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Separated pulsed laser deposition for nanostructured thin films

Kenji Ebihara *, Sang-Moo Park, Koji Fujii, Tomoaki Ikegami

Department of Electrical and Computer Engineering, Graduate School of Science and Technology, Kumamoto University, Kurokami 2-39-1,
Kumamoto City, 860-8555 Japan

Abstract

We have developed an alternative laser deposition technique for preparation of droplet-free thin films and fine particles. This separated pulsed laser deposition (SPLD) consists of an ablation chamber and a deposition chamber which are independently evacuated under different ambient gases.

High quality ZnO films exhibiting both particle-free and uniform deposition were obtained such as at an ablation pressure of 5 mTorr (Ar) and a deposition pressure of 10 mTorr (O_2). It is shown that, when the bias voltage and magnetic field are simultaneously applied in the deposition chamber, the $E \times B$ drift motion of about 70 km/s over the substrates contributes to deposit the smooth and high quality films. XRD and optical transmittance for the deposited films were investigated to clarify the operating properties of the SPLD assisted by the electric field and magnetic field. This SPLD is a promising technique for preparation of films and nanostructured particles.

Keywords: Pulsed laser deposition (PLD); Nanostructures; Oxidation; Optical properties characteristics

1. Introduction

Pulsed laser deposition (PLD) is a widespread and useful technique possessing many advantages including stoichiometry, lowering deposition temperature and high deposition rate in arbitrary atmosphere [1]. However, the PLD has inherent problems such as deposition of droplets, limited deposition area, and expensive instrument system. Several novel systems assisted by plasma, electric and magnetic fields have been proposed to improve the deposited film quality. Giardini et al. [2] and Cappelli et al. [3] used reactive pulsed laser ablation and deposition technique which combines the several advantages of conventional PLD with the enhancement of the reactivity in RF plasma. Kobayashi et al. have developed Aurora PLD under application of the magnetic field (0.45 T). This method is characterized by an enhanced ionization of the ablated particles during transport from the target to substrate through magnetic influence on electrons and ions [4]. Zhang et al. utilized an excimer UV source (Xe2*, 172 nm excimer lamp) in conjunction with the conventional PLD in order to assist the growth of oxide dielectric films in oxygen radicals [5].

We have developed an alternative laser deposition technique to improve the film qualities by the conventional pulsed laser ablation system [6]. Here, we propose the separated pulsed laser deposition (SPLD) consisting of an ablation chamber and a deposition chamber which are independently evacuated under different ambient gases. In order to prepare the high quality PLD films, electric and magnetic fields were applied in the deposition chamber. Photonic material of ZnO was deposited to clarify the features of this SPLD system.

2. Experimental

Fig. 1 shows the geometry of the SPLD system [6]. We can independently control the ambient pressures of the ablation chamber and the deposition chamber. The ablation chamber is a stainless steel globe with 300 mm diameter. The deposition chamber is made of a quartz tube of 100 mm diameter and a metallic conic wall with variable orifice diameters. For the ablation process we use a KrF excimer laser with $\lambda = 248$ nm and 25 ns pulse duration. Different gas pressures in two chambers having the differential evacuation system allow us to provide optimal control of the plasma plume, the gas phase reaction and the film growth by applying variable voltages between the conic wall and the substrate under the magnetic field.

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* Corresponding author. Tel.: +81 96 342 3628; fax: +81 96 342 3630.
E-mail address: ebihara@eecs.kumamoto-u.ac.jp (K. Ebihara).

