Available online at www.sciencedirect.com

SCIENCE DIRECT

Thin Solid Films 471 (2005) 48–52

thin solid films

www.elsevier.com/locate/tsf

Preparation and conducting performance of $LaNiO_3$ thin film on Si substrate

Yongfa Zhu*, Hai Wang, Peng Liu, Wenqing Yao, Lili Cao

Department of Chemistry, Tsinghua University, Beijing 100084, PR China

Received 26 September 2003; received in revised form 23 November 2003; accepted 3 April 2004
Available online 25 May 2004

Abstract

$LaNiO_3$ thin film with perovskite structure was successfully prepared on Si (111) substrate via an amorphous heteronuclear complex as precursor. The annealing temperature had a significant effect on the crystallization of $LaNiO_3$ film. The crystallization temperature of the film was higher than that of the powder samples due to the interface reaction between the layer and the substrate. The thickness of $LaNiO_3$ thin film increased with the precursor concentration and the texture of the film could be improved significantly by adding some polyethylene glycol (PEG) as additive. A remarkable decline of the electrical resistivity was observed when the calcination temperature was raised to 800 °C. The conductivity of $LaNiO_3$ film increased gradually when the temperature decreased and the film showed a metallic behavior.

Keywords: $LaNiO_3$; AES; SEM; Resistivity

1. Introduction

Mixed-metal oxides with perovskite structure have received considerable attention in recent years. Their preparation routes and properties have been widely studied [1–3]. Among these materials, lanthanum nickel oxide ($LaNiO_3$) with perovskite structure is considered important due to its electronic properties and has been used as electrode material and catalyst [4].

$LaNiO_3$ with perovskite structure shows metallic character, which is quite uncommon in oxides. It is well known to be a rhomboidal weakly distorted perovskite which exhibits a metallic character down to 4.2 K [5]. When the distortion of the perovskite structure increases, like in semiconductor such as $SmNiO_3$, the metallic property no longer exists. The electrical and magnetic properties of this oxide are governed by strong electronic correlation effects. Thus, it is important to investigate the effect of the preparation route and conditions on the crystalline structure and morphology of synthesized $LaNiO_3$ films. The structure and morphology are considered important due to their effect on electronic properties, which affect the conductivity.

Much work has been done on the preparation and the characterization of $LaNiO_3$ powder and some works on thin films [6,7]. Different preparation methods of perovskite oxides have been studied in the last decades [8,9]. Because amorphous complex method has many advantages [10], this work attempts to synthesize $LaNiO_3$ film via amorphous complex and reveals the influence of precursor concentration and additive on the thickness and texture of the $LaNiO_3$ thin film as well as the effect of the calcination temperature on the crystallization and resistivity of $LaNiO_3$ thin film.

2. Experimental section

2.1. Preparation of $LaNiO_3$/Si (111) thin film

Firstly, $La(NO_3)_3{\cdot}6H_2O$ and $Ni(NO_3)_2{\cdot}6H_2O$ powder with a molar ratio of 1:1 was dissolved in distilled water. Then, excess NaOH solution (1.0 M) was added in drops into the solutions to prepare the fresh $La(OH)_3$, $Ni(OH)_2$ mixture precipitates. Mixture precipitates were separated by filtration and washed with distilled water for several times to remove the excess of OH^-. Then, mixture precipitates were added into diethylenetriaminepentaacetic acid (H_5DTPA) solutions. The mixture was stirred and heated at about 80 °C to promote dissolution and reaction until the mixture

* Corresponding author. Tel.: +86-10-62783586; fax: +86-10-62787601.
E-mail address: zhuyf@chem.tsinghua.edu.cn (Y. Zhu).

0040-6090/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2004.04.023

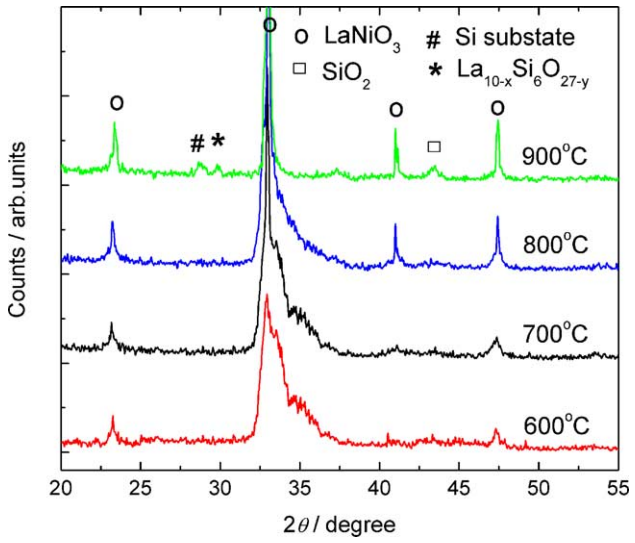

Fig. 1. XRD patterns of $LaNiO_3$/Si thin film calcined at different temperatures for 2 h.

