

Relaxation of nanopatterns on Nb-doped SrTiO₃ surface

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By atomic force microscopy (AFM), we have realized nanolithography and changed the physical properties within a desired nanosized region on Nb-doped SrTiO₃ single-crystal substrate. Importantly, a considerable relaxation of these written patterns was observed directly, which evidently indicates that a significant chemical transport occurs during and after the AFM lithography. Furthermore, we found that defects introduced by Ar bombardment can stabilize these patterns, which is quite effective for the application of AFM lithography in perovskite oxides. © 2004 American Institute of Physics. [DOI: 10.1063/1.1699478]

Nanoscaled patterning of surfaces has received considerable attention due to its potential application in the miniaturization of electric devices. In 1990, Dagata *et al.*¹ oxidized hydrogen-passivated silicon surfaces using scanning tunneling microscopy. The oxide feature with 100 nm resolution can be used as an etching mask or an insulative barrier. Since then, scanning probe microscopy (SPM) lithography became a highly promising method for nanolithography and fabricating nanodevices. This technology has been used to create nanopatterns on metal (Ti, Al, Nb, and Cr,...)^{2–7} and semiconductor (Si, Si/SiGe, and InAs/AlSb heterostructures)^{8–16} surfaces. The mechanism of the SPM lithography mentioned above has been considered mainly based on a simple electrochemical oxidation induced by intense electric field or current.

In order to fabricate multifunctional nanodevices, the perovskite oxides dubbed an “inorganic chameleon” should be excellent candidate materials due to their rich physical properties such as ferroelectric, ferromagnetic (colossal magnetoresistive manganites), superconductor, and semiconductor. Undoubtedly, extending SPM lithography into perovskite oxides is very important especially for the realm of nanodevice. Investigations on SPM lithography in oxide materials focus mainly in high- T_C superconductor materials^{17–24} so far. Recently, Pellegrino *et al.*²⁵ performed nanolithography in oxygen-deficient SrTiO_{3– δ} film by atomic force microscopy (AFM). As described by those authors, the mechanism of the SPM lithography in perovskite oxides is more complicated and more difficult to understand. In this letter, we have performed the AFM lithography and changed electric properties within nanosized regions on 1% (atm ratio) Nb-doped SrTiO₃ (Sr(Ti,Nb)O₃) single-crystal surface. The stability of

written patterns was investigated by means of AFM and current–voltage (I – V) measurements *in situ*. Considerable relaxation of these written patterns was found, which offers important information for understanding the underlying mechanism of SPM lithography in perovskite oxides. Moreover, we found that defects introduced by Ar bombardment can depress the relaxation and stabilize the patterns, which is important for the application of SPM lithography in perovskite oxides.

AFM (JEOL JSPM-4200) mounted with W₂C or Pt-coated tip was used to perform AFM lithography on a Sr(Ti_{0.99}Nb_{0.01})O₃ single-crystal substrate. A 5×5×0.5 mm³ Sr(Ti,Nb)O₃ substrate was fixed on a copper sample stage by conductive paste. The AFM tip was grounded. The AFM lithography was performed by tapping or contact mode. After the AFM lithography, topologies were observed by AFM *in situ* with a tapping mode. The relative humidity was 16% during our experiments.

As shown in Fig. 1(a), by tapping mode, three lines were written on the atomically flat Sr(Ti,Nb)O₃ (100) surface with a Pt-coated tip under a sample bias of +4, +6, and +8 V, respectively (from left to right). The tip scanning speed was 2000 nm/s. Similar to that in metals or Si, the height of the patterns on Sr(Ti,Nb)O₃ surface decreases with decreasing sample bias. The threshold voltage is about 2 V, below which no patterns appear. Up to now, patterns with a width below 100 nm have been obtained. Under a negative sample bias, no patterns were obtained up to –10 V. It is proposed that AFM lithography causes an electrochemical reaction by scanning a biased probe close to the sample surface. Due to ambient humidity, a water meniscus is formed between the probe and the sample surface. An electrochemical cell is thus formed, and the sample surface is oxidized in case of semiconductor (such as Si) and metal (such as Ti, Al). From this analogy of SPM lithography, in order to assist this type of

