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Lattice guiding for sputter deposition of single domain (Sr$_{0.6}$Ba$_{0.4}$)Nb$_2$O$_6$ ferroelectric thin films†

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Lattice guiding is used to synthesize preferentially oriented thin films of (Sr$_{0.6}$Ba$_{0.4}$)Nb$_2$O$_6$ by RF magnetron sputtering, with the film-substrate crystallographic relationship determined. These ferroelectric thin films guide light at 532 and 633 nm and have a single domain structure that can be written with permanent, sub-micron, anti-parallel domains.

Ferroelectric crystals are capable of manipulating light based on the distribution of their polar domains enabling functionalities such as frequency conversion and quantum information processing. The distribution of the ferroelectric domains in the crystals determine the conversion characteristics and efficiency, with random distribution having broadband performance and periodic distribution enabling highly coherent conversion. To enhance the performance of ferroelectric materials for applications in frequency conversion and quantum information processing, confined light propagation in thin film waveguides is advantageous. This requires the growth of near epitaxial and domain patternable ferroelectric thin films, the combination of which allows waveguiding and efficient light manipulation.

Experimental demonstrations have shown that strontium barium niobate (SBN) ferroelectric crystals with random ferroelectric domains are effective second harmonic generation (SHG) materials, with a particular SBN composition of (Sr$_{0.6}$Ba$_{0.4}$)Nb$_2$O$_6$ (denoted henceforth as SBN60, due to 60% SrH$_2$O material, with a particular SBN composition of) being very efficient. Synthesis of SBN60 in thin film form will enable controlled patterning of ferroelectric domains, allowing quasi phase matching for forward and backward SHG, in addition to facilitating incorporation of waveguides and couplers, creating a platform for hybrid integration.

To achieve growth of epitaxial thin films, pulsed laser deposition (PLD) is the technique usually adopted. PLD has also been used to achieve epitaxial thin films of SBN on MgO substrates. The use of PLD in this instance is encumbered by two major drawbacks. Firstly, the laser ablation process results in large crystalline deposits on the surface on the thin films. While this can be reduced by off-axis depositions, it cannot be fully controlled. Secondly, the distribution of the plasma plume limits the growth of uniform epitaxial films by PLD to relatively small areas. Considering potential applications of epitaxial SBN thin films for SHG in integrated optic devices, uniform and high quality films over large areas to enable devices 10-50 mm long is critical for maximum light interaction with the materials and efficient conversion in the case of SHG. Moreover, even with epitaxial PLD films, single domain SBN60 films which can be controllably patterned have not been demonstrated.

In this work, we utilise RF magnetron sputtering, which is reputed for large area and uniform thin film quality to deposit SBN thin films. RF magnetron sputtering is known to generally result in polycrystalline films, unless optimised conditions or lattice guiding or a combination of the two are employed. The sputtering process was carried out using a stoichiometric (Sr$_{0.6}$Ba$_{0.4}$)Nb$_2$O$_6$ target at 200 W forward power in an argon atmosphere (see ESI† for details). SBN60 has a tetragonal structure with lattice parameters $a$ and $c$ being 12.46 and 3.93 Å, respectively. In order to synthesise highly oriented thin films, a combination of lattice guiding and thermodynamics was utilised. Strontium titanate (SrTiO$_3$, STO) and 0.5 wt% niobium-doped strontium titanate (Nb:STO) substrates of (001) orientation with lattice parameter of 3.91 Å were chosen to minimise misfit strain. This level of niobium doping does not influence the substrate crystallography, but provides DC conductivity utilised for ferroelectric characterisation. The deposition was carried out at a substrate temperature of 700 °C, followed by controlled cooling at 5 °C min$^{-1}$ to maximise the crystalline quality of the films. The resulting thin film deposition rate was ~175 nm h$^{-1}$.

X-ray photoelectron spectroscopy (XPS) was utilised to determine the composition of the deposited thin films. The experimental conditions and results are described in detail in the ESI† (see Fig. S1). The composition of the films was verified as matching that of the sputtering target and the desired SBN60 composition. The crystallography of the thin films was determined using X-ray diffraction (XRD) (see ESI† for experimental details). The resulting diffractionogram is shown in Fig. 1 and was indexed based on reference powder diffraction files 01-072-6171 for SBN61† and 00-035-0734 for STO‡ from the International Centre for Diffraction Data (ICDD). The overlap of the (002) planes of SBN60 and STO observed in Fig. 1 is indicative of the guiding effect exerted by STO on the orientation of the SBN60 thin films. The diffractionogram also indicates that the SBN thin films are preferentially oriented given the dominant (001) and (002) peaks. Identical XRD results were obtained for SBN60 on Nb:STO substrates.
Cross-sectional transmission electron microscopy (XTEM) was used to determine the microstructure, thickness, and crystallography of the thin films. Figure 2 presents the high resolution cross-sectional microstructure of the SBN60 thin films on the STO substrate, which shows a polycrystalline microstructure and a film thickness of 170-178 nm for a 1 h deposition. Selected area electron diffraction (SAED) was used to determine the crystallographic relationship between the crystallites in the SBN60 thin film and the STO substrate. The SAED pattern obtained in the vicinity of the film-substrate interface is shown in Fig. 3(a) (and Fig. S2 in the ESI†). The diffraction pattern shows contributions from both the STO (red) and SBN60 (green). Figures 3(b) and 3(c) show each of these diffraction patterns indexed and reveal that the electron beam is [011] direction in STO and [001] in SBN60. The diffraction pattern show that there is a strong crystallographic orientation relationship between SrTiO$_3$ and SBN60 with the overlap of the (211) STO and (200) SrTiO$_3$ diffraction spots. The ~35° tilt angle between the diffraction patterns corresponds to the (211)^*(200) interplanar angle. It can also be seen in Fig. 3(c) (and Fig. S2 in the ESI†) that there are intermediate spots between the indexed spots. These arise due to SBN60 having a superlattice structure of strontium niobate and barium niobate.

