ROOM TEMPERATURE GROWTH OF CONDUCTING ZnO FILMS

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ABSTRACT

Single and dual-laser ablation techniques have been used to grow conductive ZnO films at room temperature by ablating a Zn metal target in oxygen ambient. The emission spectroscopy of the material plumes shows a significant presence of oxygen ions and Zn ions in the dual-laser ablated plume. Furthermore, dual-laser ablated plumes expanded rapidly in the radial direction resulting in large-area uniform films. The electrical properties of the films deposited on glass substrates depend critically on the ambient oxygen pressure. Conductivities of the order of 10^3 $(\Omega.cm)^{-1}$ have been obtained for films deposited at room temperature by the dual-laser ablation process.

INTRODUCTION

The advantages offered by excimer laser ablation for film growth include the formation of highly excited plumes resulting in high species energy at the substrate and enhanced gas phase reactions [1,2] as well as congruent evaporation of the components in a multi-component target leading to stoichiometric film deposition [3]. Since the remarkable success of this technique in the growth of high quality in-situ high temperature superconductors [4], a large variety of materials from insulators to metals in their thin film form have been grown by this method. However, two major drawbacks associated with this method of film growth, namely, the deposition of sub-micron and micron particulates on the film as a result of the explosive evaporation in the target-laser interaction [5], and the non-uniform deposition as a result of the highly forward directed expansion of the material plume [6], have stifled the development of laser ablation as a viable industrial process for film growth. The dual-laser ablation process we have developed eliminates particulate ejection and enhances the radial expansion of the plume to overcome both these drawbacks [7]. In this process an excimer laser pulse and a CO_2 laser pulse are spatially overlapped on the target with an optimum delay of 50 ns between the two pulses. The intense heating of the initial plasma plume by the CO_2 laser under these optimum conditions has been shown to re-evaporate the particulates and promote radial expansion of the plume. The mechanisms involved in the dual-laser ablation process towards the elimination of particulate ejection have been discussed in previous publications [7]. In addition, different species in the plume have been observed to follow similar expansion profiles leading to stoichiometric film growth. The enhancement of the high energy species in the plume affects the growth process, and thus, alter the properties of the deposited films.

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In this paper we report the room temperature growth of ZnO films from a metallic Zn target on glass substrates by both single and dual-laser ablation methods. Since the carrier density of pure ZnO is derived from the oxygen vacancies, films were deposited at different oxygen ambient pressures to determine the extent of the gas phase reaction. Furthermore, as the conductivity of the films depends on the morphology and the densification of the films, the high energy of the species in the dual-laser ablated plume is expected to produce better electrical properties. A comparison of the properties of the films grown by the two ablation methods is presented.

EXPERIMENTAL TECHNIQUE

An excimer laser of wavelength 248 nm and pulse width of 25 ns, and a CO_2 laser of wavelength 10.6 μm and pulse duration of 200 ns, are spatially overlapped on a Zn target in a turbo-pumped vacuum system. The two laser pulses arrive at the target with an inter-pulse delay of 50 ns. At this delay, the coupling of the CO_2 laser pulse to the excimer laser generated plasma has been shown to be optimum [8]. The details of the dual-laser ablation system are described in a previous publication [7]. The Zn target was prepared by pressing high purity Zn powder into a pellet with a pressure of 10 tons/(in)^2.

RESULTS AND DISCUSSION

The expansion characteristics of the laser generated plume, which determines the uniformity of the deposited film, were studied by depositing ZnO films on silicon substrates. The excimer laser and CO_2 laser fluences used for the film growth were 1 J/cm^2 and 5 J/cm^2, respectively. The thickness profiles were obtained by ellipsometric measurements and fitted by a distribution of the form $cos^n\theta$. The Fig.1

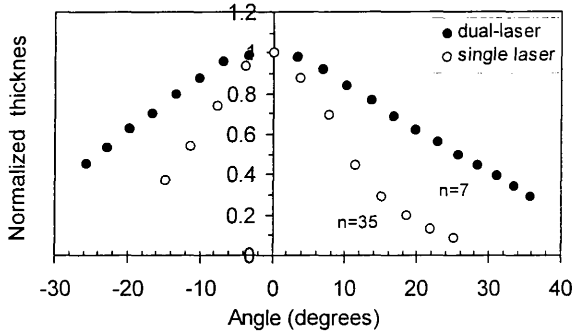

Fig. 1 Thickness profiles of single laser and dual-laser ablated ZnO films deposited in an oxygen ambient pressure of 10 mTorr on silicon substrates.

