Deep-patterning of complex oxides by focused ion beam with PMMA-assisted hybrid protective layer

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Abstract

Studying novel properties of complex oxides in nanoscale has become a popular research interest. Nanofabrication of complex oxides without damaging its intrinsic structure, however, is still challenging. In this work, we investigated the commonly used focused ion beam (FIB) technique for deep-patterning SrTiO\(_3\) (STO) using Cr as a surface protective layer and found that it was insufficient in protecting STO against the damage caused by the FIB beam tail effect. We further developed a new method for effectively deep-patterning STO using FIB. Our approach adopted a hybrid surface layer of Cr and polymethyl methacrylate (PMMA) to protect the STO surface during the FIB milling process against the damage caused by the beam tail. This PMMA-assisted hybrid protective layer can effectively prevent the damage resulting from the energetic ion beam, as verified by high-resolution transmission electron microscopy characterization. It was found that PMMA is not spun off during the FIB process but forms bubbles and likely absorbs the energy from the ion beam during this process. At the same time, a thin Cr layer of this hybrid served as a charge-releasing path and kept the patterning precise. This mechanism is very different from simply using Cr as a scarifying surface layer for ion bombardment.

1. Introduction

Research in complex oxides has attracted a lot of interest in recent years because oxide materials possess many intriguing functionalities, such as piezoelectricity and colossal magnetoresistance [1–4]. However, studying these novel physical properties of complex oxides with 3D structure in nanoscale is still challenging because deep-patterning complex oxides into structures in nano- to submicron-scale range is not easy [5–7]. Preserving the intrinsic properties of the complex oxides after patterning is essential for any post-studies related to their novel functionalities, while such fabrication is inherently difficult because of the structural complexity and chemical instability of these oxide materials. Deep-patterning of oxides are difficult because oxides generally have slow etching rates. Conventional direct etching approaches, such as wet etching and dry etching methods, would damage the oxide materials, consequently resulting in the loss of properties [4, 8]. An indirect approach, using the stenciled mask method to grow the oxides with the desired shapes on the substrates without any harsh post-treatment, can effectively pattern desired complex oxides with submicron scale [9]. Nevertheless, this approach is not suitable for growing a device with a closed loop shape, such as ring shaped geometry, since floating a part on the stencil mask to achieve the closed loop shape would be unrealistic, as depicted in figure 1(a).

The technique of focused ion beam (FIB) offers a powerful, alternative way to deep-pattern oxide materials in nano to submicron scales with any geometry, including closed loop shaped structure. With the high-energy Ga ion beam, FIB is used for high-precision localized milling. It has been proven to be very effective at milling semiconductor materials with high aspect ratios. The surface damage caused by the intensive ion beam on such materials and the ways to protect the milled samples have been intensively studied [10–12]. However, the investigations and understandings on using FIB for patterning complex oxides are limited. A few studies
suggested FIB milling would cause an essential damage to the oxide materials, and the property changes of the oxides after FIB irradiation could raise a concern for adopting FIB patterning on oxides \[13, 14\]. Another concern is that oxide materials are mostly insulators, and therefore a charging problem would occur during the FIB process. Charging is a notorious phenomenon well known in the field of electron/ion microscopy, which is caused by the charged particles continuously hitting the observed/milled area, resulting in an uneven local field and consequently the distorted imaging or imprecise milling of the local sample area.

To resolve these issues, a straightforward approach would be to deposit a metal surface layer on top of the oxide material and let the metal layer serve as a charge-releasing layer as well as a sacrificial layer during the FIB process in order to protect the oxide against the FIB beam damage. However, complex oxides often have low sputtering yields, while metals usually have relatively high sputtering yields. Whether a simple metal protective layer is effective requires detailed studies, particularly whether the after-patterning oxide can still preserve its structure in nanoscale.

