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The effect of seed layer on morphology of ZnO nanorod arrays grown by hydrothermal method

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ABSTRACT

Well-aligned ZnO nanorod arrays were synthesized by hydrothermal method on Si substrates that were covered with pre-deposited ZnO films as seed layers. The ZnO seed layers were deposited by RF magnetron sputtering. It is found that the seed layers prepared under different oxygen partial pressure sputtering parameters and annealing treatment have a great influence on the morphology of the ZnO nanorod arrays grown subsequently on them. Furthermore, growth positions of nanorod/microrod arrays were selectively controlled on the lithography-assist ZnO seed layer.

1. Introduction

With a large direct band gap (3.37 eV), large exciton binding energy (60 meV), excellent chemical and thermal stability, ZnO is one of the most important multifunctional semiconductors due to its wide range of potential photo-electrochemical applications such as light-emitting diodes, optical waveguides, dye-sensitized photovoltaic cells, conductive gas sensors and transparent electrodes, etc. [1–5]. Therefore, fabrication of ZnO nanostructures in highly oriented, aligned and ordered arrays is of critical importance for the development of novel devices. During the past several years, various methods have been developed for the synthesis of oriented arrays of ZnO nanorods and nanowires, including vapor–liquid–solid (VLS) [6], metal–organic chemical vapor deposition (MOCVD) [7], template-assisted [8], and solution method [9]. Among the various growth techniques developed, the low cost, low temperature hydrothermal method holds great promise for devices application. Recently, several studies have grown highly oriented ZnO nanorods, via two-step process, on substrates with the use of preexisting textured ZnO seeds such as a ZnO nanoparticle layer or ZnO films [10–12]. Alignment of the ZnO nanocrystals is substrate-independent and occurs on flat surfaces regardless of their crystallinity or surface chemistry, including Al_2O_3 single crystals, transparent conducting oxides such as indium tin oxide (ITO) and fluorine doped tin oxide (FTO), amorphous oxides including glass and silicon with its native oxide. For the integrated applications of nanodevices, it is necessary to control the exact growing positions of the zinc oxide nanorods on the target substrate. Several methods have demonstrated the selective-area growth of ZnO nanowires using selective-area chemical vapor deposition (CVD) or electrochemical process [13,14]. Unfortunately, these approaches need high temperature environment, expensive single crystalline substrates, and expensive low-write speed electron beam lithography. A method combined with conventional lithography methods need to be developed to exhibit advantages of the solution-based ZnO growth method, i.e., low temperature, low cost, high growth rate, and scale-up possibilities.

Although the influences of growth conditions in hydrothermal method such as growth temperature, deposition time and the concentration of the precursors on the morphology and the alignment of ZnO nanorod arrays have been demonstrated [15], and the characteristics of ZnO thin films prepared by magnetron sputtering with different parameters have been widely studied [16], to our best knowledge, the effect of seed layers prepared under different sputtering parameters on the morphology of ZnO nanorod arrays prepared by two-step hydrothermal method has never been investigated yet. In this study, highly oriented ZnO nanorods were successfully synthesized on various sputtered ZnO seed layers through aqueous solution method at low temperature. The effect of sputtering parameters such as oxygen partial pressure and annealing treatment of seed layers on the morphology of ZnO nanorod arrays were discussed. Besides, a simple aqueous solution route to selective-area grow ZnO nanorods on the substrates was demonstrated. Positions of the ZnO nanorods grown by hydrothermal process were controlled via conventional lithography.

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Table 1
Detailed preparing parameters to grow different ZnO seed layers on Si substrates.

ZnO thin film	Sputtering temperature (°C)	Ar:O_2	Working pressure (Pa)	Power (W)	Annealing(°C)
ZnO-A	200	20:3	3×10^{-5}	100	No
ZnO-B	200	20:7	3×10^{-5}	100	No
ZnO-C	200	20:7	3×10^{-5}	100	400

2. Experimental details

To grow well-aligned ZnO nanorods, different ZnO thin films were deposited on silicon wafers using RF magnetron sputtering depositions. These ZnO thin films were then used as seed layers for growing nanorods. For sputtering, argon and oxygen were used as the working gases with at least 99% purity. Prior to deposition, the Zn target was sputter-cleaned. Films were sputtered onto [1 0 0] silicon wafers which were heated to 200 °C. The working pressure was 3×10^{-5} Pa with a sputtering power of 100 W. The volume ratio between argon and oxygen of seed layer A and seed layer B were 20:3 and 20:7, respectively. Films with same sputtering parameters as seed layer B were annealed at 400 °C in the air for 1 h after sputtering, marked as seed layer C. Detailed preparing parameters to prepare different ZnO seed layers are summarized in Table 1. The film thickness was around 100 nm.

