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Plasma etching dynamics of $Ca_xBa_{1-x}Nb_2O_6$ (CBN) material

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ABSTRACT

This work reports an extensive study on the etching of Calcium Barium Niobate (CBN, a novel electro-optical material), using high density plasma processes. Different plasma chemistries (inert, chlorine and fluorine plasmas) are used to etch $Ca_{0.28}Ba_{0.76}Nb_2O_6$ (CBN-28) thin films at pressures going from 1 to 10 mTorr, bias voltages going from 0 to 600 V and substrate temperatures ranging from −75 to 375 °C. For all the conditions investigated, the experimental data are compared with a simple sputtering model and completed with TOF-SIMS measurements of some of the samples processed. This study shows that there is no chemical enhancement or inhibition in the case of chlorinated plasma (Cl_2) regardless of the ion energy or the substrate temperature. In the case of an SF_6-Ar plasma, it is shown that the observed increase of the etch yield above 150 °C results from a reduced inhibition as the temperature increases, this inhibition being caused by F and F_2 species adsorption at the surface of the material.

1. Introduction

The very promising properties of electro-optic (EO) materials have opened the way to the development of new active photonic devices such as tunable band gap photonic crystal [1], ring resonators [2] and high-speed electro-optic modulators [3–5]. The key parameter for the performance of these devices is the electro-optic coefficient r_{33} of the guiding material. Nowadays, most of the active photonic devices are based on bulk lithium niobate ($LiNbO_3$, LN), an electro-optic material that has an EO coefficient of 31 pm/V [6]. Many ferroelectric materials recently investigated such as Barium Strontium Titanate ($Ba_xSr_{1-x}TiO_3$, BST) [7], Strontium Barium Niobate ($Sr_xBa_{1-x}Nb_2O_6$, SBN) [8] and Calcium Barium Niobate ($Ca_xBa_{1-x}Nb_2O_6$, CBN) [9–12] have much higher EO coefficients (up to 1400 pV/m for the SBN [13]). Among them, CBN has the advantage to combine a high linear electro-optic coefficient (r_{33} = 130 pm/V) [14] and a high Curie temperature (260 °C) [11], which makes it a very interesting candidate for the development of high performance electro-optic devices [15].

Up to now, these ferroelectrics were hardly integrated into active devices for two main reasons: first, they are difficult to grow as thin films while keeping high electro-optic coefficients and, secondly, there are no established process to pattern these films as waveguides. In the case of CBN, it was recently demonstrated that it can be grown as thin film while keeping properties close to those of bulk material [12]. In order to control all the etching parameters and to separate physical and chemical material etching, plasma etching is the preferred way of patterning thin films. However, very few studies are devoted to the etching of ferroelectrics, and especially CBN [16]. The large number of non-conventional elements composing this material and the lack of literature on ferroelectric plasma etching makes a suitable chemistry very difficult to identify. To overcome these difficulties, we propose in this paper a thorough study of CBN etching, the goal being to understand the dynamics governing plasma etching of this material and find the optimum patterning conditions.

2. Experimental setup and diagnostics

For this etching study, CBN thin films were grown on Si (100) substrates by pulsed laser deposition (PLD) using a CBN-28 commercial ceramic target from K.J. Lesker. The deposition is carried out at 800 °C in an oxygen ambient pressure of 1 mTorr with a laser fluence of 2 J/cm^2. After deposition, in situ annealing is performed at 800 °C in 300 mTorr of oxygen to minimize the oxygen vacancies. Detailed description of the conditions used for the deposition is provided in a previous paper [12]. X-ray Diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS) characterizations show that all of the films are polycrystalline with a composition close to that of the bulk material. The atomic density of these films was calculated from the mass of the thin film measured with a precision scale before and after film deposition on a 3 inch Si wafer, considering a thickness of 1 μm (as measured by Scanning Electron Microscopy (SEM) and profilometry). This density was found to be 6.04×10^{22} at/cm^3, i.e. slightly lower than the theoretical density of epitaxial thin films (assuming a unit cell volume of 61.3 nm^3, this theoretical value is 6.51×10^{22} at/cm^3). Etching

