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On-axis radio frequency magnetron sputtering of stoichiometric $BaTiO_3$ target: Localized re-sputtering and substrate etching during thin film growth

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ABSTRACT

$BaTiO_3$ thin films were prepared on Nb–$SrTiO_3$ (100) and Pt/Al_2O_3/SiO_2/Si substrates by radio frequency (rf) magnetron sputtering using a stoichiometric $BaTiO_3$ ceramic target. This on-axis $BaTiO_3$ thin film growth encountered severe re-sputtering and substrate etching, above a threshold power density (4 W/cm^2), due to negative ion formation at the target surface and subsequent acceleration towards the substrate. However, the film deposition with reduced or negligible re-sputtering was possible below 4 W/cm^2 of rf-power. The rf-voltage vs. power curve showed two distinct linear regimes with high and low slopes; the change in the slope coincides with substrate etching. Optical emission spectroscopy was employed to establish the link between the onset of excessive re-sputtering and could be used as a control tool. Since, negative oxygen ions (O^-) are responsible for the re-sputtering, additional processing parameters like the oxygen partial pressure [$P_o = (O_2 / O_2 + Ar)$ %] and total pressure were also adjusted to realize target stoichiometry on the grown films. Finally, through optimization steps, as revealed by the X-ray photoelectron spectroscopy, stoichiometric $BaTiO_3$ films were obtained, at a pressure ≥2.7 Pa, power density of 2 W/cm^2 and P_o around 50%.

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1. Introduction

Barium titanate ($BaTiO_3$), the first perovskite ferroelectric oxide discovered in the 1940s (after the discovery of water-soluble, order–disorder type ferroelectrics, sodium potassium tartrate tetrahydrate and potassium dihydrogen phosphate), is a prototypical displacement type ferroelectric for which the origin of ferroelectricity is derived from the displacement of ions relative to each other [1]. Even after 70 years of that discovery, $BaTiO_3$ is still the most widely used material in multilayer capacitors. $BaTiO_3$, in single crystal, ceramic, and thin film forms has been studied extensively due to the superior electrical and optical properties, which are exploited in electro-optic switches, pyroelectric detectors, optical modulators, shutters, imagers, and displays to name a few [2]. However, the recent interest in $BaTiO_3$ is due to the existence of ferroelectric properties down to a thickness of about 2–3 nm. This offers the possibility of exploiting the polarization in controlling the tunneling current as predicted theoretically, the hysteretic current–voltage characteristics [3]. The control or dependence of tunneling current on the polarization direction resulted in the realization of ferroelectric tunnel junctions (FTJs) that are attracting increasing attention due to the possibility of realizing ultra-fast, high density non-volatile memory, paving the way for "oxide electronics" into the standard semiconductor industry [4–9].

Thin films of $BaTiO_3$ can be realized with methods such as hydrothermal, pulsed laser deposition, metal organic chemical vapor deposition (MOCVD), various forms of sputtering, molecular beam epitaxy, evaporation, and sol-gel. Among these methods, radio frequency (rf) magnetron sputtering is considered here due to the fact that it offers medium deposition rate, uniformity over large area with additional interest in industrial mass production. Transferring the target stoichiometry to the growing films is challenging with on-axis rf-magnetron sputtering from $BaTiO_3$ targets due to the by-production of negative ions (O^-) along with the production of neutral target atoms during the sputtering of target with positively charged ions (Ar^+). These negative ions get sufficient kinetic energy along the axis from the target rf-bias field to bombard the substrate, which significantly alters the stoichiometry of the deposit and in the worst case, even a substrate etching might occur [10]. Typical threshold energies for knocking out atoms from the surface are in the 20–50 eV range [11], which is much higher than the surface binding energy (4 to 8 eV) of the atoms. The −ve ions produced at the target surface are accelerated towards the substrate direction and bombarded the film surface with energies that could be as high as the bias voltage on the target. At 100 V, these −ve ions cause significant re-sputtering and etching of the substrate. To avoid this effect, in rf-magnetron sputter deposition of $BaTiO_3$, off-axis

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geometries are generally employed, where the substrate is kept away from the target axis. Hence, for on-axis sputter deposition, the processing parameters must be optimized, in order to minimize the energy of negative ions impinging the substrate, hence reduce their effect on the deposited film. In the present paper, process optimization of $BaTiO_3$ is discussed to avoid the substrate etching and to get uniform stoichiometric $BaTiO_3$ film on Nb–$SrTiO_3$ (100) and $Pt/Al_2O_3/SiO_2/Si$ substrates.

2. Experimental details

Conducting single crystalline and polycrystalline substrates were used for the $BaTiO_3$ deposition in the present study. In the case of conducting polycrystalline substrates, as bottom electrodes, a double-layer structure consisting of 100 nm-thick platinum films on a 5 nm-thick Al_2O_3 film was used. The latter serves as an adhesion layer to improve the sticking of platinum on the SiO_2/Si substrates and the resulting structure was $Pt/Al_2O_3/SiO_2/Si$. In the case of conducting single crystalline substrates, Nb:$SrTiO_3$ ($5 \times 5 \times 0.5$ mm, miscut angle $< 0.5°$, 0.5 wt.% Nb) with (100) orientation from Crystec GmbH was used for realizing epitaxial $BaTiO_3$ films. The surface morphology was investigated by using atomic force microscopy (Smart SPM1000-AIST-NT Inc.) in tapping mode.

