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The influence of the prefiring temperature on the structure and surface morphology of sol-gel derived ZnO film

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C-axis oriented ZnO thin films were prepared on silica glass substrates by the sol-gel method using a zinc naphthenate precursor. As-deposited films were prefired at 250 °C for 60 min, at 350 °C for 30 min, and at 500 °C for 10 min, followed by final annealing at 600–900 °C in air. Crystal structure, surface morphology, surface roughness and transmittance at the visible range were analyzed by high resolution X-ray diffraction, field emission scanning electron microscopy, scanning probe microscopy, and ultraviolet spectrophotometry. (002)-oriented ZnO films were obtained by annealing at 600 °C, and at higher temperatures for the films prefired at 350 °C and 500 °C. All the films exhibited a high transmittance, above 80%, in the visible region, and showed a sharp fundamental absorption edge at 0.38–0.40 μm. The most highly *c*-axis oriented ZnO with a homogeneous surface was observed at a prefiring temperature of 350 °C.

Key words: *ZnO thin film; sol-gel method; zinc naphthenate*

1. Introduction

The wet sol-gel method provides a simple and versatile alternative for crystalline thin film preparation [1–5]. In terms of stability in air and ease of handling, metal naphthenates are more advantageous as starting materials than metal alkoxides [6, 7]. Preparation of the coating solution using zinc naphthenate was easy by the addition of toluene, while a complicated procedure was needed for coating a metal alkoxide-

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derived solution. Furthermore, it should be noted that vaporization of additives such as alcohol, H_2O and catalyst etc. during prefiring and final heat treatment might cause cracks and pores in the product layer, and this disturbs the preparation of high quality oxide layers. However, the sol-gel method is relatively new and requires a greater understanding of the relation between processing and defects in order to optimize the film quality. Although the film shows a high orientation, pores and cracks due to vaporization of organics in film are easily recognizable in highly oriented films [8].

The authors suspected that the films might be excessively locally heated to high temperatures such as 600–900 °C because organic compounds that decompose and evolve during the pyrolysis are rapidly burned out. This may cause random nucleation and heterogeneous crystal growth, thus disturbing high orientation or epitaxy. Thus, comparison between the prefiring temperatures was considered to be important in order to achieve homogeneous nucleation resulting in high orientation.

In order to develop high quality ZnO films for devices with good performance, it is necessary to clarify the effect of heating conditions on growth. This will result in different microstructures suitable for various applications. The thermal analysis on zinc naphthenate shows that pyrolysis begins at 200 °C and is completed below 500 °C. Thus in the presented study prefiring temperatures were varied at 250–500 °C in order to clarify the effect of organics on the properties of ZnO.

2. Experimental

Zinc naphthenate (Nihon Kagaku Sangyo Co., Ltd., Japan) was used as a precursor in the sol-gel process by diluting the sol with toluene. The concentration of metal ions in the coating solution was about 4 wt. %.

Thin films were fabricated by spin coating onto 2.5 cm×2.5 cm×1 mm substrates made of silica glass at the rotation speed of 1500 rpm for 10 s. After each deposition, the coating film was pyrolyzed in air at 250 °C for 60 min, 350 °C for 30 min, and 500 °C for 10 min to decompose the organic species. For multiple coatings, the above-mentioned processes were repeated five times to obtain the resultant films approximately 0.5– 0.6 μm thick. The resultant films were directly annealed in a preheated furnace at 600–900 °C for 30 min in air. Table 1 shows the symbols used for the products.

Table 1. Symbols of the product films

Final annealing	Prefiring		
	250 °C	350 °C	500 °C
600 °C	A1	B1	C1
700 °C	A2	B2	C2
800 °C	A3	B3	C3
900 °C	A4	B4	C4