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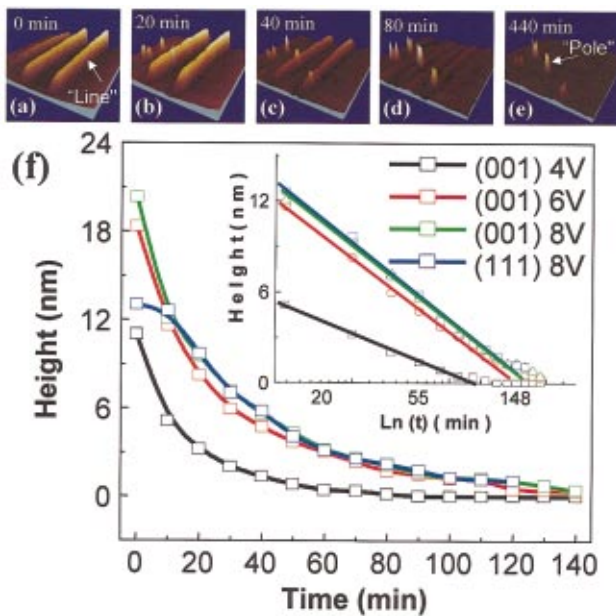


FIG. 1. (Color) (a)–(e) Topography of patterned Sr(Ti,Nb)O₃ (100) surfaces as a function of time after patterning; the scanning scale is 5×5 μm; (f) time dependence of line height on Sr(Ti,Nb)O₃ (100) and (111) surfaces, the inset shows the relationship between the line height and ln(time).

reaction, electrons should flow from tip to surface with the energy to cut chemical bonding (or to decompose materials).²⁷ Therefore, SPM nanolithography could be conducted only in positive sample biases over the threshold voltage.

Surprisingly, these nanopatterns on Sr(Ti,Nb)O₃ surface exhibit a significant relaxation after patterning. For example, as shown in Figs. 1(a)–1(e), the lines obtained under a sample bias of +4 V became smaller with time, and almost disappeared completely after 40 min except for several “poles” remained. After long enough time (440 min), the entire surface relaxed to an atomically flat surface except for several “poles” on some special spots. Figure 1(f) and its inset show the time evolution of line height on Sr(Ti,Nb)O₃ (100) and (111) surfaces. Though there is an obvious differ-

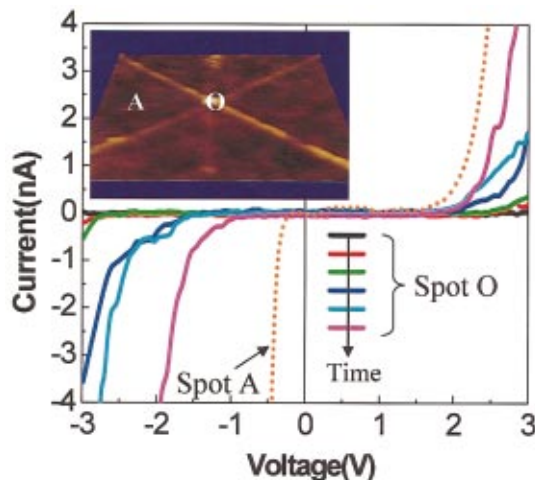


FIG. 2. (Color) The evolution of *I*–*V* characteristics of the patterned region on Sr(Ti,Nb)O₃ (100) surface (the spot O shown in the inset) with time; the orange dotted line shows the *I*–*V* characteristics of the nonpatterned region (spot A shown in the inset)

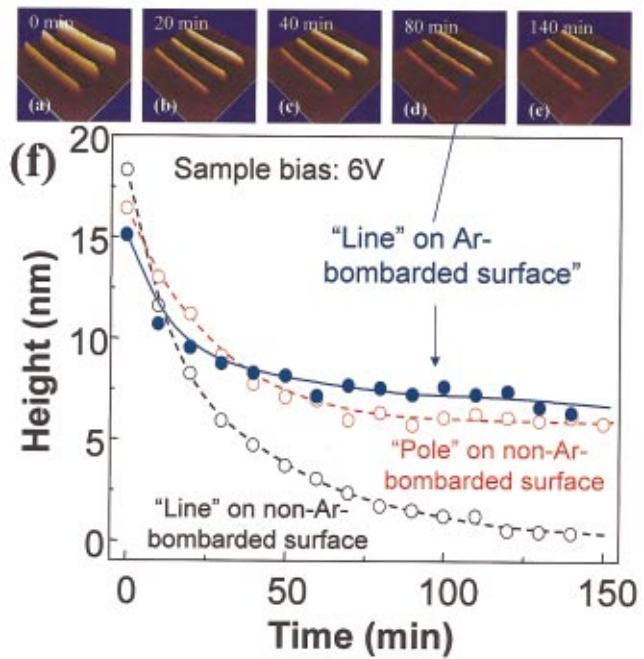


FIG. 3. (Color) (a)–(e) Topography of patterned Sr(Ti,Nb)O₃ (100) surface bombarded by Ar ions, as a function of time after patterning; the scanning scale is 5×5 μm; (f) time dependence of the heights of “line” patterns on Ar-bombarded Sr(Ti,Nb)O₃ (100) surface (blue solid line), compared with that of “line” patterns (black broken line) and “pole” (red broken line) on non-Ar-bombarded Sr(Ti,Nb)O₃ (100) surface.

ence between the initial line heights, the patterns on both Sr(Ti,Nb)O₃ (100) and (111) surfaces show basically consistent relaxation behaviors, decreasing exponentially with time.

