recherche, 39 quai Lucien Lefranc, BP 135, 93303 Aubervilliers Cedex, France

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ABSTRACT

The application of alumina-doped ZnO (AZO) films as luminescent material for large area lighting sources has been evaluated. Thin films were grown on quartz using magnetron sputtering and subsequently annealed under argon atmosphere in a rapid thermal annealing experiment. Below 550 °C, red-shift of the optical band gap and increase of the visible emission are observed in agreement with Al diffusion and formation of interstitial oxygen atoms. At temperatures higher than 800 °C, diffusion is activated and Ostwald ripening leads to the formation of larger grains and an increase of the crystalline phase. The photoluminescence (PL) intensity is enhanced, specifically in the UV range. As a result the emission spectrum of AZO thin films can be adjusted by the annealing conditions, with equal contributions from the UV and orange parts of the PL spectrum resulting in an efficient white emission as quantified using the color space map of the Commission Internationale de l'Éclairage.

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1. Introduction

Zinc oxide (ZnO) is an abundant and non-toxic oxide, which has been widely used as catalyst, sun screen or for medical applications [1]. A more recent interest focuses on the optoelectronic properties of ZnO. With a direct band gap of 3.37 eV and an exciton binding energy of 60 meV, ZnO is a promising candidate for room temperature ultraviolet optoelectronic devices, such as light emitting diodes [2].

The luminescence of ZnO presents a wide variety of emission lines, with strong dependence to structural details. Photoluminescence (PL) spectra are usually separated in two contributions: a UV-peak around 380 nm and a visible contribution. Whereas the UV line is associated with the exciton recombination, the exact origin of the visible luminescence is still controversial [3]. Defects inside the material act as strong recombination centers and emission bands are generated by donor–acceptor pair transitions. Those defects can be oxygen or zinc vacancies or interstitial atoms, or even pollutants [4].

A large variety of n-dopants can be incorporated inside the ZnO to increase the range of applications from spintronics [5],

ferroelectric layers [6], or transparent conductive oxide [7]. Doping or co-doping the layer (with elements from the groups I, IIIb, or V) modifies the energy levels and is also widely used to adjust the luminescence properties of ZnO thin films, by either shifting or broadening the several emission peak [8]. Al doping leads particularly to a yellow luminescence [9], whereas Li doping is used to adjust the peak position and its intensity [10]. Co-doping of these elements therefore leads to a broad-band yellow–white emission [11]. Obtaining a white luminescence with alumina-doped ZnO (AZO) is therefore a challenge.

There is an emergent need for large lighting sources. To obtain AZO thin films on large areas and achieve a precise control over the doping, solution-based processing (like the sol–gel method) is widely used [12,13]. However, the large solvent content inside the material leads to porosity and reduces coating life-time. Along the physical method used for the AZO deposition, magnetron sputtering emerges as an easy way to coat surfaces at the window scale. The versatility of this method enables the deposition on various substrates such as sapphire [14], silicon [15], or glass [16].

To improve the coating properties after deposition, samples are subsequently annealed. Control over the annealing atmosphere is of great importance to obtain the desired properties. Annealing in air or oxygen generally leads to a strong increase of the visible luminescence and a reduction of the UV peak [17,18]. This can subsequently be recovered by annealing the sample under reducing atmosphere [19]. Furthermore, annealing in vacuum

* Corresponding author at: Surface du Verre et Interfaces, UMR 125 CNRS/Saint-Gobain, 39 quai Lucien Lefranc, BP 135, 93303 Aubervilliers Cedex, France. Tel.: +33 1 48 39 59 56; fax: +33 1 48 39 55 62.

E-mail address: alban.letailleur@saint-gobain.com (A.A. Letailleur).

or under nitrogen leads to a specific increase of the UV part of the spectrum [20].

In applications, fast annealing is a requisite. In this work, we have probed the impact of Rapid Thermal Annealing on the luminescence of AZO thin films on quartz. The films were annealed during 5 min under argon atmosphere at temperatures up to 950 °C. The structural and optical properties of the obtained films were investigated. Impact on the luminescence was determined. In particular we show that white luminescence can be obtained in specific conditions.

2. Materials and methods

The AZO films were grown on quartz substrates (synthetic quartz, Shin-Etsu, Japan) by RF magnetron sputtering from an AZO target (GfE Fremat, Germany). Quartz was chosen as substrate because of its high transparency in the visible and UV ranges and for its chemical stability. The doping amount of Al₂O₃ in the AZO target ranged between 1 and 4 wt%.

Quartz wafers (10 × 10 cm²) were used as received and placed onto a 30 × 30 cm² glass plate into the sputtering chamber. The chamber was evacuated to 10⁻⁶ mbar. Argon was introduced through a mass flow controller and the working pressure was maintained to 8–10 × 10⁻³ mbar. The input power was kept at 2 000 W. The substrates are in translation under the AZO target and the growth rate is 30 nm m⁻¹ min⁻¹.

The thickness of the films was 750 nm as measured with a surface profilometer (DEKTAK 3, USA) and scanning electron microscopy (SEM, LEO DSM 982 Gemini).

