Polymer-assisted deposition of perovskite dielectric oxide thin films

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Abstract: Perovskite dielectric oxide thin films are tremendously important because of their promising applications in microelectronics and optoelectronic devices. Towards scalable applications of these materials, the development of well-controlled and cost-effective fabrication techniques is still under development. Here, recent progresses in the fabrication of perovskite dielectric oxide thin films by using a generic chemical solution deposition technique named polymer-assisted deposition (PAD) are reviewed. In this technique, metal ions are bonded to water-soluble polymers, forming stable and homogeneous precursor solutions of metallic ions surrounded by polymers which prevent hydrolysis of metal ions. Fabrication of the perovskite dielectric oxide thin films using the PAD technique, both on single crystal substrates and base metallic substrates, has been realised with good controllability. The qualities of the films are comparable with those of the ones prepared by physical-vapour deposition techniques.

1 Introduction

Perovskite dielectric oxide thin films have been extensively investigated due to their special dielectric properties and potential applications [1–5]. Generally, these films are grown by physical-vapour deposition, [5, 6] chemical-vapour deposition, [7, 8] or chemical solution deposition (CSD) [9, 10]. Among them, CSD is noted for its easy-setup, low-cost and the ease of coating on irregular surfaces. However, the quality control of complex oxide thin films is somehow a big challenge for most of the traditional CSD techniques. For example, the sol–gel method is a well-known CSD technique [10–12]. A key step in the sol–gel method is the hydrolysis of ester. The hydrolysis reaction in the presence of water and alcohol cannot be stopped once it happens. This results in an ageing effect of the gel which increases the difficulty in controlling the structural and physical properties of the final production. Another CSD technique, metal-organic deposition, using the carboxylate-carboxylic acids system in precursor solution preparation, can overcome the issue of the ageing effect in hydrolysis [13–15]. However, the solvents used in this technique are generally organic solvents, which will increase the cost of the whole fabrication process and may cause possible environmental pollution.

Polymer-assisted deposition (PAD) was invented in 2004 to solve the aforementioned issues [16–19]. In this method, inorganic metal ions are bonded with a water-soluble polymer, such as polyethyleneimine (PEI), to form the water-based precursor solution. Since the metal ions are bonded with the polymer, the hydrolytic reactions in water are avoided by the ligands that block the access of water molecules to the metal ions. The unique solution preparation of PAD has greatly improved the stability of the solution. The majority of the functional materials have been prepared using the PAD technique, including oxides [16, 20–26], nitrides [27–30], carbides [31, 32] and some metals such as Ge [33]. Specifically, deposition of the perovskite dielectric oxide thin films on both single crystal substrates and base metallic substrates has been demonstrated [23, 34, 35]. Good controllability in stoichiometry, crystal structures, interfacial properties and electric properties has proved that PAD is a feasible approach for the growth of high-quality perovskite dielectric oxide films.

2 Processing of PAD

Similar to other typical CSD techniques for thin film deposition, PAD includes three steps starting from the precursor solution preparation followed by thin film deposition on specific substrates via either spin or dip coating. Finally, the freshly prepared thin films are treated at the desired temperature in an oxygen environment to remove the polymer and to form the metal-oxide film.

The precursor solution preparation is actually the main feature that differs PAD from other CSD techniques. In the PAD processing, inorganic metal ions are chelated into a water-soluble polymer, such as PEI, to form the water-based precursor solution, as schematically shown in Fig. 1a. The precursor solution is then filtered by a filtration equipment as shown in Fig. 1b. Thus, the non-coordinated cation and anion species can be removed. The concentration of effective ions in the precursor solutions can be measured exactly by the inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Some requirements should be carefully taken into consideration when preparing the precursor solutions [36]:

(i) the precursor solution should be uniform, stable and no phase separation;
(ii) the soluble polymer should have a clean decomposition under certain calcination conditions, so that the final metal-oxide film can be free of side products;
(iii) the wetting between the precursor and the substrate should be as good as possible and the interdiffusion during the thin film preparing should be well controlled;
(iv) the viscosity of the precursor solution should be properly adjusted to avoid thickness variations and crack formation;
(v) the solubility of the solute should be as high as possible to form the precursor solution with a high concentration of desired ions.

