STUDY ON ZNO FILM PROPERTIES UNDER THE EFFECTS OF PH VALUE

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Abstract

This study investigated the influences of pH values on the morphology and properties of ZnO:Al (AZO) films by sol-gel technique. Spectroscopic Ellipsometry (SE) technique was developed to characterize the microstructure properties of AZO films. Results show that film crystalline orientation was affected by the pH value and the aging time of the solution while highly-oriented AZO films did not have the highest conductivity. Besides, the film conductivity was also affected by its relative density which could be quickly obtained by SE technique after appropriated optical models had been established.

Introduction

Among many deposition techniques for ZnO films [1-8], the sol-gel method is not only simple and low-cost for coating large area high quality TCO films, but also enables us to tailor the film properties with the chemistry of the sol-gel synthesis. Unfortunately, sol-gel derived crystalline structure suffers quality limitation regarding electrical and optical properties. The high density of carrier traps and potential barriers at grain boundaries deteriorate film properties sharply. However, several studies reported that the AZO film properties can be improved by optimizing deposition parameters such as the preparation and annealing conditions [7, 8]. As for deposition parameters, the relation between microstructure and opto-electrical properties of ZnO films is further to be understood and clarified. Particularly in the sol-gel procedure, different nucleation and growth processing can result in similar conductivity values [9]. Thus, in order to precisely control the stability of the conductivity of AZO films, the microstructural properties of these films need to be taken into account. For this reason, we investigated the influences of the pH values of the sol solution on the structural and electrical properties of AZO films. The refractive indices and thickness of the AZO films were then estimated by a spectroscopic ellipsometry.

Experimental

A solution of 0.5M was prepared with zinc acetate and methanol. Then, proper amount of aluminum nitrate was added to make the ratio of Al/Zn atoms 1 at.%. As stabilizer, monoethanolamine (MEA) was added to prepare solution A, B, and C. The molar ratio of MEA:ZnAc in solution A is 1:1; the pH value is 7.4. The molar ratios of both solution B and C are 4:1, and both solutions had the pH value of 10.5. Solution A, B, and C were heated at 45℃ for 3 h, 3h, and 24h respectively. A silicon substrate was dipped into the solution and withdrawn at a speed of 10cm/min. Then, the substrate was dried at 70℃ for 10min in a furnace and undergone pre-heat treatment at 600℃ for 1h. After repeating this procedure for 4~5 times, post-heat treatment was carried out under vacuum (~1 mtorr) at 600℃ for 1h. For solution A, B and C, samples A, B, and C were respectively marked.

Results and Discussion

Though film thickness and relative density could be quickly obtained by SE procedure, the deviation in the VU region became very obvious as the film thickness increased. This implied that with increasing thickness the film properties became different. Fig. 1 shows the relation of film thickness and layer number between samples A and B. However, sample C turned white and opaque at the fourth layer. Thus, it was impossible to measure its thickness with SE method. Fig. 2 shows the refraction index (with respect to wavelength 550 nm) and the relative density of each layer of samples A and B. Both values increased along with layer number. However, after the 4th layer, the refraction index and the relative density didn't increased after reaching a certain value, which implied the films are porous. This might be one of the reasons for the high resistance of the films.

Relative intensity of (002) peak obtained from the XRD pattern showed that a higher pH value can enable the crystalline to grow in direction (002), see fig. 3a, 3b. The (002) of sample B with 5 layers was found to have the highest intensity. By comparing fig. 3b and 3c, we can understand the influence of heating time on the nucleation behavior. Longer heating time caused methanol to evaporate. Thus, the viscosity of sol solution became higher, and more nuclei were produced. As a result, the XRD pattern is similar to that of ZnO powder. By using the Scherrer formula [11], the crystalline size of sample A with 5 layers was found to be ca. 28.3nm, of sample B with 5 layers ca 24.3nm, and sample C with 5 layers ca. 30.8nm. The measurement of electricity showed that the resistances of the samples were C＜A＜B, see table 1. These values are in consistence with the crystalline size. It is to be noticed that the pH values of solution B and C were both 10.5. However, the

resistance of sample C can be as low as 7.585×10-3Ωcm. It is because the solution needs a longer time to become homogeneous when more MEA is added. Therefore, due to the uncompleted polycondensation, sample B didn't have the higher conductivity crystalline though it was highly oriented. This also led to inferior crystallinity.

Conclusion

In this study, the SE optical models of AZO films were successfully established and applied to measure film thickness and relative density. It is found that the change of pH values can be used to control the grow direction of thin film. However, highly-oriented AZO films do not necessarily have the highest conductivity since conductivity is also affected by the relative density. Based on these results and our early works, we believe that the developed techniques in this study enable us to further improve film quality by controlling chemistry of the sol-gel technique.

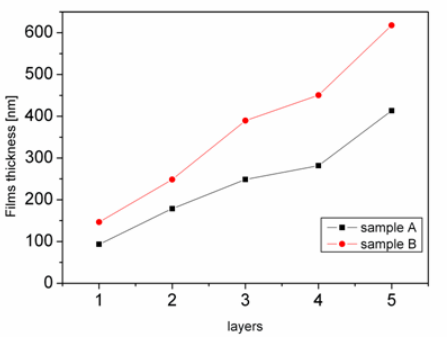


Fig. 1: Comparison of film thickness and layer number of samples A and B

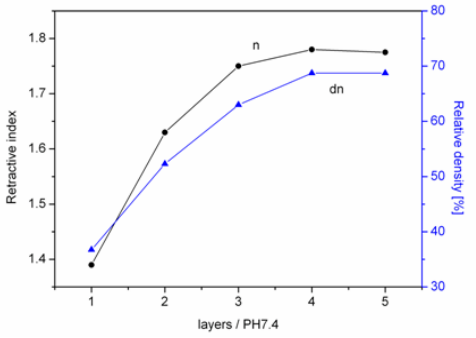
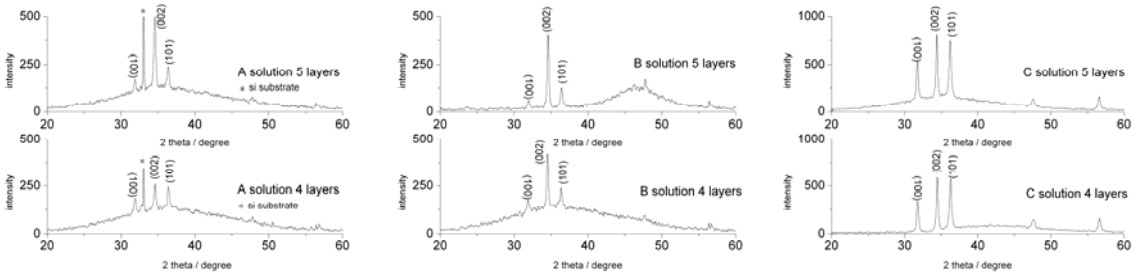


Fig. 2: Relative index and relative density of each layer obtained with SE, sample A.



(a) (b) (C)

Fig. 3: XRD patterns of sample A, B, C

Table 1: Resistance according to layer number

Ω CM	A	B	C
4 layers	1.863×10^{-2}	2.475×10^{-2}	1.053×10^{-2}
5 layers	1.653×10^{-2}	2.126×10^{-2}	7.585×10^{-3}

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