December 2006 Volume 2 Issue 6

Trade Science Inc.

Materials Science
An Indian Journal

Full Paper

MSAIJ, 2(6), 2006 [268-273]

Electric Properties Of $BiFeO_3$ Modified PZT Solid Solution Films Prepared By Sol-Gel Process

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Received: 2nd December, 2006

Accepted: 16th December, 2006

Web Publication Date : 27th December, 2006

ABSTRACT

$(PbZr_{0.5}Ti_{0.5}O_3)_x$-$(BiFeO_3)_{1-x}$ films have been prepared on $LaNiO_3/SiO_2/Si$ substrates by sol-gel process at an annealing temperature of 600°C. X-ray diffraction patterns indicate that the samples show (110) preferred orientation or random orientation according to the x and no impure phase was observed for all films. The study of ferroelectricity shows that the saturated polarizations are enhanced by the incorporation of $BiFeO_3$. Remnant polarization of 33.7 μC/cm^2, 36.8 μC/cm^2, 34.4 μC/cm^2 and 37.6 μC/cm^2 are observed for the films with x=0 to 0.20. In addition, dielectric properties were enhanced through the solid solution with $BiFeO_3$. Leakage conduction was also increased by the incorporation of $BiFeO_3$.

KEYWORDS

$(PbZr_{0.5}Ti_{0.5}O_3)_{1-x}$-$(BiFeO_3)_x$ films;
Sol gel;
Ferroelectricity;
Dielectric property;
Leakage current.

INTRODUCTION

In recent years, extensive attention has been focused on multiferroic materials, in which both electrical and magnetic ordering can coexist. They are also called magnetoelectric materials[1] and have many potential applications in information technology, sensors, (MEMS) devices, and spintronics devices etc. $BiFeO_3$ (BFO) is such material and reported to exhibit magnetic ordering with a relatively high Neel temperature (T_N~370°C) and ferroelectric ordering with cure temperature (T_C~850°C)[2], its atomic structure was determined from single crystal and powder X-ray and neutron diffraction studies, and the results reveal that BFO has a rhombohedrally distorted perovskite structure with space group R3c[3]. A ferroelectric hysteresis loop of BFO single crystal with polarization values of 3.5-6.1 $\mu C/cm^2$ has been confirmed at liquid nitrogen temperature[4].

The works focused on the study of solid solutions of BFO and other ABO_3 type perovskite ferroelectrics such $BaTiO_3$, $PbTiO_3$ and $PbLaZrTiO_3$ etc al.[5-7]. The structural, dielectric, ferroelectric and magnetic properties with the content of BFO have been studied. BFO has also been used to modify other ferroelectrics such as $SrBi_2Nb_2O_9$ and $SrBi_2Ta_2O_9$ and obtained enhanced dielectric properties[8,9]. $PbZr_{1-x}Ti_xO_3$ (PZT) is classic ABO_3 type ferroelectrics with large remnant polarization and was intensively used in memory device and piezoelectric device. It has been deposited on all sorts of substrates such as Pt/Ti/SiO_2/Si, ITO/glass and $LaNiO_3$/Si substrates[10-12]. In general, PZT films deposited on $LaNiO_3$ (LNO) bottom electrodes adopted (100) or (001) preferred orientation and has the small remnant polarization than the (111) preferred orientation films on ITO/glass or $LaNiO_3$/Si. More over, there were works on the substitution of PZT on A or B site and obtained enhanced ferroelectricity and dielectric properties[13,14]. The incorporation of BFO with other ABO_3 type perovskite ferroelectrics is co-substitution on A and B sites in essential. Since the incorporation of $BiFeO_3$ with other ferroelectrics can enhance the dielectric property, it may be the same to PZT. Further more, there is no reports on the BFO modified PZT films as our knowledge. For the purpose, PZT_{1-x}-BFO_x films with x=0, 0.05, 0.10 and 0.2 were prepared by sol-gel process on $LaNiO_3/SiO_2$/Si substrates and the ferroelectric, dielectric and leakage conduction properties were studied in our work.

