Spray pyrolysis deposition of Al-doped ZnO thin films as potential UV scintillator materials

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INTRODUCTION

Among the potential scintillator materials, bulk zinc oxide (ZnO) crystals have been extensively studied because of their intense UV emissions and picosecond to nanosecond emission lifetimes at room and even higher temperatures [1]. However, despite these excellent properties, bulk crystals are difficult to form into thin micrometer plates which are typically required for high-resolution scintillators. Aside from micrometer thicknesses, potential scintillator materials should have excellent optical properties such as nanosecond to picosecond emission decays for better detection rates and appropriate (blue to UV) emission wavelengths and visible region transparency for spectral matching considerations. Although sparsely investigated, zinc oxide thin films also exhibit excellent scintillation properties which can be further developed to satisfy the conditions for potential scintillator materials.

Different fabrication techniques have then been implemented to produce a wide array of ZnO in the form of films and nanostructures. Among common physical vapor deposition techniques such as magnetron sputtering, pulsed laser deposition (PLD), and molecular beam epitaxy (MBE), the spray pyrolysis technique is one of the most convenient ways to synthesize ZnO films. Spray pyrolysis technique is a simple and versatile method to synthesize ZnO films at relatively low temperatures without any vacuum requirements and accurate gas concentrations. Furthermore, the technique utilizes cost-effective materials while affording ease and flexibility in varying the deposition parameters and doping concentrations.

In this regard, we investigate the optical properties of aluminum (Al)-doped ZnO thin films grown using spray pyrolysis technique. Al has been chosen as a dopant to further improve the ZnO emission lifetimes. More specifically, this work aims to identify and compare the photoluminescence (PL) emissions of undoped and Al-doped ZnO thin films, to identify the effects of Al-doping on the thin film's optical emission, and to evaluate the viability of Al-doped ZnO thin films as potential scintillating materials.

METHODOLOGY

Undoped and Al-doped ZnO thin films were deposited on seeded glass substrates using spray pyrolysis technique. The glass substrates were then set on a digital hot plate which was placed 30 cm from the spray pyrolysis setup. This setup included an atomizer which sprays the substrates automatically with the precursor solution through a 0.5 mm nozzle every 15 s. For the seed layer preparation, the substrates were sprayed with 50 mL 50 mM zinc acetate dihydrate [$Zn(CH_3COO)_2{\cdot}2H_2O$, ZnAc] solution while being maintained at 350 °C for 60 min. The seeded substrates were subsequently annealed at 350°C for 20 min in ambient air to improve the seed layer crystallinity. For the undoped thin film preparation, a seeded substrate was sprayed with 200 mL ZnAc solution while also being maintained at 350 °C for 60 min. After film deposition, the sample was cooled naturally to room temperature before subsequent characterization. On the other hand, for the Al-doped thin film preparation, a similar method was implemented but with aluminum chloride ($AlCl_3$) being first added to the ZnAc solution. The appropriate amounts of $AlCl_3$ were based on the calculated molar percentage (mol %) concentration of Al ions present in the final 200 mL precursor solution. Samples with 3 and 5 mol % Al-doping concentrations were fabricated along with the undoped ZnO thin film.

PL spectroscopy was performed to investigate the undoped and Al-doped ZnO thin films deposited via spray pyrolysis technique. The experimental characterization was conducted using the frequency-tripled (290 nm) output of a Ti:sapphire laser system which was focused on the sample at an angle of 45° from the normal. For time-integrated PL (TIPL)

spectroscopy, the sample emission was collected through reflection geometry and was fiber-fed to a handheld spectrometer. For time-resolved PL (TRPL) spectroscopy, the sample emission was focused on an imaging spectrograph which was coupled to a streak camera and a high-resolution digital CCD camera. The spectral and temporal resolutions of the TIPL and TRPL setups were 1 nm and 10 ps, respectively. All spectroscopy measurements were obtained at room temperature.