It is required that the soluble polymer has suitable interactions with the metal ions such that the precursor solution is stable and no phase separation occurs during the deposition processes. For example, a special challenge exists in preventing the precipitation in the titanium solutions. Most titanium complexes such as titanium chloride (TiCl4) and titanium hydroxide (Ti(OH)3) are unstable in water and will readily hydrolyse to form partial hydroxides or various titanium oxo compounds, even the Ti(cat)3−
The binding ability for different metals can be controlled by designing the ligands of the polymer [16]. Different binding sites can be generated by choice of monomers pre-polymerisation or by post-polymerisation functionalisation of the polymer. To prepare the BST thin films, three separate solutions of Ba, Sr and Ti that are bound to polymers were first prepared. Titanium precursor solution was made as described above, i.e. bound to the PEIC polymer. Strontium was bound to PEI as an ethylenediaminetetraacetic acid (EDTA) complex by mixing a solution of EDTA in deionised water with PEI. The solution was agitated until everything dissolved and then strontium nitrate was added. Then, the solution was filtered and concentrated by using an Amicon ultrafiltration unit. ICP-AES was employed to measure the concentrations of metal ions in the final solutions. Proper amounts of the final solutions containing titanium and strontium, respectively, were mixed up, based on designed stoichiometry, to yield a solution with equal molar in Ti and Sr. This mixed solution was spin coated onto LaAlO₃ (LAO) substrates. The resultant coating was gradually heated from room temperature to about 1200°C over a period of about 1 h under an oxygen atmosphere. The XRD patterns of the film prepared from the precursor solution without filtration exhibits only (00l) diffraction peaks of BaTiO₃ and the SrTiO₃ substrate, showing that the film is pure phase without any other detectable intermedial phases.

Both simple and complex epitaxial metal-oxide films have been successfully grown by PAD [16]. A representative example of perovskite dielectric material is SrTiO₃ [16]. Solutions containing titanium and strontium bound to polymer were prepared, respectively. Titanium precursor solution was made as described above, i.e. bound to the PEIC polymer. Strontium was bound to PEI as an ethylenediaminetetraacetic acid (EDTA) complex by mixing a solution of EDTA in deionised water with PEI. The solution was agitated until everything dissolved and then strontium nitrate was added. Then, the solution was filtered and concentrated by using an Amicon ultrafiltration unit. ICP-AES was employed to measure the concentrations of metal ions in the final solutions. Proper amounts of the final solutions containing titanium and strontium, respectively, were mixed up, based on designed stoichiometry, to yield a solution with equal molar in Ti and Sr. This mixed solution was spin coated onto LaAlO₃ (LAO) substrates. The resultant coating was gradually heated from room temperature to about 1200°C over a period of about 1 h under an oxygen atmosphere. The XRD patterns of the film produced demonstrated that the SrTiO₃ film was successfully deposited on the LaAlO₃ substrate, which was highly oriented out of the plane and with no detectable second phase. The epitaxial nature of the SrTiO₃ on LaAlO₃ is evidenced by the XRD phi-scans, as shown in Fig. 3. The high-resolution TEM images illustrate the high quality of the as-prepared film by the sharp interface between the film and the substrate, the non-existence of any second phases and the absence of any voids in the film. The root mean square surface roughness of a 100 nm thick SrTiO₃ film, scanned from a 5 μm × 5 μm area by an atomic force microscope, is <2 nm, suggesting that the morphology of films deposited by PAD are quite smooth. Dielectric property measurements further confirmed the high quality of the film deposited by using PAD, i.e. a dielectric constant of over 200 and a dielectric loss <1% at 1 MHz and room temperature, which are as good as the SrTiO₃ epitaxially grown on LaAlO₃ by pulsed laser deposition (PLD) [16]. Other metal-oxide films can also be prepared by the similar procedure. Table 1 lists the metal salts and polymer to prepare the precursor solutions with the desired metal ions.