Thermogravimetric analysis (TGA, DTG-60, Shimadzu, Japan) was performed using an α-alumina reference and the heating rate of 10 °C/min in the range 16–600 °C. The phase evaluation of the films was examined by a high resolution X-ray diffractometer (HRXRD, X'pert-PRO, Philips, Netherlands) using CuK$_\alpha$ radiation in θ–2θ geometry. The surface morphology and composition of the films were evaluated from the field emission scanning electron microscopy (FE-SEM, S-4700, Hitachi, Japan) micrographs and energy dispersive X-ray spectrometry (EDS). The growth mechanism and surface roughness of the films were studied with a scanning probe microscope (SPM, Nanoscope IV, Digital Instruments, U.S.A.). All the SPM measurements were performed in air using the tapping mode. The transmittance in the visible spectra range was measured with an ultraviolet–visible–near infrared spectrophotometer (CARY 500 Scan, Varian, Australia). The transmittance was automatically calibrated against a bare glass substrate as a reference sample, and the absorption coefficient was obtained from the transmittance curve.

3. Results and discussion

Figure 1 shows the TGA curve of the starting solution dried at 80 °C for 24 h to remove the solvent. Weight loss corresponding to pyrolysis of the metal naphthenate began at around 160 °C and was completed at below 500 °C. Therefore, it was concluded that pyrolysis of the starting metal naphthenate solution is completed below 500 °C. Thus, to investigate the effects of conditions of the pyrolysis on metal naphthenate during the final heat treatment, we prepared ZnO thin films via the prefiring conditions described in the Experimental.

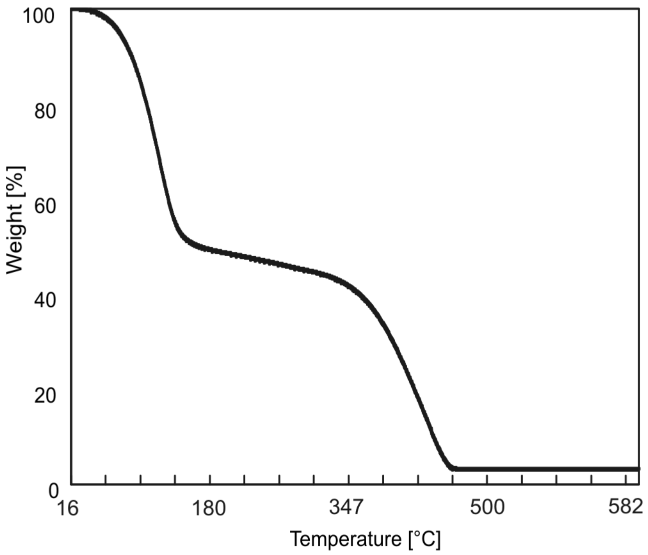

Fig. 1. TGA curve of the coating solution used in this work

All the precursor films, pyrolyzed through three paths, were found to be amorphous by XRD, and have smooth surfaces without cracks or voids as confirmed by FE-SEM observation. No significant difference was identified among these films. There were differences, however, in the content of residual carbon or carbon hydroxides in the precursor films. Residual carbon content in the films was investigated by EDS.

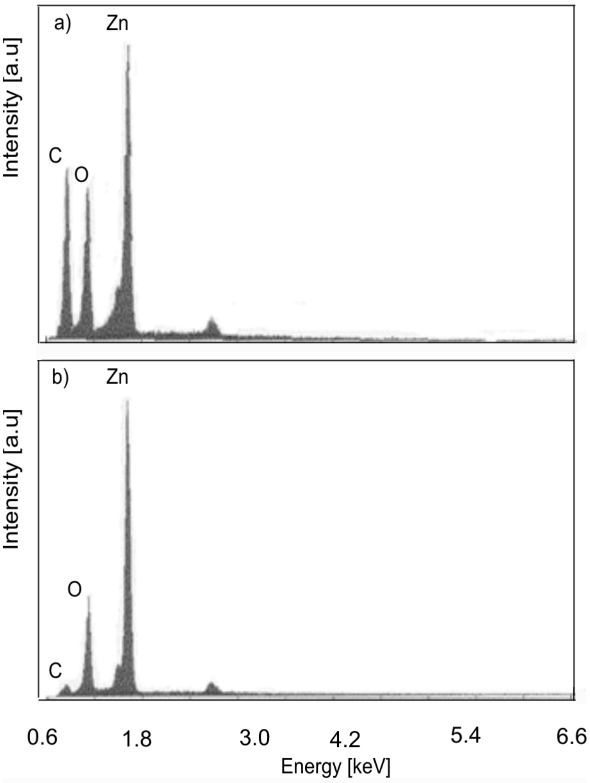

Fig. 2. EDS spectra for the surfaces of the films after prefiring:
a) at 250 °C for 60 min, b) at 500 °C for 10 min

