Effect of Substrate Temperature on the Structural and Morphological Properties of Nano-structure ZnO films by Pulsed Laser Deposition

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Abstract

In this work, ZnO thin films were grown on sapphire (0001) substrate by Pulsed Laser Deposition using SHG with Q-switched Nd:YAG pulsed laser operation at 532nm in O_2 gas ambient 5×10^{-2} mbar at different substrate temperatures varying from room temperature to 500°C. The influence of the substrate temperature on the structural and morphological properties of the films were investigated using XRD and SEM. As result, at substrate 400°C, a good quality and crystalline films were deposited that exhibits an average grain size (XRD) of 22.42nm with an average grain size (SEM) of 21.31nm.

Keywords: PLD; ZnO films; Substrate temperature; Crystal quality; Grain size; Optical properties, Nanostructures, Nd: YAG Q-Switching (SHG)

تأثير درجة حرارة القاعدة على الخواص التركيبية والطبوغرافية لأغشية أوكسيد الخارصين النانوية والمرسبة بالليزر

الخلاصة

في هذا العمل، تم أنماء أغشية اوكسيد الخارصين على قواعد من الالومينا ذات الاتجاهية (0001) باستخدام ليزر النيوديميوم ياك النبضي العامل بتقنية عامل النوعية وبنمط التولد التوافقي الثاني عند الطول الموجي 532 نانومتر بضغط اوكسجين(5 ×10^{-2}) ملي بار وبتغيير درجات الحرارة للقاعدة من درجة حرارة الغرفة إلى 500 درجة مئوية. تم دراسة تأثير درجة الحرارة على الخواص التركيبية والطبوغرافية للأغشية المحضرة بوساطة حيود الأشعة السينية والميكروسكوب الالكتروني الماسح. أظهرت النتائج عند درجة حرارة 400 درجة مئوية للقاعدة، تم الحصول على أغشية اوكسيد الزنك المتبلورة، وعند هذه الظروف تم الحصول معدل الحجم الحبيبي من خلال حيود الأشعة السينية هو 22.42 نانومتر أما معدل الحجم الحبيبي من خلال الميكروسكوب الالكتروني الماسح هو 21.31 نانو متر.

Introduction

In the early of 80’s of the last century, various methods have been employed to prepare ZnO films such as chemical vapor deposition (CVD) [1], RF magnetron sputtering [2], sol–gel process [3], metal oxide chemical vapour deposition (MOCVD) [4], molecular beam epitaxial (MBE) [5], and pulsed laser deposition (PLD) [6-8].

Pulsed laser deposition has become a widely used deposition technique for thin film growth. PLD presents several advantages with respect to other deposition techniques. In fact, due to the high energetic content of the ejected species, it allows

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low temperature deposition process. Moreover, its ability to congruently transfer the stoichiometry from the target to the film, allows the growth of complex materials. The technique is based on the vaporization process induced by focusing a high energy pulsed laser on the surface of the material. When the energy laser density is higher than a threshold value, which depends both on the material and the laser wavelength, a stream of atoms, molecules, and clusters is ejected from the target surface. Such a stream, known as a plume and being also composed of excited neutral and ionized species, emits radiation.[9]

Zinc oxide (ZnO) belongs to II–VI compound semiconductor and crystallizes in hexagonal wurtzite structure. At room temperature, ZnO films exhibit very strong emissions by excitons because of the large excitonic binding energy of 60 meV. Furthermore, ZnO has been recognized as a promising photonic material in the UV region due to its wide band gap of 3.37 eV at room temperature. [10]

Sapphire has been widely used as the substrate for the growth of ZnO films and high-quality films have been obtained [11]. The mechanism for ZnO/□-Al_2O_3 epitaxial growth is characterized by domain-matching epitaxy. ZnO thin films on sapphire are used in light-emitting diodes in which emission from both sides is desired [11].

In this work, we report the fabrication of ZnO films on single crystalline Sapphire (0001) using the ns-PLD technique and investigate the effects of substrate temperature on the structural and surface morphological properties of the films.

