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Nanoscale structuring of $SrRuO_3$ thin film surfaces by scanning tunneling microscopy

C.C. You [a,*], N.V. Rystad [b], A. Borg [b], T. Tybell [a]

[a] Department of Electronics and Telecommunications, Norwegian University of Science and Technology, 7491 Trondheim, Norway
[b] Department of Physics, Norwegian University of Science and Technology, 7491 Trondheim, Norway

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Abstract

Surface modifications through line etching of $SrRuO_3$ thin films have been carried out using a scanning tunneling microscope under ambient conditions. The line etching is found to be dependent on both bias voltage and scan speed for a given number of scan repetitions. We observe that an applied voltage above a threshold value is required for successful line etching. The depth of the etched lines is increasing with increasing bias voltage and scan repetitions as well as with decreasing scan speed. Moreover, sub-50 nm laterally confined mesa structures could be reproducibly etched on the $SrRuO_3$ thin film surfaces.

Keywords: Nanostructuring; Scanning tunneling microscopy; Sputtering; $SrRuO_3$

1. Introduction

Functional oxide materials possess interesting electronic and mechanical properties for nanoelectronic applications [1]. As the material dimensions are scaled down to the nanometer length scale, the physical properties are expected to be altered by the size reduction. In order to study and understand the size effects it is important to develop new nanostructuring methods. The downscaling can be achieved by employing conventional top-down techniques such as photo and electron beam lithography or novel bottom-up approaches. Alternative nanostructuring routes based on scanning probes offer an exciting possibility in the development of nanoscale-engineered templates for growth of epitaxial oxide nanostructures.

Scanning probes have been intensively used to obtain nanoscale surface modifications of a variety of materials, for example graphite [2,3], gold [4–7], silicon [8,9], and $YBa_2Cu_3O_7$ (YBCO) [10–12]. The dependence of surface modification on bias voltage and tunneling current has been investigated under various chemical environments in some of these experiments. For example, a fixed threshold voltage for surface modification was found when a graphite surface was covered with water [2], whereas no surface modification was observed in vacuum or dry gases [2,3]. Above a critical relative humidity, a nearly constant threshold voltage was observed for hole formation on gold [6]. For the hole formation on silicon, the threshold voltage was found to be dependent on the tunneling current [8], and the success rate of hole formation was increasing with decreasing tip-sample separation [9]. The ambient was also found to be important for surface modification of YBCO, investigations showed that water vapor and CO_2 are needed in order to achieve appreciable etching [11]. Based on these observations, several possible mechanisms have been proposed for the surface modifications in the various experiments, including mechanical contact [4,5], chemical reactions [2,6,11], field-induced evaporation [7–12], local heating [13], electromigration [14], and combinations of these.

In this paper, we report on scanning tunneling microscopy (STM) etching experiments carried out on metallic $SrRuO_3$ (SRO) thin films under ambient conditions. SRO is a chemically inert material well lattice-matched to most perovskites, which makes it an interesting material for the fabrication of nanoscale templates. We demonstrate the feasibility of using STM to etch the SRO film surface and to pattern nanoscale templates. Moreover, we present data on how bias voltage, tunneling current, and scan speed affect STM etching of SRO thin films.

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* Corresponding author. Tel.: +47 73 59 07 04; fax: +47 73 59 14 41.
E-mail address: chang.chuan.you@iet.ntnu.no (C.C. You).

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2. Experimental

Thin films of ∼ 500 Å (1 1 0)-oriented SRO were epitaxially grown on (0 0 1)-oriented $SrTiO_3$ (STO) substrates by off-axis radio frequency magnetron sputtering. The films were deposited in a mixed atmosphere of oxygen and argon ($O_2 : Ar = 4 : 10$) at a total pressure of 100 mTorr. The substrate temperature was varied between 750 and 850 °C. Atomic force microscopy (AFM) and STM topography measurements revealed a step and terrace structure consisting of 150–250 nm wide terraces, separated by steps with a height of one to two unit cells. The root-mean-square surface roughness at the terraces was found to be typically ∼ 1 Å. X-ray diffraction analysis revealed single-crystal thin film growth, and the rocking curves measured around the (1 1 0) reflection showed a mosaic spread of less than 0.1°.

