Optimized growth and dielectric properties of barium titanate thin films on polycrystalline Ni foils*

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(Received 22 February 2012; revised manuscript received 28 February 2012)

Barium titanate (BTO) thin films were deposited on polycrystalline Ni foils by using the polymer assisted deposition (PAD) technique. The growth conditions including ambient and annealing temperatures were carefully optimized based on thermal dynamic analysis to control the oxidation processing and interdiffusion. Crystal structures, surface morphologies, and dielectric performance were examined and compared for BTO thin films annealed under different temperatures. Correlations between the fabrication conditions, microstructures, and dielectric properties were discussed. BTO thin films fabricated under the optimized conditions show good crystalline structure and promising dielectric properties with $\varepsilon_r \sim 400$ and $\tan\delta < 0.025$ at 100 kHz. The data demonstrate that BTO films grown on polycrystalline Ni substrates by PAD are promising in device applications.

Keywords: polymer assisted deposition, barium titanate, nickel foils, thin films, thermodynamics, dielectric properties

PACS: 77.84.–s, 77.55.fe, 77.55.Nv **DOI:** 10.1088/1674-1056/21/6/067701

1. Introduction

Ferroelectric oxide thin films with excellent ferroelectric, dielectric, piezoelectric, and optical properties have been widely investigated and have shown great potential in many applications.[1−3] Most of the previous reports on ferroelectric oxide thin films are the integration of this kind of material with single crystal oxides or Si substrates. Deposition of ferroelectric thin films on polycrystalline base-metallic foils such as nickel and copper foils, is interesting and valuable for its potential applications in structural health monitoring systems, embedded capacitors, MEMS, etc.[4−8] However, so far, it is still a great challenge to grow high quality ferroelectric oxide thin films on polycrystalline base-metallic substrates due to the difficulties in controlling the interface. It is well known that the properties of the oxide thin films are strongly dependent on the substrates which they grow on. Compared to substrates such as ceramic oxides (such as $SrTiO_3$, $LaAlO_3$, etc.) and noble metals (such as Pt, and Au etc.) coated Si, the base-metallic substrates such as nickel and copper are much easier to oxidize. To grow oxide thin films on base-metallic foils, we have to consider both the protection of metallic foils from oxidation and the crystallization of oxide thin films. On the one hand, to avoid the serious oxidation of the base-metallic substrates, the fabrication should be performed in a reducing ambient temperature. On the other hand, to ensure the oxygen content in the oxide thin films, a proper source of oxygen needs to be provided during the process. Moreover, the interdiffusion between the oxide thin film and the base-metallic substrate at a high deposition temperature will result in a thick "dead layer" at the interface. Thus, control of the oxidation process and the interdiffusion at the interface is extremely critical for the content of oxygen vacancies and the interface properties, which are the most important factors for the electric properties of the oxide thin films.

A few groups have conducted their research on the integration of ferroelectric thin films with base-metallic substrates, using various techniques such as

*Project supported by the National Natural Science Foundation of China (Grant Nos. 11028409 and 60976061) and the Fundamental Research Funds for the Central Universities of China (Grant No. ZYGX2009Z0001).

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chemical solution deposition (CSD),[7,9] pulsed laser deposition (PLD),[5,10] and sputtering.[6,11] Among these techniques, CSD methods have the advantages of low costs, easy setup, and the ability for large area coating. However, chemical stability and reproducibility are often challenging for general CSD techniques. Recently, a polymer-assisted deposition (PAD) technique was developed for the synthesis of oxide thin films with controllable structures and excellent physical properties.[12] The unique feature of this technique is that metal ions are bonded to a water-soluble polymer to form a precursor, which can prevent the hydrolysis of the metal ions and thus greatly improve the chemical stability and reproducibility. PAD has been employed to synthesize various oxide thin films on different single crystal oxide substrates and Si wafers.[13,14] Therefore, integrating ferroelectric thin films on metallic substrates by using this technique may open a new avenue for the development of various devices. However, the water-based solution used in PAD is likely to increase the risk of oxidation of the base-metallic substrates. More efforts are needed to control the oxidation and interdiffusion at the interface to use the PAD technique to deposit metal oxides on base-metallic substrates. A good understanding of the thermodynamics during the growth of ferroelectric oxides on the base-metallic substrates is necessary to use this technique.