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experiments were conducted in a cylindrical Inductively Coupled Plasma reactor (ICP) from Oxford instruments (Plasmalab 100 model ICP 380). In this system, the ICP plasma is generated using a 2 MHz RF signal applied on the plasma coil (here at a power of 1 kW). The kinetic energy of the ions is controlled by applying RF power at 13.56 MHz on the chuck table. The experiments were carried out in pure Ar, in Cl_2 and in SF_6-Ar, the pressure of these gases or of the gas mixture being set independently of gas flows by dynamically controlling a throttling valve located at the bottom of the process chamber. The proportion of each gas in the chamber is determined from the gas flow ratios. As sulfur hexafluoride (SF_6) is strongly electronegative, it creates plasmas with a significant negative ion content and a reduced electron and positive ion density. To increase the positive ion density, it is often preferable to mix SF_6 with another gas such as Ar or He. In this work, we have chosen Ar because of its higher ionization efficiency as compared to helium. The table temperature was controlled by a heater or a liquid nitrogen flow depending on the temperature range. Helium backside cooling was used to ensure a good thermal contact between the clamped carrier wafer and the chuck table. In order to conveniently control the temperature on small CBN samples (25.4 × 25.4 mm), those samples were thermally bonded to a Si carrier wafer using either perfluoropolyether oil in the temperature range of −75 °C/+125 °C or high temperature vacuum grease for temperatures above 125 °C.

The average ion density of the plasma is measured by using a Langmuir probe, assuming a collisionless probe theory which is suitable for the low pressure conditions used (from 1 to 10 mTorr) [17,18]. The relative concentration of the positive ion species in the plasma was measured with a plasma sampling mass spectrometer (model HAL511S/2) positioned between the ICP source and the table. The etch rate is determined either ex-situ (using cross section SEM measurements) or in situ using laser interferometry considering the refraction index of the CBN thin film (n_{CBN}) to be 2.20 as determined by ellipsometry. The film being transparent and the incident laser ($\lambda = 675$ nm) being perpendicular to the surface, the period of the oscillating signal during etching corresponds to a thickness variation of $\lambda/2n_{\mathrm{CBN}}$, which allows the calculation of the etch rate. In order to determine the atomic composition of the sample surface exposed to different plasmas, time-of-flight secondary ion mass spectrometry (TOF-SIMS) was used. The samples were analyzed in the static mode using a $^{83}Bi^+$ ion beam accelerated at 15 keV and a current density of 1.8 pA, the analyzed surface being 50 × 50 μm. In order to obtain the in depth profiles close to the surface, two different species were used for positive and negative ions: O^+ ions at 1 keV and 0.58 nA and Cs^+ ions at 1 keV and 4.8 nA. The sputtered surfaces (500 × 500 μm wide) were scanned by stylus profilometry after the analysis in order to measure the sputtered depth.

3. Experimental results and discussion

3.1. Etch yield as a function of the incident ion energy

To cancel the dependence of the etch rate (*ER*) on the positive ion flux J_+, we introduce the etch yield *Y* calculated according to [19],

$$Y = \frac{\mathrm{ER} \times N_t}{J_+} \quad (1)$$

where J_+ is determined from the saturation current of the Langmuir probe in the plasma bulk for all the conditions investigated and where N_t is the CBN thin film mass density determined experimentally.

In order to investigate the mechanisms involved in Ar, Cl_2 and SF_6 etching of CBN, the experimental data obtained were compared to a physical sputtering empiric model. This model relies on the theoretical sputtering yield model developed by Yamamura et al. [20] for low energy ions incident on a target. For single element ions (as for Ar and Cl_2 plasmas), Y_i, the etch yield for the element *i*, can be expressed as:

$$Y_i = 0.163\alpha_i \frac{Y_i^{\frac{3}{4}}}{U_0^{\frac{1}{2}}} E_i^{\frac{1}{2}} \left(1 - \sqrt{\frac{E_i^{th}}{E_i}}\right) \quad (2)$$

where α_i is a dimensionless factor given by $\alpha_i = 0.10 + 1.55x_i^{-0.73} + 0.001x_i^{-1.5}$ for ions with normal incidence (x_i being the mass ratio between the incident ion *i* and the material sputtered), γ_i is the energy transfer factor for elastic collision and is calculated as $\gamma_i = 4x_i/(1 + x_i)^2$, U_0 is the surface binding energy of the material, E_i is the incident ion energy and E_i^{th} is the threshold energy for sputtering that can be approximated as $E_i^{th} \approx 8U_0x_i^{2/5}$ if the ion to material mass ratio $x_i > 0.3$.