The AZO samples were subsequently cut into pieces of 2 × 2 cm² and placed into the annealing oven. The chamber was flushed with argon during 10 min prior to annealing, and the gas flow (50 sccm) was maintained during annealing. The heating time was set to 10 s and the cooling rate was about 5 K s⁻¹. Samples were annealed at different temperatures T_a (between 350 and 950 °C) for various times t_a (between 15 and 300 s).

X-ray diffraction (XRD) film patterns were obtained with a PHILIPS PW1830 diffractometer (θ - 2θ Bragg–Brentano geometry) operating with CuK α radiation (λ = 1.5418 Å) and equipped with a graphite back monochromator.

Optical transmissions of the films were measured under normal incidence by a UV–vis spectrophotometer between 350 and 800 nm. Photoluminescence (PL) spectra were collected at room temperature under normal incidence using a 50 cm focal length spectrometer with a 300 gr/mm grating, coupled to a Peltier-cooled CCD camera. Samples were excited at an incidence angle of 50° using a 325 nm He–Cd laser with an output power of 5 mW. The laser beam was focused to 100 μ m with a 35 mm aspherical lens. The presented spectra were corrected by the spectral responses of the measurement set-up.

3. Results and discussion

3.1. Effect of annealing temperature on the structural properties

Fig. 1a–d presents top views of the surface of the AZO films obtained by SEM, before (a) and after thermal annealing during 300 s at T_a = 650 °C (b), 800 °C (c), and 900 °C (d). The as-deposited film is well crystallized with an average grain size of 40 nm. Fig. 1e presents a side view of the as-deposited film. The film is about 750 nm thick and presents a columnar structure with a lateral size of the columns of the order of 40 nm, which is consistent with the top view [21]. The columns are not perfectly straight because the substrate is moving under the target in the

magnetron chamber during the sputtering deposition. At the beginning of the sputtering, the substrate is not under the target and the flux of atoms arrives at the surface under an angle, which results in the tilt of the columns. Upon translation, the substrate arrived right under the target, and no angle is observed. Finally, when the sample is far away from the target a tilt in the other direction is observed. Thermal annealing at temperatures lower than 750 °C does not induce modifications of the surface morphology and grain size (Fig. 1b). At 800 °C, the grains start growing and an average grain size of 60 and 100 nm is observed after thermal annealing at 800 and 900 °C, respectively. Moreover, the geometry of the grain is also affected by the annealing and a faceting of the grains is observed, with the formation of a 120° angle at the boundary between three grains (shown on Fig. 1d). This increase of the grain size and the modifications in the grain morphology may be induced by Ostwald ripening; zinc oxide diffusion becomes significant at temperatures higher than 800 °C and allows for the formation of larger grains [22].

The crystalline structure of the samples was further investigated by X-ray diffraction (XRD). Fig. 2a presents the diffraction patterns of the films before and after annealing at 950 °C. The diffraction patterns are dominated by a peak at around 34.5° and a smaller one at 74°. These peaks are, respectively, assigned to the [0 0 2] and [0 0 4] orientations [23], demonstrating the marked texture of the film along the *c*-axis of the hexagonal structure in complete agreement with the columnar structure observed by SEM. The inset on Fig. 2a shows the position of the [0 0 2] peak after annealing at various temperatures for t_a = 300 s. A progressive shift to higher 2θ value is observed even at relative low temperatures. It has been previously shown that, after the deposition, the AZO layers are in slight compression [24]. This initial compressive stress along with the compressive thermal stress is relaxed during annealing, due to the formation of a larger crystalline phase. After full thermal treatment the residual stress is tensile, resulting in the shift shown on Fig. 2a [25].

Another evidence of the modification of the crystalline structure is obtained from the shape of the XRD peaks. Fig. 2b presents the peak area and the full-width at half-maximum (FWHM) for the [0 0 2] peak after annealing at various temperatures. As T_a increases, the FWHM decreases, reflecting an increase in the grain size [26]. Very little variations are observed for T_a < 750 °C, while the grain size increases significantly above 800 °C, as previously demonstrated on Fig. 1. On the other hand, At 800 °C (resp. 900 °C), the peak intensity increases by 25% (resp. 60%). This shows the formation of a larger crystalline phase inside the materials.

3.2. Effect of annealing temperatures on the optical properties

The electronic properties of the ZnO samples can be derived from the optical transmission spectrum. The gap energy can be measured using the following formula [27]:

$$Ah\nu = C(E_g - h\nu)^{1/2} \quad (1)$$

where α is the absorption coefficient of the sample, h the Planck constant, ν the frequency of the incident light, E_g the gap energy, and C the constant. Fig. 3 presents the evolution of $(\alpha h\nu)^2$ as a function of the photon energy $h\nu$. For the as deposited sample, the absorption is not sharp and the gap energy is 3.42 eV. After thermal annealing at 350 °C, the gap increases to 3.54 eV. For thermal annealing at higher temperatures, the gap progressively shifts to lower values to finally reach E_g = 3.27 eV. A first possible explanation is a Moss–Burnstein shift due to the progressive reduction of the charge carrier density inside the material with the thermal annealing. In the initial state, the presence of electron

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