### 3 Controlling ability on the stoichiometry

It should be specifically noted that the ability of PAD in controlling the stoichiometry is outstanding, as proved by the epitaxial growth of BaₓSr₁₋ₓTiO₃ (BST) thin films with different Ba/Sr ratio (x = 0.1–0.9 with an interval of 0.1) on (001) LaAlO₃ substrates [23]. BST thin films exhibiting high dielectric constants are promising candidates for green energy storage devices and tunable capacitors [44]. To prepare the BST thin films, three separate solutions of Ba, Sr and Ti that are bound to polymers were first prepared. Titanium and strontium were bound to a PEIC polymer and PEI–EDTA complex, respectively, as aforementioned. Barium was bound to the PEI–EDTA complex by dissolving EDTA and PEI in water followed by the addition of barium nitrate, similar to the process of making the Sr solution. After determining the concentrations of Ba, Sr, and Ti in their solutions, respectively, by ICP-AES, these separate solutions were then mixed accordingly to the final solution for BST with different Ba, Sr and Ti ratios. The resulting solutions were spin coated on the LaAlO₃ (LAO) substrates. The thermal
treatment was then performed in flowing oxygen. The polymer was pyrolysed by initially slowly heating at the rate of 1–10°C/min to 500°C. Samples were then annealed by heating at 1000°C for 1 h for crystallisation. A series of BST films with various x values but the same thickness of 150 nm were prepared and compared.

XRD and TEM analyses show that all the BST films are epitaxial. Only (00l) peaks of BST and LAO are observed in the XRD θ–2θ scans, suggesting that all the BST films are single phase with a preferential c-axis orientation. The φ scans results show the films to be of good epitaxial quality. Cross-sectional TEM, as shown in Fig. 4a, analysis demonstrated that the surface of the BST film is very smooth and the interface between BST and LAO is flat. Corresponding selected area diffraction (SAD) pattern (Fig. 4b) taken from the interface area confirmed the orientation relations between the film and the substrate. Diffraction dots from BST (Fig. 4c) are sharp and distinguished, indicating the high crystallinity of the film.

It is interesting to notice the different strain states of the epitaxial BST thin films grown by PAD and PLD, which should result from the different growth mechanisms. The out-of-plane and in-plane lattice parameters were calculated from the XRD data for all BST films, as demonstrated in Fig. 5. The a- and c-axis lattice constants of bulk BST are also plotted for comparison [23]. It is clearly shown that the lattice parameters of the 150 nm-thick PAD-grown films exactly follow the same trend of the bulk BST. The phase boundary occurs at x = 0.3 where the crystal structure of the film changes from tetragonal to cubic. It is interesting to compare these results with the 150 nm-thick BST films deposited by PLD [45]. The films grown by PLD have shown strong distortions compared to the bulk, especially the phase boundary of tetragonal and cubic structure has shifted to 0.4 instead of 0.3. Moreover, the films with x > 0.6 grown by PLD have been distorted to tetragonal

structure. This distortion was not observed in the 150 nm-thick films grown by PAD. In other words, in contrast to the strained films grown by PLD, the films grown by PAD are relaxed. This means that the critical thickness (above which the film is totally strained) of the PAD-films is <150 nm. On the other hand, for the PLD-films, the critical thickness is larger than 300 nm.

Dielectric constants of the PAD-prepared BST films were measured using coplanar stripline electrodes. Figs. 6a and b compare the zero-field dielectric constant (ɛ₀) and tunability [(ɛ₀−ɛ_E)/ɛ₀, where ɛ_E is the dielectric constant at an applied field E] versus x for the films. The dielectric values of the films grown by PAD are comparable with the reported values of the films grown by PLD, [45] demonstrating the good quality of the BST films grown by PAD. The change of the dielectric properties of the BST films with the variation in the x values is also very similar to the BST films grown by PLD [45]. However, it should be pointed out that the highest dielectric constant is obtained at x = 0.4 for the films deposited by PLD but at x = 0.3 for the films deposited by PAD. Among the films grown by PAD, the BST film with x = 0.3 exhibits the highest ɛ₀ (∼1010) and tunability (∼69%). This should be attributed to the different strain states in the BST films. The phase boundary between the tetragonal and the cubic occurs at x = 0.3 for the PAD films but at x = 0.4 for the PLD films. It is believed that the highest dielectric constant can be obtained at the phase boundary, as many other material systems [46, 47].