The etching experiments were performed in a commercial STM system using mechanically cut Pt/Ir tips. The STM was operated in air and at room temperature. Constant current mode was employed for the investigation and the feedback loop was switched on for both etching and imaging. For normal imaging, a positive bias voltage of typically 500 mV and a tunneling current of 300 pA were used. The nanostructuring was achieved by controlling bias voltage, tunneling current and scan speed. The bias voltage was varied between 1.6 and 3.0 V, the scan speed between 100 and 1500 nm/s, and 50–200 scan repetitions were used. Prior to etching, the setpoint tunneling current was set to 40–60 pA with an imposed ac component with a frequency of 50 Hz and an amplitude of 30–65 pA as shown in Fig. 1. Since the feedback loop was on during etching, the imposed ac oscillation at the given setpoint tunneling currents results in a vertical displacement of the tip in the range of 1–2 nm. The ac component originates from the power line, and by carefully choosing the integral gain in the feedback loop and the setpoint tunneling current the ac component can be controlled. As can be seen in Fig. 1, the amplitude of the ac current oscillations is increasing with decreasing setpoint tunneling currents.

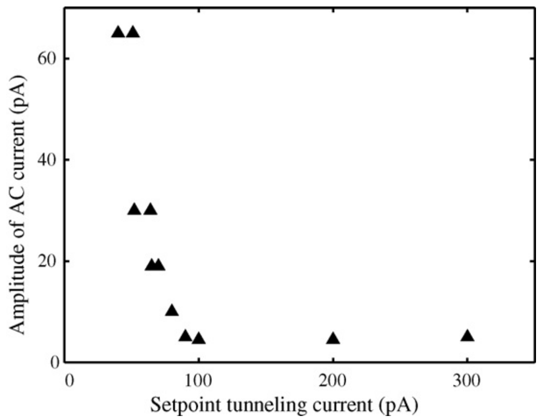

Fig. 1. The amplitude of ac current oscillations vs. setpoint tunneling current obtained at an integral gain of 0.5 and a bias voltage of 500 mV. The STM tip was positioned above a fixed point on the film surface during the measurements.

In order to perform line etching the STM tip was programmed to scan back and forth repeatedly over a preselected area. For the present experiments, eight lines were consecutively etched by moving the tip starting in the upper left and ending in the lower right corner of the selected area. The lines were approximately 100 nm long with a separation of 50 nm. The STM image in Fig. 2(a) displays a data set typical for the line etching experiments obtained at bias voltage 2.2 V, setpoint tunneling current 60 pA, scan speed 100 nm/s and 50 scan repetitions. As can be seen in Fig. 2, there is an evolution of the etching from line to line in the upper row. After three to four lines the etching process is more reproducible. This is illustrated by the shown surface profiles along line A (Fig. 2(b)) and line B (Fig. 2(c)). For this reason, only the four lower lines were used for data analysis of each data set.

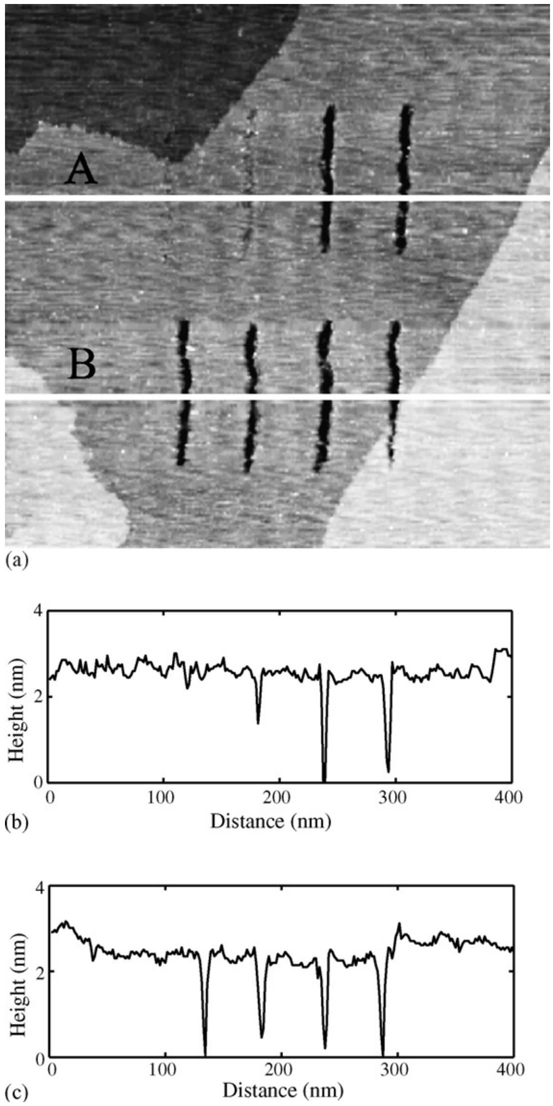

Fig. 2. (a) STM image (400 nm × 400 nm) of a typical data set for line etching experiments. Eight lines ∼ 100 nm long were consecutively etched on the SRO film surface using bias voltage of 2.2 V, setpoint tunneling current of 60 pA, scan speed of 100 nm/s and 50 scan repetitions. (b and c) The surface profiles along the marker lines A and B in (a), respectively.