Figures 2a, b show EDS spectra of the precursor films pyrolyzed at 250 °C for 60 min and at 500 °C for 10 min, respectively. Comparing these spectra, a large peak of CK_α was recognized in Fig. 2a. It is apparent that precursor films pyrolyzed at 250 °C for 60 min contained a larger amount of carbon than those pyrolyzed at 500 °C for 10 min.

Figure 3 shows XRD θ–2θ scans of the ZnO thin films pyrolyzed at 250 °C for 60 min (3a), at 350 °C for 30 min (3b), and at 500 °C for 10 min (3c), followed by final heat treatment at various temperatures. The (002) oriented ZnO thin films were obtained by final heat treatment at 600 °C and at higher temperatures for the films pyrolyzed at 350 °C and 500 °C. When the pyrolysis temperature was too low, at 250 °C, crystallization and orientation of ZnO thin films was very difficult to induce:

the resultant ZnO thin films A1–A4 were found to be amorphous or non-oriented. By contrast, in the films B1–B4, a distinct (002) peak of ZnO was recognized. Upon increasing the final heat treatment temperature to 800 °C and 900 °C, a strong ZnO (002) peak was seen. It should be noted that the peak intensity of ZnO thin films was significantly affected by the pyrolysis temperature, although the final heat-treatment temperature was the same. The lower peak intensity of resultant films, shown in Fig. 3a, may be attributed to the presence of residual organic components.

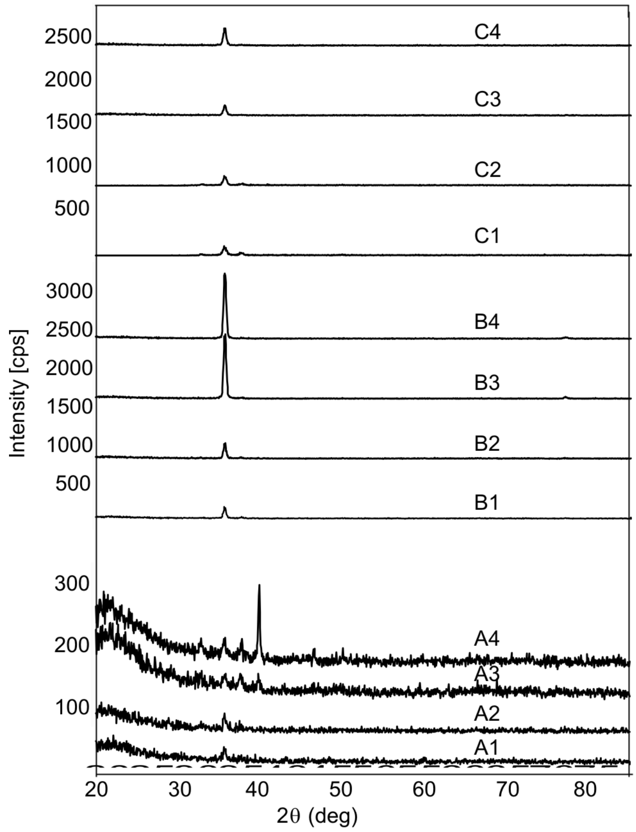

Fig. 3. XRD spectra of finally annealed films prefired:
a) at 250 °C for 60 min, b) at 350 °C for 30 min, c) at 500 °C for 10 min

EDS analysis indicated that the ZnO thin films which had been pyrolyzed at 250 °C contained much residual carbon or carbon hydroxides. In this case, crystallization of the film and decomposition of organic compounds proceeded concurrently during the final heat treatment. Crystal growth may be suppressed by residual carbon during the final heat treatment, resulting in the low peak intensity of ZnO thin films A1–A4 [9].