EXPERIMENTAL

The $BiFeO_3$ precursor solution was prepared using Bi $(NO_3)_3 \cdot 5H_2O$ and Fe $(NO_3)_3 \cdot 9H_2O$ as staring materials. $Bi(NO_3)_3 \cdot 5H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ were mixed with a mol ratio of 1/1 and dissolved at room temperature in 2-methoxyethanol and stirred for 30 minutes. Then acetic anhydride was added to dehydrate and ethanolamine was added to adjust the viscosity under constant stirring. The stock solution was adjusted to 0.3 M by adding methoxyethanol. The above process was performed in an ambient atmosphere at room temperature.

The $Pb(Zr_{0.5}Ti_{0.5})O_3$ precursor solution was prepared using $Pb(CH_3COO)_2 \cdot 3H_2O$, $Zr(NO_3)_4 \cdot 5H_2O$ and $Ti(C_4H_9O)_4$ as staring materials. $Pb(CH_3COO)_2 \cdot 3H_2O$ was dissolved in 2-methoxyethanol and circumfluence for 30 minutes. Then $Zr(NO_3)_4 \cdot 5H_2O$ and $Ti(C_4H_9O_4)_4$ were dumped into 2-methoxyethanol and stirred for 30 minutes to dissolved respectively. The mol ratio of $Pb(CH_3COO)_2 \cdot 3H_2O$, $Zr(NO_3)_4 \cdot 5H_2O$ and $Ti(C_4H_9O_4)_4$ were 1.1:0.5:0.5 (10 % Pb excess to compensate the Pb loss during the annealing process). Then the above solutions were mixed under constant stirring, ice acetic acid was added to stabilize the solution. The concentration was adjust to 0.3 M by add 2-methoxyethanol.

The $Pb(Zr_{0.5}Ti_{0.5})O_3$ precursor solution and $BiFeO_3$ precursor solutions were mixed with proper volume ratio of 1:0, 0.95:0.05 and 0.9:0.10 and 0.80:0.20 to obtain $(PZT)_{1-x}$-BFO_x total precursor solution. $LaNiO_3/SiO_2$/Si was used as substrates, the preparation technology refer to[12]. The depositions were carried out by spin coating at 6000 rpm for 20 s. Each deposition layer was pre-annealing at 350°C for 3 minutes and crystallized at 600°C for 3 minutes in air atmosphere. Then the temperature was rapidly dropped to 300°C in 3 minutes. The spin coating was repeated several times to obtain the desired thickness. Structure of the films was analyzed by X-ray diffraction. The XRD patterns were recorded with X-ray diffraction meter with Cu Ka radiation. The surface and cross section morphology are analyzed by scanning electric microscopy (AFM) and atom force microscopy (SEM) respectively. For electrical measurements, Pt dots of $0.01mm^2$ were deposited through a mask on the films by sputtering. The ferroelectric hysteresis loops and leakage conductions were obtained using a precision work station (Radiant Technology). Dielectric constant and loss tangent were measured with HP 4284A LCR meter

RESULTS AND DISCUSSIONS

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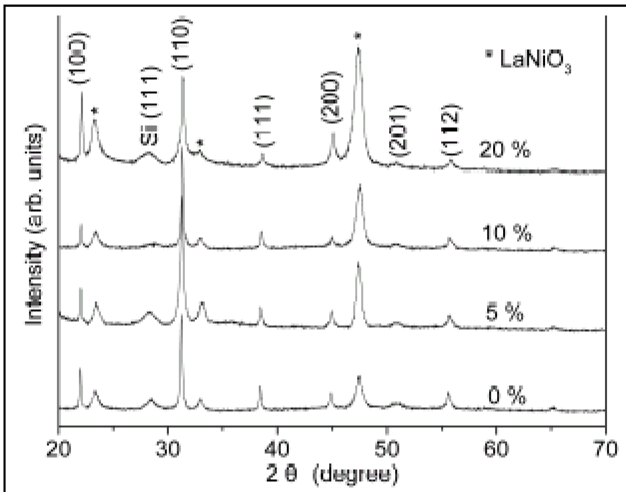
The XRD diffraction patterns obtained for the $PZT_{1-x}BFO_x$ films where x=0.0, 0.05, 0.10, and 0.20 are shown in figure 1. All films are well crystallized since the peaks for the $(PZT)_{1-x}(BFO)_x$ phase are sharp and slim. It is easy to see that all films show perovskite structure and no impure phase such as pyrochlore phase was identified up to x = 0.20. Moreover, only tetragonal phase (PZT phase) can be observed and no rhombohedra phase ($BiFeO_3$ phase) was identified in the whole composition range, therefore solid solution phase was formed in the whole composition content range for all films. The films with x = 0 to 0.10 show (110) preferred orientation and the film with x = 0.2 show random orientation. In our work, the LNO bottom electrodes are (100) preferred oriented, while we did not obtain (100) preferred oriented PZT film. The results are different from most already reported results[15,16,17], in the above work, pure PZT films adopted (100) preferred orientation on (100) preferred oriented $LaNiO_3$ bottom electrodes because of crystal lattice match. In our work, the (110) preferred orientation of pure PZT is very likely caused by the stress during the rapid cooling. In addition, the distortion of crystal lattice by the co-substitution in A site and B site by Bi and Fe respectively may attribute to the orientation of the films.