ZnO nanorods were grown on ZnO seed layer coated substrates by an aqueous chemical method in 60 ml of aqueous solution containing 0.1 M zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and 0.1 M hexamethylenetetramine ($(CH_2)_6N_4$) in a sealed teflon lined autoclave. The ZnO seed layer coated substrates were immersed parallel with the sidewall of the autoclave into aqueous solution. The autoclave was kept in a conventional laboratory oven at a constant temperature of 95 °C for 8 h. After the reaction, the substrates were rinsed with de-ionized water and dried in air at room temperature to remove residual salts and organic materials. To control the growth position of ZnO nanorod arrays, photoresist AZ5214 was spin coated on the ZnO–C seed layer and formed a photolithographic mask covered substrates. Using conventional lithography, circular hole array patterns were made on the organic mask after exposure and development. Then, the mask covered substrates were immersed in equimolar mixed nutrient solution of 0.1 M $Zn(NO_3)_2 \cdot 6H_2O$ and hexamethylenetetramine and that of 0.025 M $Zn(NO_3)_2 \cdot 6H_2O$ and hexamethylenetetramine at 95 °C for 6 h, respectively. Selective growth was achieved by the absence of ZnO nucleation sites on photoresist “mask”. Morphological microstructures of ZnO nanorods were characterized by field emission scanning electron microscopy (FE-SEM).

3. Results and discussion

3.1. Effect of oxygen partial pressure of seed layers on the morphology of ZnO nanorod arrays

Fig. 1 shows the plane view of the nanorod arrays grown on various ZnO seeded substrates, when the reaction time was fixed at 8 h. As observed, the morphologies of the nanorods are different in terms of the shape, diameter, and orientation. The nanorod arrays grown on ZnO-A seed layers deposited via RF magnetron sputtering at Ar/O_2 ratio of 20:3 had an average diameter of about 200 nm and grew on the substrate in a high density. These nanorods exhibited a relatively poor alignment and disordered polygonal shapes on the end. ZnO nanorods on ZnO-B seed layers which deposited at Ar/O_2 ratio of 20:7 grew in a direction almost perpendicular to the surface of the substrate. Most of the nanorods exhibited hexagonal rod shape, implying good qualities of these ZnO crystals that grew along the [0 0 0 1] direction. These nanorods also grew in a very high density with an average diameter of about 200 nm. Uniformity and alignment are better for the ZnO nanorods grown on the ZnO-B seeded substrates compared with those on ZnO-A seeded substrates. Apparently, prior seeding of the surface by ZnO layer leads to nucleation sites on which ZnO nanorod arrays can grow in a highly aligned fashion and has significant influence on the morphology of ZnO nanorods.

It is generally agreed that ZnO seeding is required for the aligned ZnO nanorods growth on the substrates [10]. We believe the poor orientation and crystallization of the nucleuses are responsible for the bad alignment of nanorods in the final deposits. Studies have explored the influence of oxygen partial pressure on the structure of ZnO films deposited by RF magnetron sputtering [16]. It was indicated that when the working pressure was kept constant, the growth behavior of the ZnO thin film was mainly decided by the density of oxygen in the space where the sample was deposited, and the crystallization of the ZnO thin films was promoted by desirable argon/oxygen ratio. It is known that ZnO nanorods are formed due to the high growth rate along (0 0 0 1) direction (*c*-axis) [9], which is also the preferential growth direction of the ZnO thin film. In other words, the nanorods with hexagonal cross-section