In this paper, we report the successful fabrication of ferroelectric oxide BTO thin films on polycrystalline Ni foils by using the PAD technique. The thermodynamics have been investigated to optimize the growth conditions. The correlation between the fabrication condition, microstructures, and electric properties of the films will be discussed.

2. Experimental

To control the interdiffusion between the film and the substrate, a buffer layer is normally adopted. In our experiments, we chose nickel oxide as the buffer layer due to its advantages such as easy fabrication, controllable dimensions, and self-attainment. The nickel oxide layers were formed on Ni substrates by pretreating the Ni foils in a hydrogen peroxide (H_2O_2) solution. Commercial polycrystalline nickel foils (99.9%) with a thickness of 0.5 mm were mechanically polished to remove the natural oxidized layers on the Ni surface as well as the surface contaminations. The as-polished nickel surface is shiny and has a very poor wet ability to the water-based precursor solutions used in PAD. So, after ultrasonic cleaning in acetone, the foils were then immersed into 10% H_2O_2 solution for 2 hours at 50 °C to form the oxide buffer layer as well as to improve the wet ability.

Details for the preparation of the precursor solutions containing the Ba^{2+} and Ti^{4+} ions have been reported in earlier publications.[15] The concentration of the Ba^{2+} and Ti^{4+} ions in the precursor solutions were measured using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). Then the Ba^{2+} and Ti^{4+} precursor solutions were mixed in a molar ratio of 1:1 to yield a precursor solution for BTO. The as-prepared solution was spin-coated on the pretreated nickel foils with a spin rate of 3000 rpm for 30 s to form the precursor films. The precursor films were then put into a tube furnace for heat treatment. As mentioned above, in order to suppress the oxidation of the nickel substrates as well as decrease the density of oxygen vacancies in the oxide films, it is critical to carefully control the processing conditions such as the oxygen partial pressure, the annealing temperature, and the annealing time, etc.

A proper oxygen partial pressure is important to ensure the nickel foils maintain a metallic status while elements of Ba and Ti can react with oxygen to form oxides. Figure 1(a) is the equilibrium oxygen partial pressure curves versus temperatures for barium, titanium, nickel metals, and their oxides.[16] It is obvious that the shaded region can fulfil our request. In our experiment, a forming gas containing 94% N_2 + 6% H_2 with a flow rate of 100 ml/min was chosen as the heat treatment ambient, in which the oxygen partial pressure is about 10^{-18} atm (1 atm = 1.01325×10^5 Pa). Thus, any temperature in the range of 700 °C–1000 °C falls into the shaded area in Fig. 1(a). It should be noted that in this processing window, the nickel oxide decomposes into nickel and oxygen, which would act as another oxygen source for the BTO films.

To decompose the polymer, the precursor films were first heated to 510 °C and maintained at that temperature for one hour. The spin coating and thermal treatment were repeated for 5 times to yield thicker films. Then, the films were further heated up to an annealing temperature for crystallization. This annealing temperature must ensure the BTO thin films have good crystallization, meanwhile, serious interdiffusion between the oxide thin films and the Ni substrates must be avoided. The crystallization of BTO thin films is in general enhanced with an increase of the annealing temperature in the range

of 600 °C–1000 °C. However, the diffusion coefficient of the nickel metallic is a function of temperature, as shown in Fig. 1(b).[17] In the temperature range of 600 °C–1000 °C, the diffusion coefficient of Ni increases about one order of magnitude as the temperature increases 100 °C. So, the annealing temperature of BTO thin films has to be carefully chosen. To find out the optimal growth condition, samples annealed at temperatures of 700, 800, 900, and 1000 °C were prepared and compared, named as A700, A800, A900, and A1000, respectively. The final thicknesses of BTO films are about 500 nm for all the samples. Microstructures of the films were examined by the X-ray diffraction (XRD) technique and an atomic-force microscopy (AFM). Dielectric properties of the samples were tested using an Agilent-4284A Precision LCR meter.