became transparent solution. After the solution was vaporized, the mixture became a glass-like gel.

The amorphous precursor LaNi(DTPA)·$6H_2O$ added into deionizer water to prepare precursor solution with 0.1 M. About 2 wt.% of polyethylene glycol (PEG; mol. wt. of 4000) was directly added into precursor solution. Si wafer was cleaned in deionized water using ultrasonic bath. The precursor films with various thicknesses were formed on Si wafer by spin coating precursor solution with the LaNi(DTPA)·$6H_2O$'s concentration of 10, 15, 25 and 30 wt.% at the rate of 3000 rpm for 1 min. The $LaNiO_3$ film was obtained by annealing the precursor film sample in air. At first, the temperature was raised to 400 °C at a slow heating rate (5 °C/min). Then, the sample was kept at 400 °C for 30 min to promote the decomposition of organic components. Finally, the temperature was increased to various preset temperatures and maintained for a definite period of time to promote the formation of perovskite-type $LaNiO_3$ film.

2.2. Analysis techniques

Auger electron spectroscopy (AES) spectra were obtained using PHI 610 SAM system. A coaxial electron gun with a single-pass cylindrical mirror analyzer (CMA) was used. The energy resolution of the CMA was set at 0.3% to obtain a good energy resolution. For AES analysis, the electron beam energy and the beam current were 3.0 keV and 0.5 μA, respectively. The electron beam was incident at an angle of 60° with respect to the specimen surface. The base pressure of the analysis chamber was better than 3×10^{-7} Pa. During the depth profile analysis, the energy and beam current of the Ar ion beam were 3.0 keV and 6 μA, respectively. The diameter of beam was 1 mm and the sputtering rate was calibrated to be 30.0 nm/min by using thermal oxidized SiO_2 thin film. No electron charge effect was observed during AES analysis.

Scanning electron microscopy (SEM) experiments were carried out in KYKY-2800 scanning electron microscope. X-ray diffraction (XRD) experiments were carried out in Bruker D8 Advance X-ray diffractometer with Cu K_α radiation.

The resistance was measured with a four-probe method in an air flow. The measurement was carried on the Potentiostat/Galvanostat electrochemistry analyzer. The electrical current was 1 mA. The electrical resistance measured between the Pt legs of the thermocouples is converted into electrical conductivity based on the dimensions of the resistors (260 nm thick, 5.8 mm long and 4.48 mm wide).

3. Results and discussion

3.1. Crystallization and interface reaction of $LaNiO_3$ thin film

Fig. 1 showed the XRD patterns of $LaNiO_3$ thin films, which were calcined at different temperatures for 2 h. A sharp peak and a broad peak around 33° were observed when the calcination temperature was 600 °C. The sharp peak at 33° can be attributed to the perovskite structure of $LaNiO_3$ (110) and the broad peak from 32° to 38° was resulted from the amorphous $LaNiO_3$, which indicates that the perovskite structure of $LaNiO_3$ was not formed perfectly at 600 °C. However, our previous work has demonstrated that $LaNiO_3$ powder with perfect perovskite structure can be obtained at this temperature [12]. Thus, the crystallization of the $LaNiO_3$ film on Si substrate *is* more difficult than that of the powder. Several other sharp peaks that can be attributed

