Dependence of the sputter-etching characteristics of strontium–titanate–oxide thin films on their structural properties

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Sputter-etching characteristics of polycrystalline strontium–titanate–oxide (STO) thin films are investigated using a high-density argon plasma. STO thin films were grown by means of a reactive pulsed-laser deposition technique in which the buffer oxygen pressure was varied to change the structural properties of the films. The sputter-etch rate of the rf-biased films is found to linearly increase with the oxygen deposition pressure. This result is shown to be related to the corresponding decrease of the film density. This dependence of the etch rate on the structural properties of the films has very important consequences on etching studies and on the optimization of etching processes.
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The control of the etch rate is one of the critical issues related to the patterning of functional thin films relevant for applications in photonics and telecommunications. This etch rate is known to be strongly influenced by the plasma environment (reactive neutral and ion density, ion energy, etc.). For this reason, most studies reported in the literature are devoted to the influence of the plasma parameters on the etch rate in a more or less exhaustive manner. However, in addition to the plasma parameters, it is expected that the film properties somewhat impact the etching characteristics. Even though the crystalline orientation of single-element solids is known to influence sputtering,[1] the role of the film structural properties on the etching characteristics was never explicitly addressed in the literature. To examine this question, we investigate the structural dependence of the sputter-etching characteristics of strontium–titanate–oxide (STO) thin films, using a parametric approach. This material is characterized by high transparency in the visible and infrared regions and specific electro-optic properties that make it suitable for integration into photonic devices.

Polycrystalline STO layers were grown on (100) silicon substrates by means of a reactive pulsed-laser-deposition technique, using a KrF excimer laser (wavelength: 248 nm).[2] Ablation was achieved by focusing the laser beam (energy density of 1.5 J/cm^2 and repetition rate of 50 Hz) on a rotating $SrTiO_3$ target. The structural properties of the films can be tuned by varying the deposition conditions, for example substrate temperature and oxygen buffer gas pressure.[3–6] Throughout this work, the substrate temperature was kept constant at 540 °C while the O_2 pressure was varied from 1 to 100 mTorr. Dry etching of the STO layers was subsequently performed using a magnetized high-density argon plasma sustained by a traveling electromagnetic surface wave.[7–9] The absorbed power (i.e., incident minus reflected power), the magnetic field intensity and the argon pressure were set to 400 W, 600 G, and 1 mTorr, respectively. The substrate holder was rf biased using a 13.56 MHz source with a power of 40 W. In such experimental conditions, considering both the dc bias voltage and the sheath potential, the energy of the ions impinging onto the substrate is about 115 eV. The sputter-etch rate of the bare STO layer was determined from He–Ne laser interferometry ($\lambda = 632.8$ nm),[8,10] using the STO refraction index values measured by variable angle spectroscopic ellipsometry.[6] For $\lambda = 632.8$ nm, the refraction index of the layers was found to vary between 2.4 at 1 mTorr and 1.8 at 100 mTorr.

Figure 1 shows the STO sputter-etch rate as a function of the oxygen pressure used during STO deposition. The etch rate is seen to increase linearly with O_2 pressure, which clearly indicates some dependence on the film properties. To understand this result, we recall that the sputter-etch rate (ER) of plasma-immersed substrates is[7,11]

$$\mathrm{ER} = (1 - RR) J_+ Y / N_t, \tag{1}$$

where *RR* is the redeposition factor resulting from collisions between sputtered species and plasma particles in the sheath,

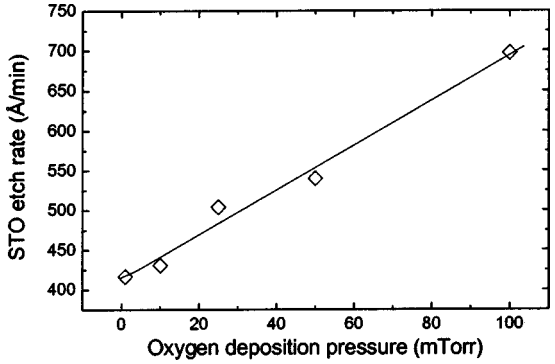

FIG. 1. STO sputter-etch rate as a function of the oxygen deposition pressure.

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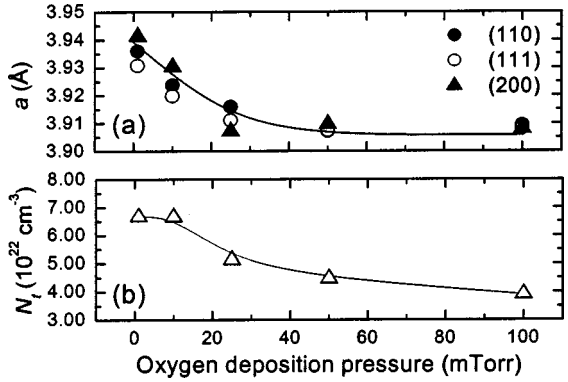

FIG. 2. Lattice constant a (a) and film density N_t (b) of STO thin films as a function of the oxygen deposition pressure.