From the report of Ohyama et al. [10], for ZnO thin films prepared by using sol-gel with zinc acetate–2 methoxyethanol–monoethanolamine solution, when the heating rate is low, the gel film is given enough time to structurally relax before crystallization, resulting in denser ceramic films. Moreover, when the prefiring temperatures are too high (higher than 300 °C), vaporization of the solvents, and thermal decomposition of zinc acetate may take place abruptly and simultaneously with the crystallization, disturbing the unidirectional crystal growth [10]. However, in our work ([11] and present work), highly *c*-axis-oriented ZnO films were obtained by prefiring at higher temperatures, specifically at 350 °C and 500 °C. Previously, we reported that structural relaxation of the precursor gel before crystallization, by employing solvents having high boiling points about 200 °C is unessential for obtaining oriented ZnO thin films when using a zinc naphthenate precursor [11]. We prepared ZnO thin films exhibiting a strongly preferred orientation by using toluene which has a relatively low boiling point.

However, it should be noted that when the prefiring temperatures are too high, such as 500 °C, crystallinity of the ZnO thin films is decreased. This result suggests that abrupt and simultaneous thermal decomposition of zinc naphthenate, probably due to a high prefiring temperature, may slightly corrupt unidirectional crystal growth. In the sol-gel process, several actions occur simultaneously in the thermal treatment process, such as the evaporation of the dissolvent, the decomposition and evaporation of organics and the growth of ZnO grain, etc. [12]. At an excessively high prefiring temperature, the decomposition process is hastened and less time is left for gel films to undergo structural relaxation which induces a decrease in the quality of ZnO.

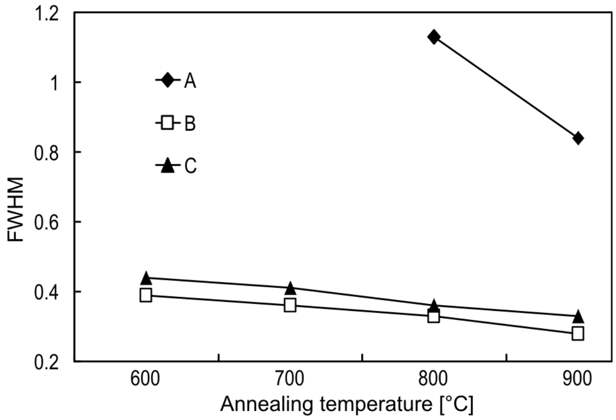

Fig. 4. FWHMs of finally annealed films in function of prefiring temperature

We also observed that with an increase in heat treatment temperature, the full width at half-maximum (FWHM) decreases, as shown in Fig. 4. In addition, the highest crystallinity is observed for the films pyrolyzed at 350 °C. These results indicate that ZnO thin films prepared with zinc naphthenate and prefired at 350 °C can be expected to have high crystallinity. For the films prefired at 350 °C, the (002) peak intensity of the ZnO films markedly improves with an increase in the annealing temperature. The increase in intensity of the (002) orientation may be attributed to reorientation of the crystallites obtaining sufficient energy at higher annealing temperature. This results in obtaining ZnO with superior crystallinity and a higher degree of orientation. More research for the relation between the crystallization and the exact organic species and contents will be done.

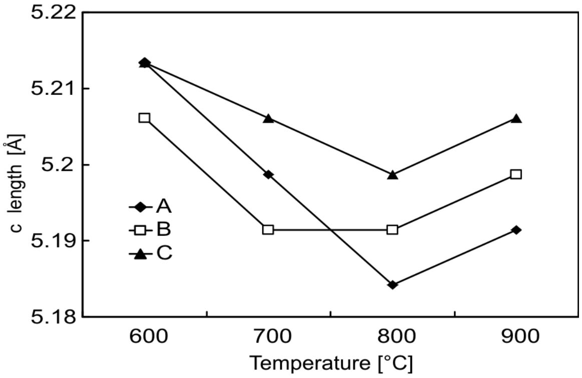

Fig. 5. Length of the *C* period of finally annealed films in function of prefiring temperature

Based on the XRD data, the lattice *c* parameter has been estimated to be 5.1842 –5.2134 Å, as shown in Fig. 5. These values are similar to the ASTM value of 5.2066 Å for the bulk ZnO. The larger value of the lattice constant for the thin film at 600 °C as compared with the standard powder value shows that the unit cell is elongated along the *c* axis, and that compressive forces act in the plane of the ZnO thin film. These compressive forces disappear as the heat treatment temperature is increased.