Having established lattice guided growth of preferentially oriented thin films of SBN60 on STO substrates, the ability of these films to serve as light guiding layers and domain patternable ferroelectrics was examined by prism coupling and piezoresponse force microscopy, respectively. Prism coupling is an efficient technique for coupling light into a thin film, using a precisely polished prism, overcoming the need to fabricate a waveguide.$^{10}$ The observation of coupling modes is indicative of the ability of the thin film layer to guide light in a film-substrate arrangement, and sufficient number of modes can be utilised to extract the refractive index and thickness of the thin film. A Metricon prism coupler was used to study the SBN60 thin films (see ESI† for details). The measurements were undertaken at 532 and 633 nm to determine the ability of the films to guide both wavelengths. In order to have sufficient film thickness to support optical modes, the films utilised for these experiments were obtained by a 6 h deposition (~1.05 μm).

Figure 4 presents prism coupling results for the SBN60-STO film-substrate structure. Dips seen in the spectra correspond to optical modes supported by the film with the position of each mode representing the effective modal index $\beta$. Optical modes are supported by the SBN60 thin film at both 532 and 633 nm, demonstrating the ability of these films to guide light. From the effective modal indices $\beta$, the ordinary refractive index ($n_o$, TE mode) was determined at 532 and 633 nm as 2.367 and 2.334, respectively. This refractive index is in agreement with 2.30 at 633 nm obtained for highly oriented SBN60 thin films on platinised MgO substrates.$^{11}$ The film thickness extracted from the prism coupling measurements was 1.02 μm, which matches the expected value of ~1.05 μm.
topography changes were observed, which did not affect the 30
film with sub-micron resolution, as shown in Fig. 5(b). Some
applied to the AFM tip, inverse domains could be written in the

determine piezoelectric displacements under applied bias.

The technique uses an atomic force microscope (AFM) to
parallel 180º ferroelectric domains, which are usually observed
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films revealed a very smooth surface (see ESI†, Fig. S3), with 20

Piezoresponse force microscopy (PFM) is increasingly used to
characterise the ferroelectric properties of thin films, and, in particular, to study the distribution and polarity of domains. The technique uses an atomic force microscope (AFM) to determine piezoelectric displacements under applied bias. The SBN60 thin films on STO and Nb:STO substrates were both studied by PFM, with Nb:STO providing a conductive substrate to serve as the bottom ground electrode, while in the case of STO the piezoelectric response is purely determined by bias-induced electric field at the AFM tip. The surface topography of these films revealed a very smooth surface (see ESI†, Fig. S3), with root mean square roughness of 126 pm (~0.1 nm). PFM phase maps, which provide information about the orientation of the ferroelectric polarization, for a set of measurements are presented in Fig. 5. The as-deposited thin films have a uniform piezoelectric phase response as seen in Fig. 5(a) and hence a uniform polarization direction, and thus appear to be comprised exclusively of a single ferroelectric domain. Using a ±6 V bias applied to the AFM tip, inverse domains could be written in the film with sub-micron resolution, as shown in Fig. 5(b). Some topography changes were observed, which did not affect the switchability of the domains. No in-plane displacements were observed, confirming the domains being formed were anti-parallel 180º ferroelectric domains, which are usually observed for tetragonal unit cell structure materials, as in the case of SBN60. Written domains remained stable for at least one week.

In summary, we have demonstrated the use of lattice guiding for the synthesis of preferentially oriented thin films of SBN60 on STO substrates. The interfacial crystallographic relationship was examined using XRD and SAED. These films are shown to be suitable for optical waveguiding at 532 and 633 nm. The as-deposited single domain ferroelectric structure of the films can be patterned with sub-micron inverse domains. These SBN60 thin films have the potential to be an efficient platform for high efficiency nonlinear optical processing.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental conditions for thin film deposition and for characterisation processes; X-ray photoelectron spectroscopy results; as-collected electron diffraction pattern; topography of film surface. See DOI: 10.1039/c0xx00000x/
7 Powder Diffraction Pattern Files, International Centre for Diffraction Data (ICDD), Newtown Square, PA 19073, Card 00-035-0734.

Fig. 4 Prism coupling spectra for SBN60 thin films. The modes observed confirm optical guiding at 532 and 633 nm.

Fig. 5 Piezoresponse force microscopy results showing phase maps of ferroelectric domains in SBN60 thin films on Nb:STO. The single domain characteristic of the films is shown in (a). The ability to write micro- and nano-scale domains with a ±6 V tip bias is shown in (b), where the contrast depicts anti-parallel 180º domains.