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Growth Dynamics of Barium Titanate Thin Films on Polycrystalline Ni Foils Using Polymer-Assisted Deposition Technique

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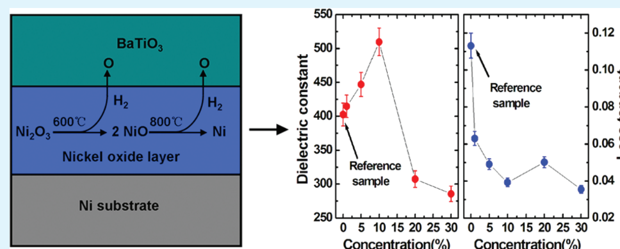
ABSTRACT: Polymer-assisted deposition (PAD) technique was developed to fabricate ferroelectric $BaTiO_3$ (BTO) thin films directly on polycrystalline nickel foils. The growth dynamics was systematically studied to optimize the single-phase BTO films with good dielectric properties. It is critical to pretreat nickel foils with hydrogen peroxide (H_2O_2) solution to form thin nickel oxide layers on the surfaces for the growth of BTO films. Both the concentration of H_2O_2 solution and the pretreated time were found to strongly affect the dielectric constant of BTO films, which may be associated with the oxygen diffusion from nickel oxide buffer layers to BTO layers during annealing. The BTO thin films with optimized growth conditions have good crystal structure and electrical properties, suggesting that the as-grown BTO films by PAD technique can be utilized for new devices development and energy storage applications.



KEYWORDS: *polymer-assisted deposition, barium titanate, thin films, nickel foils, hydrogen peroxide*

1. INTRODUCTION

Environmentally friendly lead-free ferroelectric $BaTiO_3$ (BTO) with good dielectric, ferroelectric, and piezoelectric properties has attracted tremendous interest as promising materials for various devices applications.[1−5] Especially, the growth of BTO thin films directly on the surfaces of metallic or structural materials has become a critical issue on the development of devices such as structural health monitoring systems, super-capacitors, embedded capacitors, and MEMS.[6−15] Various techniques such as chemical solution deposition (CSD),[8−10] pulsed laser deposition (PLD),[11−13] and sputtering[14,15] were employed to deposit BTO thin films on nickel foils. Among these techniques, CSD methods show advantages of low cost, easy setup and ability for large area coating. However, for the general CSD techniques such as sol−gel, it is not easy to ensure a high chemical stability and reproducibility because of the time-dependent hydrolysis of its precursor. Recently, a CSD technique named polymer assisted deposition (PAD) was developed for the synthesis of various oxide thin films with good controllability.[16] In this technique, metal ions are bonded to a water-soluble polymer to form a precursor, which can prevent the hydrolysis of the metal ions and yield a more stable and homogeneous solution than other general CSD techniques. PAD has shown a unique ability in precise controlling both structures and stoichiometry of films. This technique has been employed to synthesize various oxide thin films on different single crystalline substrates.[16−19] The dielectric properties of the $Ba_{1-x}Sr_xTiO_3$ (BST) thin films on $LaAlO_3$ substrates grown by PAD demonstrated the comparable physical properties as the films deposited by PLD.[19] Therefore, growth of ferroelectric thin films on base metallic foils by using PAD technique may open a new avenue for development of various devices. However, so far, no report has been found on the deposition of metal-oxide films on metallic substrates using PAD, to our knowledge. The water based solution used in PAD is likely to increase the risk of oxidation of the base metallic substrates. An effective way to control the oxidation and interdiffusion at the interface is critical for using PAD technique to deposit metal oxide on metallic substrates. In this paper, we report the successful fabrication of BTO thin films on polycrystalline nickel foils with promising dielectric properties using PAD technique.