The $BaTiO_3$ thin film deposition was then realized on these substrates by conventional on-axis RF magnetron sputtering at various temperatures (25 °C to 800 °C). The sputtering unit used in this study was a computer controlled table top deposition system, *SPT310 Plasmionique Inc.*, equipped with three guns at the top and a heated substrate holder block at the bottom along the axis of the sputter-guns. The deposition geometry is shown in Fig. 1. The symmetry axis passed through centers of both the target holder and the substrate holder which allows for a slight off-axis positioning. Such an inverted conical design ensured equal distance between various targets (at the perimeter of circular base) and substrate (at the vertex), was due to the possibility of exploiting the system for multi-target deposition at the same time (Fig. 1b). A polycrystalline $BaTiO_3$ ceramic disc (2.54 cm diameter and 0.317 cm thickness) was used as the sputtering target. Prior to the deposition, the chamber was evacuated to at least a base pressure of ~7 mPa using a dry pumping station, although a residual pressure in the range of 0.27 mPa could be achieved. The sputtering medium was a gas mixture of Ar and O_2 [oxygen partial pressure, $P_o = O_2 / (Ar + O_2) = 0$ to 100%] and the operating pressure was in the range 0.7–4 Pa. An upstream PID (proportional-integral-derivative) controller, maintained the constant pressure throughout the deposition. The target was pre-sputtered for 15 min, while keeping the shutter on the substrate surface, in order to eliminate contamination and maintain homogeneity of the target composition. The sputtering conditions are listed in Table 1.

Optical emission spectroscopy (OES) was used for understanding the plasma composition, and the substrate etching during $BaTiO_3$ deposition. Two compact spectrometers, provided with the deposition system, having different spectral resolutions were used to monitor the $BaTiO_3$ sputtering process. The sensitivity of this process control was analyzed with the study of emission intensity of Ti, Ba, O and Ar spectral lines and their ratios. All the data were analyzed using "OES Capture" software developed by Plasmionique Inc. Ba and Ti incorporation in the films was routinely determined with X-ray photo-electron spectroscopy (VG Escalab 220i XL). Al Kα (1486.6 eV) radiation from a monochromatic x-ray source operating at 400 W was used for the study. Spectra were calibrated using carbon by assigning the binding energy of 284.6 eV to the C1s peak position to compensate shift in the peak position due to charging effects.

Table 1
Summary of sputtering conditions used for the deposition $BaTiO_3$ thin films.

Substrate	$Pt/Al_2O_3/SiO_2/Si$ and Nb–$SrTiO_3$
Target	$BaTiO_3$ ceramic disc
Target dimension	2.54 cm diameter; 0.317 cm thickness
Power	10–65 W
Target–substrate spacing	9 cm
Sputtering medium	Ar and O_2 mixture
Sputtering pressure	0.7–4 Pa
Substrate temperature	RT-800 °C
Pre-sputtering duration	15 min
Sputtering time	180 min

3. Results and discussion

3.1. Deposition and substrate etching

Prior to deposition as-received Nb: $SrTiO_3$ was etched hydrothermally in water and then annealed in oxygen ambient to ensure single termination (Fig. 2a) [12]. The AFM characterization revealed an average rms roughness around 0.15 nm. As can be seen in the inset of Fig. 2a, the line scan showed an average step height of 0.4 nm, suggesting single termination of SrO or TiO_2 [12]. In Fig. 2b, the AFM surface morphology showed polycrystalline granular features of the platinum surface (x-ray diffraction studies revealed Pt orientation along (111) direction, results not shown) with an rms roughness of about 1.6 nm. As the actual surface morphology of the as-received $Pt/Al_2O_3/SiO_2/Si$ substrate was found to be dependent on the deposition temperature, we used a standard pre-anneal, i.e., 30 min at 700 °C, to stabilize the 'Pt' microstructure before deposition.

To understand the on-axis and off axis effects and uniformity of $BaTiO_3$ deposition with the table top sputtering unit, a 5.08 cm diameter platinized silicon was kept at the center of the substrate holder, without rotation and the deposition was performed at 700 °C and 0.7 Pa. Now rf-power was varied while keeping the oxygen partial pressure, P_o at 50% and the photographs of the substrate after deposition for about 3 h are depicted in Fig. 3. At low power ≤20 W (4 W/cm^2) deposition was observed all over the surface with severe thickness non-uniformity over

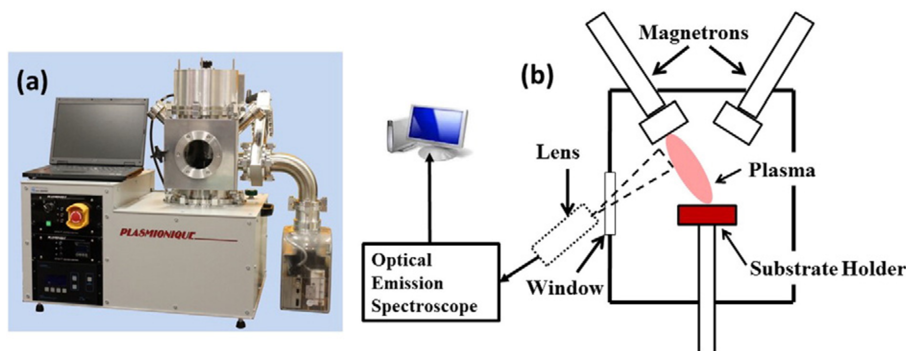

Fig. 1. (a) Table top deposition system (*SPT310 Plasmionique Inc.*) used for the present study; (b) schematic diagram of the sputtering chamber.

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