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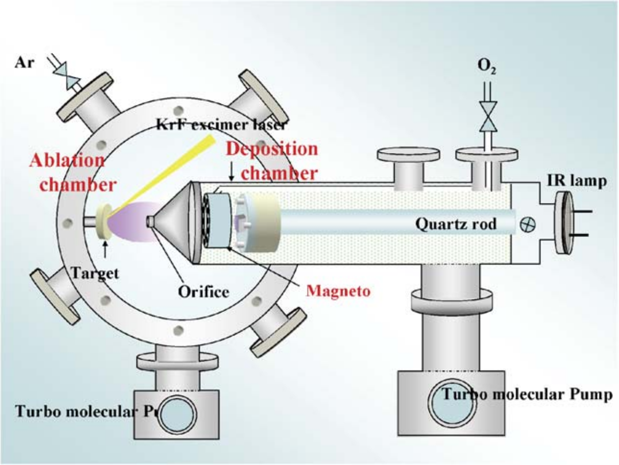


Fig. 1. Separated pulsed laser deposition.

Fig. 2 is the configuration of the components for the SPLD. The magnetic induction (*B*) is generated by the permanent magnets in the deposition chamber. The electric field (*E*) was directed toward the left-hand side due to applied positive bias voltage between the substrate and the conical capsule. Since the radial component of the magnetic induction (B_r) crosses vertically with *E*, the drift motion of ions and electrons given by

$$V_d = E \times B/B^2\,(\mathrm{m/s})$$

provides the velocity $V_d = E/B_r$ [7].

This azimuthal averaged motion causes the plasma to flow by sweeping over the deposited film.

We studied the dynamics of the plasma plumes of this SPLD assisted by the applied electric and magnetic fields. The surface morphology of the deposited films was observed by using atomic force microscopy (AFM) (Seiko: SPI3800N).

3. Results and discussion

In order to evaluate the operation condition of this SPLD system, we have studied the dynamics of the plasma plume as well as the film qualities of the deposited films. The plasma plumes of the zinc oxide (ZnO) target in Ar and O_2 atmosphere of the ablation chamber ($P_a = 20$ mTorr) were studied when the deposition chamber was filled with oxygen gas of deposition pressure ($P_d = 10$ mTorr). It was noticed that the emission from the argon plasma in the ablation chamber is strong and large volume comparing with the plasma in oxygen atmosphere. Since excitation and ionization of Ar gas are easier than these of oxygen, the Ar plasma plume can enhance the ionization and reaction of the ejected species.

In order to visualize and digitally record the plasma emission spectra a linear CCD Ocean Optics spectrometer was used. The emission spectra from the plasma were measured at the metallic conic wall orifice with the help of a fibre optic and a collimator attached to the spectrometer entrance slit. The time integrated spectral intensity of the laser produced plasma at $P_a = 10$ mTorr O_2 and $P_b = 20$ mTorr O_2 showed three strong lines from Zn (468.0, 472.2, 468.8 nm) and a band from O_2^+ at 637 nm.

The effect of magnetic field on the plasma plumes is shown in Fig. 3. Plasma plume showed large emission volume in the ablation chamber when the mirror type magnetic field ($B = 0.1$ T) was applied. The emission in the deposition chamber was too weak to measure using our optical system. The magnetic field was extended to trap the charged particles near the capsule type wall.

We deposited the ZnO films when pressures in both ablation chamber and deposition chamber were changed. Fig. 4 shows AFM images of the films deposited at $P_a = 5$, 10, 20 mTorr (Ar) under a deposition pressure (P_d) of 10 mTorr (O_2). We cannot observe droplet-like particles on the films. The small grain of the size of 60 nm was obtained at lower pressure of $P_a =$ 5 mTorr.

Fig. 5 shows the transmittance spectra of these films. The film deposited at 5 mTorr exhibits higher optical transmittance above 350 nm. The Tauc plot of this film indicates the optical band gap of 3.1 eV. Increase of the ambient pressure decreases optical band gap to about 2.6 eV.

Fig. 6 shows the XRD patterns of same ZnO films in Fig. 4. The film deposited at $P_a = 5$ mTorr and $P_d = 10$ mTorr exhibits the crystal structure with high preferential orientation of (002) plane indicating good crystallinity.

