TWO-STAGE CHEMICAL DEPOSITION OF OXIDE FILMS

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Abstract Two-stage chemical deposition (TSCD) technique is used to produce ZnO, Mn_2O_3 and NiO films on soda-lime glass (SL-G) from an aqueous solution of zinc, manganese and nickel complex, respectively. The TSCD method enables the deposition of metal oxide thin films with a thickness which can be controlled during the preparation procedure. The ZnO, Mn_2O_3 and NiO thin films were polycrystalline films which were adherent well to the substrates. The SEM micrographs clearly indicate that the zinc oxide layer is composed of oval shaped crystallites preferably orientated perpendicular to the surface of the substrate. The Mn_2O_3 and NiO layers were closely packed on the substrate. These particles seem to grow from the surface of the substrate.

Keywords Zinc Oxide, Manganese Oxide, Nickel Oxide, Soda-Lime, Oval-Shaped Particles

چکیده در این مقاله از تکنیک رسوب شیمیایی دو مرحله ای (TSCD) برای تولید لایه های نازک اکسید روی (ZnO)، اکسید منگنز (Mn_2O_3) و اکسید نیکل (NiO) روی شیشه سودا لایم به ترتیب با استفاده از محلول آبی شامل کمپلکس روی، منگنز و نیکل استفاده شده است. روش TSCD قابلیت رسوب لایه های نازک اکسید فلزی با ضخامت مشخص که می‌تواند در حین فرآیند تولید کنترل شود را دارد. لایه های نازک اکسید روی، اکسید منگنز و اکسید نیکل، پلی کریستالی بوده و چسبندگی خوبی به سطح زیر لایه دارند. میکروگراف های SEM به خوبی نشان می دهند که لایه اکسید روی از کریستالیت‌های دوکی شکل که ترجیحاً در جهت عمود بر سطح زیر لایه آرایش گرفته اند، تشکیل شده است. لایه های اکسید منگنز و اکسید نیکل روی سطح زیر لایه فشرده بوده و به نظر می‌رسد که این ذرات از سطح زیر لایه شروع به رشد کرده اند.

1. INTRODUCTION

Several methods are applied to prepare metal oxide films, both physical and chemical deposition technologies including sputtering [1], pulsed laser deposition [2], chemical vapor deposition [3], molecular beam epitaxy [4], sol-gel process [5], spray pyrolysis [6], electroless bath deposition [7] and chemical bath deposition [8-12]. However, most of the methods were not well suited for large area coating, low-temperature processing, and low process cost. So far, the above mentioned methods could not be used for ZnO crystal fabrication below 150˚C. Again, the equipment is expensive for large area process. Therefore, chemical bath deposition has been an attractive technology which is simple and low cost for thin-film fabrication. Preparation of oxide film in a chemical solution bath presents several advantages: (1) films can be obtained on substrates at low temperature, below 100˚C (2) the thickness and morphology of film can be controlled by deposition parameters, (3) the equipment is relatively cheap, (4) the technique is more environmentally friendly, and (5) the deposition can be performed onto any kind of substrate that is inactive with respect to the chemicals used [8]. These supply the technique compatibility for the low-cost process and good quality. Two-stage chemical deposition (TSCD) is an advantageous technique for formation of a

largely surfaced thin film. Deposition of ZnO, Mn_2O_3 and NiO films with controllable thickness is made possible by using this method. Although an overwhelming volume of literature confines to the deposition of ZnO, Mn_2O_3 and NiO, very little attention has been paid to the two-stage ZnO chemical deposition and no studies have been conducted on the preparation of chemically deposited manganese and nickel oxide. In this paper, we present the results obtained from the preparation of various metal oxides such as ZnO, Mn_2O_3 and NiO films using the TSCD method and their material characterization.

2. EXPERIMENTAL PROCEDURE

2.1. Raw Materials The initial materials such as zinc chloride, manganese chloride, nickel chloride, ammonia, and Tiron were purchased from Merck and used without further purification.

