



## Reactive ion etching of ferroelectric SrBi<sub>2</sub>Ta<sub>x</sub>Nb<sub>2-x</sub>O<sub>9</sub> thin films

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# Reactive ion etching of ferroelectric $\text{SrBi}_2\text{Ta}_x\text{Nb}_{2-x}\text{O}_9$ thin films

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Ferroelectric  $\text{SrBi}_2\text{Ta}_x\text{Nb}_{2-x}\text{O}_9$  thin films were patterned using reactive ion etching. Considering the environmental impact effect,  $\text{CHClFCF}_3$ , a special etching gas, known to be less environmentally hazardous compared to the other hydrofluorocarbons, was employed in this study. The etch rates as a function of etching parameters were investigated. An etch rate of 20 nm/min was obtained. Surface compositional change during etching was monitored by x-ray photoelectron spectroscopy. Surface residues were removed by a postetching cleaning process. © 1996 American Institute of Physics. [S0003-6951(96)01504-8]

Recently, there has been increasing interest in ferroelectric thin films for semiconductor nonvolatile random access memory applications (FRAM).<sup>1,2</sup> Using ferroelectric thin film capacitors, FRAMs display fast switching speed, low operating voltage (<5 V), wide operating temperature range, and high radiation hardness. Furthermore, the manufacturing processes for ferroelectric thin films, electrodes, and passivation layers are quite compatible with existing silicon very large scale integrated (VLSI) processing. FRAMs are expected eventually to replace static random access memory (SRAMs) in the cache memory, dynamic random access memory (DRAMs) in the main system memory, and magnetic hard disk drive. Currently,  $\text{Pb}(\text{Zr,Ti})\text{O}_3$  (PZT) is considered to be the primary candidate ferroelectric material for this application as a result of its excellent ferroelectric properties and high Curie temperature.<sup>1-3</sup> However, its commercial usage has been hindered by serious degradation problems such as fatigue, imprint, and leakage current which limit the lifetime of these devices.<sup>4-8</sup> Research is being conducted to improve the longevity by doping La or Nb donors into the PZT films and by using conductive electrodes such as Y-Ba-Cu-O,  $\text{RuO}_2$ , La-Sr-Co-O, etc., instead of platinum.<sup>8-10</sup> An alternate approach is to find new ferroelectric materials which do not have the degradation problems.

Recently, it has been found that ferroelectric Bi-layered structure oxides such as  $\text{SrBi}_2(\text{Ta}_x\text{Nb}_{2-x})\text{O}_9$  thin films are very promising for degradation-free FRAM application on Pt electrodes.<sup>11-13</sup> We have manufactured these films by metalorganic deposition (MOD) and pulsed laser ablation (PLD) on a platinum substrate.<sup>12,13</sup> These ferroelectric capacitors show very good hysteresis characteristics with a remnant polarization value of 11  $\mu\text{C}/\text{cm}^2$  and no fatigue up to  $10^{11}$  switching cycles.

Patterning the  $\text{SrBi}_2(\text{Ta}_x\text{Nb}_{2-x})\text{O}_9$  films is another important issue in the integration of the films into a RAM cell. Reactive ion etching (RIE) has been chosen for patterning the  $\text{SrBi}_2(\text{Ta}_x\text{Nb}_{2-x})\text{O}_9$  films because it exhibits superior directional etching, critical dimension control, and compatibility with the other dry processes such as chemical vapor deposition (CVD), sputtering, molecular beam epitaxy (MBE), etc., than wet chemical and ion beam etching. To select reactive gases several factors should be considered; the reac-

tivity of the reactive species with the films, the volatility of possible etch products, and finally the environmental impact of the gases.  $\text{CHClFCF}_3$  (DuPont trade name HCFC-124) was selected for this particular study, because it has been proven effective for complex metal oxides etching and is known to be less environmentally hazardous compared to the other hydrofluorocarbons.<sup>14</sup>

In this letter, the preliminary experimental results on reactive etching of  $\text{SrBi}_2\text{Ta}_2\text{O}_9$  and  $\text{SrBi}_2\text{Nb}_2\text{O}_9$  are presented. The dependence of etch rates on chamber pressure and rf power are presented. The surface compositional change during etching is monitored through x-ray photoelectron spectroscopy (XPS) analysis.

