$PbZr_{0.4}Ti_{0.6}O_3$ and $Ba_{0.9}Sr_{0.1}TiO_3$ reflectors derived from chemical solutions containing polymers

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$Ba_{0.9}Sr_{0.1}TiO_3$ (BST)-based and $PbZr_{0.4}Ti_{0.6}O_3$-based quasi-periodic multilayers consisting of dense and porous ferroelectric layers have been fabricated by solgel technique using chemical solutions containing polyethylene glycol (PEG) or polyvinylpyrrolidone k30 (PVP). All multilayers exhibit good performance as dielectric mirrors. For each multilayer, the maximum peak reflectivity is over 90% and the photonic stopband width is no less than 30 nm at room temperature. The reflection-band position can be easily tuned by varying the thickness of the bilayer. With the same processing conditions and number of periods, the Bragg reflection performance is almost the same for quasi-periodic PZT multilayers derived from two precursors containing different polymers. The BST multilayers deposited by using a PVP-containing precursor are superior in optical properties, including peak reflectivities and stop-band width, to those deposited by using the PEG-containing solution. © 2008 Optical Society of America

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Dielectric reflectors, extensively used in optical systems, are periodic stacks of two dielectric materials. When the average optical thickness of each layer in a periodic dielectric multilayer is a quarter of the central wavelength λ_0, the spectroscopic reflectivity is enhanced at λ_0. Such a dielectric Bragg mirror has many advantages over its metal counterpart, such as low optical loss, high reflectivity, and high mechanical robustness. The conventional material pairs for construction of Bragg reflectors include ZnS/Na_3AlF_6, TiO_2/SiO_2, $GaAs/Al_xGa_{1-x}As$, $Al_xGa_{1-x}N/Al_yGa_{1-y}N$, $GaAs/Al_2O_3$, SnS/SiO_2, polyethylene/tellurium, and so on [1–8]. However, the performance of Bragg reflectors made of these materials cannot be dynamically tuned by an applied electric field owing to their very weak electro-optical effects.

On the other hand, ternary ferroelectric oxides, such as $PbZr_xTi_{1-x}O_3$ and $BaTi_xSi_{1-x}O_3$, are ideal candidates for manufacturing photonic devices with controllable characteristic parameters. Those materials have the advantages of high transparency over a wide spectral range and large electro-optical coefficients. As a result, one-dimensional periodic structures based on ferroelectrics are interesting both for fundamental research and for technological applications.

It is, however, rather difficult for the conventional coating techniques such as molecular beam epitaxy, metal–organic chemical vapor deposition, thermal evaporation, and magnetron sputtering to fabricate one-dimensional ternary ferroelectric-based photonic crystals. Recently we developed a simple and feasible method to grow quasi-periodic ferroelectric multilayers with a total thickness of a few micrometers based on one single chemical solution with polyvinylpyrrolidone k30 (PVP) additive [9–11]. The method is based on phase separation as briefly described as follows. During spin coating, the PVP additive is phase segregated from the rest of the solution and driven to the bottom vicinity of the wet gel layer, where it condenses into nanosize polymer domains, with the driving force being the differences in the chemical properties and physical sizes of the two solvated constituents [12,13]. When the gel film is sintered at high temperature, the nanosize PVP droplets are thermally decomposed. A gel film with nanosize pores is then left. A distinguishable bilayer consisting of a dense ferroelectric and a pore-embedded ferroelectric layers is formed. By repeating the spin-coating /annealing step a ferroelectric multilayer was formed. Although the prepared ferroelectric multilayer stacks are not strictly periodic owing to the limitation of solgel processing, they exhibit high optical reflectivity at given frequency ranges, and the optical reflectivity in the reflection band can be further increased by adding more number of bilayers in ferroelectric multilayers. Additionally, these multialyers show excellent electric properties, such as low leakage current density, high remanent polarization, and dielectric permittivity [14,15].

In this work, we demonstrate that quasi-periodic $PbZr_xTi_{1-x}O_3$ and $BaTi_xSi_{1-x}O_3$ multilayers could also be fabricated by using one single chemical solution with polyethylene glycol (PEG) additive. The grown ternary ferroelectric multilayers also display good performance as a one-dimensional photonic crystal. The optical properties have been compared for ferroelectric multilayers with the same composition, derived from precursors containing PEG and PVP.