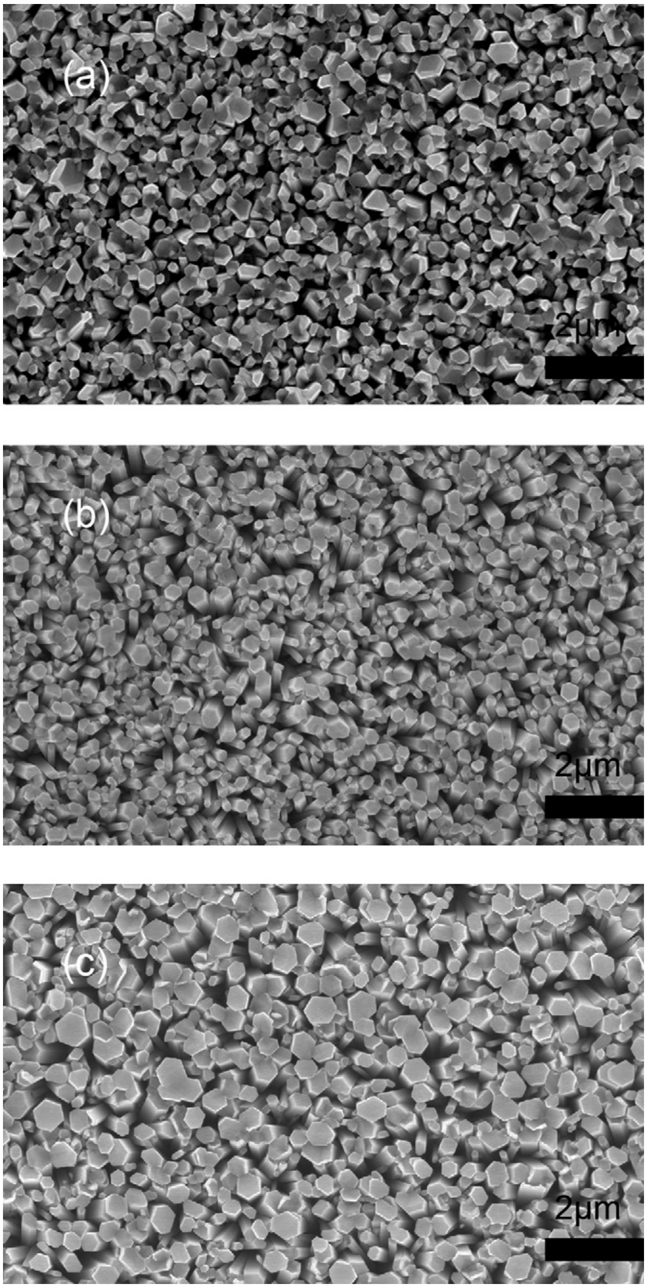

Fig. 1. SEM images of ZnO nanorods grown on Si substrates with different ZnO seed layers: (a) plane view of ZnO nanorod arrays grown on ZnO-A seed layer; (b) plane view of ZnO nanorod arrays grown on ZnO-B seed layer; and (c) plane view of ZnO nanorod arrays grown on ZnO-C seed layer.