![Fig. 3 XRD phi-scans and high-resolution TEM images of epitaxial SrTiO₃ films deposited by PAD on LaAlO₃. (Jia et al. [16]; reproduced with permission from Nature Publishing Group)](image1)

![Fig. 4 Cross-sectional TEM images from BaₓSr₀.₅TiO₃ on LaAlO₃ along LAO (100) zone axis](image2)

| Table 1 | Metal salts and polymer in preparing metal ions |
|---------|---------------------------------------------|
| Metal ions | Metal salts               | Polymer | Reference |
| Al³⁺     | Al(NO₃)₃                | PEI     | [37]      |
| Ca²⁺     | Ca(NO₃)₂                | PEI     | [38]      |
| Ti⁴⁺     | TiCl₂(NH₄)₂             | PEI/C   | [16, 34]  |
| V⁵⁺     | NH₄VO₃, NaVO₃          | PEI     | [20, 39, 40] |
| Mn²⁺     | MnCl₂                  | PEI     | [21]      |
| Fe³⁺     | Fe(NO₃)₃               | PEI     | [41]      |
| Cu²⁺     | Cu(NO₃)₂               | PEI     | [38]      |
| Sr²⁺     | Sr(NO₃)₂               | PEI     | [42]      |
| Y³⁺     | Y(NO₃)₃                | PEI     | [41]      |
| Ru⁴⁺     | RuCl₃, poly (acrylic acid) (PAA) |        | [42]      |
| Ba⁹⁺     | Ba(NO₃)₂               | PEI     | [34]      |
| La⁹⁺     | La(NO₃)₃               | PEI     | [21]      |
| Eu³⁺     | EuCl₃·6H₂O             | PEI     | [43]      |
| Bi³⁺     | Bi(NO₃)₃               | PEI     | [40, 44]  |

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The results demonstrated that the PAD technique has superior advantages in controlling the stoichiometry of complex dielectric oxide thin films and the dielectric properties of these films are comparable with the films grown by PLD. Considering the complication to adjust stoichiometry of thin films by changing various targets for the physical-vapour deposition techniques such as sputtering and PLD, the convenience of the PAD technique is obvious, which is just by simply mixing up the separate solutions with different metal ions according to the required stoichiometry.

4 Strain engineering

The epitaxial growth capability enables the PAD technique as an excellent tool to manipulate the strains in the dielectric thin films, which can tailor the dielectric properties accordingly. Besides the generally used methods such as adjusting the film thickness or choosing different substrates, several eye-catching methods have been reported using films grown by PAD.

Interesting results have been reported that by using a proper design of vicinal single-crystal substrate, the interface strain in epitaxial thin films can be well controlled by adjusting the miscut angle via a surface-step-terrace (SST) matching growth mode. Besides the lattice mismatch between the film and the substrate, the unit cell mismatch between the epitaxial film and the surface step terrace dimension of the substrate need to be considered in the SST model [48, 49]. The unit cell mismatching strain can be tuned by controlling the surface step terrace dimension via adjusting the miscut angle of the vicinal substrate. Therefore, the SST model provides a new way to tailor the strain in the epitaxial oxide thin films. The key point to utilise this method is high-quality epitaxial growth. Using the PLD technique, some results supporting this model have been reported. Nevertheless, by using CSD techniques, epitaxial quality of thin films might be a concern.

On account of the feature of PAD which could easily prepare high-quality epitaxial metal-oxides thin films, the SST model has been well demonstrated on CaCu$_3$Ti$_2$O$_7$ (CCTO) and BST thin films were grown by PAD [38, 44]. The CCTO thin film has ultra-high and stable dielectric constant, which is considered as a promising dielectric material for capacitance [38, 44]. Highly epitaxial CCTO and BST thin films on vicinal (001) LAO substrates with miscut angles of 1.0°, 2.75° and 5.0° along the [100] axis or [110] axis were designed and fabricated by using the PAD technique. Thin films on an ordinary LAO (001) substrates, i.e. substrates with no intentional miscut, were also prepared as a reference.

Ideally, substrates which are with miscut along the [100] direction can produce vicinal surface with step edge along [010], as schematically shown in Fig. 7a. However, substrates which are with miscut along the [110] direction will introduce plenty of zig-zag or sawtooth-shaped step edges, as schematically shown in Fig. 7b. The sizes of the nanosteps should be determined by the miscut angle and the surface step terrace energy under the optimised growth conditions [50].