A SAMCO RIE-1C compact reactive ion etcher, with an electrode separation of 5 cm and a cathode area of 127  $\text{cm}^2$ , was used for this work. The cathode and the etching samples are water cooled during the etching process.  $\text{SrBi}_2\text{Ta}_2\text{O}_9$  and  $\text{SrBi}_2\text{Nb}_2\text{O}_9$  samples, 350 nm in thickness, were prepared by MOD, precursors were spin coated onto 5.1 in. Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/Si substrates, followed by a firing process to form the proper crystal structure. Details of the procedure appear elsewhere.<sup>11,13</sup> Changes in film thickness due to etching were measured by variable angle spectroscopic ellipsometry (VASE). The etch rates, defined as change in thickness divided by etch time, were recorded as a function of process controllable parameters, chamber pressure, and rf power. Surface composition analysis was carried out using a Kratos x-ray photoelectron spectrometer with a  $\text{MgK}\alpha$  x-ray source. Gold 4f peaks were used to calibrate the binding energies.

Figure 1 shows the etch rates of  $\text{SrBi}_2\text{Ta}_2\text{O}_9$  and  $\text{SrBi}_2\text{Nb}_2\text{O}_9$  films as a function of reactive gas pressure at a fixed rf power of 150 W. In general, the etch rates of both films decrease with increasing gas pressure. For a parallel plate reactor, increasing the discharge pressure will cause the decreasing of sheath potential across the cathode<sup>15,16</sup> which thereby reduces the kinetic energy of the bombarding ions. Liu *et al.*<sup>17</sup> studied the dc self-bias (sheath) potential effect on etching rates in a parallel plate reactor. They found that etching rates were related to the self-bias potential in the following format:

$$\text{ER} = \nu Z(V_{\text{sb}})[\text{RS}] \exp(-E_a/RT_s),$$

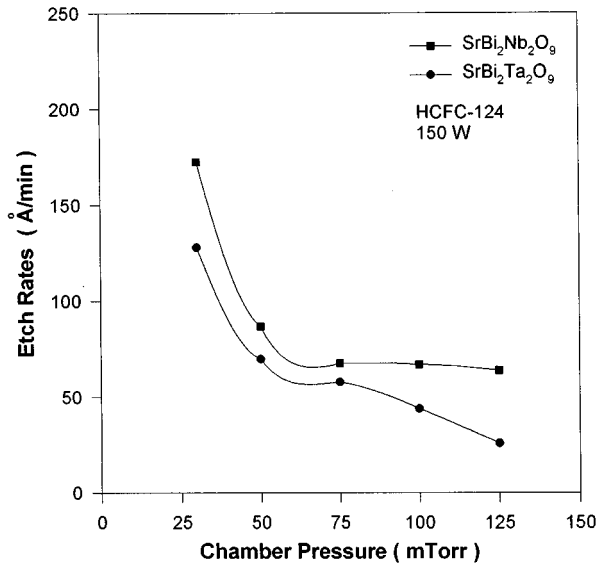


FIG. 1. The etch rates of SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> and SrBi<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub> films as a function of chamber pressure at a fixed rf power of 150 W.

$$Z = 1 + \sigma V_{sb}, \quad \sigma > 0,$$

where  $\nu$  is a term that represents the effective rate of transport of reactive species (RS) to the wafer surface;  $Z(V_{sb})$  is a dc self-bias factor that deals with the effect of the self-bias potential on the etching reaction rate;  $[RS]$  represents the concentration of reactive species at the wafer surface;  $E_a$  is the activation energy for the reaction,  $R$  is the gas constant, and  $T_s$  is the substrate temperature. Obviously, the etching rates will decrease with decreasing self-bias potential  $V_{sb}$ . Additionally, the increase in the gas pressure reduces the mean-free path of the reactive species and further reduces their concentration at the film surface. Figure 1 also indicates that the etch rate of SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> films is lower than that of SrBi<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub> films. This may be correlated to the lower melting and boiling points of niobium halides than corresponding tantalum compounds.<sup>17</sup> From these results, it is reasonable to expect that the etch rate of solid solution SrBi<sub>2</sub>(Ta<sub>x</sub>Nb<sub>2-x</sub>)O<sub>9</sub> films would lie between the rates of SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> and SrBi<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub>.