Figure 2 shows the cross section SEM photo of pure PZT, which indicates that the film has a homogeneous thickness. The thickness, judged from the photo, is about 400 nm.



Figue 1: XRD patterns of $PZT_{1-x}BFO_x$ annealed at 600°C

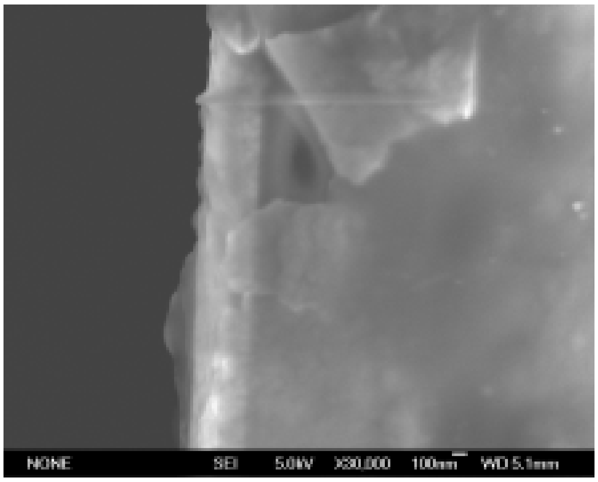


Figure 2: Cross section SEM photo of pure PZT film

Figure 3 presents the AFM images of $PZT_{1-x}BFO_x$ thin films with x = 0.00 to 0.20 annealed at 600°C. The AFM image shows that the pure PZT film is made of uniform fine grains and the fine grain begin to growth into larger grains with the increasing of x.

The film with x = 0.20 has the largest and even grain. More over, the coarseness of the film is increased with x. The film with x = 0.20 has the largest surface coarseness. Therefore the incorporation of BFO is attributed to enhance the nucleation rate and therefore the films with the incorporation of BFO are easier to grow into larger grains.

Figure 4 shows the electric hysteresis loops of PZT_{1-x}-BFO_x films with x = 0.00 to 0.20 annealed at 600°C. The films show different saturate polarization (Ps) and nearly same remnant polarization. The saturate polarizations for the films with x = 0.00 to 0.20 are 80.7$\mu C/cm^2$, 91.1$\mu C/cm^2$, 83.7 $\mu C/cm^2$, 64.9 $\mu C/cm^2$ and the remnant polarizations (Pr) are 33.7 $\mu C/cm^2$, 36.8 $\mu C/cm^2$, 34.4 $\mu C/cm^2$ and 37.6 $\mu C/cm^2$ at an applied field 726 kV/cm., respectively. The films with x < 0.2 show small coercive filed and large saturation polarization. The Pr of the pure PZT is larger than that of Zhu and less than the (111) oriented PZT films on Pt/Ti/SiO_2/Si substrates[18,19]. From the results above we can find that through the solid solution with $BiFeO_3$, the saturate polarization is substantially enhanced since the Ps value for the film with x = 0.05 is 10 $\mu C/cm^2$ larger than that of the pure PZT. There is no substantially change in