Correlation between grain size and optical properties has been discussed from a viewpoint of the band gap energy of the deposited ZnO films. The existence of the grain boundary causes a band bending to reduce the band gap energy because

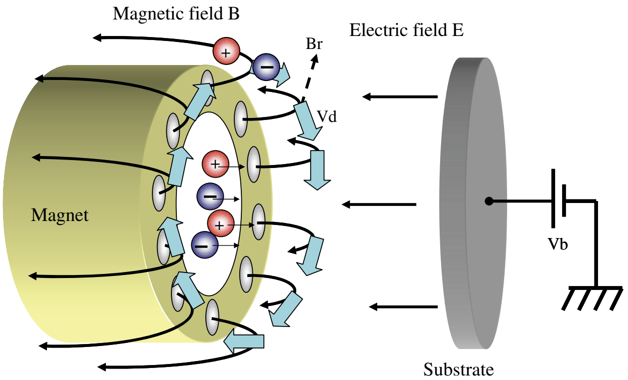
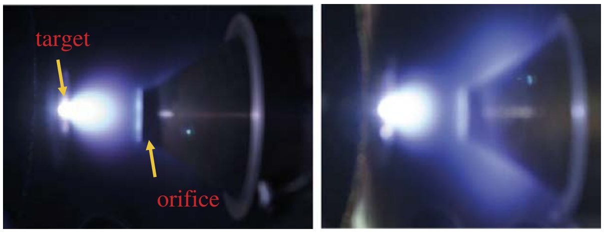


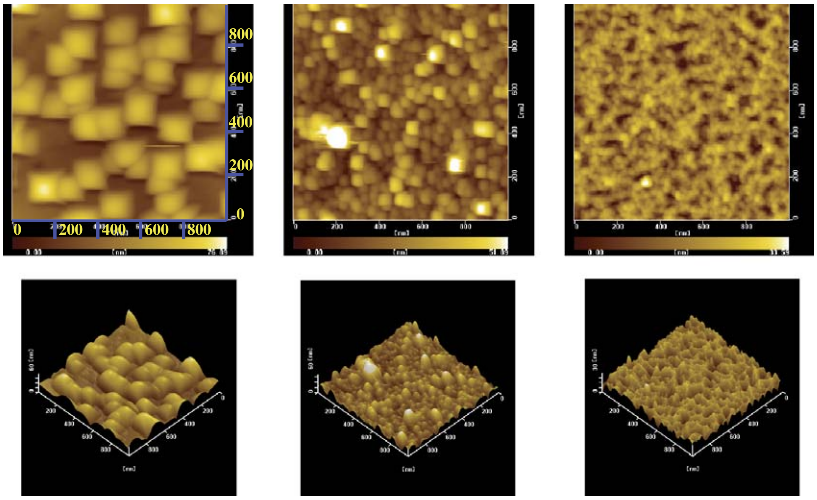
Fig. 2. *E*×*B* drift motion in the SPLD.



B=0 **B=0.1T**

Pa=5mTorr(Ar), Pd=10mTorr(O_2), Laser fluence: 3J/cm^2

Fig. 3. Effect of magnetic field on the emission of SPLD plasma.

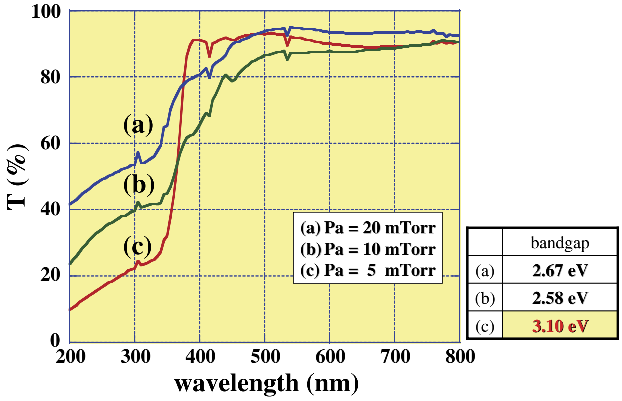


(a) **Pa:Ar, 20 mTorr**
Pd:O_2, 10 mTorr
RMS 14.46nm
Grain Size 149nm

(b) **Pa:Ar, 10 mTorr**
Pd:O_2, 10 mTorr
RMS 9.65nm
Grain Size 68nm

(c) **Pa:Ar, 5 mTorr**
Pd:O_2, 10 mTorr
RMS 5.2nm
Grain Size 61nm

Fig. 4. AFM images of ZnO films deposited at various values of P_a. Bias voltage = 500 V DC.