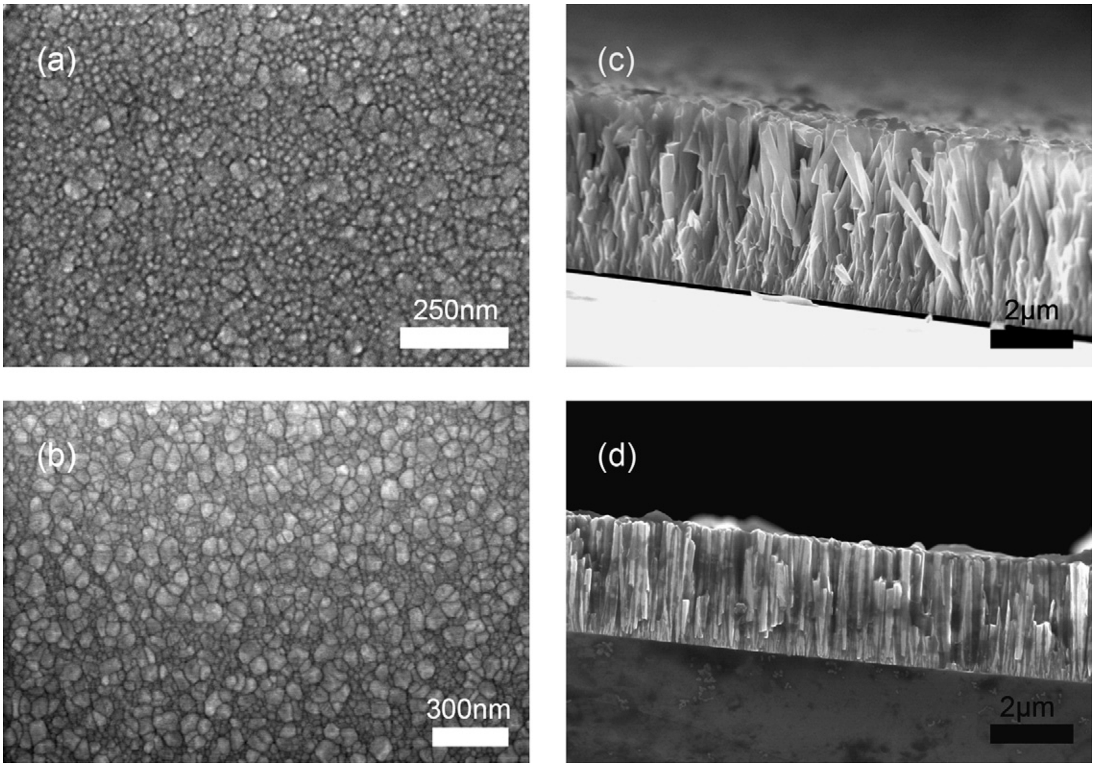

Fig. 2. (a) Plane view SEM image of ZnO-B seed layer; (b) plane view SEM image of ZnO-C seed layer; (c) cross-sectional view of ZnO nanorod arrays grown on ZnO-B seed layer; and (d) cross-sectional view of ZnO nanorod arrays grown on ZnO-C seed layer.

are grown along the normal direction of the ZnO thin films. Thus, the nanorod arrays grown on relatively poor orientation and crystallization seed layer A, which resulted from improper spurring parameters of argon/oxygen ratio, have a relatively poor alignment and disordered polygonal performance compared with nanorod arrays grown on seed layer B prepared under more desirable magnetron sputtering parameters.

3.2. Effect of annealing treatment of seed layers on the morphology of ZnO nanorod arrays

Fig. 1c shows the plane view of the nanorod arrays grown on ZnO-C seed layer, which is different from seed layer B by undergoing annealing treatment. Nanorods with an average diameter of 300–400 nm were obtained on seed layer C. Compared with Fig. 1b, the nanorod arrays grown on ZnO-C seed layer have larger average diameters than nanorods with the size of 200 nm grown on ZnO-B seed layer. ZnO-B and ZnO-C seed layers have columnar grains in high density as shown in Fig. 2a and b. The sizes of crystal nucleus on ZnO-C seed layer are larger than those on ZnO-B. Apparently, the seed grains in layer C grew up when annealing at high temperature, which resulted in the larger diameters of nanorods in subsequent deposition process. Fig. 2c and d shows the cross-sectional view of the nanorod arrays grown on ZnO seeded layer B and C, respectively. The lengths of the nanorods synthesized in our experimental conditions are around 4 μm. Alignment is better for the ZnO nanorods grown on the ZnO-C seed layer compared with those on ZnO-B seed layer that have an inclination away from vertical direction. The orientation of the ZnO seed films could be further enhanced during annealing process [17]. These oriented seed layers help form well-aligned ZnO nanorods in the hydrothermal process as nanorods are grown along the normal orientation of the ZnO thin films. In general, the underneath pre-annealing treated seed grains play a crucial role in the growth of high-oriented ZnO nanorod arrays.