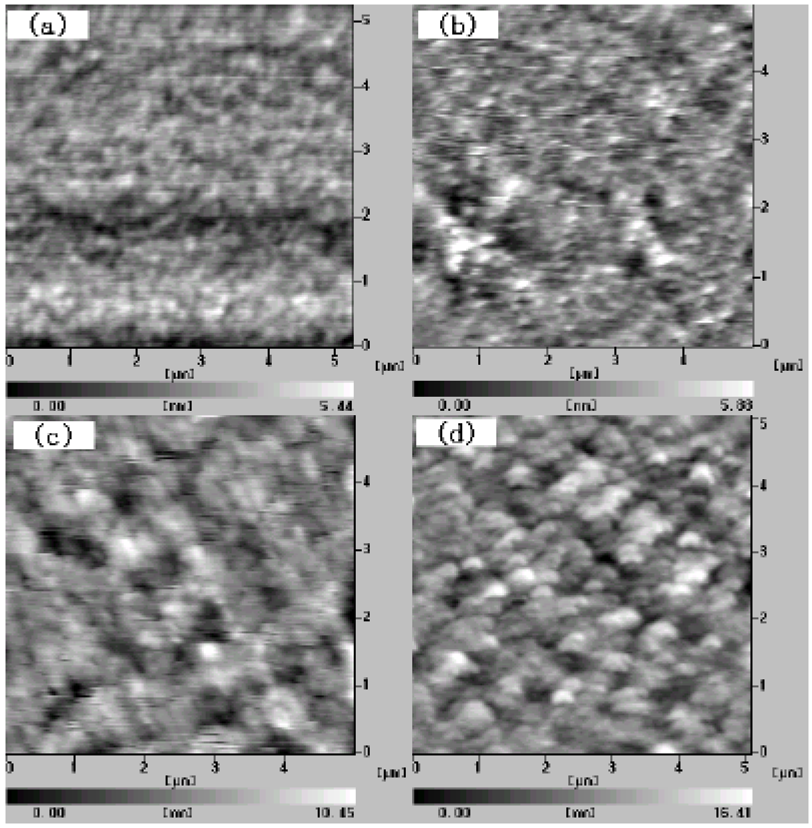


Figure 3: AFM photos of PZT_{1-x}-BFO_x films for x = (a) 0.00, (b) 0.05, (c) 0.10 (d) 0.20

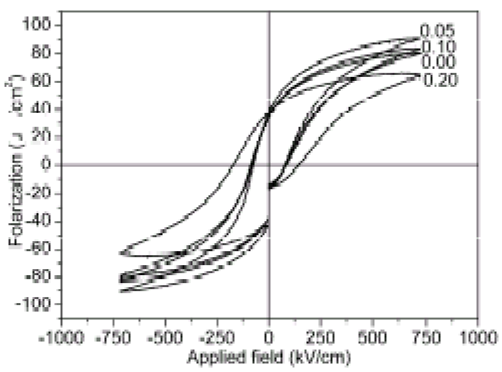


Figure 4: Electric hysteresis loops for PZT_{1-x}-BFO_x films

the coercive filed since the films with $x < 0.2$ have the nearly same coercive fields. While large coercive field is obviously for the film with x = 0.20. We suggest that the large coercive field is from the pin of domain wall by the space charges originate from the A and B sites substitution by Bi^{3+} and Fe^{3+}. The ions radius of Fe^{3+}, Zr^{4+}, Ti^{4+}, Bi^{3+} and Pb^{2+} are 0.64 Å, 0.72 Å, 0.68 Å, 1.03 Å and 1.32 Å, respectively. Because of the similar ion radius of Fe^{3+} to Zr^{4+} and Ti^{4+}, Bi^{3+} to Pb^{2+}, the incorporation of $BiFeO_3$ will result in A site occupation for Bi^{3+} and B site occupation for Fe^{3+} to form stabilize perovskite structure. Since the radius of Fe^{3+} is less than that of Zr^{4+} and Ti^{4+}, we expect larger vibrating space for the Fe^{3+} in the oxygen octahedron thus obtains more intense polarization. On the other hand, the susceptibility of Fe^{3+} is less than that of Ti^{4+} and Zr^{4+} and the excess substitution of Ti^{4+} and Zr^{4+} with Fe^{3+} will lead to the reduction therefore the film with x = 0.2 has the least Ps.