2.2. Deposition Processing of Oxide Films Soda-lime glass plates with 25×15×1 mm dimensions were used as the solid substrate for film growth. After degreasing, the plates were washed with deionized water and dried in a stream of hot air. The final solution composition and the bath conditions are shown in Table 1. The zinc, manganese and nickel complex solutions having the composition shown in Table 1 were prepared by mixing concentrated NH_4OH with 0.5M $ZnCl_2$, $MnCl_2$ and $NiCl_2$, respectively. After mixing concentrated ammonia with chloride compounds, white $Zn(OH)_2$, brown $Mn(OH)_2$ and green $Ni(OH)_2$ were precipitated. Further addition of NH_4OH resulted in dissolving of these precipitates. The solutions were diluted up to appropriate concentrations of Zn^{+2}, Mn^{+2} and Ni^{+2} complexes. This was found to be the most convenient concentration for production of a good quality films on the substrate then Cleaned substrates were immersed into a cold complex-containing solution and then in hot water for 2 seconds. After a required number of dipping, the substrates which were immersed in the complex solution contained Zn^{+2}, Mn^{+2} and Ni^{+2} were deposited with ZnO, Mn_2O_3 and NiO films, respectively. The substrates with the deposited ZnO, Mn_2O_3 and NiO films were annealed at 400˚C in a tube furnace for 1 h.

2.3. Deposit Characterization The oxide films produced in this work were characterized by their surface morphology and preferred orientation. The surface morphology was studied by scanning electron microscopy (SEM) using a Philips model MV 2300 operated at 25 kV. The chemical composition of the deposits was determined using the Kevex model energy dispersive X-ray

TABLE 1. Bath Conditions and Chemical Deposition Parameters with their Various Ranges for ZnO, Mn_2O_3 and NiO Deposition.

Variable	Range
$ZnCl_2$ ($g.l^{-1}$)	20-100
$MnCl_2$ ($g.l^{-1}$)	20-100
$NiCl_2$ ($g.l^{-1}$)	20-100
NH_3 (ml)	10-50
Additive (Tiron)*	1 Drop Per Liter
pH	8-11
Temperature of Complex Solution (˚C)	10-20
Temperature of Hot Water (˚C)	90-105

*A compound based on the benzene molecule.

spectroscopy (EDAX) system attached to the SEM. All chemical composition values are quoted by weight percentage and represent the average of at least five measurements, In order to verify the accuracy of the EDAX analysis, one deposit of ZnO, Mn_2O_3 and NiO was also analyzed by wet chemistry using atomic absorption spectroscopy (AAS).

Knowing the surface area of the substrate and the deposited mass of the layer, the thickness of the film was determined by assuming the density of ZnO, Mn_2O_3 and NiO precipitated at 5.606, 4.44, and 4.67 $g.cm^{-3}$ respectively. Thickness measurements were made by scanning electron microscopy of the samples gave similar results.

X-ray diffraction (XRD) was used to determine the phase present and the preferred orientation of the deposits. A Philips Xpert-Pro X-ray diffractometer with a Cu Kα radiation (λ=1.5418Å) was employed to obtain XRD spectra using standard θ-2θ geometry. A computer-base search and match was used for phase identification.

3. RESULTS AND DISCUSSION

The increasing effect on the thickness of the layer by the number of dipping and the deposited ZnO, Mn_2O_3 and NiO film is presented in Figure 1. It shows the average deposition rate of zinc oxide film is lower than Mn_2O_3 and NiO films. The deposition rate per dipping was averaged at 0.012 μm, 0.015 μm and 0.016 μm for ZnO, Mn_2O_3 and NiO films, respectively. Figure 1 shows that the thickness variation vs. dipping number is linear and the thickness increasing rate is constant. The unchanged concentration of the solution during the growing process, seems to be responsible for this effect.