As shown in the inset of Fig. 2, by contact mode, three lines were written on Sr(Ti,Nb)O₃ (100) surface with a W₂C-coated tip under a sample bias of +10 V. The tip scanning speed was 500 nm/s. *I*–*V* characteristics for the unpatterned and patterned regions (spots A and O in the inset of Fig. 2) were measured by AFM mounted with W₂C-coated tip with a contact mode *in situ*. The current flowed through the thickness of the substrate. As shown in Fig. 2, the unpatterned region showed an insulative behavior due to Schottky potential between the metallic tip and the semiconductor sample. The patterned region is more insulative than the unpatterned one. For example, under a sample bias of +3 V, the resistance of the patterned region (~10¹¹ Ω) is three orders of magnitude larger than that of the unpatterned region (~10⁸ Ω). With prolonging time after patterning, the diffusion potential voltage at which point the current started to increase and the resistance under a same voltage of the patterned region decreases. Moreover, *I*–*V* curve approaches gradually that of an unpatterned region. Consistent with the relaxation behaviors shown in Figs. 1(a)–1(e), the evolution of *I*–*V* characteristics also indicates the written pattern is not so stable, and the height of the insulative pattern decreases with extending time.

The relaxation behavior of the written patterns is obviously disadvantageous for constructing nano-devices by SPM lithography. Because the insulative material newly created by SPM lithography can be directly used as a barrier, or is removed by wet etching to obtain a vacuum barrier, the relaxation behavior limits the lifetime of the barrier or re-

quires a rapid wet etching soon after SPM lithography (within several minutes), which is a serious obstacle for applying this technology, especially in use of single crystal substrates. Fortunately, these remaining “poles” [as shown in Figs. 1(a)–1(e)] suggest the patterns are stable at some special places. It may be defects that stabilize the pattern. In order to verify this hypothesis, we bombarded the Sr(Ti,Nb)O₃ (100) surface by Ar ions with 100 V accelerating voltage to create more defects. After that, AFM lithography has been performed on the Ar-bombarded Sr(Ti,Nb)O₃ surface, and the stability of the created patterns was investigated. As shown in Figs. 3(a)–3(e), the patterns on the Ar-bombarded surface at first show a relaxation behavior, and then stabilize with a height about several nanometers. What we emphasize is, as shown in Fig. 3(f), by comparing the “poles” of the non-Ar-bombarded surface, the whole “line” pattern on the Ar-bombarded surface shows very similar relaxation behaviors, even having almost the same final height (about 7 nm for that under the sample bias of +6 V). Furthermore, much slower relaxation behaviors of nanopatterns created by AFM lithography were also observed in SrTiO_{3-δ} and La_{0.8}Ba_{0.2}MnO₃ films, in which more defects are expected compared to the single crystal sample. These results support the fact that defects depress the relaxation and stabilize the written patterns.

Although the mechanism of SPM lithography in metals or Si is considered in terms of an electrochemical oxidation, that in perovskite oxides is still unclear. In addition, compared to the oxygen-deficient SrTiO_{3-δ} film used in Ref. 25, oxygen vacancies are not very serious in a Sr(Ti,Nb)O₃ single crystal. It seems that oxygen vacancies are not indispensable for SPM lithography in perovskite oxides. In order to understand the large volume expansion of the patterned region, it is proposed that a significant chemical transport (for example, electromigration or field-induced diffusion^{22,26,27}) due to an intensive electric field, beside the electrochemical oxidation (decomposition) of the surface may create a poorly dense SrTiO₃ during the AFM lithography. The considerable relaxation of the patterns can be attributed to recovering from a poorly dense SrTiO₃ to initial state via chemical transport in nano-scale. Defects at surface prevent ion migration so that lines formed by SPM lithography remain on the Ar-bombarded surface and poles remain even on untreated single crystal surface, respectively. Of course, in order to find out the exact mechanism, more efforts are needed.

In summary, we performed AFM lithography on Sr(Ti,Nb)O₃ single-crystal surface. Importantly, considerable relaxation of the written patterns was observed directly, and

defects introduced by Ar bombardment can be used to stabilize the pattern. The relaxation behaviors of the written patterns and stabilization by Ar bombardment observed herein evidently indicate that a significant chemical transport occurs during and after the SPM lithography. This offers important information for exploring the underlying mechanism of SPM lithography in perovskite oxides. Furthermore, the stabilization of patterns by Ar bombardment is quite effective for the application of SPM lithography in perovskite oxides.

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