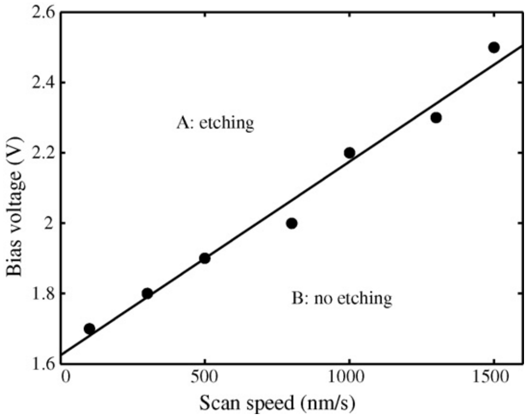

Fig. 3. The dependence of successful etching on bias voltage and scan speed when scanning each line 50 times. The points correspond to the threshold voltage at which etching occurs. The line is guide to the eye.

3. Results and discussion

Fig. 3 shows the dependence of successful etching on bias voltage and scan speed when scanning each line 50 times. Here we have defined the etching to be successful if the resulting line is continuous for at least 50 nm with a minimum average depth of half a unit cell. The points in Fig. 3 show the lowest voltage at which etching is observed for a given scan speed. For voltages below this value no etching is observed. The line through the data points thus indicates the division between combinations of applied voltage and scan speed where etching occurs (region A) and where etching does not occur (region B). Thus we find that the etching process requires a bias voltage larger than a threshold value, which depends on the scan speed of the STM tip. In contrast, no such threshold voltage could be established for line etching of SRO thin films under ultra-high-vacuum conditions using tungsten tips [15]. A threshold voltage has previously been observed for other systems [2,6,9]. However, this study shows that such threshold voltages in general may depend on scan speed. For the $SrRuO_3$ system, we note that the tip quality quickly deteriorates for bias voltages above 2.8 V by the formation of multiple tips or strongly altered tip shape.

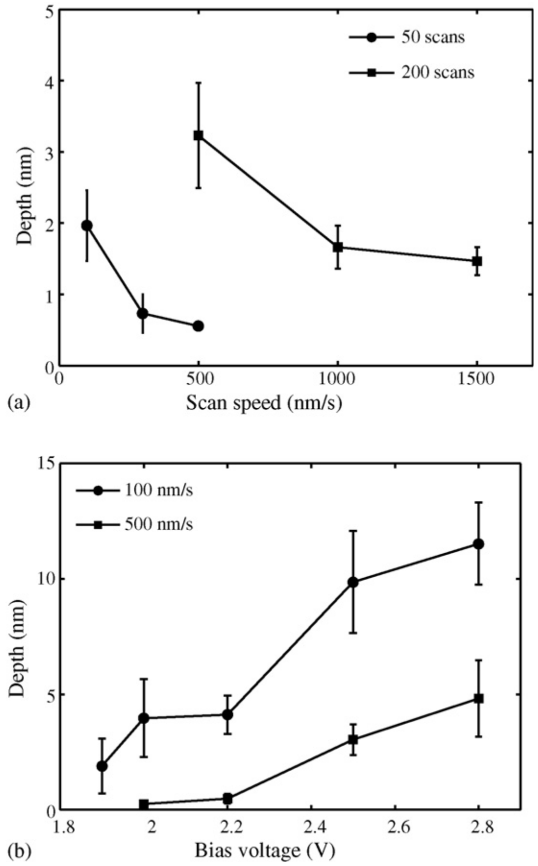

Fig. 4. (a) Depth vs. scan speed at a bias voltage of 2.2 V for 50 and 200 scan repetitions, respectively. The general trend is that the line depth decreases for increasing scan speed. (b) Depth vs. bias voltage using 50 scan repetitions for scan speeds of 100 and 500 nm/s, respectively. The data indicate that the line depth increases with increasing bias voltage. The error bars indicate the standard deviation. The lines are guides to the eye.