RESULTS

Figure 1 shows the normalized TIPL spectra of the undoped and Al-doped ZnO thin films deposited via spray pyrolysis technique. The undoped and Al-doped films exhibit similar intense UV emissions and broad visible emissions around 381 nm (UV) and 540 nm (green), respectively. The UV emissions, which correspond to the near-band-edge emission of ZnO [1], are similar for the undoped and Al-doped samples. Considering the spectral resolution and fitting deviation, the UV emissions do not shift nor broaden with increasing doping concentration, and the peak positions and spectral linewidths remain constant around 381 and 28 nm, respectively. On the other hand, the visible emissions, which are associated with defects or impurities [1], slightly increase in intensity with Al-doping. Compared to the undoped sample, the 3 and 5 mol % Al-doped thin films have visible emissions which are higher by one order of magnitude. These results indicate that the undoped and Al-doped ZnO thin films fabricated by spray pyrolysis technique exhibit intense UV emissions and that Al-doping results in an increase in the films' defect-related visible emission intensities.

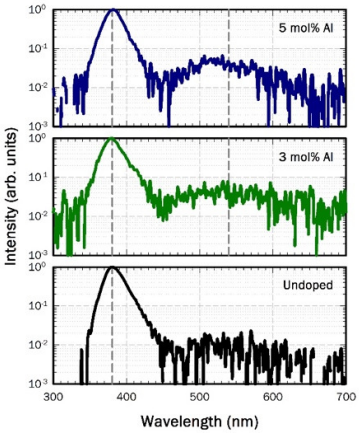

Fig. 1. TIPL spectra of undoped and Al-doped ZnO thin films deposited via spray pyrolysis technique

Figure 2 shows the normalized UV emission temporal profiles of the undoped and Al-doped ZnO thin films deposited via spray pyrolysis technique. Exponential functions are fitted to each profile to determine the corresponding emission lifetimes. Instead of the usual double exponential functions, the decaying parts of all profiles fit well to single exponential functions. The undoped, 3 mol % Al-doped, and 5 mol % Al-doped thin films have UV emission lifetimes of 28, 20, and 23 ps, respectively. The fast lifetimes are comparable to those of hydrothermal-grown ZnO nanorods (24 ps) [2] and intentionally doped bulk ZnO single crystals (15 to 130 ps) [3, 4] and can be largely attributed to the effective nonradiative recombination with the activation of nonradiative centers at room temperature [5-7]. Considering the instrumental resolution and fitting deviation, all samples exhibit similar emission lifetimes of 20 to 30 ps. These results reveal that the undoped and Al-doped ZnO thin films fabricated by spray pyrolysis technique exhibit fast picosecond UV emissions and that Al-doping does not affect UV emission lifetimes of the fabricated thin films.

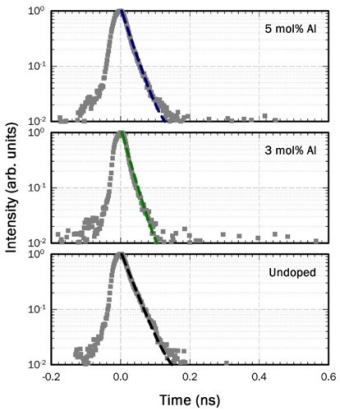

Fig. 2. UV emission temporal profiles of undoped and Al-doped ZnO thin films deposited via spray pyrolysis technique.

SUMMARY

We have reported the optical properties of Al-doped ZnO thin films deposited via spray pyrolysis technique. Both undoped and Al-doped thin films exhibit intense picosecond (< 30 ps) emissions in the UV region (381 nm). Additional investigations are currently underway to elucidate a precise relationship between Al-doping and optical properties of ZnO thin films. Our present findings nonetheless suggest that the spray-pyrolysis-deposited and intentionally-doped ZnO thin films can be used as ultrafast UV scintillators.

ACKNOWLEGEMENT

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