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Photoluminescence of chemical bath deposited ZnO:Al films treated by rapid thermal annealing

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Abstract

Aluminum-doped zinc oxide (ZnO:Al) films fabricated by chemical bath deposition are characterized using scanning electron microscopy and photoluminescence (PL) spectroscopy. The impact of rapid thermal annealing (RTA) upon the morphology and luminescence characteristics of ZnO:Al layers is studied in an annealing temperature interval up to 650 °C. The as deposited films consist of high quality microcrystalline grains surrounded by a material of poor quality. RTA at temperatures around 650 °C proves to increase the grain size, enhance the ultraviolet PL with simultaneous suppression of the visible luminescence, and activate the Al donor impurities.

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1. Introduction

Aluminum-doped zinc oxide (ZnO:Al) films are promising for various applications including gas sensors [1], solar cells [2], optical waveguide and exciton related devices [3], transparent conductors in thin-film transistors [4]. The defect chemistry of ZnO:Al films is the key factor defining the application. The properties of such films prove to be strongly dependent on the fabrication method, co-doping species and conditions of postgrowth treatment. A wide variety of synthetic methods has been used to fabricate high quality ZnO:Al thin films, some of which are radio-frequency thermal plasma evaporation [5], pulsed laser deposition [6], chemical vapor deposition [7], metalorganic chemical vapor deposition and sputtering [8]. Over the past years, the method of chemical bath deposition became widely used for the fabrication of ZnO:Al thin films due to its simplicity of preparation, satisfactory stability, low cost equipment and low deposition temperatures.

Annealing is the most important and widely used process for removing the defects and improving the properties of the oxide films. Rapid thermal annealing (RTA) was proposed as an alternative thermal processing solution. The lamp-based RTA systems provide short cycle time and flexibility compared to batch-type furnaces.

Strong demand in thermal load reduction and cycle time reduction made RTA a very popular processing method in recent years [9,10]. In this paper, we report the fabrication of ZnO:Al thin films from an aqueous solution at low temperatures. Undoped films were also grown for comparison purpose. The impact of the RTA on the morphology and luminescence properties of ZnO:Al films is studied.

2. Experimental details

The ZnO:Al films were deposited on Corning glass (Vycor 7913) substrate by chemical bath deposition using a

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beaker placed upon a heater during the growth process. Before the deposition, the substrates were cleaned in dilute HCl (1:5 by volume) for 10 min, and then rinsed in deionized water (DI). After that the glass slides were rinsed in ethanol:acetone (1:1) mixture, DI and dried in a nitrogen flux. The cleaned substrates were immersed in an aqueous-solution bath for definite periods of time in order to fabricate films of desired thicknesses. The aqueous solution comprises a mixture of 0.5 M zinc sulphate ($ZnSO_4$) in 40 ml of DI, 0.005–0.015 M aluminum sulphate ($Al_2(SO_4)_3$) in 10 ml of DI mixed until complete dissolution, then was added 0.5 M ethylenediamine [EN] in 100 ml and diluted to 1 l with deionized water. The pH value of the reaction bath was 9.2 and was raised to 11 by addition of 4 M sodium hydroxide (NaOH). The freshly prepared solutions were mixed thoroughly until complete dissolution. The starting chemical bath prepared in the described manner initially appeared turbid before the addition of sodium hydroxide. The various baths were set up by changing the Zn:Al:[EN] ratios, by adding 100 ml of deionized water in each case. The aqueous bath for sample preparation selected have the following ratios: Zn:Al:[EN] (0.02 M: 1 mM:0.045 M, pH=11). The cleaned glass substrates were vertically fixed in the beaker containing the complex solution. The temperature of the cation precursor was kept at room temperature or at 60 °C during the deposition. The thin films were grown for 0.5 h at 60 °C. After deposition the as grown samples were rinsed in deionized water and dried in air at 150 °C. The film thicknesses have been measured from scanning electron microscope (SEM) cross-section images.

The surface morphology of the ZnO:Al films was studied using a VEGA TS 5130MM, 20 keV scanning electron microscope equipped with an Energy Dispersive X-ray (EDX) system for chemical composition microanalysis. The ratio of Al and Zn in the doped film was investigated by EDX analysis made in plane detection mode.