Figure 5 shows the dielectric constant and dissipation factor as a function of frequency range from 1100 Hz to 1.0 MHz at room temperature for the PZT_{1-x}-BFO_x films with x=0.00 to 0.20. The films show enhanced dielectric property for the dielectric constants of the films with x=0.10 and 0.20 are larger than the pure PZT film below 400 kHz. The film with x=0.05 has the least dielectric constant above 80 kHz. It is suggested that the dielectric constant is determined by the polarization in ferroelectrics. As has been discussed above, the incorporation of $BiFeO_3$ leads to the enhanced ionic displace in octahedral therefore results in enhanced polarization,

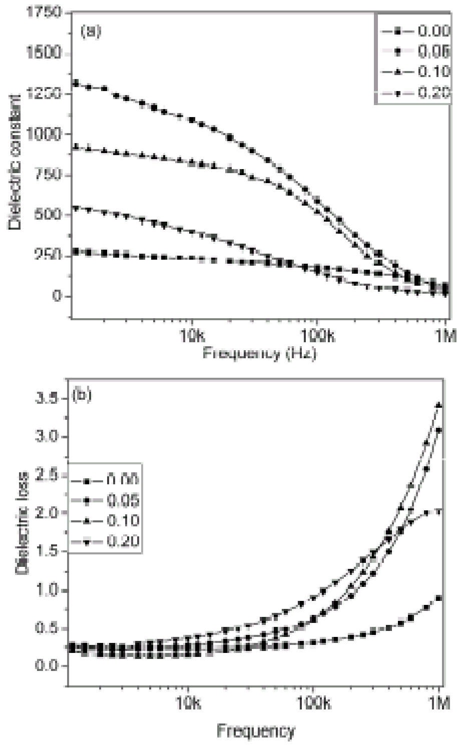


Figure 5: Dielectric properties of the (a) dielectric constant and (b) dielectric loss of the PZT_{1-x}-BFO_x films with x= 0.0 to 0.20

which brings on the increase of dielectric constant. We can also observe the drastic decrease of dielectric constant above 100 kHz for the film with x=0.2. As discussed in our previous work[20], the falling in dielectric constant arises from the fact that polarization does not occur instantaneously with the application of the electric field because of inertia. At low frequencies, all the polarizations contribute. As frequency is increased, those with large relaxation times cease to respond and hence the decrease in dielectric constant.

The dielectric loss is shown in figure 3 (b), the films with x = 0 and 0.10 have low dielectric loss at low frequencies and the dielectric loss begin to increase drastically near 100 kHz. For the film with x = 0.10, dielectric loss was observed to decrease with frequency between 110 kHz to 10 kHz and it is attribute the effects of DC conduction. The large DC conduction is attributed to the space charges introduced by aliovalent substitution of Pb^{2+} and Fe^{3+}. Below 300 kHz, the film with x = 0.2 has the largest dielectric loss at the same frequency and it may be related to the larger crystal grain of it.

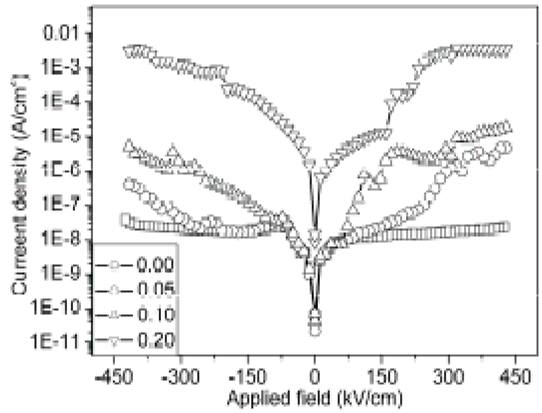


Figure 6: J-E characteristics of PZT_{1-x}-BFO_x films with x=0 to 0.2

Figure 6 shows J-E characteristics of the PZT_{1-x}-BFO_x films with x=0, 0.05, 0.10 and 0.20 at both polarities of the applied voltages. From which we find that the pure PZT film has the lowest current densities at the same applied field. Obviously, the leakage currents density is increased with the x monotonously. Comparing with the pure PZT film, the leakage current density increased by nearly six orders of magnitude for the film with x=0.2. It has been well established that the leakage current in ferroelectrics is dominated by space charges. Therefore abundant space charges were produced by the incorporation of $BiFeO_3$. We suggest that the space charges are originated from the following three reasons: (1) cation vacancies created by the substitution of Ti^{4+} with Fe^{3+}. (2) anion vacancies created by the substitution of Pb^{2+} with Bi^{3+}. (3) oxygen vacancies created by the valence reduction of Fe^{3+} species to Fe^{2+}. As discussed above the increasing is attributed to the increasing of space charges by the incorporation of BFO.