Scanning probe microscopy (SPM) was employed to characterise the morphologies of the vicinal LAO substrates after a thermal treatment of 240 min at 900°C in the flowing O$_2$. As predicted, the LAO substrates with miscut along [100] direction can produce surfaces with step edges along [010], while the miscut along [110] forms plenty of zig-zag or sawtooth-shaped step edges. Line scans across the selected 300 nm-wide sections on each vicinal LAO substrate indicated that terraces on the vicinal surfaces of the LAO substrates can be well fit by a number of steps with average width (T$_w$) and height (T$_h$). Specifically, for the 1.0° vicinal substrate, two kinds of steps with 1 and 2 unit cells in height, respectively, were clearly seen to present alternately. For the vicinal substrate with 2.75° miscut angle, average terrace height corresponding to 4.5 unit cells was detected, which can be considered to consist of two kinds of steps with 4 and 5 unit cells in height. For the substrates with miscut angle of 5.0°, average terrace height is about 6 unit cells of LAO. The SPM results revealed that the thermodynamically unstable atomic steps tend to reduce the surface energy by bunching together into wider terraces separated by steps with n$\times$ d$_{LAO}$ in height [50].

The out-of-plane and in-plane lattice parameters of the as-grown BST films on [100]-miscut and [110]-miscut substrates are shown in Fig. 8. For convenience, the lattice parameters along [100], [010] and [001] directions are defined as a, b and c, respectively. As for BST films grown on [100]-miscut substrates (Fig. 8a), obvious different behaviour along the a- and b-directions has been observed, which should be attributed to the miscut direction for the substrates. In other words, different strains have been induced in parallel and perpendicular to the surface step terrace edge directions. In comparison, for the films grown on [110]-miscut substrates (Fig. 8b), similar behaviour and strain states were detected along the two in-plane directions. The phenomenon is easy to understand considering the miscut along [110] direction which produces plenty of zig-zag, or sawtooth-shaped, surface step terraces edges on the surface of the substrates [50]. In this case, the edges of BST films would grow segmentally along a- and b-directions conformal to the sawtooth-shaped nanosteps, leading to similar behaviour along the two in-plane directions. The ratios a/c and b/c were defined as tetragonality and plotted versus the miscut angles in Figs. 5c and d. The values of a/c are obviously larger than b/c for samples on [100]-miscut.
tensile strains exist locally in the film. Various miscut angles in group 110. (Yao et al. [44]; reproduced with permission from Royal Society of Chemistry).

substrates. However, they are much closer to each other for samples on [110]-miscut substrates.

To understand the lattice deformation mechanism, mismatching strains induced by surface step terraces of the vicinal substrates should be carefully considered. Briefly, the lattice of the film would be stretched or compressed depending on the terrace dimensions so as to occupy the entire width of each terrace with integral unit cells of thin film material, introducing ‘SST strain’ in the film. However, since the theoretically calculated terrace width usually cannot exactly accommodate integer unit cells of LAO substrate while the crystal structure of the substrate would not deform to fit the terrace, the quantity of LAO unit cells accommodated on each terrace should be one of the two adjacent integers. Although the surface step terrace is preferred to bunch together upon annealing, it is still true that terraces with different widths co-exist on the surface. Correspondingly, based on the SST model, the crystal of the film would be strained to fit each terrace during the film growth, which may form various strain states on different terraces of one substrate. In each film on the [100]-miscut vicinal substrate, along the [100] direction, both compressive and tensile strains exist locally in the film. Various miscut angles induce different percentages of compressive and tensile strained domains. For example, for the CCTO film grown on the LAO substrate with 1.0° miscut angle, which processes two kinds of terrace steps (one or two LAO unit cells in height), a higher percentage of the steps bare tensile strain, leading to an overall tensile strain along the [100] direction of the film. For the CCTO film grown on the substrate with 5.0° miscut angle, the numbers of the steps baring tensile strain or compressive strain are close to each other, which would minimise the overall internal strain along the [100] direction of the film. Similarly, based on the SST model, the crystal of the film would be strained to fit each terrace during the film growth, which may form various strain states on different terraces of one substrate. In each film on the [100]-miscut vicinal substrate, along the [100] direction, both compressive and tensile strains exist locally in the film. Various miscut angles induce different percentages of compressive and tensile strained domains. For example, for the CCTO film grown on the LAO substrate with 1.0° miscut angle, which processes two kinds of terrace steps (one or two LAO unit cells in height), a higher percentage of the steps bare tensile strain, leading to an overall tensile strain along the [100] direction of the film. For the CCTO film grown on the substrate with 5.0° miscut angle, the numbers of the steps baring tensile strain or compressive strain are close to each other, which would minimise the overall internal strain along the [100] direction of the film. The overall strain states are highly determined by the ratio of the compressive and tensile strained domains, which can be tuned by the miscut angle. The calculated results agree very well with the [100] lattice parameters deduced from the XRD measurements, implying that the SST strains have been successfully induced in the [100] direction of the films and dominate the strain states along this direction. Similarly, the corresponding information for films grown on [110]-miscut substrates could also be calculated. The obvious difference between the films on the [100]-miscut and the [110]-miscut substrates is that the former one would induce anisotropic strain while the latter one would not.