After the deposition, ZnO:Al films (6mm × 6 mm, 700 nm thickness) were subjected to RTA at different temperatures from 350 to 650 °C, for 20 s under low vacuum (10^{-1} Pa) conditions using the RTA system schematic illustrated in Fig. 1.

An example of wafer temperature profile during 15 s processing at 650 °C is shown in Fig. 2.

Photoluminescence (PL) was excited by the 351.1 nm line of an Ar^+ SpectraPhysics laser and analyzed in a quasi-backscattering geometry through a double spectrometer with

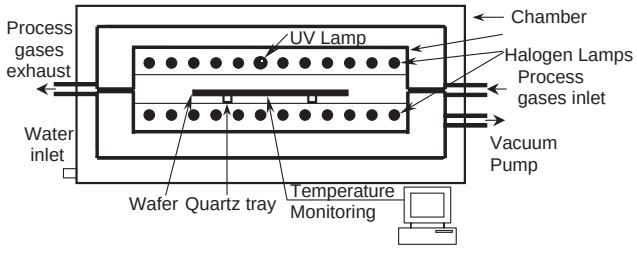

Fig. 1. Schematic diagram of the rapid thermal annealing RTA system.

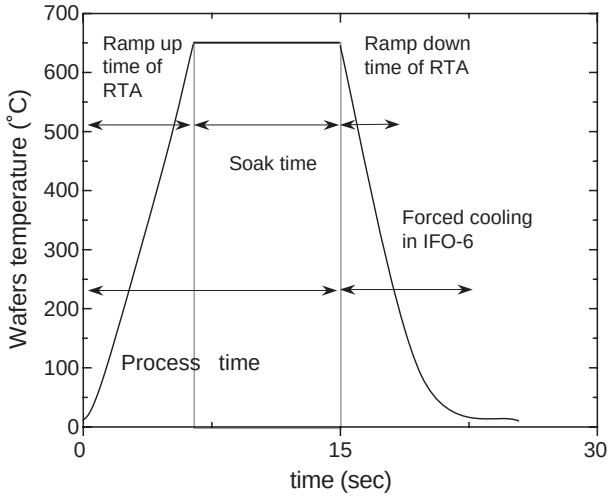

Fig. 2. The temperature profile during a 15 s, 650 °C process in the rapid thermal annealing RTA system.

1200 grooves/mm gratings assuring a linear dispersion of 0.8 nm/mm. The spectrometer was equipped with a photomultiplier with SbKNaCs photocathode working in a photon counting mode. The spectral resolution was better than 0.5 meV. The samples were mounted on the optical cryogenic systems cold station.

3. Results and discussions

Fig. 3 presents the effect of RTA treatment on the surface morphology of a ZnO:Al films chemically deposited from Zn:Al:[EN] (0.02 M:1 mM:0.045 M, pH=11) aqueous bath: (a) as grown without RTA (sample 1), and (b) treated by RTA at 650 °C for 20 s (sample 4). The as grown films microcrystallites mean size is 200 nm. RTA leads to the increase of the grain sizes by a factor of two.

Fig. 4 shows the PL spectra of ZnO:Al films (700 nm thickness) chemically deposited from Zn:Al:[EN] (0.02 M:1 mM:0.045 M, pH=11) aqueous bath and annealed at different RTA temperatures for 20 s: sample 1 is the as grown film; 2—treated by RTA at 400 °C; 3—treated by RTA at 500 °C; 4—treated by RTA at 650 °C (the morphology is presented in Fig. 3b). One can see that the emission from the as grown sample is dominated by resonant Raman scattering (RRS) labeled as 2LO–4LO (longitudinal-optical) peaks, i. e. the near bandgap luminescence is weaker than the RRS.

The difference between the position of the nLO_{RRS} peak and the excitation energy (3.530 eV) is n times the energy of the A_1(LO) phonon in wurtzite-type ZnO (72 meV). It means that this emission originates from the n-order Raman scattering.

Resonant Raman scattering from solids can be observed if the energy of the incoming or scattered photons matches real electronic states in the material. One refers to incoming and outgoing resonance (see, e.g., [11]). Multiphonon