1. Experimental Work

A ZnO target of high – purity 99.99% was mounted in a locally designed vacuum chamber and ablated by a second harmonic generation (SHG) with Q- switched Nd: YAG pulsed laser operated at 532 nm. Pulse width of 10 ns, repetition rate of 6Hz and operated at 1.6 J/cm^2 energy density was focused by positive lens with focal length 5 cm on the target to generate plasma plume as shown in fig. 1. Prior to deposition, both polished sapphire substrates were etched in H_2SO_4:H_3PO_4=3:1 followed by ultrasonic cleaning in deionized water, and finally dried. In order to get a uniform film thickness, substrates were kept rotating during the deposition. All samples were grown at an optimal oxygen background pressure of 5×10^{-2} mbar. The substrate temperature was varied from RT to 500°C. The film thickness is measured by using optical interferometer method and its found (150nm). The film morphology was investigated by a Scanning Electron Microscopy (SEM- FEL Quanta 200, Netherlands). X-ray diffraction (XRD) measurements were performed by a Rigaku diffractometer with Cu K□1 radiation (□□=1.5405A˚).

2. Results and Discussion

Fig. 2; shows XRD patterns for the ZnO thin films grown on sapphire substrate at different substrate temperatures. The peak at about 34.4º and 41.6º corresponding to the diffraction from the ZnO (002) and Al_2O_3 (006) planes, respectively. The

ZnO (002) peaks are observed for all the sample temperatures.

This indicates that ZnO films with a good c-axis preferred orientation can be obtained by PLD at substrate temperatures from RT to 500°C. In addition, there is one weak peak appearing at 2□=31.8º as shown in Fig. (2b, d); which is corresponding to ZnO (100). The intensity, full-width-at-half-maximum (FWHM) and position of the (002) diffraction peak are shown in Fig. 3; It is found that the intensity of (002) orientation is weak for the films grown at RT, but it increases with increasing substrate temperature to 400°C. However, the intensity decreases when ZnO is deposited at 500°C, the intensities of ZnO (002) peaks in XRD spectra are different due to the diverse crystallization quality and various substrate temperatures in spite of the same deposition condition. The FWHM of 2θ values reveals the crystalline structure of the film. The atomic kinetic energy is mainly determined by substrate temperature. Therefore, at a relatively high temperature, the atoms on the film surface can move quickly to look for the lowest energy sites and form the low energy structure [12]. As a result, the structural quality of the ZnO film deposited at high substrate temperature is better than at low temperature. Meanwhile, in the films deposited at high substrate temperature, the number of grains with the c-axis orientation is large. So the XRD curve becomes smooth and the intensity of ZnO (002) peak becomes strong with the increase of substrate temperature. The crystalline structure of the specimens becomes good. But when the substrate temperature is too high (for example 500°C), the adatoms are decomposed and re-evaporated from the surface.

By using the Scherrer equation, the grain size along the (002) orientation can be evaluated, and the values have been listed in table 1. Since the grain size is inversely proportional to the FWHM, the grain size steeply decreases from the largest value of 40.87nm to the smallest of 22.42nm as the substrate temperature increases from RT to 400°C, and it gradually increases to 28.05nm with a further increase in substrate temperature to 500°C.

Fig.4; shows the SEM images of the surface morphologies of the ZnO films deposited at substrate temperature of RT°C, 100°C, 200°C, 300°C, 400°C and 500°C, respectively. The non-dense ZnO films are obtained at RT. When the substrate temperature is 100°C, 200°C, and 300°C the grain size is smaller (29.25, 27.40, 25.31) respectively, and the films become relatively dense compared with films grown at RT°C as shown in fig.4 (b-d). But in Fig.(4e), the size of the particles is small, some holes appear and the surface of the thin film becomes coarse. The particles can crystallize easily and there are few defects in the films.

At higher substrate temperature increases to higher temperature, dense ZnO films are obtained, and their grain size obviously increase, especially the films at 500°C which have coarse grains. The surfaces of ZnO thin films were more planer and compact as the mobility of adsorbent atoms increased at higher temperatures. There are some bright spots on the surface of ZnO thin films that are considered to be micro particles and drops. Which are produced by ZnO target due to the large energy density of laser. The grain size observed from SEM pictures is also listed in Table 1. From Table 1, the average grain size obtained by the XRD method is different from that found by SEM.