angular distributions of the film thickness for single laser and dual-laser deposited films in a 10 mT ambient oxygen pressure are compared in Figure 1. As indicated in the figure, the single laser deposited films follow a highly forward directed $cos^{35}\theta$ distribution while dual-laser deposited films show a considerably more uniform $cos^{7}\theta$ distribution. This amounts to a four fold increase in the area of film growth for the dual-laser process.

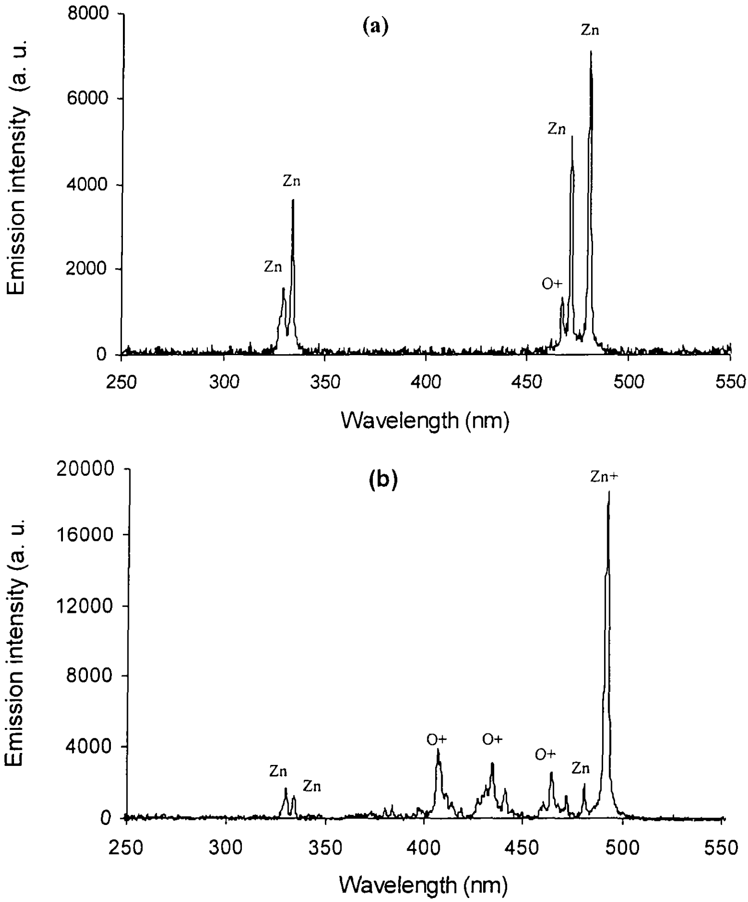

Fig. 2 Emission spectrum of a plume from laser ablation of a Zn target in a 10 mT oxygen ambient pressure, (a) by single laser, (b) dual-laser.

To study the effect of the CO_2 laser on the plume excitation, the emission of the laser generated plume was imaged onto an optical fiber which delivered the collected light to an optical multi-channel analyzer (OMA). Figure 2 shows the emission spectrum of the plume collected 6 cm from the target at an ambient oxygen pressure of 10 mT. The single laser ablated plume, Fig 2(a), contains mostly excited neutrals while the dual-laser ablated plume, Fig. 2(b), shows a significant ionization of the plume. The presence of these high energy ions is expected to promote columnar growth and increase the film densification.

Thin films of ZnO were deposited on soda-lime glass at room temperature by both techniques to study the effect of the dual-laser process on the electrical properties of these films. Along with the glass substrate a silicon substrate was mounted on the same substrate holder in order to measure the film thickness and refractive index by using ellipsometry. The crystallinity of the films was investigated by x-ray diffraction. As indicated in Figure 3, the presence of only the (00l) peaks in XRD analysis of the films points to highly c-axis oriented film growth.