To evaluate the impact from the SST strains, anisotropic dielectric properties of the films grown on vicinal substrates were demonstrated through the dielectric measurements conducted along two in-plane directions (a- and b-directions) of the BST films using Au/BST/LAO interdigital capacitors. As shown in Fig. 9a, for the BST films grown on the [100]-cut substrates, a higher dielectric constant along the a-direction than that along the b-direction can be observed in each sample. On the other hand, as for the films on the [110]-cut substrates shown in Fig. 9b, the values of dielectric constants in both in-plane directions ([100] and [010]) are very close to each other. The change percentages of dielectric constants along two in-plane directions are also labelled in Figs. 9a and b, which are obviously higher for samples on the [100]-cut substrates than those on the [110]-cut substrates, suggesting that the vicinal substrates on the [100]-cut substrates can introduce anisotropy more easily. Additionally, the evolution trend of dielectric properties fit well with the trend of the tetragonality for both groups, implying strong impact from the strain.

The results evident that the overall strain states of the epitaxial thin films grown on vicinal substrates can be tuned by the miscut angle and the miscut direction, which not only shed new light on heteroepitaxial growth mechanism, but also provide a promising platform for the design and integration of high-performance device applications. It should be noted again, the epitaxial quality of the thin films, ensured by the PAD technique, is critical in successfully inducing the strains.

Another interesting and feasible route for strain engineering, utilising the PAD technique, is demonstrated by the system with amorphous nanoparticles embedded in epitaxial thin film matrix, which shows specific advantages of this thin film deposition technique [51]. It is found that SiO\textsubscript{2} nanoparticles bind to the PEI polymer presumably by a surfactant-like interaction of the polymer with the surface of the nanoparticles. The ease of forming the soluble SiO\textsubscript{2} nano-particle solution makes it very attractive as a precursor to SiO\textsubscript{2}-metal-oxide composite films. The precursor solutions for the deposition of SiO\textsubscript{2}-metal-oxide (e.g. STO) composite films were obtained from a mixture of separate solutions of silica and the corresponding metals (e.g. Sr and Ti solutions). Silica nanoparticles with sizes of around 10 nm bind to PEI. The resulting precursor solutions were spin-coated onto the LAO substrates and then annealed in flowing oxygen for 2 h at 860°C. XRD analysis indicates that only peaks from STO and the substrate...
are present, with no peaks attributable to silica, thereby indicating that silica retains its amorphous nature in the composite films. The data also showed that the epitaxial quality for SiO$_2$-STO composite films is quite good. Figs. 10a and b show cross-section high-resolution transmission electron microscopy (HRTEM) images of an SiO$_2$-STO film on a LAO substrate from two different areas. The images clearly indicate that the STO phase has grown epitaxially on the LAO substrate and that SiO$_2$ spots (A, B, C and E) indicate epitaxy being established in the STO matrix. This successful attempt to grow such amorphous nanoparticles in an epitaxial matrix based on a chemical solution approach has provided a very convenient platform which can potentially be used to fine-tune the strain state of the epitaxial matrix.

5 Fabrication of complex oxide thin films on polycrystalline nickel foils

Besides growing thin films on single crystal substrates, the PAD technique has also been developed to fabricate oxide thin films directly on the base metallic substrates, Ni foils [52, 53]. A flexible assembly by integrating ferroelectric oxide thin films with metallic nickel (Ni) foils has potential applications in various multidisciplinary areas such as health monitoring systems, embedded capacitors, energy harvesting devices and micro-electro-mechanical system (MEMS) [54–61]. The growth of BTO thin films directly on the surfaces of metallic or structural materials has become a critical issue on the development of these devices [57–66]. Controlling the interface is always a big challenge. The growth of ferroelectric thin films on base metallic foils by using PAD technique may open a new route for the development of a cost-effective chemical solution approach. However, 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 the PAD technique to deposit metal-oxide thin films on base-metallic substrates. 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. Compared to other buffers, NiO offers advantages such as easy fabrication, self-attain and good adhesion. By taking the advantages of both PAD and the structure of nickel oxide buffer layer, synthesis of ferroelectric BTO thin films on Ni foils has been demonstrated. Instead of using the method of thermal oxidation, a simple and easily controlled method was adopted by pretreating the Ni foil in hydrogen peroxide (H$_2$O$_2$) solution to form a nickel oxide buffer layer. The thickness and quality of the oxide layer, which was found to be a vital factor for the properties of the integrated thin films, could be controlled through the concentration of H$_2$O$_2$ solution and the time of the pretreatment.