The coating solutions for deposited $PbZr_{0.4}Ti_{0.6}O_3$ (PZT) and $Ba_{0.9}Sr_{0.1}TiO_3$ (BST) multilayers were similar to those reported in [9,10] except that the PVP in the precursor was replaced by PEG. The details for sample preparation had been described in [9,10]. In order to improve lattice matching between

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the PZT film (a-axis lattice constant of bulk $Pb_{0.4}Ti_{0.6}O_3$ material ~3.982 Å) and the Si substrate, a 120 nm conductive $LaNiO_3$ buffer layer (lattice constant 3.84 Å) was grown on the Si wafer. A PZT multilayer with 17 pairs of dense-PZT/porous-PZT layers was deposited at 2500 rounds per minute (rpm) on the $LaNiO_3$-coated Si substrate. Three BST multilayer specimens with 16 bilayer dense-BST /porous-BST layers were spin-coated on $SrTiO_3$ wafers at 1800, 2400, and 3000 rpm. X-ray diffraction data show that all of the multilayers have been fully crystallized into the perovskite phase and exhibit polycrystalline structures without any preferred orientation. The cross-sectional morphologies of the multilayers were characterized by high-resolution scanning electron microscope (SEM). The reflectance spectral data were recorded by a Perkin Elmer Lambda 800/900 UV/vis spectrometer, and the incident light was perpendicular to the sample surface.

Figure 1(a) presents a typical cross-sectional SEM image for the BST multilayer deposited at 2400 rpm. The multilayer reveals a layered structure consisting of dense-BST /porous-BST bilayers, which is similar to those of BST multilayers reported in [10]. The alternating dense and porous layers along the growth direction give rise to a quasi-periodic sequence of refractive indices as Bragg reflectors.

Figure 2 shows the room temperature absolute reflectance spectra for these ternary ferroelectric multilayers in the range of 350–800 nm. The line with open circles in Fig. 2 corresponds to PZT multilayer and the other curves to the BST multilayers. As expected, each sample has a reflection band with a stop-band width no less than 30 nm and peak reflectivities over 90%, rendering these ferroelectric multilayers with good performance as a dielectric mirror. It is also found that the central wavelength of the maximum peak of the BST multilayer shifts from 492 to 402 nm and the bandwidth varies from 45 to 36 nm with increasing spinning rate, indicating that the reflection-band position of the ternary ferroelectric multilayers can be easily tailored by changing processing parameters such as spinning rate.

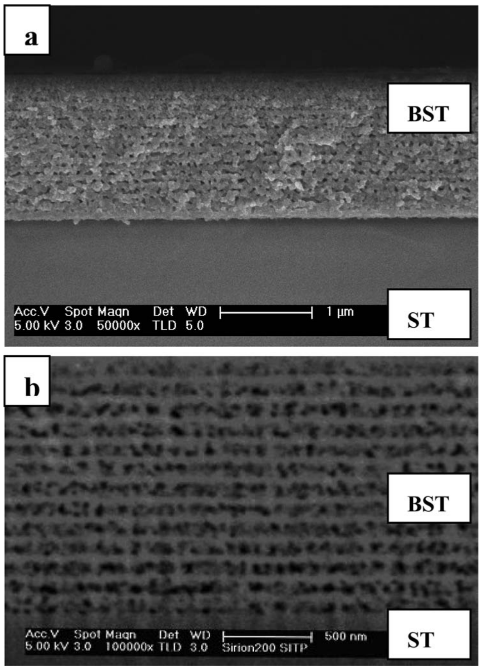

Fig. 1. a, Cross-sectional SEM image of BST multilayer deposited at 2400 rpm using a solution containing PEG additive, showing a layered structure consisting of dense-BST and porous-BST layers. The alternating of dense layers and porous layers along the growth direction gives rise to a quasi-periodic sequence of refractive indices as Bragg reflectors. b, Cross-sectional SEM photograph of a BST multilayer derived from a chemical solution with PVP polymer.