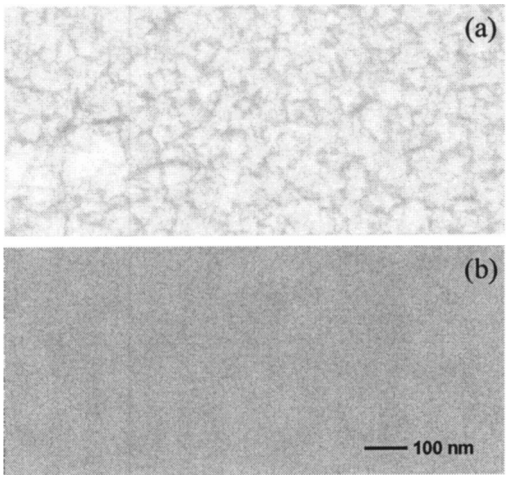

FIG. 3. Scanning electron microscopy images of STO thin films at two different oxygen deposition pressure: (a) 100 mTorr; (b) 10 mTorr. The scale is 100 nm for both images.

J_+ the positive ion flux impinging onto the substrate, Y the sputtering yield (i.e., the number of atoms ejected per incident ion), and N_t the atomic density of the film. For given plasma conditions, J_+ and RR are constants. As a consequence, the only film-dependent variables in Eq. (1) are Y and N_t.

The dependence of Y and N_t on the deposition conditions was analyzed by examining STO structural properties by means of various characterization techniques, including scanning electron microscopy (SEM), x-ray diffraction spectrometry, and Rutherford backscattering spectroscopy (RBS). The lattice parameter a was calculated from the (110), (111), and (200) x-ray diffraction peaks, using Bragg's law. The samples were additionally analyzed by RBS using a 2800 keV $^4He^{++}$ ion beam at normal incidence. We have obtained the surface atomic density of the films from the RBS spectra by using RUMP simulations.[12,13] The atomic density was subsequently calculated by dividing this surface atomic density by the sample thickness measured by cross-sectional SEM. The films used in the present work have a typical thickness varying from 350 to 550 nm.

Figure 2 shows the influence of the oxygen deposition pressure on the lattice parameter [Fig. 2(a)] and on the film density [Fig. 2(b)]. Both a and N_t increase with decreasing pressure. The increase of a at lower O_2 pressure results from the presence of oxygen vacancies in the crystal lattice.[4,6] Therefore, at lower pressure, less atoms are distributed in a larger lattice volume. *A priori*, this could suggest a decrease of the film atom density with decreasing pressure. However, the RBS results [Fig. 2(b)] clearly show that N_t increases. This apparent contradiction can be resolved considering that when the pressure increases, the films contain more voids between crystallites, resulting in a larger free volume (or micopore). This is supported by SEM observations (see Fig. 3) that show a larger concentration of grain boundaries at higher deposition pressure. A similar observation was reported by other authors in the case of tin oxide thin films grown by pulsed-laser deposition.[14] The observation of Figs. 2(b) and 3 thus clearly indicates that it is the free volume between the crystallites rather than the lattice expansion that controls the pressure dependence of N_t. Note that the measured film density remains lower than that of the bulk $SrTiO_3$ target ($N_t = 8.4\times10^{22}$ cm^{-3}) while approaching it at lower O_2 pressure.

The dependence of the STO sputter-etch rate on the film density is illustrated in Fig. 4 where ER is plotted as a function of $1/N_t$. The experimental data can be well fitted using a linear regression. According to Eq. (1), this indicates that Y is not influenced by the deposition conditions, i.e., by the film structural properties. To confirm this result, sputtering yield values were estimated from the experimental etch rate data using Eq. (1). The positive ion flux J_+ was measured using the positive ion saturation current of a cylindrical Langmuir probe placed near the substrate. Here, we found $J_+ \approx 5.9\times10^{16}$ cm^{-2} s^{-1}. Because of the very low argon pressure employed in our etching experiments, the redeposition effects can be neglected, i.e., $RR \approx 0$.[7] The corresponding Y values are presented in Fig. 5 as a function of the oxygen pressure used during STO deposition. The observed Y values are similar to the pure Ti sputtering yield under comparable conditions.[15] Figure 5 also shows that Y is independent of the O_2 pressure, thereby confirming that for polycrystalline STO films, Y is not influenced by the film properties.

The complexity of the film structure together with the complicated behavior of the sputtering yield for multicomponent structures make difficult to quantitatively support the observed independence of Y on the film structural properties. Moreover, sputtering yield models are not well documented for the low range of ion energies employed in our experiments. In order to achieve some qualitative understanding of our observations, recall that the generally accepted Sig-

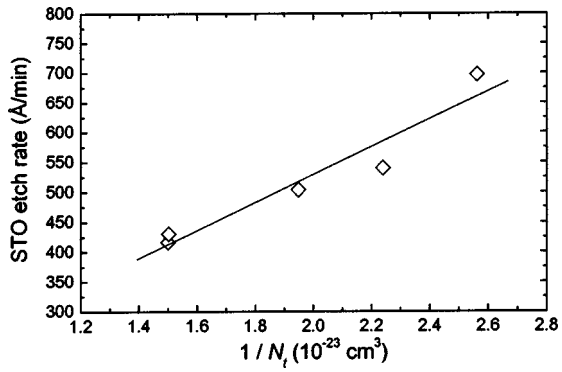

FIG. 4. STO sputter-etch rate as a function of the inverse of the film density.