3.3. Growth on patterned substrates

Growth positions of several centimeter ZnO nanorod arrays were easily controlled via coating the ZnO-C seed layer with patterned photoresist “mask” fabricated by conventional photolithography. Before lithography, substrates coated with photoresist S9912, AZ4620 and AZ5214 were placed in the growth environment of ZnO nanorods respectively, in order to verify the corrosion resistance of different photoresist during growth process. At last, AZ5214 photoresist was proved to have the best performance without any cracking, shedding or deformation in hydrothermal growth environment, as shown in Fig. 3a. The pattern was defined by an array of circles with 1 μm in diameter, and 5 μm in pitch. Since ZnO nanorods would not grow on the organic mask due to the lack of ZnO nucleation sites on the organic resist layer, they grow only on the patterned sites in the hydrothermal process subsequently. The SEM image in Fig. 3b shows the ZnO nanorod/microrod arrays, which were synthesized in equimolar mixed nutrient solution of 0.1 M $Zn(NO_3)_2·6H_2O$ and hexamethylenetetramine, were selectively grown in circular hole patterns, as desired. These rod clusters exhibit interesting flower shapes, with the diameters of nearly 1 μm. The large diameters of the rods are result from limited growing points on patterned substrates that leads to the slow consumption rate for precursors as well as relatively fast diffusion rate of the growing units and the crystal growth rate at the liquid–solid interface in high precursor concentration. When the patterned substrates were immersed in low concentration nutrient solution, the diameters of as-synthesized nanorods decreased significantly. Fig. 3c shows the SEM image of growth position controlled nanorods that were synthesized in equimolar mixed nutrient solution of 0.025 M $Zn(NO_3)_2·6H_2O$ and hexamethylenetetramine at 95 °C for 6 h. The as-synthesized nanorods, with diameters ranging from 60 to 100 nm, became much thinner, due to the decreasing of precursor concentration. This growth phenomenon is similar to aligned growth of ZnO nanorods on sub-

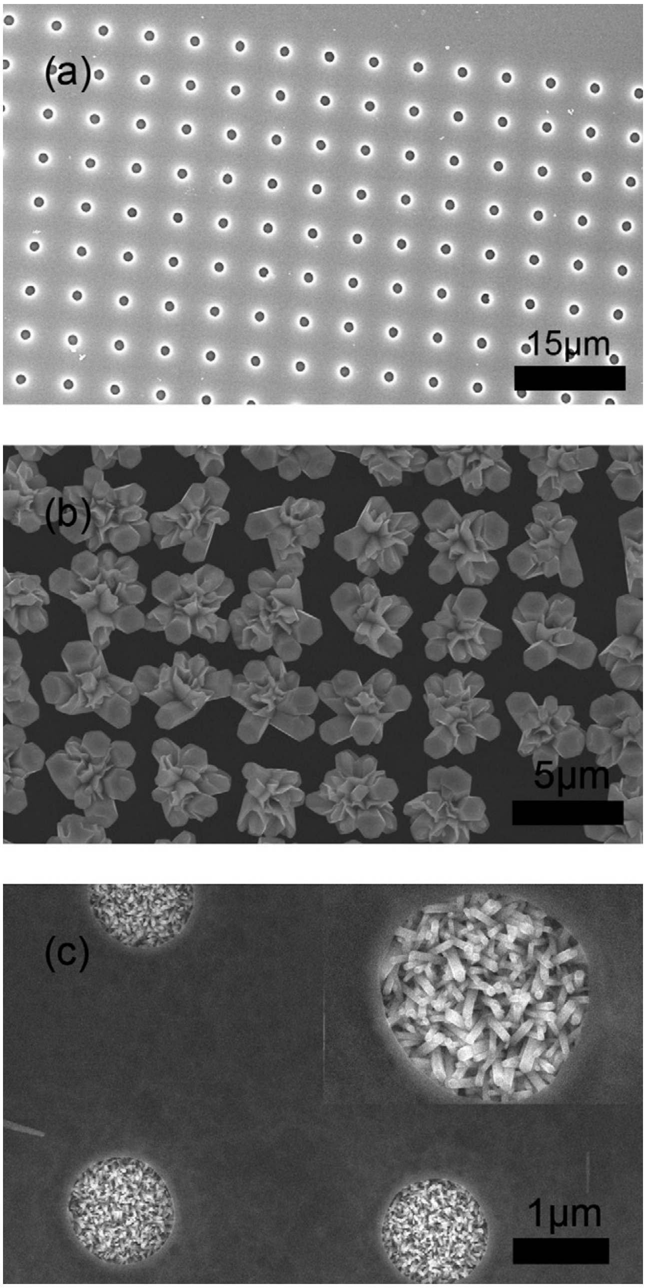

Fig. 3. (a) SEM image of patterned ZnO seed layer; (b) SEM image of growth position controlled ZnO nanorod arrays synthesized in equimolar mixed nutrient solution of 0.1 M $Zn(NO_3)_2{\cdot}6H_2O$ and hexamethylenetetramine; and (c) SEM image of growth position controlled ZnO nanorod arrays synthesized in 0.025 M $Zn(NO_3)_2{\cdot}6H_2O$/hexamethylenetetramine, inset: high magnification SEM image.

strates without patterns [9,15], the diameters of ZnO nanorods can be reduced by decreasing the concentration of the reactant while keeping the ratio of Zn^{2+} to hexamethylenetetramine constant at 1:1. These periodically ordered ZnO naonorod arrays are readily synthesized. Unlike controlled selective growth technique using E-beam lithography [14,18], which has a major drawback of throughput for device fabrication, these growth positions controlled ZnO nanorods fabricated via conventional lithography are attractive for potential applications in ZnO-based nanodevices.