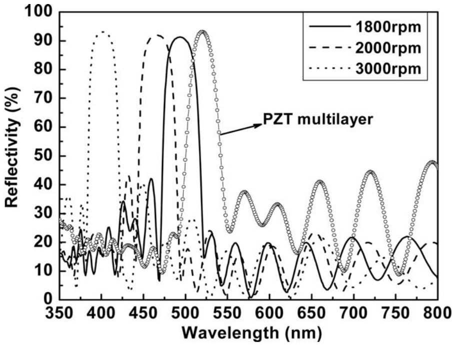

Fig. 2. Room temperature reflectance spectra for the ferroelectric multilayers derived from PEG-containing chemical solutions. The solid, dashed, and dotted curves denote three BST multilayers deposited at 1800, 2000, and 3000 rpm, respectively, while the curve with open circles corresponds to the PZT multilayer.

By close examination of the reflectance spectra of the two PZT multilayers derived from the chemical solutions containing different polymer additives, it can be found that the optical properties of both PZT multilayers, including peak reflectivity and bandwidth, are quite similar, implying that both PVP and PEG are suitable polymer additives for fabrication of periodic PZT multilayer stacks.

However, the case for the BST multilayer system is quite different. These types of polymer have a remarkable effect on their optical performance. To clearly state the discrepancy in optical properties between the BST multilayers derived from the precursor solutions containing different polymer additives, Fig. 3 shows the room temperature absolute reflectance spectra for another three BST multilayers. These BST multilayer stacks contain 16 periods of dense-BST layer/porous-BST layer and were fabricated at spinning rates of 4000, 3000, and 2500 rpm by using a PVP-containing precursor chemical solution. Comparing Figs. 2 and 3, it can be seen that the BST mutilayers derived from the solution with PVP possess broader reflection bands and higher peak reflectivities, with the reflection bands exhibiting a symmetric and flat-toped structure. This indicates that the PVP-containing precursor chemical solution is more suitable for the use to fabricate dielectric reflectors.

The quantities' peak reflectivity, bandwidth, and central wavelength of reflection band are three important parameters for characterizing the optical performance of a dielectric reflector. Both peak reflectivity and stop-band width increase with decreasing

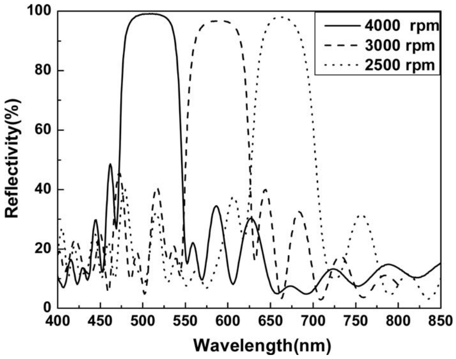

Fig. 3. Dependence of reflectivitiy of the three BST multilayers on wavelength. These multilayers with 16 periods of dense-BST/porous-BST layers were grown by using one single PVP-containing solution. The solid, dashed, and dotted curves correspond to those stacks spin-coated at 2500, 3000, and 4000 rpm, respectively

the optical thickness difference between the high and low refractive index layers for a periodic multilayer with a given period number. As shown in Fig. 1, the average physical thickness of the dense-BST layer is larger than that of the porous-BST layer in a bilayer in the BST multilayer deposited by a solution with PEG additive, which is the opposite of what occurs with BST multilayers derived from a precursor containing PVP. Thus, the optical thickness ratio of the dense and porous layers has a larger deviation away from unity for the BST multilayers fabricated by using PEG-containing chemical solution, giving rise to a narrower reflection band and a lower value of peak reflectivity for these BST multilayers. However, it should be noted that much more work is need to get further insight into the effect of polymers PVP and PEG on the Bragg reflectance performance of BST multilayers.

In summary, quasi-periodic ternary ferroelectric Bragg reflectors were fabricated by using one single precursor solution with PEG additive. With the same processing conditions and number of periods, the Bragg reflection performance of the PZT multilayers is almost the same as that of layers fabricated using precursors containing PVP polymer. The BST multilayers deposited by using PVP-containing precursor are superior in optical properties to those deposited by the PEG-containing solution.

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