

# Etching characteristics and plasma-induced damage of $\text{Ba}_{0.65}\text{Sr}_{0.35}\text{TiO}_3$ thin films etched in $\text{CF}_4/\text{Ar}/\text{O}_2$ plasma

Zuci Quan, Baishun Zhang \*, Tianjin Zhang, Tao Guo, Ruikun Pan, Juan Jiang

*School of Materials Science and Engineering, Hubei University, Wuhan 430062, PR China*

Received 7 October 2006; accepted 22 December 2006

Available online 13 January 2007

## Abstract

Sol-gel-derived  $\text{Ba}_{0.65}\text{Sr}_{0.35}\text{TiO}_3$  (BST) thin films were etched in  $\text{CF}_4/\text{Ar}/\text{O}_2$  plasma using magnetically enhanced reactive ion etching technology. The maximum etch rate of BST film is 8.47 nm/min when  $\text{CF}_4/\text{Ar}/\text{O}_2$  gas mixing ratio is equal to 9/36/5. X-ray photoelectron spectroscopy analysis indicates the accumulation of fluorine-containing by-products on the etched surface due to their poor volatility, resulting in (Ba,Sr)-rich and (Ti,O)-deficient etched surface. Compared to the unetched counterparts, the etched Ba 3d<sub>5/2</sub>, Ba 3d<sub>3/2</sub>, Sr 3d<sub>5/2</sub>, Sr 3d<sub>3/2</sub>, Ti 2p<sub>3/2</sub>, Ti 2p<sub>1/2</sub> and O 1s photoelectron peaks shift towards higher binding energy regions by amounts of 1.31, 1.30, 0.60, 0.79, 0.09, 0.46 and 0.50 eV, respectively. X-ray diffraction (XRD) analysis reveals that intensities of the etched BST (100), (110), (200) and (211) peaks are lowered and broadened. Raman spectra confirm that the Raman peaks of the etched film shift towards lower wave number regions with the values of 7, 6, 4 and 4  $\text{cm}^{-1}$ , and the corresponding phonon lifetimes are longer than those of the unetched film because of the plasma-induced damage. When the etched films are postannealed at 650 °C for 20 min under an O<sub>2</sub> ambience, the chemical shifts of Ba 3d, Sr 3d, Ti 2p and O 1s peaks, the variations for atomic concentrations of Ba, Sr, Ti and O, and the Raman redshifts are reduced, while the corresponding XRD peak intensities increase. It is conceivable that the plasma-induced damage of the etched film could be partially recovered during the postannealing process.

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**Keywords:** BST thin film; Etch rate; Chemical shifts; Plasma-induced damage

## 1. Introduction

$\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$  (BST) thin films have attracted much attention for their applications in nonvolatile ferroelectric random access memories (NVRAMs), microelectromechanical systems (MEMSs), and uncooled infrared focal plane arrays (UIFPAs), based on the merits of high dielectric constant, low dielectric loss, small leakage current density, composition-dependent Curie temperature (from 30 to 400 K), and superior pyroelectric properties [1–3]. In order to accomplish the integration of these devices, the etching process for BST films must be developed. Several techniques have been used for etching BST films: wet chemical etching, reactive ion etching (RIE), magnetically enhanced

reactive ion etching (MERIE), inductively coupled plasma (ICP) etching, electron cyclotron resonance (ECR) etching, helicon wave plasma (HWP) etching, and reactive ion-beam etching (RIBE) [4–8]. Among those technologies, MERIE system has shown high etch rate and good selectivity performance for etching BST films because of the presence of relatively intensive magnetic field and the high density plasma at low pressure. Until now, there are several works devoted to an investigation of the etching properties for BST films using various chlorine-based and/or fluorine-based plasmas [5,8–10]. Kim et al. [5] reported the etching characteristics and mechanism of BST films using  $\text{CF}_4/\text{Cl}_2/\text{Ar}$  and  $\text{BCl}_3/\text{Cl}/\text{Ar}$  gas mixtures in an ICP system. Shibano et al. [8] observed the etching behaviors of BST films using  $\text{Cl}_2/\text{Ar}$  plasma in an electron cyclotron resonance reactive ion etching (ECR-RIE) setup. They further demonstrated the etching of  $\text{BaO}_{1.1}$ ,  $\text{SrO}_{1.3}$ ,  $\text{TiO}_{0.6}$ , and  $\text{Ba}_x\text{Sr}_y\text{O}_z$  films

\* Corresponding author. Tel.: +86 27 88661682; fax: +86 27 88662550.  
E-mail address: [shichie118@sina.com](mailto:shichie118@sina.com) (B. Zhang).

with  $\text{Cl}_2$  plasma, and showed that the chemical enhancement in BST etching was related to the existence of titanium in the films. Kang et al. [9] attributed the chemical damage resulted from the contamination of the etched surface by the low-volatile reaction products, and the physical damage was represented by the formation of the surface defects in the BST crystalline structure. Wu et al. [10] studied the etching characteristics and the minimized plasma-induced damage of BST films using  $\text{Cl}_2/\text{Ar}$  plasma in an ICP system. They also discussed the mechanism of leakage current density and dielectric constant with various substrate bias and ICP power. However, it was not clear whether or not these processes were really optimum.

In this work, the etching characteristics and plasma-induced damage of BST films were investigated from MERIE processing using  $\text{O}_2$  added into the  $\text{CF}_4/\text{Ar}$  plasma. The surface composition and chemical bonding states for the unetched, etched, and postanneal-after-etched BST surfaces were examined by X-ray photoelectron spectroscopy (XPS). The plasma-induced damage including fluorine-containing chemical contamination, crystal structure, lattice distortion and physical damage for the etched BST films were characterized by XPS, X-ray diffraction (XRD), and Raman spectroscopy. The recovery mechanism of the plasma-induced damage after postannealing was also discussed.