For multi-element incident ions (as for SF_6-Ar plasmas), the formula decomposes the total yield into effective contributions of every single element. In the case of SF_6-Ar, the total yield *Y* becomes (as shown by Stafford et al. [21]):

$$\begin{aligned} Y = \frac{0.163}{U_0^{1/2}} \Bigg\{ & \alpha_S \gamma_S^{\frac{3}{4}} \Bigg[p_{S^+}\left(\sqrt{E_S^{S^+}} - \sqrt{E_S^{th}}\right) + p_{SF^+}\left(\sqrt{E_S^{SF^+}} - \sqrt{E_S^{th}}\right) \\ & + p_{SFO^+}\left(\sqrt{E_S^{SFO^+}} - \sqrt{E_S^{th}}\right) + p_{SF_2^+}\left(\sqrt{E_S^{SF_2^+}} - \sqrt{E_S^{th}}\right) \\ & + p_{SF_3^+}\left(\sqrt{E_S^{SF_3^+}} - \sqrt{E_S^{th}}\right) + p_{SF_5^+}\left(\sqrt{E_S^{SF_5^+}} - \sqrt{E_S^{th}}\right)\Bigg] \\ & + \alpha_F \gamma_F^{3/4} \Bigg[p_{F^+}\left(\sqrt{E_F^{F^+}} - \sqrt{E_F^{th}}\right) + p_{SF^+}\left(\sqrt{E_F^{SF^+}} - \sqrt{E_F^{th}}\right) \\ & + p_{SFO^+}\left(\sqrt{E_F^{SFO^+}} - \sqrt{E_F^{th}}\right) + p_{SF_2^+}\left(\sqrt{E_F^{SF_2^+}} - \sqrt{E_S^{th}}\right) \\ & + p_{SF_3^+}\left(\sqrt{E_F^{SF_3^+}} - \sqrt{E_F^{th}}\right) + p_{SF_5^+}\left(\sqrt{E_F^{SF_5^+}} - \sqrt{E_F^{th}}\right)\Bigg] \\ & + \alpha_{A\gamma} \gamma_{A\gamma}^{3/4} \left[p_{A\gamma^+}\left(\sqrt{E_{A\gamma}^{A\gamma^+}} - \sqrt{E_{A\gamma}^{th}}\right)\right] + \alpha_0 \gamma_0^{3/4} \left[p_{SFO^+}\left(\sqrt{E_0^{SFO^+}} - \sqrt{E_0^{th}}\right)\right] \Bigg\} \end{aligned} \quad (3)$$

where p_i is the fraction of the ion *i* in the plasma determined by the positive ion mass spectrometry and ε_j^{i+} is the fraction of the parent ion i^+ energy that is transferred to the atom *j*.

The values of ε_j^{i+} can be calculated from the mass ratio of the atom *j* to the ion i^+ times the incident ion energy. In this work, the effective target mass (CBN-28) was estimated as the mass of a unit cell divided by the number of atoms in this cell, i.e. $m_{\mathrm{CBN}} = 43.54$ amu. As the surface binding energy of CBN is unknown, the value of U_s was extracted from the experimental curve of the Ar sputtering of CBN, as CBN etching with argon has no chemistry involved. The value found is $U_s \approx 6$ eV, which is close to similar materials such as STO [21].

Fig. 1 shows the positive ion composition measured between the ICP source and the table in the case of an SF_6-Ar plasma with different SF_6 fractions. It shows that the plasma contains several kinds of ions, the most important being Ar^+ and S^+ as previously observed by Goyette et al. [22]. It is noteworthy that ions containing fluorine atoms become dominant only for gas mixture with SF_6 fraction exceeding 70%. We further note the presence of SFO^+, SF_2^+ and SF^+ and a low density of F^+ ions (the presence of SFO^+ ions can be attributed to the interaction between the plasma and the quartz clamp used to maintain the samples or interaction with the ICP reactor chamber walls that comprises an alumina tube). Fig. 1 also shows that heavy ions coming from the decomposition of SF_6 such as SF_3^+ or SF_5^+ represent less than 10% of the positive ions.

Knowing all the parameters of the model, the theoretical sputtering yield *Y* of CBN was calculated for each plasma composition (pure Ar, Cl_2 and SF_6-Ar) as a function of the incident ion energy.