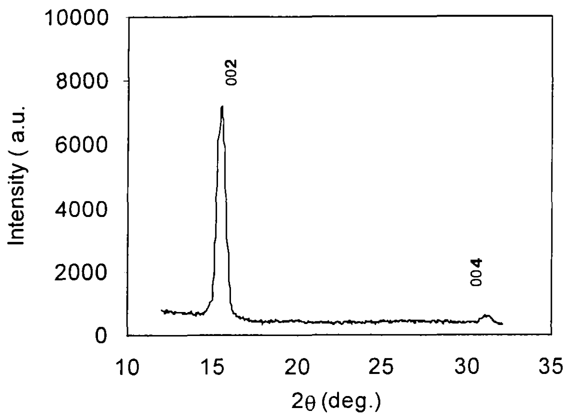

Fig. 3 X-ray diffraction pattern of a ZnO thin film deposited on a glass substrate at room temperature. The x-ray wavelength is 0.71 A.

The conductivity of the films on glass substrates was measured by the four-point probe technique while the carrier densities of the films were obtained by measuring the Hall voltage. The film thickness was determined by ellipsometric measurements of the films deposited on silicon substrates. The refractive index of the films deposited by single laser ablation ranged from about 1.85 to 1.9 while the dual-laser deposited films showed a refractive index of about 1.95, which is closer to the average bulk value. This indicates that the dual-laser deposited films are of higher density than the films grown by single laser ablation. The dependence of the film conductivity on the deposition pressure of oxygen is shown in Figure 4. The highest

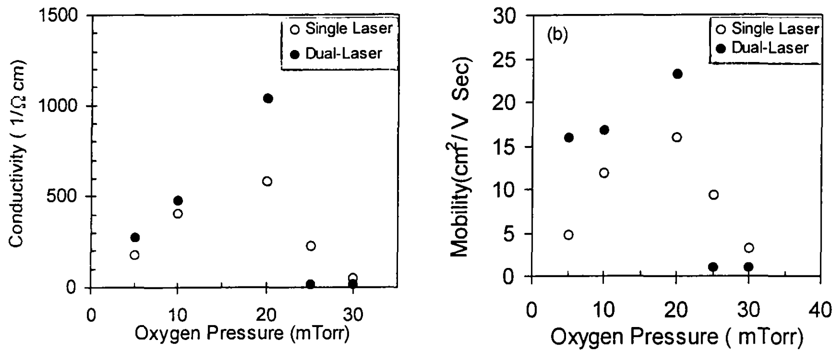

Fig. 4 The effect of oxygen ambient pressure on conductivity (a) and mobility (b) of ZnO films deposited by single laser and dual-laser ablation on glass substrates at room temperature.

conductivity was obtained for a deposition pressure of about 20 mTorr. At pressures below 5 mTorr deposited films appeared to be dark indicating insufficient gas phase reaction to form the ZnO structure. The films deposited at low oxygen pressures are significantly deficient in oxygen, and thus, show poor conductivity as a result of high scattering. Increasing oxygen pressure increases the gas phase reaction to incorporate more oxygen into the film leading to an increase in conductivity. Further reduction of oxygen vacancies for oxygen pressures above 20 mTorr sharply reduces the carrier density of the film leading to a reduction in the conductivity. In comparison to single laser deposited films, dual-laser deposited films showed a higher conductivity even at lower carrier densities. Improved crystallinity of the films produced by the higher energy species in the dual-laser ablated plume is responsible for the increase in the film conductivity. As seen in Figure 4(b), higher conductivity at a lower carrier density produced mobilities as high as 24 cm^2/V.sec.

CONCLUSIONS

We have used a dual-laser ablation technique to deposit conducting ZnO films from a metallic Zn target in an oxygen ambient. In comparison to the conventional single laser deposition, this technique significantly increases the area of film growth. In addition, the high energy of the plume species increases adatom mobility at the substrate leading to high density films. In the growth of films at room temperature the gas phase reaction is crucial for the formation of ZnO. Films grown at low oxygen pressures are less transparent and poorly conducting. The highest conductivity and mobility were produced by the films deposited at an oxygen pressure of about 20 mTorr.

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