The effect of rf power on the etch rates of SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> and SrBi<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub> films at 30 mTorr is shown in Fig. 2. Etch rates increased, in general, with increasing power density for both films. It should be noted that the sheath voltage of the cathode and discharge current increase with increasing rf power so that both physical and chemical etching effects become enhanced.

Figures 3 and 4 show typical XPS surface survey scans of SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> and SrBi<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub> specimens before and after partial etching at 30 mTorr chamber pressure, using 150 W rf power. The increase of strontium atomic concentration on the etched surface was observed for both types of specimens. It indicates that the removal of strontium oxides may be the limiting factor for RIE of SBT and SBN films. The surface residue of strontium was also detected by XPS on the surface of completely etched specimens [Fig. 5(a)], which is ex-

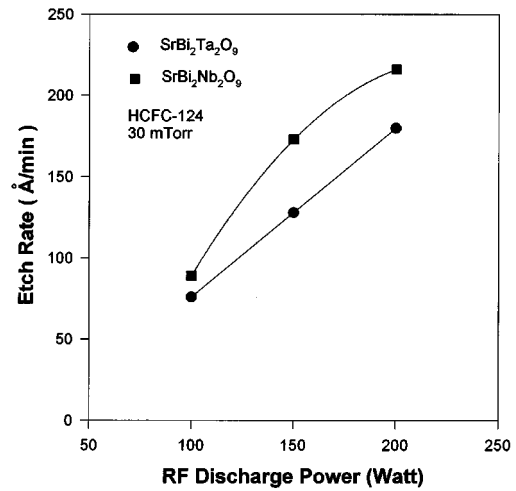


FIG. 2. The etch rates of SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> and SrBi<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub> films vary with rf discharge power at 30 mTorr chamber pressure.

pected based on the relatively high melting and boiling points of strontium halides.<sup>18</sup> However, the surface residues can be easily removed by a postcleaning process.<sup>19</sup> The evidence of which is also showed in Fig. 5(b).

Furthermore, a reduction of the oxidation state<sup>20,21</sup> from bismuth oxide to bismuth metal has occurred during RIE, which is shown in Fig. 6. Although this should not be a problem for completely etched ferroelectric capacitors, it indicates that sidewall compositional damage to a ferroelectric capacitor may happen during RIE. Additional work must be done in order to find out whether there is a reduction on the sidewall during RIE and, more importantly, what are the con-

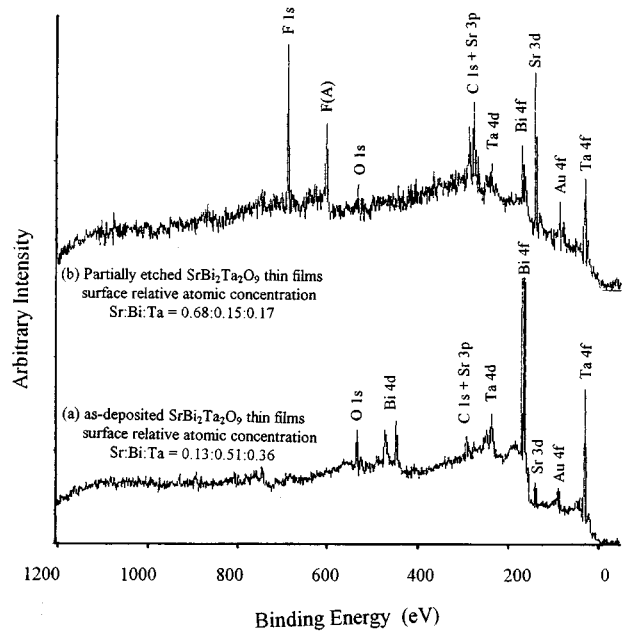


FIG. 3. XPS surface scans and surface relative atomic concentration of a SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> specimen (a) as-deposited films; (b) etched in CHCl<sub>3</sub> with 150 W and 30 mTorr for 5 min.