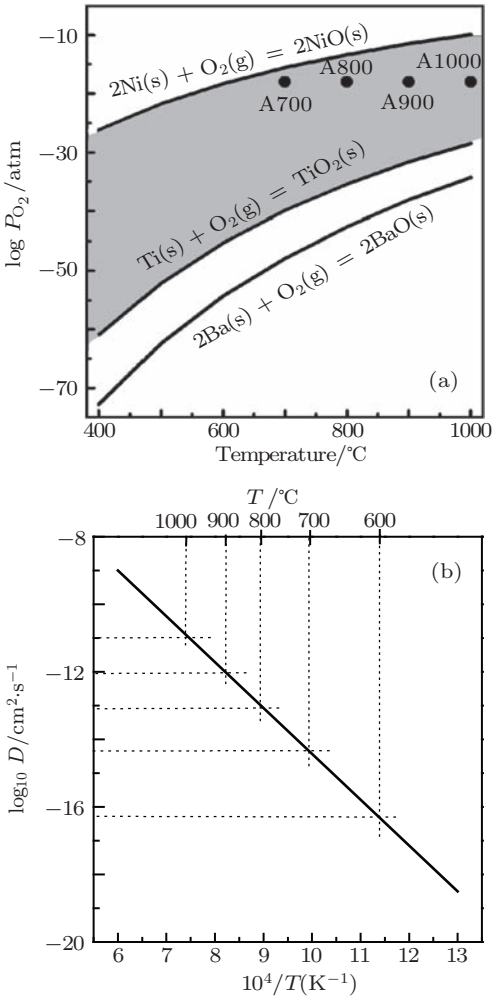


Fig. 1. (a) Equilibrium oxygen partial pressure curves versus temperature for barium, titanium, nickel metals and their oxides. The shaded region is the processing window. The annealing conditions of samples A700, A800, A900, A1000 were also shown in the figure, respectively. (b) Diffusion coefficient of nickel atoms in nickel as a function of temperature.

3. Results and discussions

XRD was performed using Cu Kα radiation to examine the crystal structure of the films. Figure 2 shows the typical XRD patterns for A700, A800, A900, and A1000 respectively. The characteristic peaks of polycrystalline nickel and pseudo-cubic BTO can be identified for all samples. No peak from either NiO or Ni_2O_3 is observed. The data demonstrated that we have successfully fabricated BTO thin films on polycrystalline nickel foils without detectable nickel oxide phases. All the diffraction peaks in the samples annealed in the range of 700 °C–900 °C can only be indexed by polycrystalline pseudo-cubic BTO and nickel. However, peaks near 27° and 29° from $Ba_2Ni_xO_z$ were observed in the diffraction pattern of the sample A1000. This may be caused by the serious interdiffusion at 1000 °C.

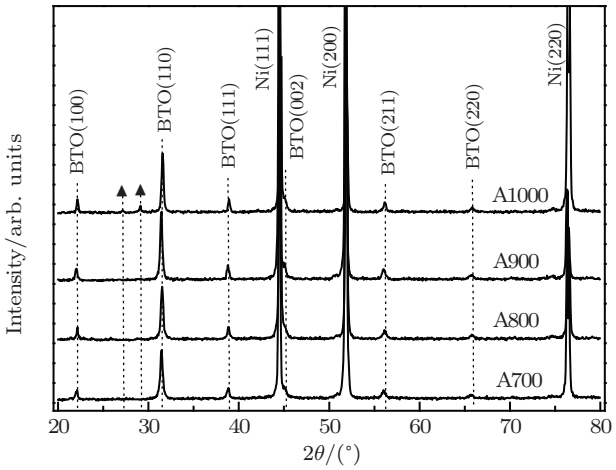


Fig. 2. XRD patterns from θ–2θ scans for the BTO thin films annealed at 700 °C–1000 °C, respectively. The symbol ▲ indicates the peaks from $Ba_2Ni_xO_z$.