## 2. Experimental procedure

The precursor solution of  $\text{Ba}_{0.65}\text{Sr}_{0.35}\text{TiO}_3$  (BST) films was prepared by acetic acid based sol–gel process. Barium acetate  $[\text{Ba}(\text{CH}_3\text{COO})_2]$ , strontium acetate  $[\text{Sr}(\text{CH}_3\text{COO})_2 \cdot \frac{1}{2}\text{H}_2\text{O}]$ , and tetrabutyl titanate  $[\text{Ti}(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_4]$  were used as starting materials. Glacial acetic acid ( $\text{CH}_3\text{COOH}$ ) was used as catalyst. 2-Methoxyethanol ( $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$ ) was used as solvent. *N-N*-dimethyl formamide  $[(\text{CH}_3)_2\text{NOCH}]$  was used to stabilize the solution. After stoichiometrically dissolved, the concentration of multi-component BST sol was controlled to 0.3 M and pH value was about 3.5. The precursor solution was spin-coated onto Pt(111)/Ti/SiO<sub>2</sub>/Si(100) substrates at 4000 rpm for 30 s. The wet films were pre-baked at 400 °C for 15 min to remove the organic contaminations. This procedure was performed several times to obtain appropriate thickness. The films were annealed at 700 °C for 20 min under an  $\text{O}_2$  ambience using a rapid thermal processor (RTP, RTP500) to form the perovskite phase.

BST films were etched in a MERIE apparatus (ME-3A) using various  $\text{CF}_4/\text{Ar}/\text{O}_2$  gas mixing ratios.  $\text{CF}_4$ , Ar, and  $\text{O}_2$  gases flowing into the chamber were controlled by mass flow controllers. The films were etched under the following conditions: the gas flow rate ratios of  $\text{CF}_4/\text{Ar}$  were equal to 50/0, 40/10, 30/20, 20/30, 10/40, 0/50; while  $\text{CF}_4/\text{Ar}/\text{O}_2$  were 10/39/1, 10/37/3, 9/34/7, 8/33/9, and 8/31/11, respectively. An 80 W radio frequency (RF) power with 13.56 MHz was applied to generate plasma. Total gas flow

rate was 50 sccm; etching time was 30 min; base pressure was better than 0.1 Pa, and working pressure was about 2.5 Pa. Furthermore, the etched BST films were postannealed at 650 °C for 20 min under an  $\text{O}_2$  ambience by RTP.

In order to measure the etch rates conveniently, a few etching samples were patterned using an 1.5- $\mu\text{m}$ -thick positive photoresist (BP212) mask with the standard photolithography process. On the other hand, the other samples were virgin BST films without any photoresist treatment before etching. The etching depths were measured by nano-step talysurf (S4C-3D). The etching rates were calculated according to the relationships between etching depths and etching times. The surface composition and chemical bonding states of the corresponding elements for the unetched, etched, and postanneal-after-etched BST surfaces were investigated by XPS (Kratos XSAM 800). The XPS Mg K $\alpha$  source operating at 200 W (12 kV  $\times$  16.7 mA) provided non-monochromatic X-rays at 1253.6 eV. The analyzer was used in the constant retarding ratio (CRR) mode applying the retarding ratio of 20. The survey spectra were taken at a base pressure of  $2 \times 10^{-7}$  Pa and a scan range from 1000 to 0 eV binding energy was sufficient to identify all detectable elements. The C 1s peak at 285.0 eV was assigned to carbon from contaminated hydrocarbon and was used to be criterion to rectify the energy of spectra. The software of XPSPEAK Version 4.1 was used to fit the narrow-scan spectra for Ba 3d, Sr 3d, Ti 2p, and O 1s peaks after Shirley-type background [11] subtraction. Narrow-scan spectra of Ba 3d, Sr 3d, and O 1s peaks were fitted by symmetrical Gaussian-Lorentzian product function [12], while the Ti 2p doublets were fitted by asymmetrical Gaussian-Lorentzian sum function [13] to adjust the multiple splitting and/or shake-up process [14] of transition-metal Ti cations. Relative atomic concentrations of Ba, Sr, Ti, and O (marked as Ba%, Sr%, Ti% and O%, respectively) were estimated from the XPS element peak areas after applying atomic sensitivity factors. The relative sensitivity factors of Ba 3d, Sr 3d, Ti 2p and O 1s are 3.13, 3.24, 2.129 and 0.914 with respect to F 1s, respectively. The crystal structures of the unetched, etched, and postanneal-after-etched BST films were analyzed by X-ray diffractometer (XRD, Rigaku D/Max- $\square$ C) with Cu K $\alpha$  radiation and Raman spectrometer (Renishaw inVia Raman spectrometer). The 632.8 nm line from a He-Ne laser with a beam diameter of about 2  $\mu\text{m}$  on the sample surface was used for Raman excitation. Incident laser power was kept at a low level (20 mW) to avoid sample heating. The Raman spectra were recorded in the range from 100 to 1200  $\text{cm}^{-1}$  with resolution of 1  $\text{cm}^{-1}$ . All measurements were carried out at room temperature.

## 3. Results and discussion

Fig. 1 shows the etch rate of BST films as a function of the various  $\text{CF}_4/\text{Ar}/\text{O}_2$  gas mixing ratios. As Ar/ ( $\text{CF}_4 + \text{Ar}$ ) increases to 80%, the etch rate increases, which reaches a maximal value of 7.68 nm/min when Ar/

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