4. Conclusions

In summary, well-aligned ZnO nanorod arrays were successfully synthesized in high density, via two-step hydrothermal method, on Si wafers coated by ZnO seed layers that were deposited using RF magnetron sputtering. The sputtering parameters like oxygen partial pressure and annealing treatment of seed layers had a great influence on the morphology of ZnO nanorod arrays. The nanorod arrays grown on seed layer B, which were deposited at more desirable magnetron sputtering parameters of argon/oxygen ratio of 20:7, had better alignment and crystallization compared with those grown on seed layer A deposited at argon/oxygen ratio of 20:3. The diameters increased and the alignment gained further enhanced for the nanorods grown on annealing treated seed layer C. We also demonstrated a simple aqueous solution route to control the growth position of ZnO nanorod arrays on the substrates via conventional lithography. Based on the compatibility with standard semiconductor microfabrication technology, this controlled selective growth technique can be a useful route to facile and quick fabricate high-performance ZnO-based nanodevices.

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References

[1] R. Konenkamp, R.C. Word, M. Godinez, Nano Lett. 5 (2005) 2005–2008.
[2] J.Y. Lee, Y.S. Choi, J.H. Kim, M.O. Park, S. Im, Thin Solid Films 403 (2002) 553–557.
[3] M. Law, L.E. Greene, J.C. Johnson, R. Saykally, P.D. Yang, Nat. Mater. 4 (2005) 455–459.
[4] J.X. Wang, X.W. Sun, Y. Yang, H. Huang, Y.C. Lee, O.K. Tan, L. Vayssieres, Nanotechnology 17 (2006) 4995–4998.
[5] C.D. Lokhandea, P.M. Gondkara, R.S. Maneb, V.R. Shindea, S.H. Han, J. Alloy Compd. 475 (2009) 304–311.
[6] M.H. Huang, Y.Y. Wu, H. Feick, N. Tran, E. Weber, P.D. Yang, Adv. Mater. 13 (2001) 113–116.
[7] K.S. Kim, H.W. Kim, Phys. B: Condens. Matter 328 (2003) 368–371.
[8] Y. Li, G.W. Meng, L.D. Zhang, F. Phillipp, Appl. Phys. Lett. 76 (2000) 2011–2013.
[9] L. Vayssieres, Adv. Mater. 15 (2003) 464–466.
[10] L.E. Greene, M. Law, D.H. Tan, M. Montano, J. Goldberger, G. Somorjai, P.D. Yang, Nano Lett. 5 (2005) 1231–1236.
[11] Q. Ahsanulhaq, A. Umar, Y.B. Hahn, Nanotechnology 18 (2007) 115603–115609.
[12] Y. Tak, K. Yong, J. Phys. Chem. B 109 (2005) 19263–19269.
[13] J. Noborisaka, J. Motohisa, T. Fukui, Appl. Phys. Lett. 86 (2005) 213102.
[14] J. Cui, U. Gibson, Nanotechnology 18 (2007) 155302.
[15] M. Guo, P. Diao, S.M. Cai, J Solid State Chem. 178 (2005) 1864–1873.
[16] C.H. Ahn, Y.Y. Kim, S.W. Kang, B.H. Kong, S.K. Mohanta, H.K. Cho, J.H. Kim, H.S. Lee, J. Mater. Sci.: Mater. Electron. 19 (2008) 744–748.
[17] G.Z. Xing, B. Yao, C.X. Cong, T. Yang, Y.P. Xie, B.H. Li, D.Z. Shen, J. Alloy Compd. 457 (2008) 36–41.
[18] B. Weintraub, Y. Deng, Z.L. Wang, J. Phys. Chem. C 111 (2007) 10162–10165.