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Random lasing from surface modified films of zinc oxide nanoparticles

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Abstract

The photoluminescence properties of zinc oxide (ZnO) ceramic thin films, prepared by spin coating of ZnO nanoparticle aqueous suspensions, were studied with emphasis on the influence of film structure and surface morphology on the observation of random laser action. Surface processing employing laser annealing transforms the particulate grain structure of the as-deposited films into a porous channel-like network. This modification was shown to be critical for achieving random laser action as it favors efficient coupling of the pump light into the film material.

Keywords: Random laser; Surface processing; Zinc oxide

1. Introduction

Zinc oxide (ZnO), a wide band gap semiconductor material, has received much attention because of its potential applications in photonic, electronic and chemical sensor devices [1–3]. Particular emphasis has been placed recently on light emitting ZnO nanostructures including nano-crystals, -rods, -wires or -walls [4–7]. For example, arrays of ZnO nanorods grown by vapor or liquid solution deposition methods have been fabricated and found to exhibit room temperature laser emission in the ultraviolet arising from individual columns defining highly efficient Fabry–Perot cavities [8–12]. Also, recently a thin film ZnO laser grown on a silicon microdisk, showed laser activity in the whispering gallery modes corresponding to the microdisk hybrid structure [13].

In parallel, significant research work has focused on highly scattering ZnO thin film or hybrid structures, which upon pumping exhibit laser-like emission

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described by the term random laser, the word "random" being used to indicate the disorder (randomness) of the medium [14–20]. It is indeed this strong scattering that induces localization of light, which, coupled to the gain capacity of ZnO, leads to light amplification. Depending on the feedback mechanism, coherent or incoherent, the random laser spectral output is characterized by sharp spectral features arising from distinct laser modes or a narrow band envelope of amplified spontaneous emission (ASE)-like emission, respectively [21]. A number of ZnO-based random lasers including ZnO polycrystalline film [22], powders [23], ZnO microlasers [24] and ZnO-based hybrids [19,20] have been developed.

Although several ZnO-based systems, exhibiting random laser action, have been fabricated, it appears that there is still scope for new approaches leading to less complicated, more versatile and inexpensive methods to produce new structures and enable better control over the lasing properties. To this end, we have worked on a variety of hybrid materials composed of ZnO nanoparticles dispersed in polymer matrices [19] or silicate glasses [25], which have shown random laser action. In the work described in this paper, the random laser behavior of ceramic ZnO thin films, grown on glass by spin coating of aqueous ZnO nanoparticle suspensions, was investigated. The random laser efficiency was found to be a function of film morphology and nanoparticle surface density and increased noticeably when the as-deposited films were subjected to additional surface processing employing laser annealing.

2. Experimental

In a typical procedure, ZnO nanoparticles (6 g) in powder form (Aldrich 20,533-2) were mixed with 9 ml of dilute acetic acid solution (pH 2–3) containing two drops of surfactant (Trinitron—X100). The resulting white suspension (slurry) was ultra-sonicated for 10 min; it was then deposited on to a glass substrate (25 mm × 25 mm) by spin coating and left to dry at room temperature. The dried films were heat-treated at 600 °C for 12 h yielding a smooth ZnO ceramic material. A quite uniform thickness, 1 μm, was achieved across the film with the exception of a small area (diameter of about 4 mm) in the center of the film, in which particles accumulated giving rise to a maximum thickness of 3 μm.

Laser annealing of the as-deposited films was carried out in air using a spatially homogenized beam from a XeCl excimer laser ($\lambda = 308$ nm; pulse duration, 30 ns), which permitted uniform irradiation of a 4 mm × 4 mm spot on the film surface. The laser beam was scanned appropriately in order to irradiate the whole film. Ten pulses at 200 mJ/cm^2 (optimum fluence) were used at each spot. It was found that irradiation at high fluence values, in the range of 300 mJ/cm^2, led to surface decomposition while in the range of 100 mJ/cm^2 the photon flux was not sufficient for annealing.

For the emission measurements a KrF excimer laser (Lambda Physik), operating at 248 nm, was employed as the excitation source. The pulse duration provided was 450 fs or 5 ps, with 2 mJ of maximum energy on the sample. The intensity of the laser beam was controlled by means of a variable attenuator and monitored through a sensitive energy meter. The irradiation area on the sample surface was adjusted by translating a spherical focusing lens ($f = +500$ mm) along the beam path. The photoluminescence emission was collected with a quartz optical fiber and analyzed in a 0.32 m imaging spectrograph (TRIAX-320, Jobin Yvon/Spex) with gratings of 600 and 2400 grooves/mm (spectral resolution 0.4 and 0.1 nm, respectively). The spectrum was recorded on an Intensified Charge Coupled Device (ICCD) detector (DH520-18F, Andor Technology) operated in the continuous mode (no gating). Emission spectra were recorded separately for each one of 10–20 successive laser pulses at a repetition rate of 1–5 Hz. This permitted monitoring of the shot-to-shot emission signal fluctuations especially around the lasing threshold.

A scanning X-ray microdiffractometer General Area Detector Diffraction System (GADDS) with ~500 μm beam size was used to characterize crystallinity and phase content of the films.

Atomic force microscopy (AFM) was used to study the surface topology of both the as-deposited and laser-annealed films. AFM measurements were performed on a Digital Instruments Multimode Scanning Probe Microscope using the Nanoscope IIIa, Version 4.23r3 software. All experiments were carried out in the tapping mode.