To control the oxidation of the Ni substrate and the interdiffusion between the film and the substrate, a buffer layer is normally adopted during the fabrication. La_2O_3, $LaNiO_3$, etc., were reported as buffers for the deposition of ferroelectric thin films on nickel or copper substrates.[20,21] Recently, it was reported that the high quality BTO thin films with preferred

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orientation were directly deposited on polycrystalline Ni tapes by using NiO buffers formed from the thermal oxidation of the Ni substrates.[11,12] Compared to other buffers, NiO offers advantages such as easy fabrication, self-attainment, and good adhesion. We take the advantages of both PAD and the structure of nickel oxide buffer layer to synthesize ferroelectric BTO thin films on Ni foils. Instead of using the method of thermal oxidation, we adopted a simple and easily controlled method by pretreating the Ni foil in hydrogen peroxide (H_2O_2) solution to form a nickel oxide buffer layer. The thickness and quality of the oxide layer were controlled through the concentration of H_2O_2 solution and the time of the pretreatment.

2. EXPERIMENTAL SECTION

Experimentally, commercial polycrystalline nickel foils with the thickness of 0.5 mm were mechanically polished to remove the deep scratches and native oxidized layers on the Ni surface as well as the surface contaminations. The foils were ultrasonically cleaned in acetone then immerged in the H_2O_2 solution at 50 °C to form the oxide layers. To optimize the conditions for the growth of nickel oxide buffer layers, two groups of the samples were prepared to study the effects from the concentration of H_2O_2 solution and the pretreatment time. Group I was prepared with different concentration of H_2O_2 solution (from 1 to 30%) and with a fixed pretreatment time (2 h). Group II was prepared with different pretreatment time (from 1 to 6 h) and with a fixed H_2O_2 solution (10%). The color of the foils surfaces gradually changes from silvery white to yellowy as the pretreatment time or the concentration of H_2O_2 solution increases, indicating that the thickness of nickel oxide layers increases accordingly. For comparison, a reference sample was also prepared by immersing the Ni foils in deionized water, instead of H_2O_2 solution, for 2 h. It should be noted that we could not use the bare Ni foils without any pretreatment as reference, because the precursor solution is hard to directly spin-coated on the nontreated shinning Ni surface.

To deposit BTO thin films by PAD, precursor solutions containing the Ba^{2+} and Ti^{4+} ions were prepared. Ba^{2+} solution was made by adding 0.9 g of barium nitrate into the mixture in which 1 g of Ethylenediaminetetraacetic acid (EDTA) and 1 g of polyethyleneimine (PEI, from Sigma-Aldrich, average $M_n \approx 60\,000$, $M_w \approx 750\,000$) were dissolved in 25 mL of distilled water. The solution was then purified and concentrated in an Amicon filtration unit to yield a solution with 19.8 mg Ba^{2+} per milliliters. To prepare the Ti^{4+} solution, we slowly added 2 mL of titanium chloride into 30 mL of 30% peroxide solution, and the solution was then added slowly into the mixture of EDTA and PEI solution; finally, the solution was purified and concentrated to get a solution containing 12.4 mg of Ti^{4+} ions per mL. The concentration of the solutions was measured by inductively coupled plasma optical emission spectrometer (ICP-OES) . The Ba^{2+} and Ti^{4+} solution were then mixed in the proportion of 1:1 to yield a homogonous 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. The as-prepared samples were then put into a furnace for heat treatment.

To find out the optimal condition for heat treatment, we studied the phase diagrams of Ba–O, Ti–O, and Ni–O. In the optimized processing window, the Ba and Ti ions should be able to get oxidized after debonding from the polymer, whereas the nickel substrates should be protected from oxidation. The requirement mentioned above could be fulfilled by controlling the oxygen partial pressure. Figure 1 shows equilibrium oxygen partial pressure curves versus temperature for barium, titanium, nickel metals and their oxides.[22] The shaded region is the processing window in which Ba and Ti can be oxidized while Ni remains a metal. The crystallization temperature we chose is 800 °C, where the BTO crystal can form. The oxygen partial pressure is 1×10^{-18} atm, provided by a forming gas of 94% N_2 and 6% H_2. The black dot in Figure 1 indicates the crystallization condition used in our experiment.