Surface morphologies of the thin films were investigated using AFM. Figures 3(a)–3(d) show the AFM images of A700 to A1000 respectively. It is obvious that the grain size increases with the annealing temperature. The films annealed at 700 °C have the smallest grain size (about 210 nm in average). Moreover, voids can be seen on the surface of A700. The average grain sizes of A800, A900, and A1000 increase to 280 nm, 310 nm, and 380 nm, respectively. Few voids were detected on their surface. The voids may form when the polymer are decomposed. During the annealing, the BTO crystals grow and reconstruct, and thus fill in these voids. The phenomenon suggests that a thermal treatment at 700 °C is possibly insufficient. This temperature could not provide enough energy to restructure the crystals to fill in all the voids.

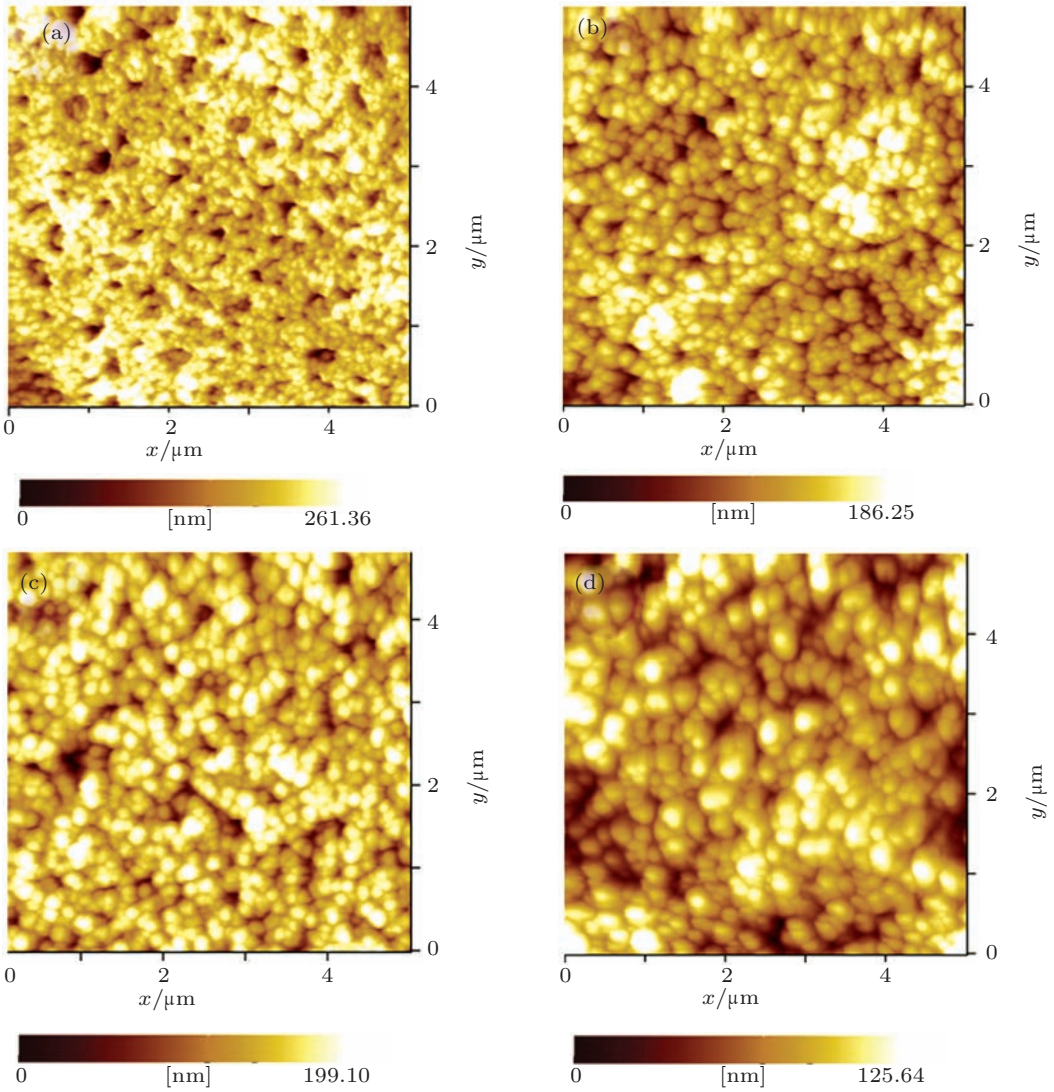


Fig. 3. (colour online) AFM images of the BTO thin films: panels (a)–(d) for samples A700, A800, A900, and A1000 respectively.

To investigate the electric properties of the BTO thin films, gold top electrodes with an area of 10^{-4} cm^2 were deposited on the surfaces of the BTO films using sputtering. Dielectric constant and dielectric loss tangent were measured using an Agilent-4284A Precision LCR meter at 100 kHz. Figure 4 shows the dielectric constant and loss tangent versus the applied electric field (E) for all the samples. It shows that the dielectric constant and the loss tangent of the BTO thin films strongly depend on the annealing temperature. For A700, A800, and A900 the dielectric constant increases and the loss tangent decreases as the annealing