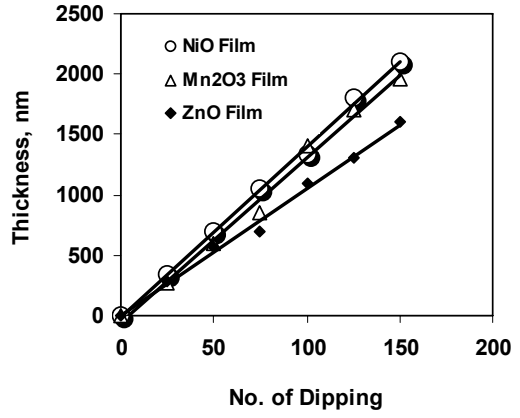
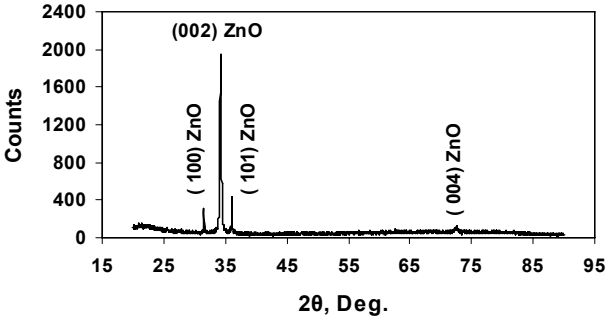
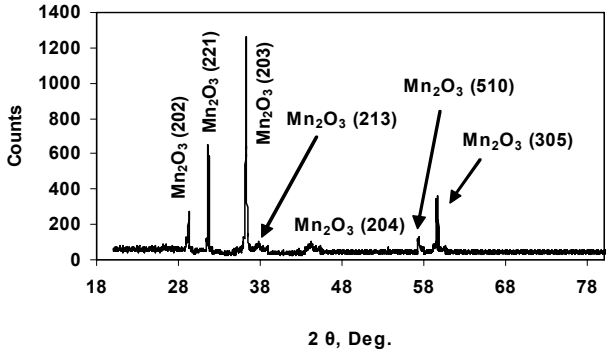


Figure 1. The variation of thickness of ZnO, Mn_2O_3 and NiO films vs. the number of dipping.



(a)



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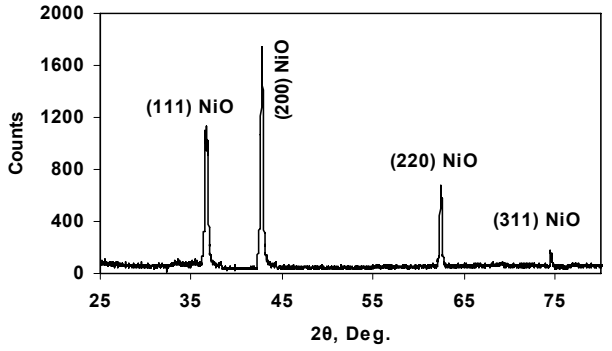


(c)

Figure 2. XRD patterns for (a) ZnO (b) Mn_2O_3, and (c) NiO deposits on SL-G substrate annealed at 400˚C.

The x-ray diffraction θ-2θ patterns of annealed ZnO, Mn_2O_3 and NiO films are shown in Figure 2. Crystal structure and chemical composition of the phases are determined from these graphs. From the presence of the diffraction peaks produced by the films and the angles of the peaks we can conclude that the films prepared from the aqueous solutions containing $ZnCl_2$, $MnCl_2$ and $NiCl_2$ have zincited ZnO, Mn_2O_3 and bunsenite NiO crystal structures, respectively. Other materials such as impurities are below limits of detection.