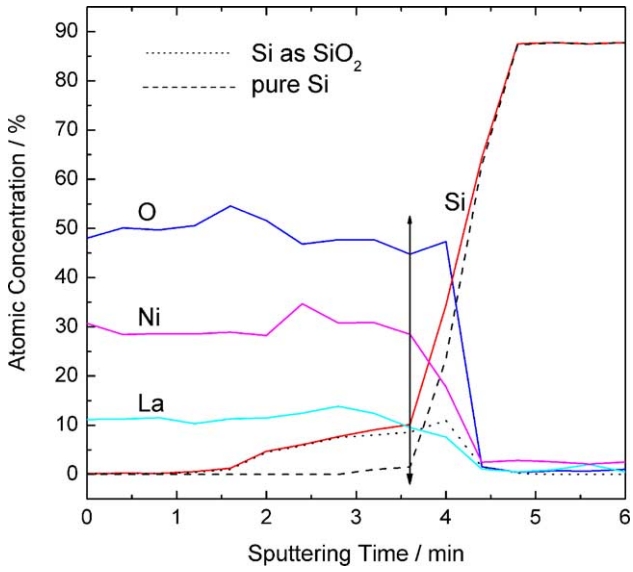

Fig. 2. A typical AES depth profile of $LaNiO_3$/Si thin film calcined at 800 °C for 2 h.

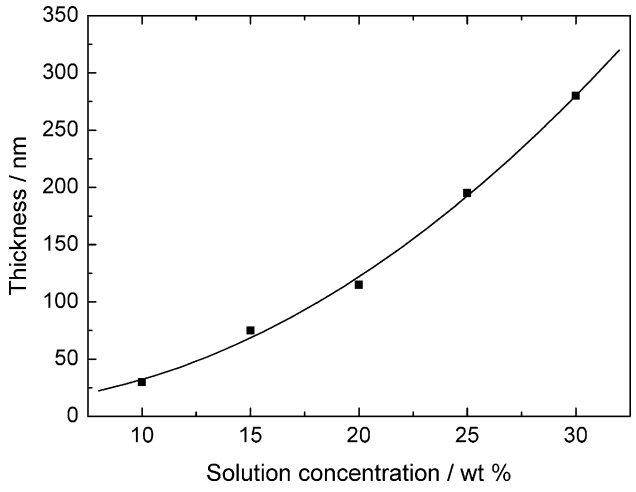

Fig. 3. The influence of the concentration of the precursor solution on the thickness of $LaNiO_3$/Si film calcined at 800 °C for 2 h.

to the perovskite structure of $LaNiO_3$ were also observed. With increasing temperature, peaks of the perovskite structure became stronger and sharper, indicating the increase of the crystal size. After the annealing temperature reached 900 °C, a well-defined (110) peak was observed, as a result of the crystallization of $LaNiO_3$. Some additional weak peaks were observed. The peaks at 28° and 43° can be attributed to Si substrate and SiO_2 species, respectively, suggesting that the reaction between the substrate and the film layer was completely and some SiO_2 was formed. The peak at 30° comes from $La_{10-x}Si_6O_{27-y}$ which is formed by an interface reaction [11]. All these results showed the annealing temperature had a significant effect on the crystallization of the thin film.

A further study of the interface reaction was carried out using AES. Fig. 2 shows a typical AES depth profile spectrum of a $LaNiO_3$/Si film sample calcined at 800 °C for 2 h. The composition distribution of the thin film with depth was not homogeneous. Because the sensitivity of Ni and La in AES is based on metallic and it is different from compounds, the signal of Ni was very weak and the ratio of Ni/La was about 0.5 due to formation of $LaNiO_3$ species. Some Si signal was found in the $LaNiO_3$ layer and the interface between the film and the substrate was quite wide. The portion of the film layer where the atomic concentration of the Si was between 13% to 87% can be considered as the interface. The position of the short arrow was settled at 13% of the Si atomic concentration in Fig. 2. Consequently, the distance from surface to the short arrow was considered as the thickness of the $LaNiO_3$ film layer. The AES result indicates that there was some interface diffusion between $LaNiO_3$ layer and Si substrate, which is consistent with the result of XRD. The Si KLL peaks indicate that different kind of Si species existed in film. SiO_2 species was formed on the film layer by the oxidation of diffused silicon from substrate. The interface reaction can enhance the binding strength between the film and the Si substrate, but it can impede the crystallization of the $LaNiO_3$ species as well. The interface reaction was the main reason why the crys-

