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Sol–gel derived amorphous/nanocrystalline MgZnO thin films annealed by atmospheric pressure plasma jets

Shao-Tzu Lien[a], Jian-Zhang Chen[a,*], Yao-Jhen Yang[b], Cheng-Che Hsu[b], I-Chun Cheng[c,d]

[a]*Graduate Institute of Applied Mechanics, National Taiwan University, No. 1, Sec. 4, Roosevelt Rd., Taipei City 10617, Taiwan*
[b]*Department of Chemical Engineering, National Taiwan University, Taipei City 10617, Taiwan*
[c]*Graduate Institute of Photonics and Optoelectronics, National Taiwan University, Taipei City 10617, Taiwan*
[d]*Department of Electrical Engineering, National Taiwan University, Taipei City 10617, Taiwan*

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Abstract

This paper reports the characterization of sol–gel derived MgZnO thin films annealed by atmospheric pressure plasma jets (APPJs). $Mg_xZn_{1-x}O$ films exhibit high transparency (> 80%) in the visible light wavelength region. When 20 at% Mg is incorporated into the film, the optical bandgap reveals a blue shift from ~3.25 to ~3.5 eV and the resistivity increases by three to four orders of magnitude, owing to the substitution of Mg atoms into the Zn lattice sites. The absorption band edge becomes sharper and the bandgap becomes slightly narrower as the APPJ treatment time increases. This can be attributed to slight grain growth in the films. When the material is amorphous/nanocrystalline, the quantum confinement effect causes a slight decrease in the bandgap as the grain size increases, resulting in slope alteration at the absorption edge. Compressive stresses caused by the difference in the thermal expansion coefficients between the film and the substrate are generated during the drying process. This leads to surface wrinkling on the sol–gel derived $Mg_{0.2}Zn_{0.8}O$ thin films.

Keywords: D. ZnO; Annealing; Atmospheric pressure plasma jet; MgZnO; Sol–gel

1. Introduction

ZnO is a promising candidate material for short-wavelength optoelectronic devices owing to its wide bandgap (≈ 3.37 eV) and large exciton binding energy (≈ 60 meV) at room temperature [1]. ZnO-based materials have been applied to various types of optoelectronic devices such as gas sensors [2,3], thin-film transistors [4–8], pn diodes [9,10], LEDs [11], UV detectors [12–16], and solar cells [17]. To modulate the bandgap, ZnO can be alloyed with MgO to form $Mg_xZn_{1-x}O$ [18–22]. It has been demonstrated that the bandgap of $Mg_xZn_{1-x}O$ increases from 3.37 to 3.99 eV when the Mg concentration is increased up to x=0.33 [20]. Similar bandgap modulation has been found in Mg alloyed InZnO material systems [23,24]. Because the ionic radii of Mg^{2+} and Zn^{2+} are similar, Zn can be substituted by Mg without much lattice distortion [20]. $Mg_xZn_{1-x}O$ can also be used with ZnO to form $Mg_xZn_{1-x}O$/ZnO heterostructures in which the polarization field at the interface can induce two-dimensional electron gases [25–33].

Several fabrication processes have been developed for $Mg_xZn_{1-x}O$ thin films. Molecular beam epitaxy (MBE) [34,35], pulse laser deposition (PLD) [36,37], metal-organic chemical vapor deposition (MOCVD) [38,39], and atomic layer deposition (ALD) [22] are frequently used for fabricating high-quality $Mg_xZn_{1-x}O$ films. However, with regard to large-area electronics, low cost large-area compatible deposition processes such as sputtering [19,40], sol–gel [41–43], and spray pyrolysis [44,45] are desired fabrication technologies. In this paper, we report the characterization of sol–gel derived $Mg_xZn_{1-x}O$ thin films annealed by atmospheric pressure plasma jets (APPJs). APPJs consist highly energetic N_2 molecules in the plasma jets that provide additional energy to assist the annealing process, which can shorten the processing time [29,46]. When oxygen is involved in APPJs, both the

*Corresponding author. Tel./fax: +886 2 3366 5694.
E-mail address: jchen@ntu.edu.tw (J.-Z. Chen).

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metastable N_2 and ozone photo-induced dissociation can assist the removal of organic residues [47]. The bandgaps of sol–gel derived $Mg_xZn_{1-x}O$ thin films are successfully engineered from ~3.25 to ~3.50 eV by varying Mg content up to 20%. The films show good transparency in the visible light wavelength region. APPJ treatment increases the top-layer grain connectivity, slightly sharpens the absorption edges, and reduces the bandgaps. APPJ is a good candidate for a rapid thermal annealing process.

2. Experimental procedures

The $Mg_xZn_{1-x}O$ sol–gel solution was prepared by dissolving zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$, ≥98%, Sigma-Aldrich) and magnesium acetate tetrahydrate ($Mg(CH_3COO)_2 \cdot 4H_2O$, ≥98%, J.T. Baker) in isopropyl alcohol. Monoethanolamine (C_2H_7NO, MEA, ≥99%, Sigma-Aldrich) was used as a stabilizer. The molar ratio of MEA to the total ion concentration was maintained at 1. The Mg content x ($x = [Mg^{2+}]/([Zn^{2+}]+[Mg^{2+}])$) was varied as 0, 0.05, 0.1, and 0.2 respectively; the total ion concentration was fixed at 0.3 M. Then, the mixture was stirred at 70 °C for 3 h to form a clear homogeneous solution. After the stirring process, the transparent solution was aged for 24 h at room temperature. Finally, the sol–gel solution was filtered using a 0.45-μm filter.