temperature increases. The zero field dielectric constants for A700, A800, and A900 are 289, 383, and 600, respectively. The zero field loss tangents for A700, A800, and A900 are 0.027, 0.021, and 0.018, respectively. It is clear that dielectric constants are tuned by the electric field for all three samples, as seen in other ferroelectric materials. Tunability is defined as $(\varepsilon_0 - \varepsilon_E)/\varepsilon_0$, where ε_0 and ε_E are the dielectric constants for the film at zero and E fields. When an electric field of 200 kV/cm was applied to the samples, the tunability for A700, A800, and A900 are 40%, 47%, and 54% respectively. The improvement of the dielectric properties at a higher temperature is likely to result from a better crystallization of the films.

However, for the films annealed at 1000 °C, the dielectric constant is as low as 18 and the loss tangent is as high as 0.7. The degradation of the dielectric properties in A1000 might be related to the serious interdiffusion, as demonstrated by the XRD pattern.

In addition, it should be noted that for the sample A900, the loss tangent shows an abnormal increase

at about 140 kV/cm (as shown in the black cycle in Fig. 4). It has been previously reported that a similar abnormality in loss tangent is associated with a region with a high oxygen-vacancies-density, which is easily formed near the surface of thin films when the sample was annealed at a high temperature in a reducing environment.[18,19] The abnormal increase in loss tangent implies that oxygen loss at the surface of the BTO thin film may occur in A900 when it was annealed in a reducing ambient.