Conclusion

In summary, we have discussed the effect or temperature on the structural and morphological of ZnO thin films, which prepared by ns-pulsed laser deposition on sapphire substrate in chamber with oxygen pressure 5×10^{-2} mbar and 1.6 J/cm^2 laser fluence energy density. The analysis of XRD and SEM results indicate that the structure and crystalline quality of the ZnO thin films improved when the deposition temperature increases from 100 to 400°C, but degrades when the temperature reaches over 400°C. The film deposited at an optimum substrate temperature of 400°C exhibited single phase of ZnO with preferred (002) orientation with an average grain size of (21.42) nm. From SEM was found that the size of the particles is small (21.31) nm and the surface of film becomes coarse with low defect.

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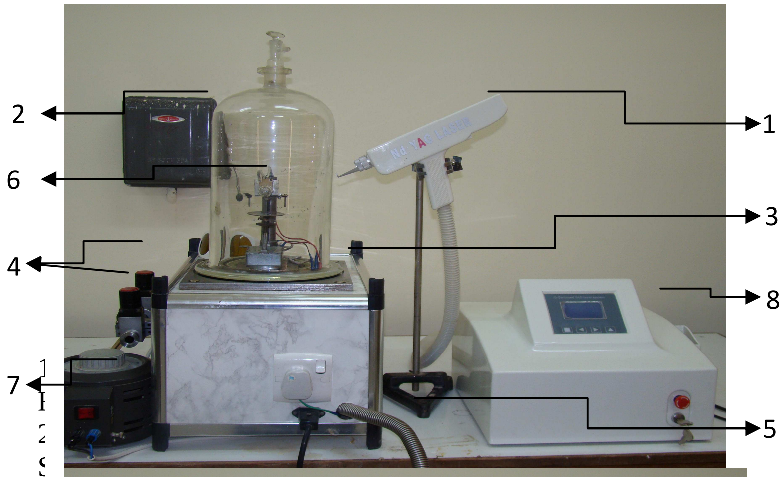
Table 1; Grain size of the ZnO films deposited at various substrate temperatures

	Substrate temperature (°C)					
	RT	100	200	300	400	500
Grain size (XRD) (nm)	40.87	33.56	29.47	26.67	22.42	28.05
Grain size (SEM) (nm)	38	29.25	27.40	25.85	21.31	76.43