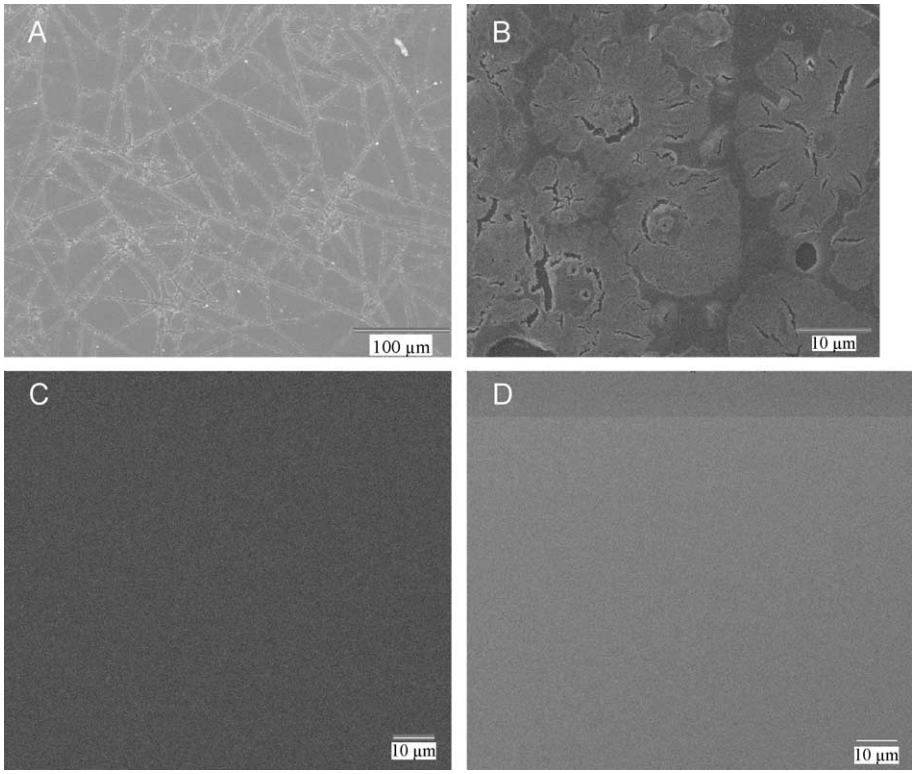

Fig. 4. The effects of precursor concentration on the texture of $LaNiO_3$/Si thin film; (A) 30 wt.%; (B) 25 wt.%; (C) 15 wt.%; (D) 10 wt.%.

tallization temperature of $LaNiO_3$ film on the Si substrate was higher than that of the powder.

3.2. Influence of precursor concentration on the thickness and texture

The texture and thickness of $LaNiO_3$ film were studied by SEM. Fig. 3 showed the effect of precursor concentration on the thickness of the thin film. All samples were calcined at 800 °C for 2 h. The thickness was defined as the perpendicular distance from the surface of $LaNiO_3$ thin film to the interface of $LaNiO_3$/Si, which was marked by the short arrow in Fig. 2. It can be observed in Fig. 3 that the thickness of the film varied from 30 to 280 nm (equivalent to Ar etched SiO_2 in the same sputtering conditions) with the increase of the precursor concentration. The dependence of the thickness on the concentration was not linear because of the viscosity of the solution. The above results demonstrated the thickness of the $LaNiO_3$ thin film can be controlled by the viscosity of the precursor solution.

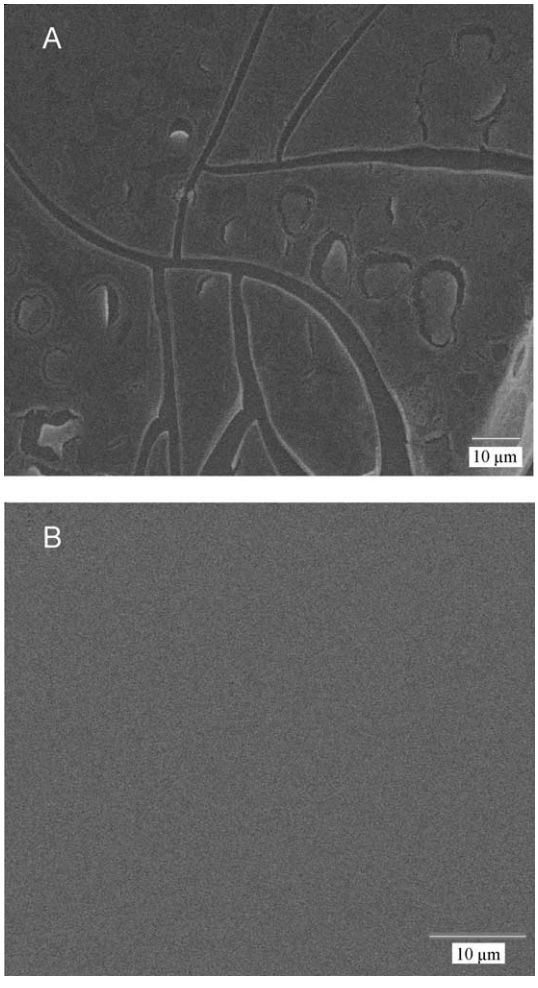

Fig. 5. Effect of (A) no PEG and (B) 2 wt.% PEG (MW 4000) addition on the surface texture of $LaNiO_3$/Si thin film prepared with 20 wt.% LaNi(DTPA) precursor solution.