In this work, we studied the effectiveness of using a simple metal layer as a protective layer for FIB deep-patterning SrTiO$_3$ (STO) and found that it was insufficient for preserving the oxide nanostructure after patterning. Among many complex oxides, STO is a well-studied material and is used in many applications \[15\], and thus it was chosen to be investigated in this work. We further developed a hybrid layer consisting of polymethyl methacrylate (PMMA) and a thin Cr layer as the surface protective layer of STO for FIB patterning. PMMA is a commonly used polymer material, which is inexpensive, can be easily spin-coated onto a flat surface and cured by a simple heating process. With high-resolution transmission electron microscopy (TEM) characterization, we show that this hybrid layer can effectively protect the oxide and preserve its crystallinity after FIB deep-patterning. Intriguingly, the protecting mechanism of this hybrid layer was found to be different from the usual sacrificial surface metal layer against FIB bombardment, and this is reported.
2. Experimental

A commercial single crystal (100) oriented SrTiO$_3$ (Shinkosha, Japan) was used as the specimen in this work. As schematically shown in figure 1(b), a surface protective layer consisting of either pure Cr (∼100 nm), or a hybrid layer of Cr (10–20 nm) and PMMA (∼200 nm) (figure 1(c)), was applied onto the STO surface prior to FIB milling. The FIB system used is a dual-beam focused ion beam system (FEI NOVA 600) equipped with a Ga ion source operated at 30 kV and a scanning electron microscope (SEM) which allows the sample to be observed using the electron beam imaging function while it is patterned by the ion beam. The beam condition was set at 10–30 pA. Cr is a metal often used in the semiconductor industry, and it has a relatively low sputtering rate against Ga ions while compared to other metals. In this study, Cr was deposited using a thermal evaporator. PMMA was applied to the STO surface using a spin coater. The patterned STO was characterized using a field-emission high-resolution TEM (JEM-2100F & Tecnai) to image the cross-sectional areas.

3. Results and discussion

Figure 2(a) shows the representative ring structures made by FIB patterning on STO coated with a pure Cr surface layer. The width of the ring is 200 nm, with an aspect ratio of height/width ∼2.5. Figure 2(b) shows the TEM cross-sectional image of the after-patterned Cr-coated STO ring area. It is clear that the pure Cr layer is insufficient in protecting the STO against the ion beam damage during the deep milling process, resulting in severe damage on the edge as well as on top of the desired structure. The severe damage on the STO stage area, the supposedly unmilled area, was caused by the wide-spreading beam tail of the ion beam, which behaves as a bi-Gaussian distribution [16, 17], as schematically explained in figure 2(c). Due to the FIB beam tail effect, the surface as well as the edges of the deep-patterned STO with a surface Cr layer was severely damaged. Even the shape of the ring stage could not be kept intact. Apparently, a simple Cr surface layer is insufficient in preserving the nanostructure of the STO after patterning.

We developed a Cr/PMMA hybrid layer as an approach for FIB deep-patterning on STO (figure 1(c)). Under the same FIB beam condition, the STO protected by the Cr/PMMA hybrid layer demonstrated a totally different result. SEM images show the representative patterned ring structures with this approach, as shown in figure 3(a). Even though they look not much different from the images shown in figure 2(a), the cross-sectional TEM characterization revealed totally different results. Figure 3(b) shows a TEM cross-sectional image of a stage of the after-patterned STO protected by the hybrid Cr/PMMA layer. Clearly, the shape of the supposedly unmilled stage area was well persevered. Intriguingly, the PMMA was not sputtered off by the beam tail but formed a bubble on top of the patterned STO, and the thin Cr floated on top of the PMMA, serving as the charge-releasing layer assisting the precision of the FIB milling.

As shown in figure 3(c), the crystallinity of the STO under the PMMA layer is well preserved, as proven by the high-resolution TEM image. This result is undoubtedly superior than the one patterned with a pure Cr surface layer (figure 2). Taking a closer look at figure 3(b), the structure on the sidewalls of the trench were damaged by the FIB beam tail. It was reported that focused ion beam milling on STO single crystal would induce a thin amorphous layer on the sidewall of the milled area, and <1% atomic fraction of Ga was found in the amorphous area after milling [18]. Such amorphization phenomenon could explain the structural change of the sidewall area shown in figure 3(b). It should be noted here that although the crystallinity in the top area of STO was preserved using this Cr/PMMA protection method, the structure of the sidewall area was changed and thus the intrinsic property of STO single crystal would not be the same.