3. Stainless steel Flange. 7.Variac devices
3. Vacuum system 8. Nd:YAG laser Power supply

Figure (1): Pulsed laser deposition (PLD) system

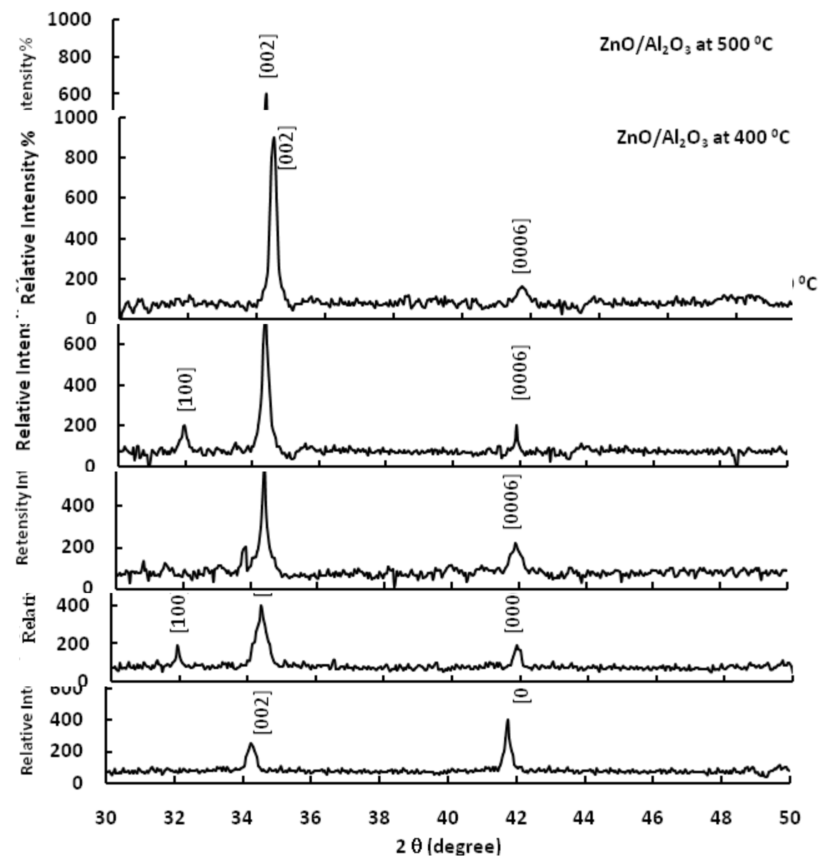


Figure 2; XRD patterns of pulsed laser deposition ZnO thin films grown on sapphire substrate at various substrate temperatures.

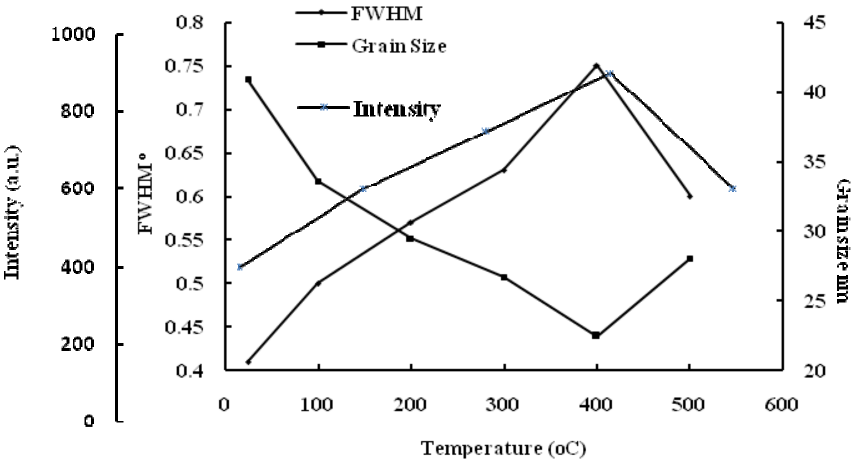


Figure 3; Intensity, position and FWHM of (002) diffraction peak for the ZnO films deposited at different substrate temperature

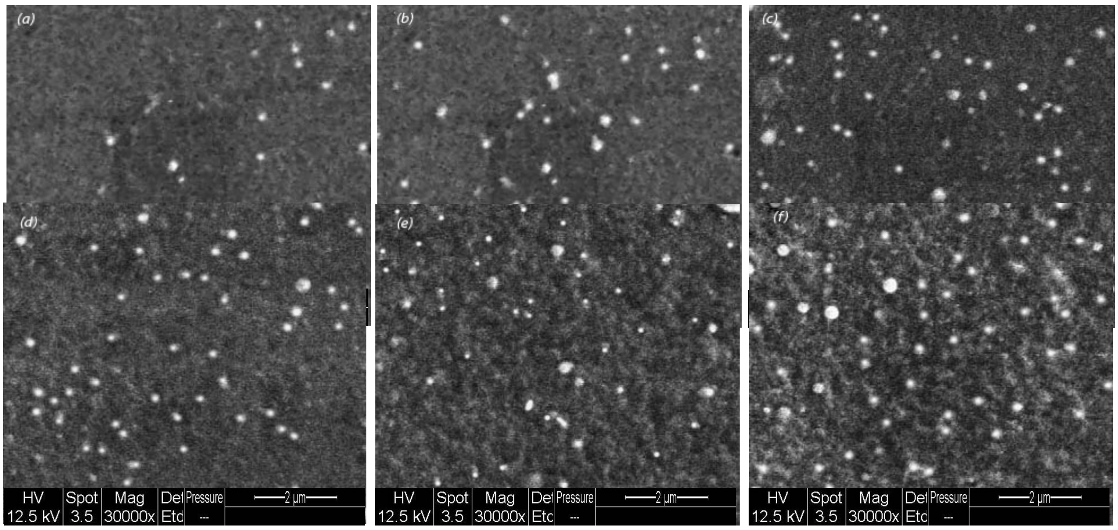


Figure 4; SEM images of ZnO films deposited at various substrate temperatures a)RT°C, b)100°C, c) 200°C, d) 300°C, e) 400°C, f) 500°C.