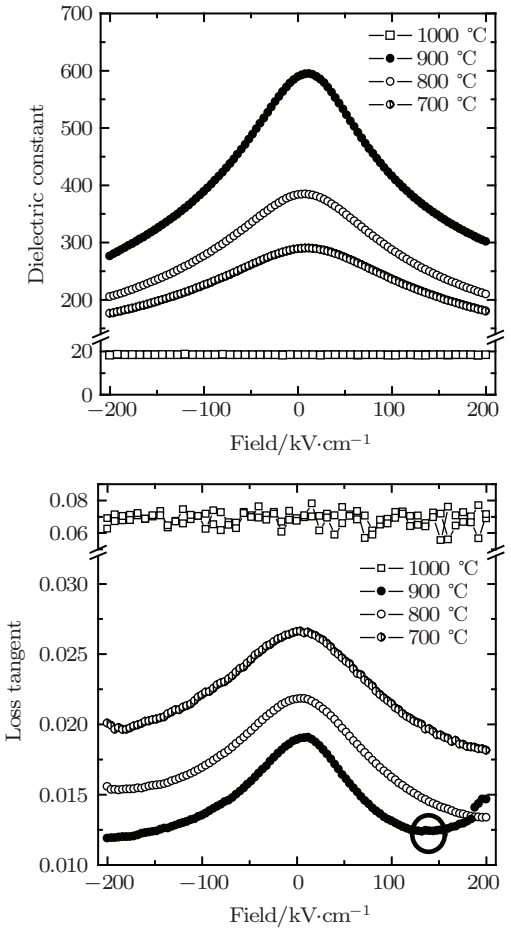


Fig. 4. (colour online) The dielectric constant and loss tangent tested at 100 kHz for samples A700, A800, A900, and A1000, respectively.

Frequency dependences of the dielectric constant and the loss tangent were also measured for A700, A800, and A900, as shown in Fig. 5. Consistent with Fig. 4, it also shows that the dielectric constant increases and the loss tangent decreases as the annealing temperature increases. Moreover, the figure shows a really high loss tangent for sample A700 in the low frequency region (i.e., when frequency is lower than 4 kHz, $\tan\delta = 0.1 \sim 1.6$). It is believed that the high loss at the low frequency region is ascribed to the space charge polarization of the thin films. The space charge polarization is associated with the migration of defects (such as oxygen vacancies) or disorder in the thin films.[20,21] This is consistent with the AFM images in which voids were observed on the surface of this sample. As discussed above, 700 °C is not sufficient for a good thermal treatment. High density of defects or disorders may have left in the film as well as the voids.

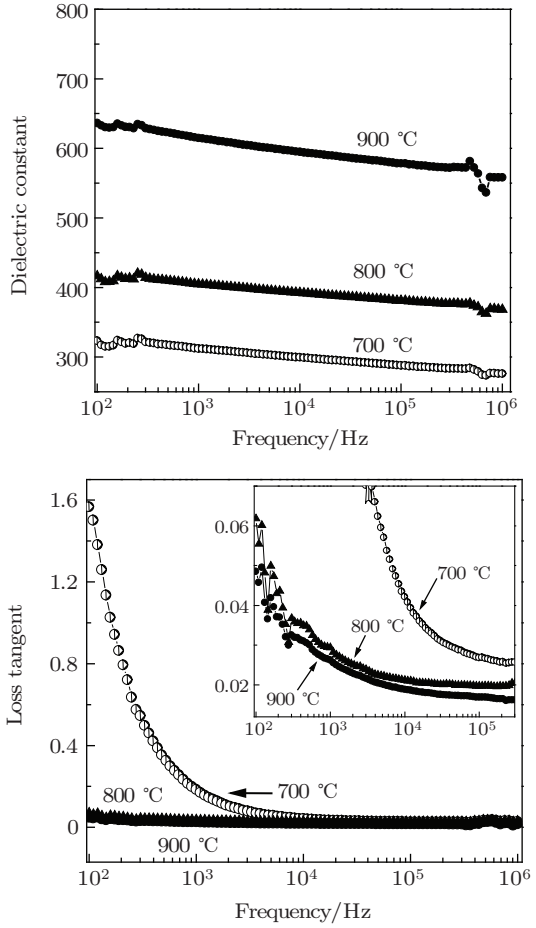


Fig. 5. The dielectric constant and the loss tangent as a function of frequency for samples A700, A800, and A900 respectively.

Based on the above data, 800 °C should be the optimal annealing temperature. The film A800 exhibits a good crystalline structure, a void-free surface morphology and excellent dielectric properties.