In order to more exactly investigate the structural properties of ZnO thin film, we calculated the stress in the film. The calculation is based on the biaxial strain model [13]. The strain $\varepsilon = [(c_{\mathrm{bulk}} - c_{\mathrm{film}})/c_{\mathrm{bulk}}]$ in the direction of the *c* axis, i.e., perpendicular to the substrate surface, was measured by XRD. To derive the stress of film parallel to the film surface, the following formula has been used [13], which is valid for a hexagonal lattice:

$$s_{\mathrm{film}} = \frac{2c_{13}^2 - c_{33}\left(c_{11} + c_{12}\right)}{2c_{13}} \frac{c_{\mathrm{film}} - c_{\mathrm{bulk}}}{c_{\mathrm{bulk}}} \tag{1}$$

Thee following elastic constants c_{ij} of single crystalline ZnO have been used: $c_{11} = 208.8$, $c_{33} = 213.8$, $c_{12} = 119.7$ and $c_{13} = 104.2$ GPa [14]. Stress in the film can be estimated using Eq. (1) and is plotted in function of final heat treatment temperature in Fig. 6. The negative sign for the films A1 and C1 heat treated at 600 °C indicates that the lattice constant *c* is elongated as compared with unstressed powder, and therefore the film is compressed in the direction parallel with the surface, i.e., when a film is constrained and compressed by a substrate, the normal direction to the substrate surface is elongated. After a further heat treatment above 700 °C, films enter into a state of compression as compared with the normal lattice state of bulk ZnO.

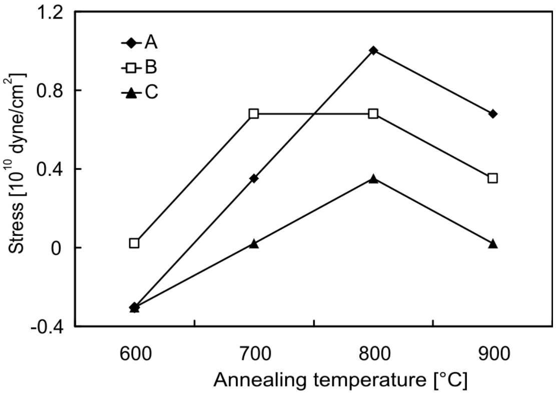

Fig. 6. Variation of stress induced in the finally annealed films in function of prefiring temperature