CONCLUSIONS

$BiFeO_3$ modified PZT films were prepared with sol-gel process. PZT_{1-x}-BFO_x films with x=0 to 0.2 were deposited on $LaNiO_3/SiO_2/Si$ substrates and fully crystalline films were obtained at an annealing temperature of 600°C. Through the incorporation of $BiFeO_3$, the ferroelectricity and dielectric property are substantially enhanced. Remnant polarizations of 33.7 mC/cm^2, 36.8 mC/cm^2, 34.4 mC/cm^2

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and 37.6 $\mu C/cm^2$ are observed respectively for the films with x=0, 0.05, 0.10 and 0.20. Enhanced ferroelectricity and dielectric property are thought to be determined by the enhanced polarization by the substitution of Zr^{4+} and Ti^{4+} with Fe^{3+}. The leakage conduction is greatly increased by the incorporation of $BiFeO_3$ and is thought to due to the cantion and anion vacancies produced by the substitution of A and B site with Bi^{3+} and Fe^{3+}.

REFERENCES

[1] M.M.Kumar, A.Srinivas, G.S.Kumar, S.V.Suryanarayana; J.Phys.Condens.Matter, **11**, 8131 **(1999)**.

[2] I.Sosnowska, T.P.Neumaier, E.Steichele; J.Phys., C., **15**, 4835 **(1982)**.

[3] C.Michel, J.M.Moreau, G.D.Achenbach, R.Gerson, W.J.James; Solid State Commun., **7**, 701 **(1969)**.

[4] J.R.Teague, R.Gerson, W.J.James; Solid State Commun., **8**, 1073 **(1970)**.

[5] K.Ueda, H.Tabat, T.Kawai; Appl.Phys.Lett., **75**, 555 **(1999)**.

[6] D.I.Woodward, I.M.Reaney, R.E.Eitel, C.A.Randall; J.Appl.Phys., **94**, 3313 **(2003)**.

[7] T.Kanai, S.Ohkoshi, K.Hashimoto; J.Phys.Chem.Solid., **64**, 391 **(2003)**.

[8] A.Srinivas, D.Kim, K.S.Hong; Appl.Phys.Lett., **83**, 1602 **(2003)**.

[9] H.Gu, J.Xue, J.Wang; Appl.Phys.Lett., **79**, 2061 **(2001)**.

[10] X.M.Lu, F.Schlaphof, S.Grafstrom, C.Loppacher, L.M.Eng; Appl.Phys.Lett., **81**, 3215 **(2002)**.

[11] Z.Liu, Q.Liu, H.Liu, K.Yao; Phys.Stat.Sol., (a), **202**, 1834 **(2005)**.

[12] X.J.Meng, J.G.Cheng, J.L.Sun, H.J.Ye, S.L.Guo, J.H.Chu; J.Crystal Growth, **220**, 100 **(2000)**.

[13] J.Zhai, M.H.Cheung, Z.K.Xu, X.Li, H.Chen; Appl. Phys.Lett., **81**, 3621 **(2002)**.

[14] J.Zhai, H.Chen; J.Appl.Phys., **94**, 589 **(2003)**.

[15] H.Miyazaki, T.Goto, Y.Miwa, T.Ohno, H.Suzuki, T.Ota, M.Takahashi; J.Eur.Ceram.Soc., **24**, 1005 **(2004)**.

[16] X.J.Meng, J.G.Cheng, J.L.Sun, H.J.Ye, S.L.Guo, J.H.Chu; J.Cryst.Growth, **220**, 100 **(2000)**.

[17] S.H.Hu, G.J.Hu, X.J.Meng, G.S.Wang, J.L.Sun, S.L.Guo, J.H.Chu, N.Dai; J.Cryst.Growth, **260**, 109 **(2004)**.

[18] T.J. Zhu, L.Lu, C.V.Thompson; J.Cryst.Growth, **273**, 172 **(2004)**.

[19] Q.Wang, Y.Ding, Q.Chen, M.Zhao, J.Cheng; Appl. Phys.Lett., **86**, 162903 **(2005)**.

[20] H.Liu, Z.Liu, Q.Liu, K.Yao; Thin Solid Films, **500**, 105 **(2006)**.