In Fig. 4(a), we plot the correlation between the depth of the etched lines and the scan speed for a bias voltage of 2.2 V. We find that an increase in scan speed results in an decrease in line depth for both 50 and 200 scan repetitions. Fig. 4(b) shows the dependence of depth on bias voltage using 50 scan repetitions for scan speeds of 100 and 500 nm/s, respectively. As can be seen, the line depth is increasing with increasing bias voltage. It should be pointed out that the discrepancy between the average depths in Fig. 4(a) and (b) for the identical set of etching parameters (i.e. bias voltage of 2.2 V, scan speed of 100 nm/s and 50 scan repetitions) could tentatively be attributed to the difference between tip shapes since different tips were used to obtain data shown in Fig. 4(b). We note that the depth of the etched lines varied using different tips even though the film surface quality and the etching parameters were not changed. Although the value of line depth varies with the tip quality, the trends indicated by Fig. 4(a) and (b) are consistent with each other. It is interesting to note that for a given bias voltage and number of scan repetitions, deeper line etching is obtained by reducing the scan speed, as shown in Fig. 4(b). This result implies that the etching process is a function of the total time that the STM tip spends above each point on the film surface. Since the surface modification of SRO was obtained at a high voltage and a low tunneling current, material removal by mechanical contact is not expected. Mechanisms responsible for the STM etching of SRO thin films that are consistent with our observations could be electric field induced evaporation [16] and chemical reactions, or a combination of these two mechanisms.

In general, upon etching we observed that the amount of residual material debris near the etched area is depending on the setpoint tunneling current. We note that by applying an ac component at small setpoint tunneling currents, hence large current oscillations as shown in Fig. 1, the material build-up is reduced as compared to large setpoint tunneling currents [17]. Remaining material debris could be removed by scanning the tip with a scan rate of 10 Hz over the etched area typically four times using normal imaging conditions. Fig. 2(a) shows an image obtained after using this procedure. No excess material accumulation near the etched area can be observed in the figure. We also note that topographic imaging using same the scan

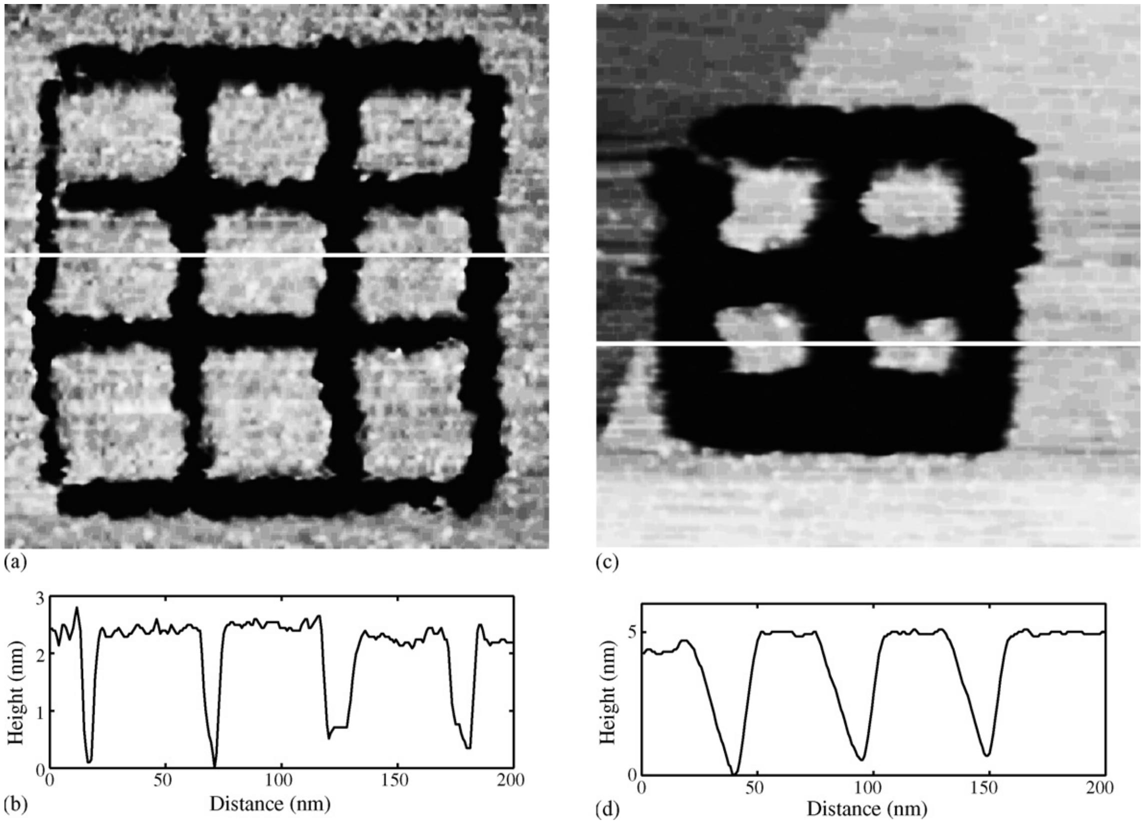

Fig. 5. (a) 3 × 3 array structure created by STM etching using bias voltage of 2.8 V, setpoint tunneling current of 40 pA, scan speed of 100 nm/s, and 7 scan repetitions. The surface profile (b) along the marker line in (a) shows that the average width and depth of the SRO mesas are 46 and 2.1 nm, respectively. (c) 2 × 2 array structure created by using bias voltage of 2.4 V, setpoint tunneling current of 60 pA, scan speed of 100 nm/s, and 20 scan repetitions. The average width and depth of the SRO mesas are 42 and 4.2 nm, respectively, as shown by the surface profile (d).