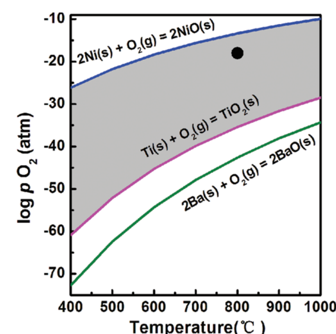

Figure 1. Equilibrium oxygen partial pressure curves versus temperature for barium, titanium, nickel metals, and their oxides. The shaded region is the processing window and the black dot indicates the crystallization condition of BTO used in our experiment.

The whole heat treatment processing can be described as the following. To depolymerize the polymer, all the samples were first heated to 510 °C with the rate of 1−10 °C/minute and maintained at that temperature for 1 h. This process was repeated for 5 times and then the samples were annealed in 800 °C for 30 min for crystallization. Forming gas (N_2 94% + H_2 6%) with a flow rate of 100 mL/min was used during the whole heat treatment processes. The final thicknesses of BTO films are about 500 nm for all the samples.

3. RESULTS AND DISCUSSION

X-ray diffraction (XRD) was performed using Cu Kα radiation to examine the crystal structure of the films. Panels a and b in Figure 2 are the XRD θ−2θ scanning patterns for samples in

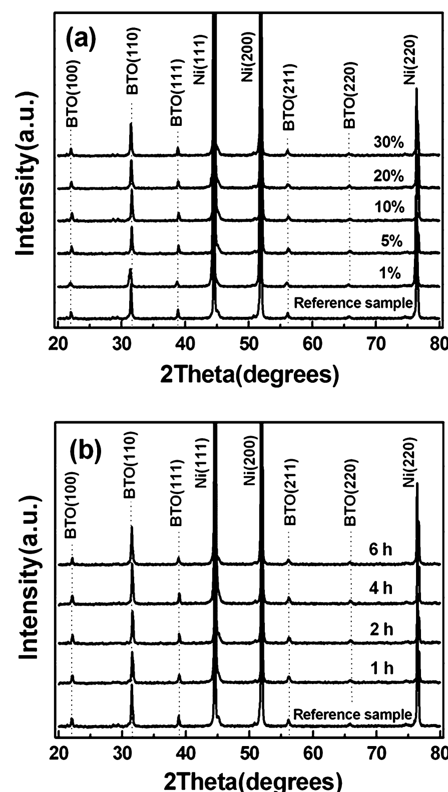

Figure 2. XRD θ−2θ scans of the BTO thin films grown on different pretreated nickel foils: (a) group I, the pretreated time was fixed at 2 h and the concentration of H_2O_2 solutions varied from 1 to 30%; (b) group II, the concentration of H_2O_2 solutions was fixed 10% and the pretreated time varied from 1 to 6 h.

group I and group II, respectively. Result from the reference sample was also included in the figures. All the peaks in the patterns can be indexed by the pseudocubic BTO and Ni, suggesting that the BTO films have been successfully fabricated with a pure polycrystalline pseudocubic phase. No NiO or Ni_2O_3 peak has been observed, implying the nickel oxide layers were too thin to be detected or were reduced into Ni nanostructures as previous reports found.[12] No significant difference among the samples was observed from the powder XRD patterns, suggesting that the crystalline phase of the BTO films in these two groups are similar, even between the reference sample and the ones pretreated by H_2O_2.

However, the atomic force microscopy (AFM) studies show quite different growth features of the BTO films on the reference sample and the others. It is found that many voids are seen on the surface of the BTO film on the reference sample and the root-mean-square (rms) surface roughness is found to be about 30 nm. However, the rms roughness of BTO thin films deposited on the H_2O_2 solution pretreated Ni foils is typically about 15 nm, which is much lower than the reference BTO film. Images a and b in Figure 3 are the AFM images

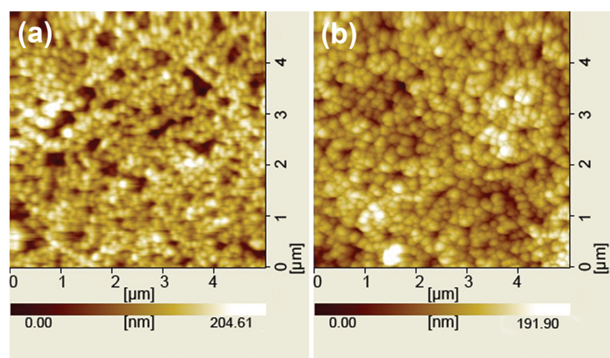

Figure 3. AFM images of the as-grown BTO thin films on (a) the reference sample and (b) the nickel substrate pretreated with 10% H_2O_2 solution for 2 h.