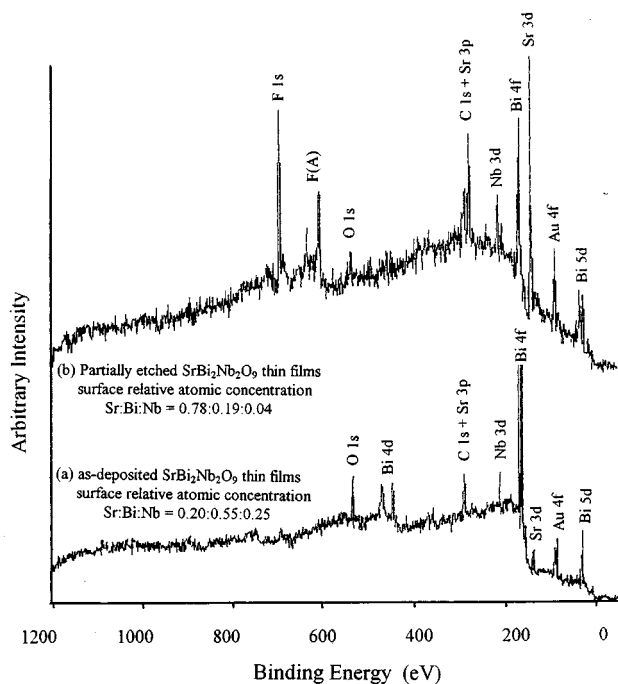


FIG. 4. XPS surface survey scans and surface relative atomic concentration of a  $\text{SrBi}_2\text{Nb}_2\text{O}_9$  specimen, (a) as-deposited films, (b) etched in  $\text{CHClFCF}_3$  with 150 W and 30 mTorr for 5 min.

sequent effects of this damage on electric properties after etching.<sup>22</sup>

The etching characteristics of SBT and SBN films were also studied using  $\text{SF}_6$  as etching gas. The etch rates of SBN films were 130 Å/min in  $\text{SF}_6$  compared to 173 Å/min in HCFC-124 at the same chamber pressure of 30 mTorr and rf power of 150 W. Whereas the etch rates for SBT films were about the same, 120 Å/min in  $\text{SF}_6$  compared to 130 Å/min in HCFC-124. In addition,  $\text{SF}_6$  discharge leaves a large amount of fluorine residues on the etched sample surface compared to HCFC-124 discharge.

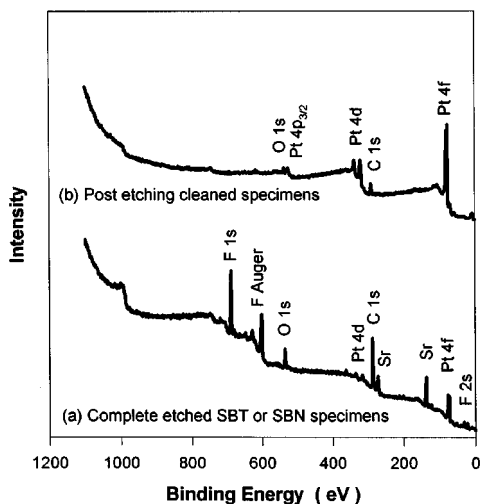


FIG. 5. XPS surface survey scans on (a) completely etched specimens, surface residue of strontium is detected and (b) postetching cleaned specimens.

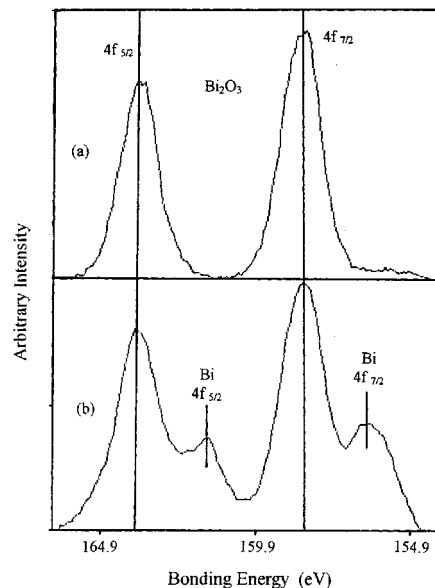


FIG. 6. Reduction effects of  $\text{Bi}_2\text{O}_3$  to  $(\text{Bi}:\text{Bi}_2\text{O}_3=0.45)$  upon reactive ion etching.

In summary, the layered structure  $\text{SrBi}_2(\text{Ta}_x\text{Nb}_{2-x})\text{O}_9$  ferroelectric films were successfully etched with  $\text{CHClFCF}_3$  as a reactive gas. The dependence of etch rates on etching conditions, rf power, and gas pressure were investigated. Surface compositional change as well as reduction effects upon etching were observed. Surface residues after etching were removed by postetching cleaning solution.

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