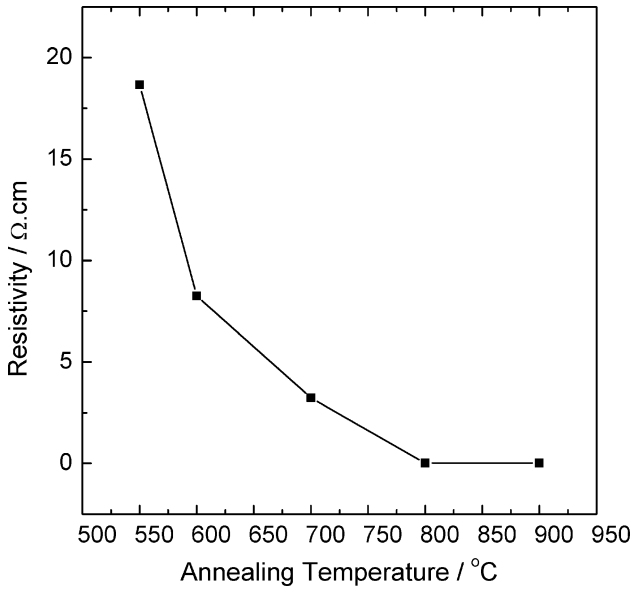

Fig. 6. Electrical resistivity of $LaNiO_3$/Si film at room temperature as a function of annealing temperatures. [The film was prepared with 20 wt.% LaNi(DTPA) precursor solution and 2 wt.% PEG additive].

The concentration of the precursor solution influenced not only the thickness of the thin film but also the texture of the film. Fig. 4 shows the SEM photos of the $LaNiO_3$/Si thin films prepared with differently concentrated precursor solutions. Some microcracks were observed on the surface of the film sample, which was prepared with a high concentrated precursor solution(c>20%). The film could also be split and dropped from the Si substrate when the concentration was extraordinarily high. The higher the concentration of the precursor solution was, the more microcracks were observed on the surface. When the precursor concentration c was reduced to 15%, the thickness of the thin film was approximately 75 nm and no microcrack was observed on the surface of the film. The thin film was even smoother when the concentration was lower. This result indicates that the surface texture of the thin films could be improved by decreasing the concentration of the precursor.

3.3. Influence of PEG additive on the thickness and texture

Polyethylene glycol (PEG) was used to increase the viscosity of solution and improve the quality of the thin film. The influence of the additive on the thickness and surface texture were investigated by using AES and SEM. Based on the AES depth profile analysis, the influence of PEG additive on the thickness of the thin film was very limited when the concentration of additive was lower than 10 wt.% in the precursor solution. It can be explained that the precursor solution had a certain viscosity itself and the addition of PEG did not change the viscosity of the solution significantly. Thus, the effect of the PEG on the thickness of the $LaNiO_3$ thin film was not obvious when the additive

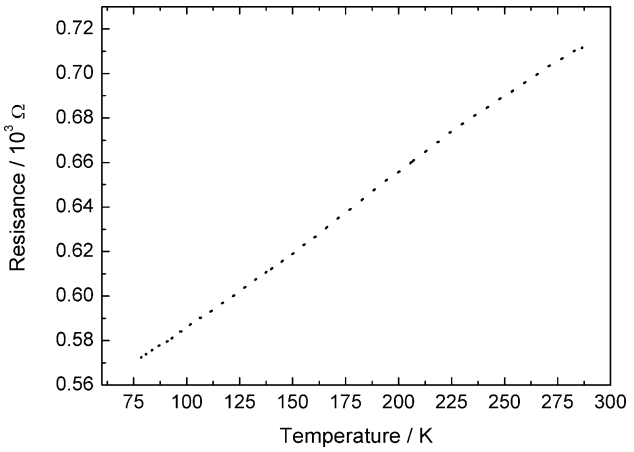

Fig. 7. Electrical resistance of $LaNiO_3$/Si film calcined at 800 °C for 2 h as a function of temperature. [The film was prepared with 20 wt.% LaNi(DTPA) precursor solution and 2 wt.% PEG additive].

concentration was less than 10 wt.% in the precursor solution.