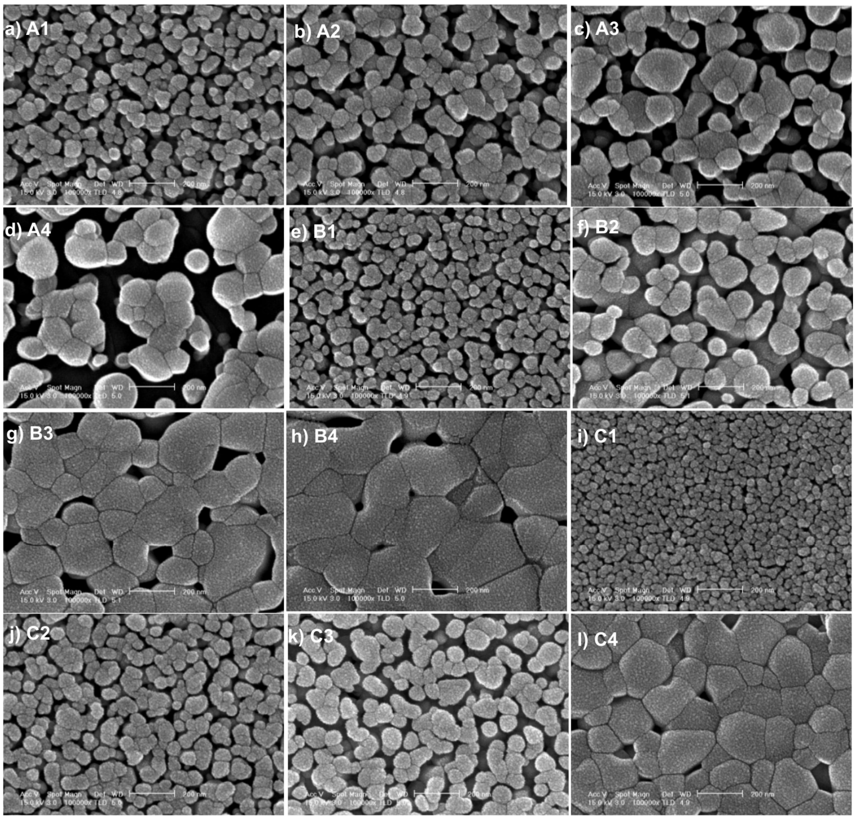

Fig. 7. FE-SEM images of the finally annealed films prefired at 250 °C for 60 min (a–d), at 350 °C for 30 min (e–h), and at 500 °C for 10 min (i–l)

Figure 7 shows the FE-SEM photographs of the ZnO thin films pyrolyzed at 250 °C for 60 min (a–d), at 350 °C for 30 min (e–h), and at 500 °C for 10 min (i–l), followed by final heat treatment at 600–900 °C for 30 min in air. Particulate structure is evident in all the films. The particle size increases with increase of the heat treatment temperature. It is obvious that the particle size increased with the increased annealing temperature which is consistent with the ZRD results. According to Hsieh et al. [15], the atoms would obtain enough energy to occupy proper sites in the crystal lattices, and grains with lower surface energy would become larger at higher temperatures. However, formation of polycrystalline films with grain boundary micropores, prefired at 250 °C, A3 and A4, is quite obvious from the micrographs. As the prefiring temperature decreases, the amount of organics in the prefired film increases, and therefore the decomposition and the crystallization may occur almost simultaneously. Since the structural relaxation of the prefired film induced by the decomposition can take place only before the crystallization, the simultaneous decomposition and crystallization may give the film less chance to be structurally relaxed, resulting in a microporous structure (see Fig. 7c and d).

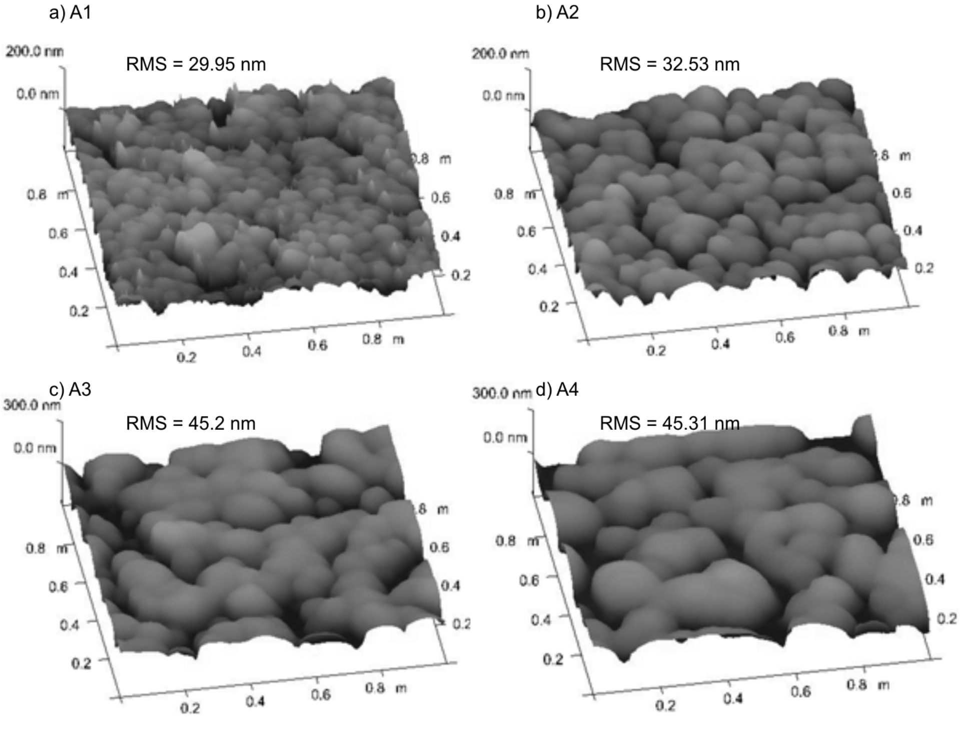

Fig. 8. SPM images (1×1 μm^2) of the finally annealed films prefired at 250 °C for 60 min