4. Conclusion

In summary, BTO thin films were successfully deposited on polycrystalline Ni foils using the PAD technique. The thermodynamics of the deposition process were systematically investigated to optimize the growth conditions. BTO thin films with good crystalline structure were achieved. The films fabricated

under an optimized condition have high dielectric constants ($\varepsilon_r \approx 400$) and low loss tangents ($\tan\delta < 0.025$, at 100 kHz), suggesting that the BTO films grown on Ni foils using the PAD technique can be utilized for various device applications.

References

[1] Choi K J, Biegalski M, Li Y L, Sharan A, Schubert J, Uecker R, Reiche P, Chen Y B, Pan X Q, Gopalan V, Chen L Q, Schlom D G and Eom C B 2004 *Science* **306** 1005

[2] Roberts S 1947 *Phys. Rev.* **71** 890

[3] Kamalsanan M N, Chandra S, Joshi P C and Mansingh A 1991 *Appl. Phys. Lett.* **59** 3547

[4] Israel C, Mathur N D and Scott J F 2008 *Nat. Mater.* **7** 94

[5] Yuan Z, Liu J, Weaver J, Chen C L, Jiang J C, Lin B, Giurgiutiu V, Bhalla A and Guo R Y 2007 *Appl. Phys. Lett.* **90** 202901

[6] Aygün S M, Daniels P, Borlands W and Maria J P 2008 *J. Appl. Phys.* **103** 084123

[7] Dechakupt T, Yang G Y, Randall C A and Trolier-McKinstry S 2008 *J. Am. Ceram. Soc.* **91** 1845

[8] Kingon A I and Srinivasan S 2005 *Nat. Mater.* **4** 233

[9] Dawley J T and Clem P G 2002 *Appl. Phys. Lett.* **81** 3028

[10] Jiang J C, Meletis E I, Yuan Z, Liu J, Weaver J, Chen C L, Lin B, Giurgiutiu V, Guo R Y, Bhalla A S, Liu D and White K W 2008 *J. Nano Research* **1** 59

[11] Bao L J, Ryley J, Li Z G, Wilker C, Zhang L, Reardon D and Guo R Y 2009 *J. Appl. Phys.* **106** 114114

[12] Jia Q X, McCleskey T M, Burrell A K, Lin Y, Collis G E Wang H, Li A D Q and Foltyn S R 2004 *Nat. Mater.* **3** 529

[13] Burrell A K, Mark McCleskey T and Jia Q X 2008 *Chem. Commun.* **11** 1271

[14] Luo H, Yang H, Baily S A, Ugurlu O, Jain M, Hawley M E, McCleskey T M, Burrell A K, Bauer E, Civale L, Holesinger T G and Jia Q X 2007 *J. Am. Chem. Soc.* **129** 14132

[15] Lin Y, Lee J S, Wang H, Li Y, Foltyn S R, Jia Q X, Collis G E, Burrell A K and McCleskey T M 2004 *Appl. Phys. Lett.* **85** 5007

[16] Barin I 1989 *Thermochemical Data of Pure Substances* (Weinheim: VCH, Federal Republic of Germany) pp. 148, 1213, 1693

[17] Atkinson A, Moon D P, Smart D W and Taylor R I 1986 *J. Mater. Sci.* **21** 1747

[18] Podpirka A, Viswanath B and Ramanathan S 2010 *J. Appl. Phys.* **108** 024106

[19] Lee J S, Li Y, Lin Y, Lee S Y and Jia Q X 2004 *Appl. Phys. Lett.* **84** 3825

[20] Yang G Y, Dickey E C, Randall C A, Barber D E, Pinceloup P, Henderson M A, Hill R A, Beeson J J and Skamser D J 2004 *J. Appl. Phys.* **96** 7492

[21] Shen M R, Dong Z G, Gan Z Q, Ge S B and Cao W W 2002 *Appl. Phys. Lett.* **80** 2538