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Etch damage evaluation on $(Bi_{4-x}La_x)Ti_3O_{12}$ thin films during the etch process using inductively coupled plasma sources

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Abstract

The etching mechanism of $(Bi_{4-x}La_x)Ti_3O_{12}$ (BLT) thin films in Ar/Cl_2 inductively coupled plasma (ICP) and plasma-induced damages at the etched surfaces were investigated as a function of gas-mixing ratios. The maximum etch rate of BLT thin films was 50.8 nm/min of 80% Ar/20% Cl_2. From various experimental data, amorphous phases on the etched surface existed on both chemically and physically etched films, but the amorphous phase was thicker after the 80% Ar/20% Cl_2 process. Moreover, crystalline "breaking" appeared during the etching in Cl_2-containing plasma. Also the remnant polarization and fatigue resistances decreased more for the 80% Ar/20% Cl_2 etch than for pure Ar plasma etch.

Keywords: $Bi_{4-x}La_xTi_3O_{12}$; Ar/Cl_2 plasma; Etch damage; QMS

1. Introduction

During the last decade, high-permittivity dielectrics have been intensively studied for ferroelectric random access memories (FRAMs) applications due to such properties as low operating voltage, fast switching speed and non-volatility [1,2]. Among the variety of ferroelectric thin films exhibiting the above advantages, $Bi_{4-x}La_xTi_3O_{12}$ (BLT) thin films attracted a significant attention because of their low processing temperature (650°C) and medium remnant polarization, as compared to $Pb(Zr_xTi_{1-x})O_3$ and $SrBi_2Ta_2O_9$ films [1,3,4]. Therefore, the development of anisotropic and non-destructive etching process for BLT thin films is an important task aimed at obtaining a small feature size as well as an accurate pattern transfer.

There is a broad experience gathered by many research groups using a variety of reactive halogen-containing plasmas to etch ferroelectric thin films, including the BLT films. Among them, the Ar/Cl_2 mixture occupies a leading place because of the following advantages. First, this system has a rather simple plasma chemistry that allows one to predict and explain the etch results. Also, the higher volatility of the most of metal chlorides compared with metal fluorides provide higher etch rates under the same operating conditions. Second, the use of Ar/Cl_2 mixture provides a flexible adjustment of chemical and physical mechanisms of the etch process, including the non-monotonic etch rate dependence on the gas mixing ratio mentioned by several researches (see, for example, Refs. [5–7]). However, from the literature data, it follows that the etch behavior of the BLT thin films has not yet

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been well studied. Particularly, this relates to the BLT etch mechanism in the Ar/Cl_2 plasma, and especially to the plasma-induced damage influencing the device characteristics. It is evident that for the given plasma system the plasma-induced damage can be caused not only by ion bombardment of the etched surface, but also by the surface contamination by the reaction products as well as by the charging between the Pt electrode and BLT thin film layer resulting from the negative potential of the substrate holder.

In this study, BLT thin films were etched using an inductively coupled plasma (ICP) system with different Ar/Cl_2 mixing ratios with the purpose of analyzing the etch mechanism and the etch damage. Plasma diagnostics were performed by a quadrupole mass spectrometer (QMS). Changes in the chemical state of the etched surface were analyzed with X-ray photoelectron spectroscopy (XPS). Physical damage was evaluated by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Polarization–electric field (P–E) curves and fatigue were measured to characterize the variations in the ferroelectric properties.

2. Experimental

BLT thin films were prepared on Pt by metal organic deposition (MOD). BLT thin films were synthesized according to the formula $Bi_{4-x}La_xTi_3O_{12}$ ($x = 0.75$), the synthesis procedure is explained in detail in Ref. [8]. The films were deposited on the substrate by a spinner operated at 4000 rpm for 30 s and subsequently dried on a hot plate at 400 °C for 10 min to remove organic contaminations. The pre-baked film was annealed at 650 °C for 1 h under an oxygen atmosphere for crystallization. BLT films obtained in this way have thickness of about 200 nm.

Experiments were carried out in a planar ICP reactor. The reactor chamber was made of stainless steel and had a shape of cylinder with an inner radius of 15 cm. On the top of the chamber, a 24-mm-thick horizontal quartz window separated the working zone and a 4-turn copper coil that was connected to rf (13.56 MHz) power supply. On the bottom of the chamber, the electrode used as the substrate holder was located. The bottom electrode was made from the anodized Al and was connected to another 13.56 MHz rf generator to control the dc bias voltage. The axial size of the working zone, i.e. the distance between the quartz window and the bottom electrode, was equal to 14 cm. The experiments were carried out under the following fixed input parameters: total gas pressure of 15 mTorr, total gas flow rate of 20 sccm, ICP power of 700 W, and dc bias voltage of −200 V. Only the Ar/Cl_2 mixing ratio was varied.

During QMS (EQP 510, Hiden Analytical Ltd) measurements, the sampling tip with an orifice of 250 μm in diameter was set through the view port on the sidewall of the reactor chamber. The chemical state of the etched BLT thin films was investigated with using XPS (VG-Scientific ESCALAB 250) spectrometer. In this measurements, the X-ray power was 220 W at 11.1 mA; using the pass energy of 25 eV, the spectral resolution of 0.45 eV was obtained. The spectrometer energy scale was calibrated to the C 1s core level line at 285.0 eV. The incident angle between the X-ray beam and the tested sample was 0°. The cross-sectional microstructure of the BLT films was examined with TEM. P–E hysteresis curves and fatigue were measured with a precision workstation ferroelectric tester (Radiant Technology, USA).

3. Results and discussion

Fig. 1 shows the etch rates of the BLT film as a function of $Ar/(Ar+Cl_2)$ mixing ratios. It can be seen that the pure Ar plasma provides a somewhat faster etching compared with the pure Cl_2 plasma, with the corresponding etch rates equal to 23 and 20.5 nm/min. Primarily, this fact allows one to make a conclusion about the dominating physical pathway in the BLT etch process. Such a conclusion becomes more justified after the analysis of the

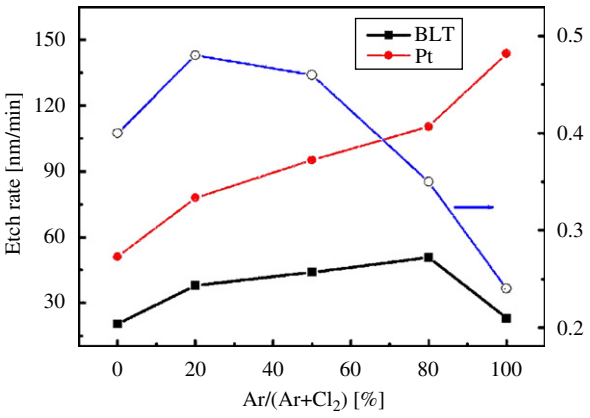

Fig. 1. Etch rate of BLT and Pt as a function of gas-mixing ratio and etch selectivity.