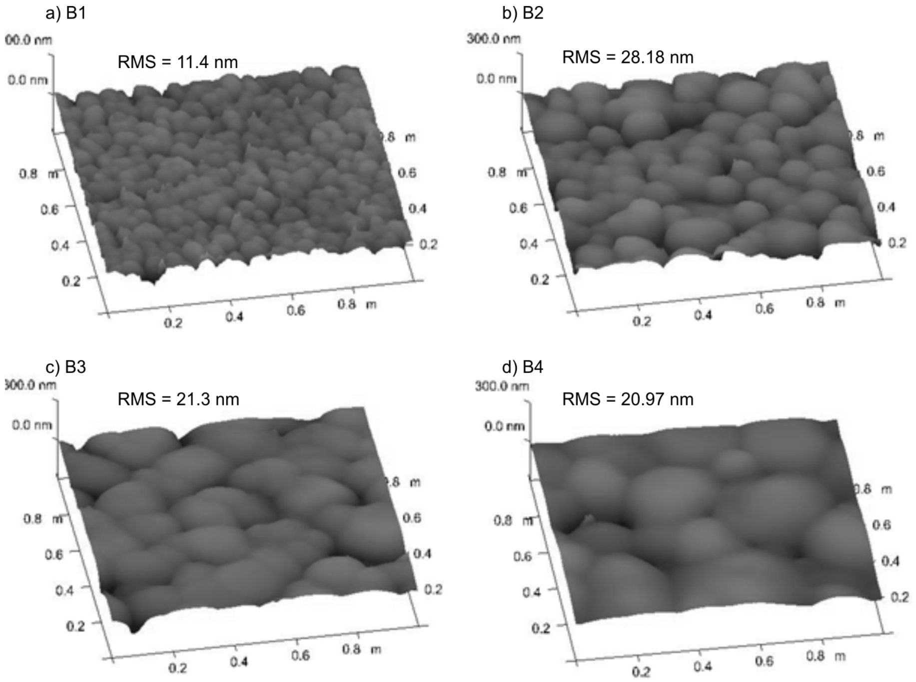

Fig. 9. SPM images (1×1 μm^2) of the finally annealed films prefired at 350 °C for 30 min