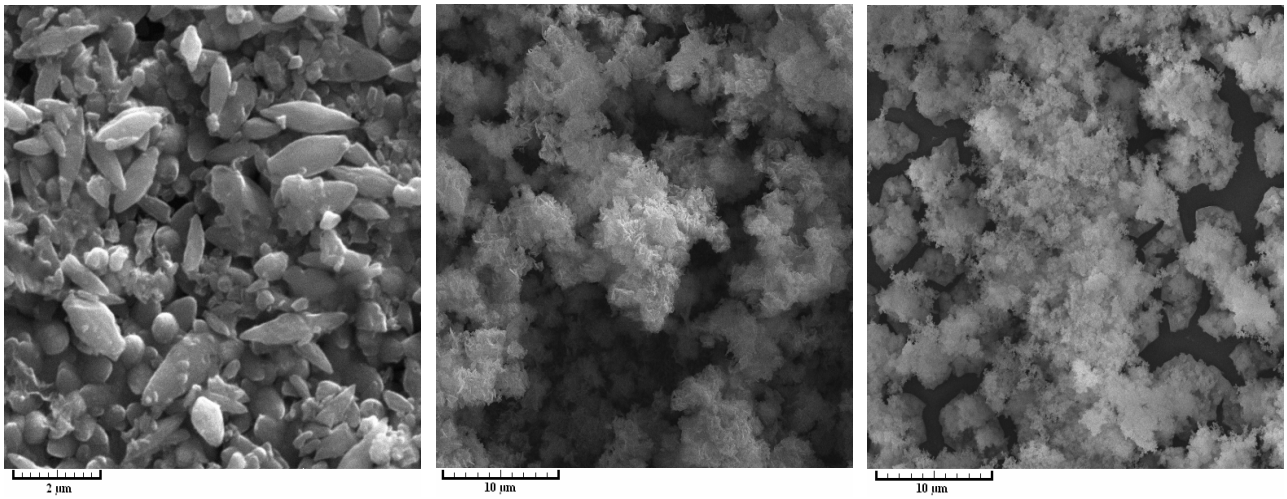
Comparing the peaks pronounced at $2\theta = 34.6$ (Figure 2a), $2\theta = 36.1$ (Figure 2b) and $2\theta = 43.4$ (Figure 2c) with standard ones shows, that the preferred orientations of the microcrystals of ZnO, Mn_2O_3 and NiO films are (002), (203), and (200) crystal planes, respectively.

The surface morphologies of the annealed ZnO, Mn_2O_3 and NiO films after 100 times dipping are shown in Figure 3. A slight morphology change is observed for Mn_2O_3 and NiO films deposited on the SL-G substrate, while a much more distinguishable change occurs when ZnO deposited on the SL-G substrate. The SEM micrograph of ZnO film clearly indicate that zinc oxide film is composed of oval shaped crystallites preferably orientated perpendicular to the surface of the substrate. It is observed from Figure 3c that the particles of Mn_2O_3 and NiO grow from the surface of substrate.

EDAX spectra of the ZnO, Mn_2O_3 and NiO films show the presence of Zn, Mn, Ni and O. Other peaks reveal the existence of Ca, Si, and Cl. The source of Si is the substrate (Figure 4). Ca may have come from the SL-G substrate. The Cl species may have come from the aqueous complex solution. As a typical example, one of the samples of ZnO, Mn_2O_3 and NiO was also analyzed by wet chemistry using atomic absorption spectroscopy (AAS). AAS analysis showed 76.4 wt % Zn, 67.94 wt % Mn and 76.4 wt Ni, while EDAX analysis indicated 78.2 wt % Zn, 69.03 wt % Mn and 77.4 wt % Ni. The difference between AAS and EDAX analysis is within the acceptable range of the experimental errors.

4. CONCLUSION

Very adherent films of ZnO, Mn_2O_3 and NiO can easily be deposited by successive immersions of the substrate in a cold ammonia complex solution and then in hot water. The thickness of the film can



(a) (b) (c)

Figure 3. SEM micrographs showing the morphology of (a) zinc oxide, (b) manganese oxide and (c) nickel oxide deposits on SL-G substrate annealed at 400˚C.