The filtered solution was spin-coated onto 2 cm × 2 cm Corning Eagle-2000 glass substrates at 3000 rpm for 30 s. This coating process was repeated five times for the film to reach ~200 nm thickness, which was measured using a profilometer (KLA-Tencor Alpha Step 500). After each coating step, a 10-min, 300 °C thermal process was performed on a hotplate. APPJ was then used to anneal the resultant $Mg_xZn_{1-x}O$ thin films. The schematic of the APPJ apparatus used in this study is shown in Fig. 1. The plasma jet consists of stainless-steel, cylindrical-type electrodes with the inner and outer electrodes being powered and grounded, respectively [48]. The diameters of the inner and outer electrodes are 1.5 and 3.5 cm, respectively. A pulsed power source supplied dc pulse voltage up to 350 V with a repetitive frequency up to 25 kHz, followed by a transformer that increases the voltage of up to 21 kV. The plasmas underwent glow to arc transition within each power period. Such an arrangement sustained a jet of high reactivity and great power controllability [49,50]. The dc pulse voltage was the control parameter of the plasma jet. A quartz tube of 2-cm length was installed at the downstream of the plasma jet to confine the convective flow and to minimize the influence of ambient air [51]. The applied conditions for APPJ surface treatment were: applied voltage, 275 V; air (79% N_2 +21% O_2, 99.995%) flow rate, 35 slm; on/off duty cycle, 7/33 μs; and 1-mm gap between the quartz tube exit and the platform. The surface temperature evolution upon the exposure to the APPJ was monitored using a K-type thermocouple. The temporal evolution of the temperature was acquired using a data acquisition device (USB-6221, National Instruments) and recorded using a computer. Fig. 2 shows the temperature evolution for the APPJ surface treatment process. From 0 to 30 s, the temperature increases rapidly, following which the temperature increases slowly and becomes steady. The temperatures of the substrate at various times are tabulated in Table 1. The highest surface temperature was ~630 °C.

We determined the stoichiometric composition of the sol–gel derived $Mg_xZn_{1-x}O$ films by using an electron probe X-ray microanalyzer (EPMA, JEOL JXA-8200) (in this particular experiment, the sol–gel derived $Mg_xZn_{1-x}O$ films were deposited on a p-Si (100) wafer). Three measurements were taken on each sample; the detected positions were 2 mm apart. The crystalline structure of the APPJ-annealed $Mg_xZn_{1-x}O$ films was examined by X-ray diffraction (PANlytical X'Pert Pro). The morphology was investigated using a scanning electron microscope (SEM, Nova™ NanoSEM 230). The transmittance was measured by a UV–vis spectrophotometer

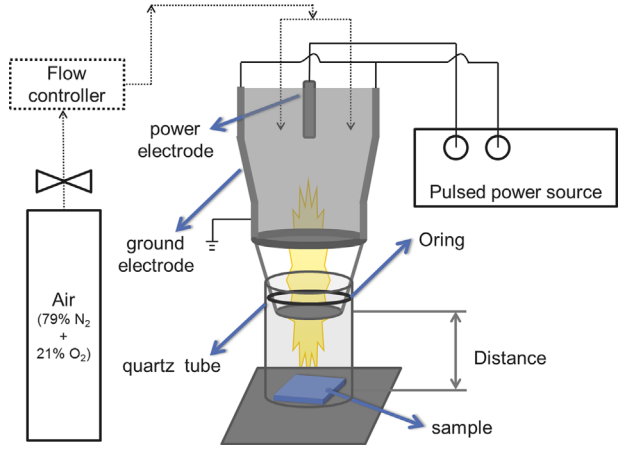

Fig. 1. The schematic of atmospheric pressure plasma jet (APPJ) apparatus.

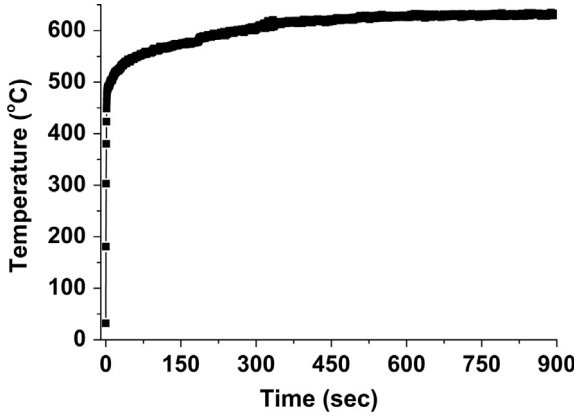

Fig. 2. Evolution of the substrate surface temperature during the APPJ surface treatment process.

Table 1
The approximate temperatures at various times.

Annealed time (min)	Temp. (°C)
1	550
5	600
10	630
15	632