The phase diagrams of Ba–O, Ti–O and Ni–O could provide necessary support in determining the optimal growth condition. Theoretically, in the optimised processing window, the Ba and Ti ions should be able to get oxidised after de-bonding from the polymer, whereas the nickel substrates should be protected from oxidation. As shown in Fig. 11, which is the equilibrium oxygen partial pressure curves versus temperature for barium, titanium, nickel metals and their oxides [67], the shaded region should be able to fulfil the requirement. Forming gas (N$_2$:94%+H$_2$:6%) with a flow rate of 100 ml/min was used during the whole heat treatment processes to provide an environment with a very low oxygen partial pressure.

XRD analysis proved that the BTO films have been successfully fabricated with a pure polycrystalline pseudo-cubic phase. Atomic force microscopy studies show improvement in the surface morphology of the BTO thin films grown on the H$_2$O$_2$-pretreated Ni foils compared with those on the non-pretreated ones.
The leakage was also effectively suppressed for the optimised pretreated sample. At an applied electric field of 200 kV/cm, the leakage current density is 0.76 A/cm² for the reference sample, while the optimal sample shows a much smaller leakage current density of $5.57 \times 10^{-4}$ A/cm². Piezoelectric force microscopy image has shown obvious ferroelectric domains in the films.

Ferroelectric measurements indicated that the highest values of $P_s$ ($\sim19.8 \mu C/cm^2$) and $P_r$ ($\sim13.2 \mu C/cm^2$) were observed for sample which was pretreated in H$_2$O$_2$ solution for 2 h, as shown in Figs. 13a and b [52]. The samples which have thicker nickel oxide buffer layers exhibit $P_s$ and $P_r$ values slightly lower. On the other hand, when the pretreatment time is $<2$ h, the $P_s$ and $P_r$ values decrease significantly with the decrease of the pretreatment time.

The magnetoelectric (ME) effect is expected to result from the coupling between the piezoelectric effect of the ferroelectric BTO film and the magnetostriiction of the Ni foil in this structure. Compared with the traditional ME heterostructures where films are deposited on rigid crystalline oxide substrates, an ME assembly with a ferroelectric or piezoelectric thin film directly on a flexible magnetic metallic substrate may exhibit an even higher ME coefficient, since the use of free-standing flexible foil would eliminate the substrate clamping effect [68, 69]. Moreover, as the magnetic substrates such as flexible Ni foils can be machined into different shapes, it is convenient to fabricate such a structure into devices with desired architectures.

A 1000 Hz ac magnetic field and a dc magnetic field were applied along the in-plane direction of Ni foils. ME voltage coefficient defined by

\[ \alpha = \frac{dP}{dH}. \]

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The leakage was also effectively suppressed for the optimised pretreated sample. At an applied electric field of 200 kV/cm, the leakage current density is 0.76 A/cm² for the reference sample, while the optimal sample shows a much smaller leakage current density of $5.57 \times 10^{-4}$ A/cm². Piezoelectric force microscopy image has shown obvious ferroelectric domains in the films.

Ferroelectric measurements indicated that the highest values of $P_s$ ($\sim19.8 \mu C/cm^2$) and $P_r$ ($\sim13.2 \mu C/cm^2$) were observed for sample which was pretreated in H$_2$O$_2$ solution for 2 h, as shown in Figs. 13a and b [52]. The samples which have thicker nickel oxide buffer layers exhibit $P_s$ and $P_r$ values slightly lower. On the other hand, when the pretreatment time is $<2$ h, the $P_s$ and $P_r$ values decrease significantly with the decrease of the pretreatment time.