parameters prior and after the etching process showed no noticeable difference, hence indicating similar tip quality.

We have also examined the feasibility of using STM etching to fabricate nanoscale SRO templates. In order to pattern a template, the horizontal lines followed by the vertical lines were consecutively etched by moving the tip to the preselected area. Fig. 5(a) shows an 3 × 3 array structure created by STM etching using bias voltage of 2.8 V, setpoint tunneling current of 40 pA, scan speed of 100 nm/s, and 7 scan repetitions. The surface profile in Fig. 5(b) along the marker line in Fig. 5(a) shows that the average width and depth of the SRO mesas are 46 and 2.1 nm, respectively. Fig. 5(c) shows an 2 × 2 array structure created by applying a bias voltage of 2.4 V, setpoint tunneling current of 60 pA, scan speed of 100 nm/s, and 20 scan repetitions. The average width and depth of the SRO mesas are 42 and 4.2 nm, respectively, as shown by the surface profile in Fig. 5(d). It can be seen by comparing Fig. 5(b) and (d) that deeper grooves around the SRO mesas could be achieved by increasing the scan repetitions.

4. Conclusion

We have used a scanning tunneling microscope to modify the surface structure of SRO thin films. The line etching is found to be dependent on both bias voltage and scan speed when scanning each line 50 times. At a given scan speed, a threshold voltage has to be applied for successful etching. The depth of the etched lines is increasing with increasing bias voltage and scan repetitions as well as with decreasing scan speed. Moreover, it is demonstrated that templates of sub-50 nm lateral size could be reproducibly etched on SRO thin films.

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References

[1] C.H. Ahn, J.-M. Triscone, J. Mannhart, Nature 424 (2003) 1015.
[2] R.M. Penner, M.J. Heben, N.S. Lewis, C.F. Quate, Appl. Phys. Lett. 58 (1991) 1389.
[3] T.R. Albrecht, M.M. Dovek, M.D. Kirk, C.A. Lang, C.F. Quate, D.P.E. Smith, Appl. Phys. Lett. 55 (1989) 1727.
[4] C.X. Guo, D.J. Thomson, Ultramicroscopy 42–44 (1992) 1452.
[5] J.I. Pascual, J. Méndez, J. Gómez-Herrero, A.M. Baró, N. García, Phys. Rev. Lett. 71 (1993) 1852.

[6] C. Lebreton, Z.Z. Wang, J. Vac. Sci. Technol. B 14 (1996) 1356.
[7] C.S. Chang, W.B. Su, T.T. Tsong, Phys. Rev. Lett. 72 (1994) 574.
[8] A. Kobayashi, F. Grey, R.S. Williams, M. Aono, Science 259 (1993) 1724.
[9] I. Lyo, P. Avouris, Science 253 (1991) 173.
[10] I. Heyvaert, E. Osquiguil, C. Van Haesendonck, Y. Bruynseraede, Appl. Phys. Lett. 61 (1992) 111.
[11] G. Bertsche, W. Clauss, F.E. Prins, D.P. Kern, J. Vac. Sci. Technol. B 16 (1998) 2833.
[12] Y.C. Fan, A.G. Fitzgerald, J.A. Cairns, J. Vac. Sci. Technol. B 18 (2000) 2377.
[13] Y.Z. Li, L. Vazquez, R. Piner, R.P. Andres, R. Reifenberger, Appl. Phys. Lett. 54 (1989) 1424.
[14] M. Ohto, S. Yamaguchi, K. Tanaka, Jpn. J. Appl. Phys. 34 (1995) 694.
[15] Ø. Dahl, S. Hallsteinsen, J.K. Grepstad, A. Borg, T. Tybell, Mater. Res. Soc. Symp. Proc. 811 (2004) 445.
[16] T.T. Tsong, Atom-probe Field Ion Microscopy, Cambridge University Press, Cambridge, 1990.
[17] S. Hallsteinsen, Nanoscale lithography of $SrRuO_3$ using an STM, Master Thesis, NTNU, 2004.