showing the surface morphology of BTO films grown on the reference sample and on a typical Ni substrate pretreated in H_2O_2 solution (i.e., 10% H_2O_2 solution for 2 h in this case), respectively. The improvement in the surface morphology of the BTO thin films may result from the change of the surface energy of the Ni substrates after the pretreatments. High-speed contact angle measurement system (model OCAH200, Data-Physics Instruments GmbH, Germany) was employed to measure the contact angles of the water droplets on the surfaces of the as-treated Ni foils. Figure 4 is the result that shows the contact angles of water drops on the Ni foil for reference sample (A), the Ni foil pretreated by H_2O_2 for 1 h (B), the Ni foil pretreated by H_2O_2 for 2 h (C). As a comparison, Figure 4 also shows the result from the as-polished and ultrasonically cleaned Ni foil (D) and a Ni foil oxidized in oxygen ambient at 300 °C for 30 min (E). Obviously, the water drop on the as-polished Ni foil (sample D) has the largest contact angle of about 100°, indicating the highest surface energy of sample D compared to others. For that of the reference sample (sample C), which was immersed in the deionized water for 2 h, the water drop has a contact angle of 80°, similar to the case of thermally oxidized sample (E), indicating a slight reduction in surface energy after these oxidation treatments. It is interesting to note that the significant

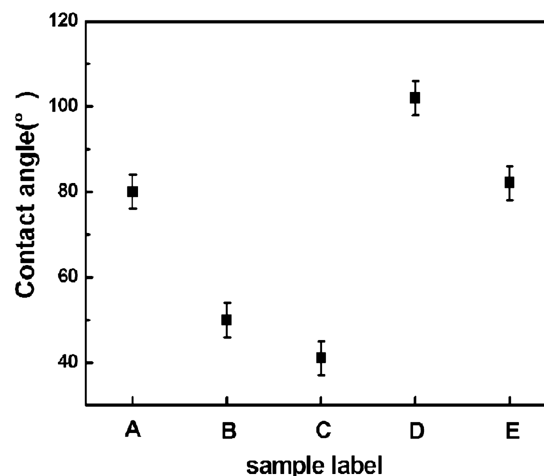

Figure 4. Contact angles of water drops on the surfaces of Ni foils with different treatments; (A) the reference Ni foil sample which was immersed in deionized water for 2 h; (B) the Ni foil pretreated in 10% H_2O_2 solution for 1 h; (C) the Ni foil pretreated in 10% H_2O_2 solution for 2 h; (D)as-polished and ultrasonically cleaned Ni foil; (E) the Ni foil oxidized at 300 °C for 30 min in an oxygen ambience.

decrease in the contact angles was observed from the samples pretreated by H_2O_2 solution (B and C), which are only about 50 and 40°, respectively. This result indicates that the nickel oxide layer formed in the H_2O_2 pretreatment have significantly reduced the surface energy compared to the reference sample. More exact to say, the wettability has been greatly improved after the H_2O_2 pretreatment and consequently yielded a more uniform coating of precursor on the pretreated nickel foils.

To examine the dielectric properties of the as-grown BTO thin films, we deposited gold top electrodes with the area of 1×10^{-4} cm^2 on the surfaces of BTO films using sputtering. Dielectric constant and dielectric loss tangent were measured by an Agilent-4284A Precision LCR meter at 100 kHz. For each sample, we measured capacitors at twenty different positions to get a statistical result. The calculated average values with error bars of the dielectric constant and loss tangent for samples in group I and II were plotted in Figure 5a−d, respectively. The results from the reference sample were also included in these figures for comparison.