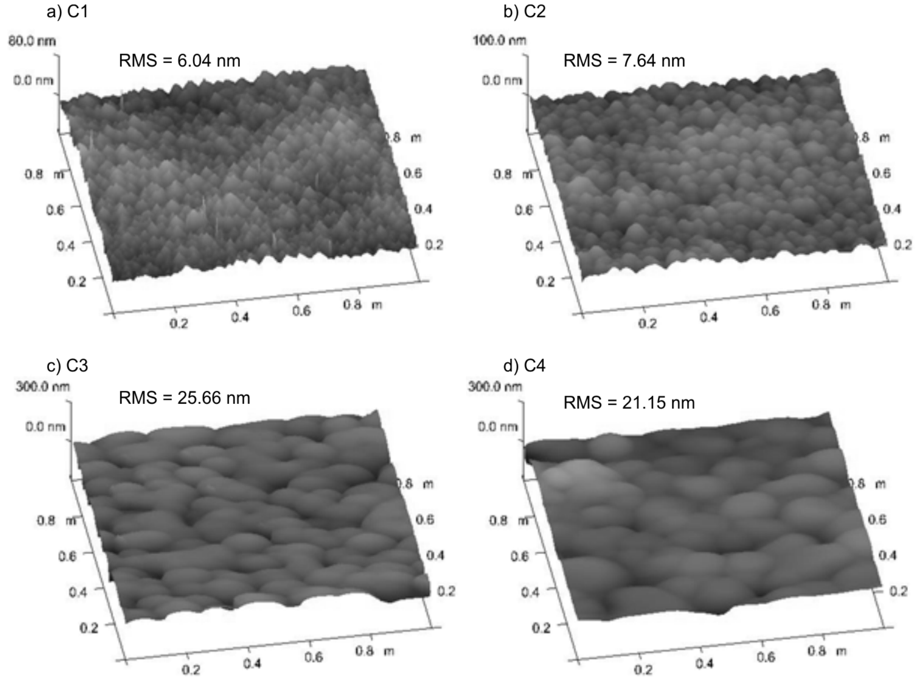

Fig. 10. SPM images (1×1 μm^2) of the finally annealed films prefired at 500 °C for 10 min

To evaluate the surface roughness and morphology of the films, SPM analysis was performed. Figures 8–10 show the SPM images (1×1 μm^2) of ZnO thin films pyrolyzed at various temperatures, followed by final heat treatment at 600–900 °C. With increasing heat-treatment temperature to 800 °C, nanosized grain growth is observed to gradually increase. At 900 °C, large grain growth is easy to identify, although the grain size uniformly increased with increasing heat treatment temperatures for all the pyrolysis temperatures. Furthermore, with an increase in annealing temperature, the root-mean-square (RMS) roughness increased to 45.2 and 45.31 nm for the films A3 and A4 pyrolyzed at 250 °C. This may be because of the pores between grains, which were confirmed by FE-SEM. On the other hand, for the films B3, B4, C3 and C4 pyrolyzed at 350 °C and 500 °C, the surface roughnesses of the annealed ZnO thin films at 800 °C and 900 °C were decreased. With increase in temperature, a smoother surface might be expected, due to an increased surface mobility of the species [16].

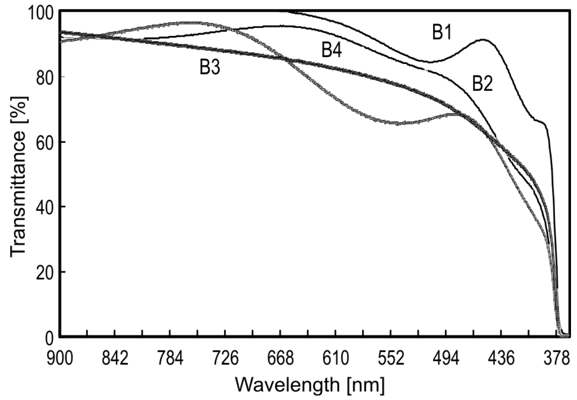

Fig. 11. Transmittance of the finally annealed films prefired at 350 °C for 30 min

Figure 11 shows transmission spectra of the annealed ZnO thin films pyrolyzed at 350 °C for 30 min. All the films exhibit transmittance higher than 80%) in the visible range and show a sharp fundamental absorption edge at about 0.38–0.4 μm which is very close to the intrinsic band gap of ZnO (3.2 eV). With an increase in annealing temperature, the transmittance decreased gradually. The high transmittance of all the films is attributed to small particle size minimizing light scattering, and low surface roughness. The optical band gap (E_g) is in the range between 3.26 eV and 3.28 eV. The estimated values of the band gap for all the films are within the range reported for such films [17]. Homogeneous transparent ZnO thin films having a high *c* axis orientation were observed at the pyrolysis temperature of 350 °C for 30 min.

4. Conclusions

Highly *c* axis oriented ZnO thin films were prepared on silica glass substrates by a sol-gel process using zinc-naphthenate as a precursor. When the prefiring temperature was too low, at 250 °C, crystallization and orientation of the films were very difficult to induce. The XRD peak intensity of ZnO films was significantly affected by the prefiring temperature, although the final annealing temperature was the same. With an increase in annealing temperature, the RMS roughness abruptly increased for the films prefired at 250 °C, while for the films prefired at 350 °C and 500 °C, the RMS roughness was somewhat decreased at 800 °C and 900 °C. Homogeneous and transparent ZnO thin film showing a high *c*-axis orientation was observed at a prefiring temperature of 350 °C for 30 min.

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