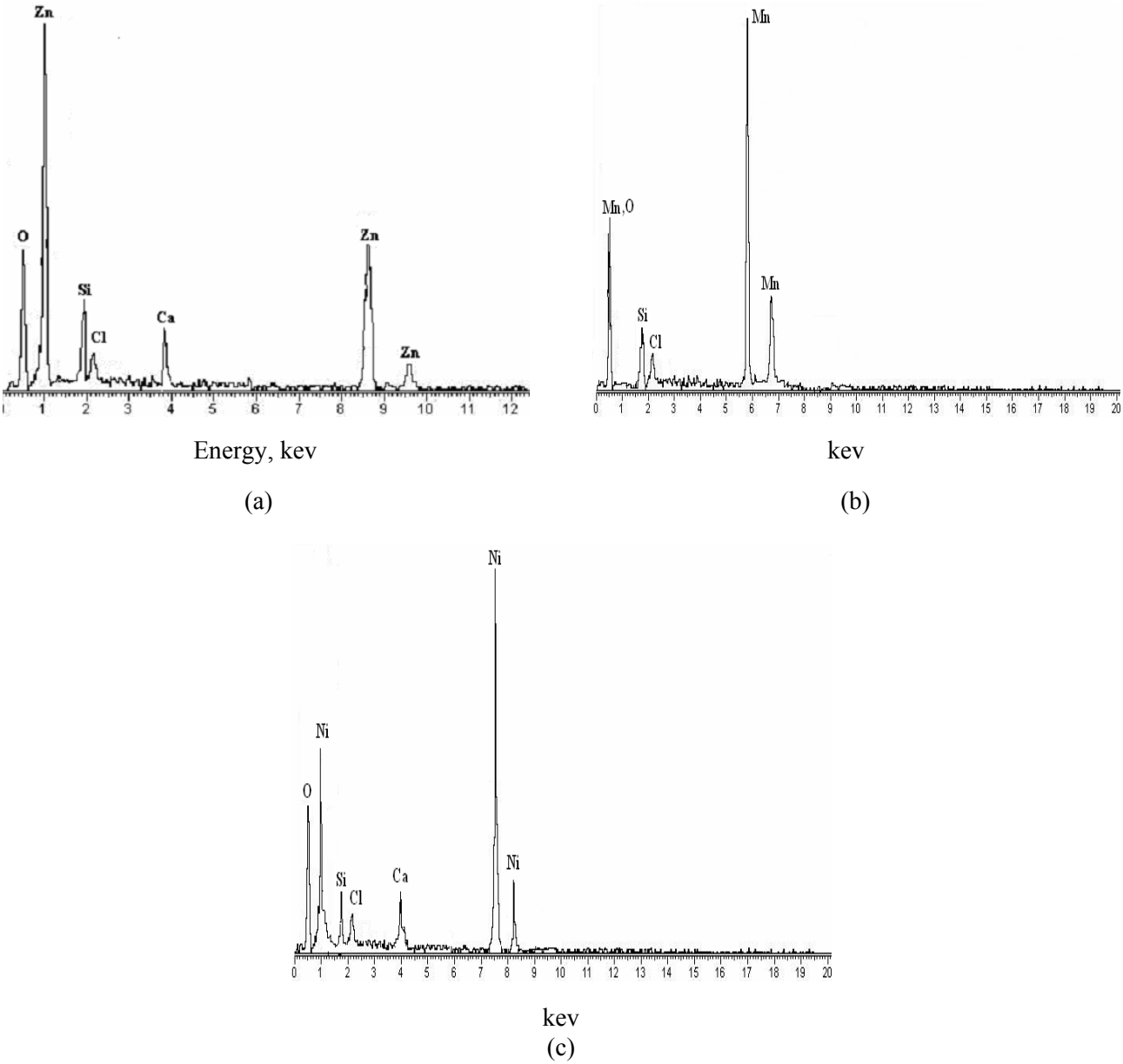


Figure 4. EDAX results of (a) ZnO, (b) Mn_2O_3 and (c) NiO film for 100 times of dipping.