	bandgap
(a)	2.67 eV
(b)	2.58 eV
(c)	3.10 eV

Fig. 5. Transmittance of ZnO films deposited at various ablation pressures.

the residual strain in the ZnO film causes the bandgap to shrink. The change of the bandgap corresponding to the strain is very small value in the range of 20–40 meV [8]. The remarkable difference in the optical properties of the present results (Fig. 5) is considered to be due to crystallinity. The sample (c) consisting of small grains is highly crystallized as shown in Fig. 6c. On the other hand the sample (a) seems to be non-crystalline (amorphous) from the XRD pattern (Fig. 6a). At low ablation pressure, the large volume plasma of ions, electrons, radicals, atoms and molecules having low density with high energy is generated to arrive on the substrate through the reaction in the deposition chamber. The rarefied ambient gas near 5 mTorr in the ablation chamber is found to contribute to formation of small crystallized grain. As the ambient pressure increases, the number of the particles and their energy (velocity) arriving on the substrate decrease due to increasing collision with ambient gas, resulting in deterioration of the deposited films.

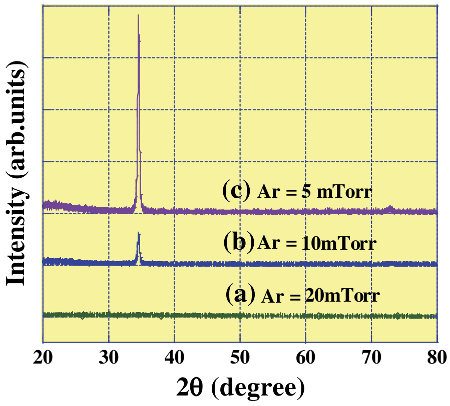
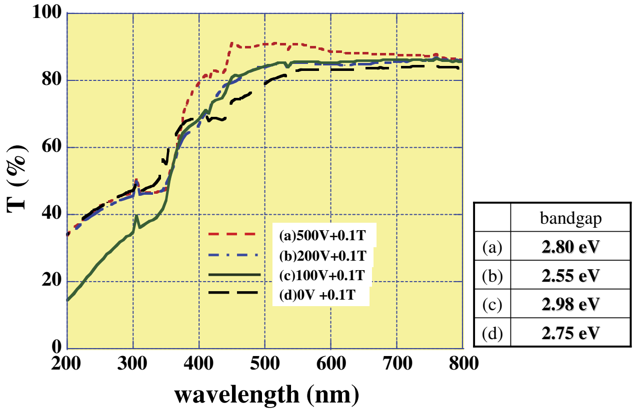
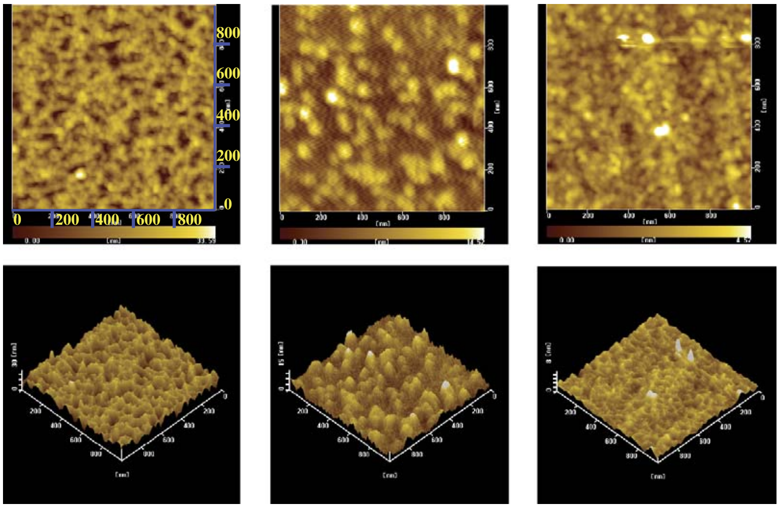


