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Structural and optical properties of hexagonal ZnO nanostructures grown by ultrasonic spray CVD

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ABSTRACT

In this paper, the growth, structural and optical properties of the hexagonal ZnO nanostructures grown by Ultrasonic Spray Chemical Vapor Deposition (USCVD) method at atmospheric pressure have been investigated. The characterizations of the grown thin films have been made with X-ray diffraction (XRD), Atomic Force Microscopy (AFM) and UV–vis Spectrophotometry measurements. Different samples have been grown on the soda-lime glass substrate with different power values of the ultrasonic transducer. Although the hexagonal ZnO nanostructures have been expected to show the polycrystalline structures, they have a strong the x-ray diffraction peaks in (0002) direction. The optical band gap, the grain size and the surface roughness of the hexagonal ZnO nanostructures have been determined. It is shown that, with the increasing power usage of the transducer, the optical transmittance of hexagonal ZnO nanostructures has decreased in the visible area. The optimum power usage of transducer used in USCVD method has been determined for the further studies.

1. Introduction

ZnO materials have been widely used in the optoelectronic applications due to its direct wide band gap of ~3.37 eV and large exciton binding energy of ~60 meV at the room temperature [1–3]. The ZnO is frequently used as an electronic and optoelectronic material in the solar cells, transparent conductor, transparent transistors [4,5]. The ZnO crystallizes in two form of hexagonal and cubic structures and it is stable in the hexagonal structure [6]. The different growth methods such as Molecular Beam Epitaxy (MBE), Chemical Vapor Deposition (CVD), RF-Magnetron sputtering, Pulsed Laser Deposition (PLD), Sol-gel dip coating are used to grow the ZnO thin films [7–11]. In order to obtain the high-quality ZnO crystal, researchers usually have been used MBE and CVD methods, although, in the recent years, the CVD with ultrasonic spray which is named as USCVD have been carried out to grow the ZnO thin films because of usage of inexpensive and non-toxic materials, and non-vacuum growth system with low cost of ownership [12–14].

Among the growth methods, the CVD growth methods are important due to the high crystal quality, easy to grow the thin film or bulk materials. In the USCVD method, the liquid precursor becomes a cold vapor by using the ultrasonic transducer, and then the cold precursor vapor is used for growth on the substrate. It is reported that the high-quality ZnO thin films were grown in the USCVD growths [15]. In these growths, the electrical power used by the ultrasonic transducer used in

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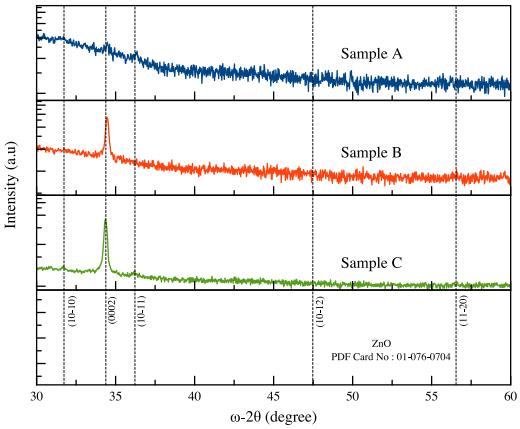

Fig. 1. XRD results of the samples.

the system is important in terms of the precursor vapor density and vapor particle size. Because the precursor vapor is proportional to the electrical power of the ultrasonic transducer, controlling the power values of the transducer is vitally important for the control of growth of ZnO with USCVD method.

ZnO can be grown with differently shaped nanostructures. Some articles have been reported ZnO nanostructures with hexagonal, flower and star shapes [16–18]. Growing differently shaped ZnO nanostructures is important in terms of the present new possibilities to fabricate new kind of devices [19]. Because of the relationship with this study, hexagonal or triangular shaped ZnO nanoplate like nanostructures can be shown as an example of these new possibilities. These structures are already reported as anode materials for the Li-ion battery in terms of high charge capacity [20].

In this paper, hexagonal ZnO nanostructures with hexagonal shape have been grown on the soda-lime glass with USCVD at atmospheric pressure. Effect of using different ultrasonic transducer power on structural, surface and optical properties of hexagonal ZnO nanostructures have been observed.

2. Experimental details

ZnO nanostructures were deposited on soda-lime glass by USCVD method. Zinc acetate dihydrate salt [$(CH_3COO)_2.2H_2O$, Sigma Aldrich ≥% 99] was dissolved in (25:75) mixture of acetic acid and deionized water (DIW). A prepared precursor solution of 0.05 M was stirred in a magnetic stirrer at the room temperature in order to adequately dissolve the zinc acetate salt. The glass substrates were ultrasonically cleaned with Ethanol, Acetic acid, and DIW and were dried in Nitrogen (N_2) atmosphere. the quartz tube was kept at the Argon (Ar % 99.99) atmosphere until reaching growth temperature. During the growth, the solution is vaporized with 1.7 MHz ultrasonic transducer and carried to the reactor with Oxygen gas (O_2) at a flow rate of 5 L/min. The time and the temperature of the growth were used as a 15 min and 450 °C. After the growth, the samples were cooled in the Ar atmosphere. The grown samples are named as A, B, and C for the increasing ultrasonic transducer electrical power usage, respectively. The crystallite characterization of the samples was done with X-Ray Diffraction (XRD) using a Rigaku ATX-G CuKα (λ = 0.154 nm) line. The surface morphology of the samples was analyzed with Atomic Force Microscopy (AFM) measurements in the sample area of $5 \times 5\ \mu m^2$. Lastly, the optical properties of the samples were investigated by UV–vis transmittance measurements using a Shimadzu UV-3600 spectrophotometer.

3. Results and discussion

Fig. 1 shows the XRD results of the hexagonal ZnO nanostructures. The sample B and C show a preferred crystalline structure in the (0002) direction. However, sample A has lower (0002) diffraction peak and therefore no dominant diffraction direction is found for the sample A. The XRD peaks are increased with increasing the electrical power usage of the ultrasonic transducer. Therefore, it can be seen the relation between the peak intensity and the electrical power usage of the transducer. To determine the grain size of the samples can be used from the XRD results with Scherrer's formula given in Eq. (1) [21];

$$D = \frac{0.89\lambda}{\beta cos\theta} \tag{1}$$

where D and λ are the grain size with a spherical approximation of the grown structure and the wavelength of X-ray used in XRD measurements, respectively. β and θ are the full width at half maximum (FWHM) of the related diffraction peak and Bragg's diffraction angle, respectively. The calculated grain sizes of the samples are listed in Table 1.