It is clearly indicated that the samples pretreated by H_2O_2 solution exhibit obvious reduction in dielectric loss compared to the reference sample, i.e., a drop from about 11% for the reference sample to about 4−6% for the pretreated samples, as shown in panels b and d in Figure 5. Moreover, the effects from the concentration of H_2O_2 and the pretreatment time are not monotonic. The BTO film grown on the Ni foil pretreated with 10% H_2O_2 solution for 2 h exhibits the highest dielectric constant of ~500, about a 20% increase compared to the reference sample. In other words, the dielectric constant of the as-grown BTO films decreases while the pretreatment time or solution concentration moves away from this optimal condition.

The experimental results suggest that the pretreatment of the Ni substrate has significantly improved the dielectric properties of BTO, especially the reduction of dielectric loss. This should be related to the improvement of the wettability of the substrate, which effectively reduces the voids and the overall surface roughness of the BTO films. On the other hand, the mechanisms of the effect from the concentration of H_2O_2 and the pretreatment time may result from the evolution of the

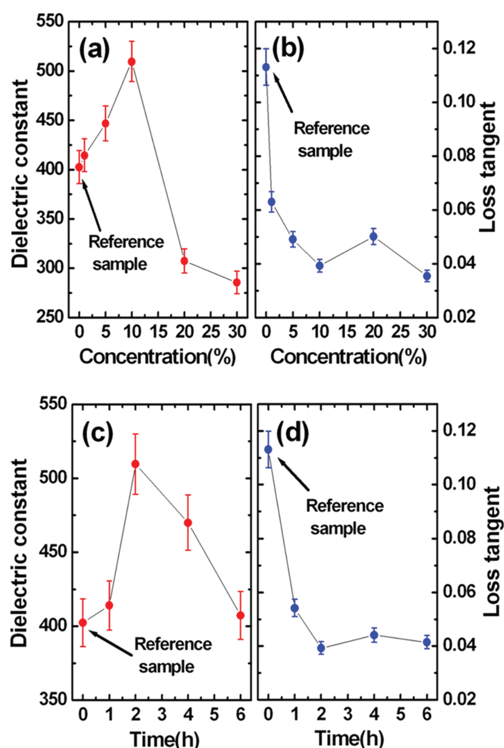

Figure 5. (a) Dielectric constant and (b) loss tangent of BTO thin films in group I; the (c) dielectric constant and (d) loss tangent of BTO thin films in group II.

nickel oxide buffer. It has been reported[23] that when Ni is reacted with H_2O_2, it is not oxidized into NiO but Ni_2O_3. On the basis of the reaction dynamics of Ni with peroxide, the higher the solution concentration and/or the longer the pretreatment time in our experiments, the thicker the Ni_2O_3 layer forms. When Ni_2O_3 is heated to about 600 °C, it can be reduced to NiO and release a part of oxygen.[24] So, when the BTO thin films were annealing at 800 °C, the Ni_2O_3 layer changed into NiO and at the same time the released oxygen diffuse into the BTO layer. It have been reported that a forming gas of 96% Ar and 4% H_2 was used to reduce the NiO on the surface of Ni substrates.[25,26] Since our BTO films were thermally treated in a reduced environment (N_2 94%, H_2 6%) where the partial pressure of O_2 was less than 1×10^{-18} atm, the NiO buffer will continue to decompose into Ni and oxygen in such an environment.[12,27] As the free energy of BTO (−1854 kJ/mol, at 1100 K)[22] is much lower than NiO (−315 kJ/mol, at 1100 K),[22] BTO is much more stable than the NiO. Thus, BTO has great ability to deprive oxygen from the NiO layer. This implies that the nickel oxide layers formed in the pretreatments not only serve as an interdiffusion barrier but also provide oxygen to the BTO layer during the heat treatment process. Thus, if the initial nickel oxide buffer is too thin, the BTO layer cannot get enough oxygen to form a stoichiometric BTO structure, which results in a low dielectric constant. This is the cases when H_2O_2 concentration was less than 10% and the pretreatment time was less than 2 h. On the other hand, if the NiO is too thick, not all the oxygen ions in the nickel oxide layer diffuse into the BTO layer after the annealing and a NiO layer is still left at the interface. The leftover NiO layer should be regarded as a small capacitor in serial with the BTO layer, which results in the decrease of the total dielectric constant. The capacitance of the leftover NiO layer is inversely proportional to its thickness. Although no direct evidence to verify if the oxide layer at the interface is completely reduced to Ni for the optimal sample, it is most likely that the leftover interfacial NiO layer in this sample is thinner than those in the samples with longer pretreated time.