Fig. 6. XRD patterns of ZnO films at various Ar pressures.



	bandgap
(a)	2.80 eV
(b)	2.55 eV
(c)	2.98 eV
(d)	2.75 eV

Fig. 7. Effect of electric field on trasmittance of ZnO films at $B_s = 0.1$ T.



(a) E(70V/cm)
RMS 5.2 nm
Grain Size 61nm

(b) B(0.1 T)
RMS 2.6 nm
Grain Size 50nm

(c) E(70V/cm) + B(0.1T)
RMS 0.84 nm
Grain Size 41nm

Fig. 8. AFM images of ZnO films deposited at magnetic field and electric field. $P_a = 5$ mTorr Ar, $P_d = 10$ mTorr O_2.

We studied the effect of the DC bias voltage and magnetic field on the film properties. Fig. 7 shows the transmittance of the ZnO films deposited at various bias voltages under a fixed magnetic field ($B = 0.1$ T). The 500 V films show the optical band gap of 2.8 eV. The effect of the electric field and the magnetic field on the surface morphology of the ZnO films is shown in Fig. 8.

The charged particles (ion and electron) in the plume plasma are affected by the electric and magnetic fields. The laser ablated plasma was generated in the magnetic field where the electric field was simultaneously applied to the substrate. The DC voltage was applied between the substrate and the capsule separated by 7 cm. In these fields, the $E \times B$ drift motion can realize the enhancement of gas ionization and the control of film growth. It is shown that the film deposited at 0.1 T and 500 V (equivalent to $E = 70$ V/cm) has smooth surface with RMS 0.84 nm. In this case, the azimuthal drift velocity V_d is estimated to be 70 km/sec from the Eq. (1). This sample consists of small grains with 40 nm. The XRD patterns for these samples show that the FWHM of the film at 500 V has small value of 0.318° indicating good crystallinity.

The charged particles moving with the azimuthal (parallel to the substrate surface) motion can sweep the deposited surface of the substrate which increases the smoothness of the films. Although the electric field forces to accelerate the charged particles (electrons at positive DC bias) toward the substrate resulting in enhancing the crystallization, the magnetic field can trap the charged particles to increase number density near the reaction area in the deposition chamber. The velocity component normal to the substrate will decrease and, as the substitution of this velocity reduction, the azimuthal drift appears resulting in decreasing the energy of the particles impinging on the substrate. In conclusion, magnetic field superposed on the electric field contributes to the smooth and uniform film deposition by suppressing the crystal growth. This is the fact that the sample (c) in Fig. 7 ($B = 0.1$ T, $E = 70$ V/cm) does not show the noticeable improvement in the optical property. When the bias voltage decreases, the surface roughness increases due to decrease of the $E \times B$ drift effect.

4. Conclusion

The separated pulsed laser deposition (SPLD) was proposed to improve the deposition characteristics by the conventional PLD. It was shown that high quality ZnO films exhibiting both particle-free and uniform deposition are obtained at ablation pressure of 5 mTorr (Ar) and deposition pressure of 10 mTorr (O_2). The simultaneous application of electric filed and magnetic field for the SPLD contributes to prepare the crystalline films with sooth surface and small grain size.

This SPLD is useful to prepare oxide and nitride thin films and nanostructured materials including carbon nanotube and nanoparticles by controlling the atmosphere in the separated deposition chamber.

Acknowledgments

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