The influence of PEG additive on the surface texture of the $LaNiO_3$ thin film was described in Fig. 5. The $LaNiO_3$/Si film sample was prepared by using the precursor solution with a concentration of approximately 20 wt.% and the thickness of the film was approximately 110 nm. When the PEG additive was not used, some microcracks and the dropped spots were found on the SEM (Fig. 5a). After 2 wt.% PEG was added into the precursor solution, the microcracks and the drop spots disappeared (Fig. 5b). The improvement of the texture probably resulted from the dispersion effect of the thermal stress in the thin film by the addition of PEG. The above results illustrates that PEG additive can greatly improve the texture of the $LaNiO_3$ thin film.

3.4. The conducting performance of the films

The effect of the annealing temperature on the resistivity of the film samples at room temperature is shown in Fig. 6. The results show a remarkable decrease in the electrical resistivity when the annealing temperature increased. When the annealing temperature was higher than 800 °C, the resistivity of the film at room temperature was fairly small. The relationship of the resistivity of the film calcined at 800 °C for 2 h as a function of the temperature was also measured. The result (Fig. 7) shows that the film had a good conductivity and the resistivity decreased gradually with the temperature from room temperature to 77 K, showing a metallic behavior.

Based on the above results, it can be concluded that a better crystal structure would lead to a decrease of the resistivity of the $LaNiO_3$ film.

4. Conclusions

$LaNiO_3$ thin film with perovskite structure was synthesized using amorphous heteronuclear complex LaNi(DTPA)·$6H_2O$ as a precursor. The synthesized film showed a good metallic conducting performance. The thickness of the $LaNiO_3$ thin film increased with the concentration of the precursor solution. When the concentration was lower than 15%, a smooth film without microcrack can be obtained. A certain amount of PEG additive can improve the surface texture of $LaNiO_3$/Si thin film significantly. The annealing temperature had a significant effect on the resistivity of the $LaNiO_3$ thin film.

Acknowledgements

This work was supported by Chinese National Science Foundation (20071021), Trans-Century Training Program Foundation for the Talents by the Ministry of Education, P.R. China and the Excellent Young Teacher Program of MOE, P.R. China.

References

[1] D.B. Meadowcroft, Nature 226 (1970) 847.
[2] Y.-F. Zhu, R.-Q. Tan, T. Yi, S.-S. Ji, X.-Y. Ye, L.-L. Cao, J. Mater. Sci. 35 (21) (2000) 5415.
[3] Y.-F. Zhu, R.-Q. Tan, T. Yi, S.-S. Ji, X.-Y. Ye, L.-L. Cao, J. Alloys Compd. 311 (1) (2000) 16.
[4] Q. Liang, Q. Li, L.-Z. Gao, Z.-L. Yu, Mater. Res. Bull. 36 (2001) 471.
[5] K.P. Rajeev, G.V. Shivashankar, A.K. Raychaudhuri, Solid State Commun. 79 (1991) 591.
[6] M.M. Cruz, M.D. Carvalho, A. Wattiaux, J.M. Bassat, A. Casaca, G. Bonfait, F.M.A. Costa, M. Godinho, Physica, B 284-288 (2000) 1477.
[7] J.M. Tranquada, D.J. Buttery, V. Sachan, Phys. Rev., B 54 (1996) 12318.
[8] N.I. Matskevich, F.A. Kuznetsov, D. Feil, K.J. Range, Thermochim. Acta 319 (1998) 1.
[9] A.K. Norman, M.A. Morris, J. Mater. Process. Technol. 92–93 (1999) 91.
[10] Y.-X. Zhang, Y.-F. Zhu, R.-Q. Tan, W.-Q. Yao, L.-L. Cao, Thin Solid Films 388 (2001) 160.
[11] Powder diffraction data, JCPDS-International Centre for XRD Diffraction Data, 1998, Card 76-0340.
[12] H. Wang, Y.-F. Zhu, P. Liu, W.-Q. Yao, J. Mater. Sci. 38 (9) (2003) 1939.