The leakage current densities were measured for the BTO film fabricated with the optimal pretreated condition and the reference sample and plotted in Figure 6a. Obviously, the

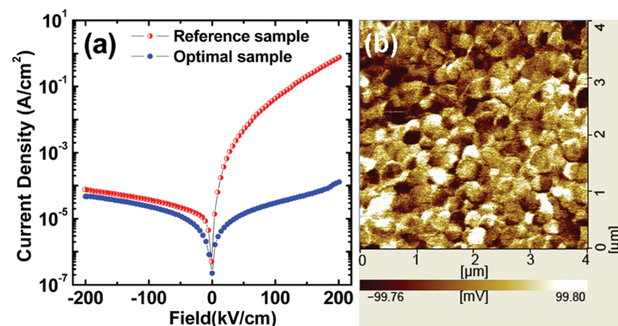

Figure 6. (a) Leakage current density of the optimal sample and reference sample. (b) Piezoresponse force microscopy image of the optimal sample.

leakage was effectively suppressed for the optimized pretreated sample. At an applied electric field of 200 kV/cm, the leakage current density is 0.76 A/cm^2 for the reference sample, while the optimal sample shows a much smaller leakage current density of 5.57×10^{-4} A/cm^2. It should be noted that the leakage current density of the reference sample exhibits an asymmetry with the applied field. As we know, the asymmetry of the leakage current density of the films is related with the different work functions of electrodes materials and the different electron affinities for the bottom and top surface of the thin films.[28] The work functions of our bottom electrodes (Ni) and top electrodes (Au) are 5.15 and 5.1 eV, respectively. The difference in the work functions of these electrodes is not big enough to induce such an obvious asymmetry in the leakage current density. Similar phenomena were previously reported in (Ba,Sr)TiO_3/Ni/Si, (Ba,Sr)TiO_3/$SrRuO_3$/Si, and (Ba,Sr)-TiO_3/$SrRuO_3$/$SrTiO_3$ thin films, which were believed to be related to the formation of a degraded region containing oxygen vacancies near the surface of the BST thin films when the samples were annealed in a reducing ambience.[29,30] When the oxides thin films are annealed in a reducing ambience, oxygen vacancies are normally formed near the top surface of the films to alter the electron affinities of the top surface[29,30] and to lower the Schottky barrier of electrode contact at the top surface.[31] In the optimal sample, it is likely that the oxygen vacancies in the BTO film can be compensated by depriving the oxygen from the nickel oxide layer since the BTO has much lower free energy.[11] Thus, the asymmetry of the leakage current density and the overall dielectric loss can be suppressed. The piezoelectric property of the optimized pretreated sample was checked by piezoelectric force microscopy (PFM) and the image is shown in Figure 6b, in which obvious ferroelectric domains were observed.

4. CONCLUSIONS

In summary, ferroelectric BTO thin films were fabricated on polycrystalline nickel foils by polymer-assisted deposition. Microstructure studies indicate that BTO thin films have single

phase BTO polycrystalline structures. A nickel oxide layer formed by pretreating the Ni substrate in the H_2O_2 solution is a key factor for controlling the growth of BTO films. Pretreatment of the Ni substrate is important to improve the dielectric properties, especially the reduction of the dielectric loss. Both the concentration of H_2O_2 solution and the pretreated time were found to strongly affect the dielectric constant of BTO films, which may be associated with the oxygen diffusion from nickel oxide buffer layers to BTO layers during annealing. Dielectric measurements reveal that BTO thin films grown under optimized conditions have high dielectric constants of about 500 and low loss tangent values of about 4%.

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Notes

The authors declare no competing financial interest.

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