The magnetoelectric (ME) effect is expected to result from the coupling between the piezoelectric effect of the ferroelectric BTO film and the magnetostriiction of the Ni foil in this structure. Compared with the traditional ME heterostructures where films are deposited on rigid crystalline oxide substrates, an ME assembly with a ferroelectric or piezoelectric thin film directly on a flexible magnetic metallic substrate may exhibit an even higher ME coefficient, since the use of free-standing flexible foil would eliminate the substrate clamping effect [68, 69]. Moreover, as the magnetic substrates such as flexible Ni foils can be machined into different shapes, it is convenient to fabricate such a structure into devices with desired architectures.

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A 1000 Hz ac magnetic field and a dc magnetic field were applied along the in-plane direction of Ni foils. ME voltage coefficient defined by

\[ \alpha = \frac{dP}{dH}. \]
interface coupling between the BTO and the Ni, which results in the top surface of the films. In the optimal sample, it is likely that the extent.

leakage current density and the overall dielectric loss can be much lower free energy [59]. Thus, the asymmetry of 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 [59]. Thus, the asymmetry of the leakage current density and the overall dielectric loss can be suppressed.

The different ferroelectric and ME properties among the samples are likely to be related with the evolution of the nickel oxide at the interface between the BTO and the Ni substrate. Clearly, the ME coefficient depends strongly on both the piezoelectric and magnetostrictive properties of the ferroelectric BTO films and the magnetic Ni foils. Equally important is the ME coupling at the interface. For a magnetostrictive/piezoelectric bilayer structure with an ideal interface, the strain in the magnetostrictive phase induced by the magnetic field should be effectively coupled to the piezoelectric phase. In reality, however, the imperfect interface would affect the coupling of the strain between the two phases. Many studies have indicated that the ME coefficient decreases rapidly as the interface coupling is weakened [71]. In this research, the existence of a thin nickel oxide layer between the BTO and the Ni substrate affects the interface coupling and consequently affects the ME coefficient to some extent.

Thus, if the initial nickel oxide layer is too thin, oxygen deficient BTO can lead to degraded ferroelectricity and piezoelectricity as indicated by the low \(P_s\) and \(P_r\) values for samples whose pretreatment time is \(<2\) h. The degraded piezoelectricity can apparently cause a low ME coefficient. On the other hand, if the NiO\(_x\) layer is too thick, the whole NiO\(_x\) layer cannot be fully reduced into Ni and is still left at the interface after the annealing. The leftover NiO\(_x\) layer may significantly reduce the interface coupling between the BTO and the Ni, which results in the dramatic decrease of the ME coefficient. In other words, the thicker (than its optimised thickness) the nickel oxide layer at the interface, the weaker the interface coupling is. Comparing the maximum ME voltage coefficient of the optimised sample (90 mV/cm Oe) with the data from similar structures in literatures, such as 55 mV/cm Oe for the BTO thin films on metallic glass substrate annealing in oxygen would further improve the electric properties for all the samples, suggesting oxygen vacancies may still exist even in the H\(_2\)O\(_2\)-pretreated ones. Although the present data have proved an acceptable electric property for the as-grown H\(_2\)O\(_2\)-pretreated samples, there is still room for further improvement.

6 Conclusion

In summary, it has been demonstrated that PAD is a feasible technique to fabricate oxide dielectric thin films with good dielectric properties. The unique feature of the precursor solution preparation by binding the metal ions to a water-soluble polymer, not only ensures high stability of the precursor solution and controllability of the process, but also promises a convenient way to control the stoichiometry of complex oxide thin films. For deposition on single crystal oxide substrates, PAD has proved its strong capability for epitaxial growth, which would provide an excellent platform for strain engineering. Furthermore, the successful fabrication of BTO thin films on Ni substrates with good electric properties has convinced the competence of PAD in controlling the interface properties, which is extremely critical for integrated thin film systems. The development of the PAD
technique would pave a cost-effective way for the applications of perovskite oxide dielectric thin films.

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8 References

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9 Conclusions

This work presents a cost-effective and scalable method for the preparation of high-temperature tolerant BaTiO3 thin films with improved electrical properties. The approach involves the use of a specially designed sol-gel process that allows for the deposition of high-quality BaTiO3 thin films. The results demonstrate that the sol-gel method can significantly reduce the processing temperature while maintaining high electrical and magnetic performance. The study also highlights the potential applications of these thin films in various high-temperature systems, including energy conversion and storage systems. Further research is needed to optimize the processing conditions and to investigate the long-term stability and reliability of these BaTiO3 thin films.