be controlled by varying the number of successive immersions and the thickness variation vs. dipping number is linear. The X-ray diffractograms of ZnO, Mn_2O_3 and NiO films show that the preferred orientations of the microcrystals are (002), (203) and (200) planes, respectively. The results obtained from XRD and EDAX techniques also reveal that the deposited films prepared from the aqueous solutions containing $ZnCl_2$, $MnCl_2$ and $NiCl_2$ are pure ZnO, Mn_2O_3 and NiO, respectively. The SEM micrographs show that the surface morphology of the Mn_2O_3 and the NiO films are the same and their particles grow away from the surface of the substrate, but that of ZnO film is composed of oval-shaped crystallites grown on the substrate.

5. REFERENCES

1. Lee, C. C., Tang, C. J. and Wu, J. Y., "Rugate Filter Made with composite Thin Films by Ion-Beam Sputtering", ***Appl. Opt***., Vol. 45, (2006), 1333-1337.
2. Cruciun, V., Elders, J., Gardenievs, J. G. E. and Boyd, I. W., "Characteristics of High Quality ZnO Thin Films Deposited by Pulsed Laser Deposition", ***Appl. Phys. Lett***., Vol. 65, (1994), 2963-2965.
3. Nutsume, Y., Sakata, H. and Hirayama, T., "Low-Temperature Electrical Conductivity and Optical Absorption Edge of ZnO Films Prepared by Chemical Vapour Deposition", ***Phys. Status Solidi A***, Vol. 148, (1995), 485-495.
4. Ogata, K., Sakurai, K., Fujita, S. Z., Fujita, S. G. and Matsushige, K., "Effects of Thermal Annealing of ZnO Layers Grown by MBE", ***J. Cryst. Growth***, Vol. 214, (2000), 312-315.
5. Natsume, Y. and Sakata, H., "Zinc Oxide Films Prepared by Sol-Gel Spin-Coating", ***Thin Solid Films***, Vol. 372, (2000), 30-36.
6. Gopala Swamy, H. and Jayarama Reddy, P. J., "Preparation of ZnO Films Films by Activated Reactive Evaporation", ***Semicond. Sci. Technol***., Vol. 5, (1990), 980-981.
7. Ristov, M., Sinadinovski, G. J., Grozdanov, G. J. and Mitreski, M., "Chemical Deposition of ZnO Films", ***Thin Solid Films***, Vol. 149, (1987), 65-71.
8. Chatterjee, A. P., Mitra, P. and Mukhopadhyay, A. K., "Chemically Deposited Zinc Oxide Thin Film Gas Sensor", ***J. Mater. Sci***., Vol. 34, (1999), 4225-4231.
9. Cheng, H. C., Chen, C. F. and Lee, C. C., "Thin-film Transistors with Active Layers of Zinc Oxide (ZnO) Fabricated by Low-Temperature Chemical Bath Method", ***Thin Solid Films***, Vol. 498, (2006), 142-145.
10. Shishiyanu, S. T., Lupan, O. I., Monaico, E. V., Ursaki, V. V., Shishiyanu, T. S. and Tiginyanu, I. M., "Photoluminescence of Chemical Bath Deposited ZnO: Al Films Treated by Rapid Thermal Annealing", ***Thin Solid Films***, Vol. 488, (2005), 15-19.
11. Saeed, T. and Obrien, P., "Deposition and Characterisation of ZnO Thin Films Grown by Chemical Bath Deposition", ***Thin Solid Films***, Vol. 271, (1995), 35-38.
12. Ramamoorthy, K., Arivanandhan, M., Sankaranarayanan, K. and Sanjeeviraja, C., "Highly textured ZnO thin films: A Novel Economical Preparation and Approachment for Optical Devices, UV Lasers and Green LEDs", ***Mater. Chem. Phys***., Vol. 85, (2004), 257-262.