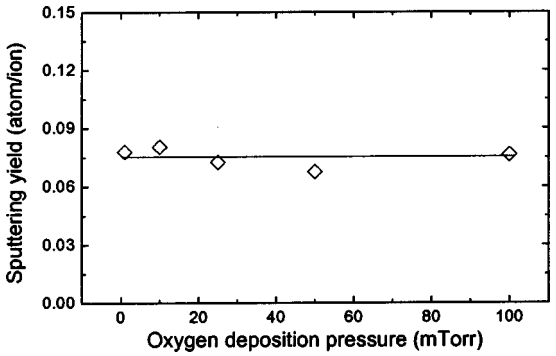

FIG. 5. STO sputtering yield as a function of the oxygen deposition pressure.

mund's model for physical sputtering predicts that Y varies inversely to the surface binding energy.[16] According to Hiratani *et al.*,[4] the lattice expansion observed at lower O_2 pressure is a consequence of an increase of the bond distance between atoms. We believe that this should result in lower surface binding energies between Sr, Ti, and O atoms. Thus, the results displayed in Fig. 5 clearly indicate that such variations in surface binding energies are not significant for the sputter-etching process of polycrystalline STO films.

In summary, we have examined the influence of the film structural properties on the sputter-etching characteristics of pulsed-laser-deposited STO thin films. Our results demonstrate that the film density is a crucial factor governing the etch rate. This has very important consequences on etching studies. For example, to identify an optimized process for a given material, one should be very careful in comparing the optimized etching conditions achieved by various authors, since the characteristics of the etched thin films is likely to differ from one author to the other. Finally, note that the conclusions reached in this letter are expected to be applicable to other thin films, especially those having complex compositions. They should also remain valid for chemically assisted etching processes, provided ion bombardment plays a significant role.

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[1] H. E. Roosendaal, in *Sputtering by Particle Bombardment I: Physical Sputtering of Element Solids*, Topics in Applied Physics Vol. 47, edited by R. Behrisch (Springer, Berlin, 1981), pp. 219–260.
[2] M. A. El Khakani, M. Chaker, and E. Gat, Appl. Phys. Lett. **69**, 2027 (1996).
[3] M. H. Yeh, K. S. Liu, and I. N. Lin, Jpn. J. Appl. Phys., Part 1 **34**, 2447 (1995).
[4] M. Hiratani, K. Imagawa, and K. Takagi, Jpn. J. Appl. Phys., Part 1 **34**, 254 (1995).
[5] F. Sanchez, M. Varela, X. Queralt, R. Aguiar, and J. L. Morenza, Appl. Phys. Lett. **61**, 2228 (1992).
[6] L. Stafford, M. Gaidi, M. Chaker, O. Langlois, J. Margot, and M. Kulishov, 50th International Symposium of the American Vacuum Society, November 2003, Baltimore, MD, J. Vac. Sci. Technol. A **21**, A23 (2003); M. Gaidi, A. Amassian, L. Stafford, M. Chaker, J. Margot, L. Martinu, and M. Kulishov (unpublished).
[7] S. Delprat, M. Chaker, and J. Margot, J. Appl. Phys. **89**, 29 (2001).
[8] L. Stafford, J. Margot, S. Delprat, M. Chaker, and D. Queney, J. Vac. Sci. Technol. A **20**, 530 (2002).
[9] J. Margot, F. Vidal, M. Chaker, T. W. Johnston, A. Aliouchouche, M. Tabbal, S. Delprat, O. Pauna, and D. Benhabid, Plasma Sources Sci. Technol. **10**, 556 (2001).
[10] L. Stafford, J. Margot, O. Langlois, and M. Chaker, J. Vac. Sci. Technol. A **21**, 1247 (2003).
[11] M. Lieberman and A. Lichtenberg, *Principles of Plasma Discharge and Materials Processing* (Wiley, New York, 1994), Chap. 10.
[12] L. R. Doolittle, Nucl. Instrum. Methods Phys. Res. B **15**, 227 (1986).
[13] K. C. Park, K. B. Kim, I. J. M. M. Raaijmakers, and K. Ngan, J. Appl. Phys. **80**, 5674 (1996).
[14] R. Dolbec, M. A. El Khakani, A. M. Serventi, M. Trudeau, and R. G. Saint-Jacques, Thin Solid Films **419**, 230 (2002).
[15] H. Oechsner, Z. Phys. **261**, 37 (1973).
[16] P. Sigmund, Phys. Rev. **184**, 383 (1969).