We also tested using a higher current FIB beam condition of 500 pA to mill a few trenches on STO protected with the surface Cr/PMMA hybrid layer, and then used TEM to characterize the results. As shown in figure 4, all
the after-patterned STO stages are preserved with sharp edges, and the PMMA layer still covers the top with some bubbles forming. With such results, the effectiveness of this hybrid layer approach is verified. It was reported that focused ion beam milling on PMMA would induce thermal reflow of PMMA as a result of localized heat generated during the ion bombardment with the polymer [19]. PMMA would be heated to its glass transition temperature and reflow under direct FIB milling, and then it would be etched away giving a longer milling time [19]. In the case of STO with the Cr/PMMA protection layer reported here, the PMMA bubbles likely formed because the PMMA reflows under the ion beam but could not be etched away because the Cr layer was on top of it. Instead of being a sacrificial layer, the PMMA layer likely absorbs the ion energy and keeps the thin Cr layer floated on top of it without being sputtered out, and thus it can continue to serve as the charge-releasing layer to maintain the precision of the patterning.

4. Conclusion

In conclusion, we develop a hybrid surface layer suitable for protecting complex oxides undergoing high-energy focused ion beam deep-patterning by combining the advantages of Cr and PMMA. Proven by high-resolution TEM characterization, the nanostructure of the after-patterned STO was well protected by this hybrid layer. The crystallinity of the FIB deep-patterned STO was found to be well preserved. PMMA can serve as an energy-absorbing material. It is able to keep the Cr floating on top of it and preserve the fragile oxide structure beneath it. The Cr/PMMA hybrid layer can effectively prevent the damage caused by the energetic beam tail and preserve the material integrity of the STO. On the other hand, a simple Cr surface layer coated on STO was found to be insufficient in protecting the unmilled area.
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References

[1] Tokura Y and Hwang H Y 2008 Complex oxides on fire Nat. Mater. 7 694–5
[2] Zubko P, Gariglio S, Gabay M, Ghiore P and Triscone J 2011 Interface physics in complex oxide heterostructures, Annu. Rev. Condens. Matter Phys. 2 141–65
[3] Hwang H Y, Iwasa Y, Kawasaki M, Keimer B, Nagaosa N and Tokura Y 2012 Emergent phenomena at oxide interfaces Nat. Mater. 11 103–13
[4] Chakhalian J, Millis A J and Rondinelli J 2012 Whither the oxide interface Nat. Mater. 11 92–4
[5] Ma W, Hesse D and Gösele U 2006 Nanostructure patterns of piezoelectric and ferroelectric complex oxides with various shapes, obtained by natural lithography and pulsed laser deposition Nanotechnology 17 2536–41
[6] You C C, Takahashi R, Borg A, Grepstad J K and Tybell T 2009 The fabrication and characterization of PbTiO₃ nanomesas realized on nanostructured SrRuO₃/SrTiO₃ templates, Nanotechnology 20 235705
[7] Jesse S et al 2016 Directing matter: toward atomic-scale 3D nanofabrication, ACS Nano 10 5600–18
[8] Balcells L, Abad L, Rojas H and Martinez B 2008 Material damage induced by nanofabrication processes in manganite thin films Nanotechnology 19 135307
[9] Nechache R et al 2011 Epitaxial patterning of Bi₂FeCrO₆ double perovskite nanostructures: multiferroic at room temperature, Adv. Mater. 23 1724–9
[10] Kempshall B W, Giannuzzi L A, Prenitzer B I, Stevie F A and Da S X 2002 Comparative evaluation of protective coatings and focused ion beam chemical vapor deposition processes J. Vac. Sci. Technol. B 20 286–90
[11] Langford R M, Nellen P M, Gierak J and Fu Y 2007 Focused ion beam micro- and nanoengineering MRS Bull. 32 417–23
[12] Mayer J, Giannuzzi L A, Kamino T and Michael J 2007 TEM sample preparation and FIB-induced damage MRS Bull. 32 400–7
[13] Pallecchi I, Pellegrino L, Bellingeri E, Siri A S, Marre D and Gazzadi G C 2008 Investigation of FIB irradiation damage in La₀.₇Sr₀.₃MnO₃ thin films J. Magn. Magn. Mat. 320 1945–51
[14] Siemens W et al 2014 Focused-ion-beam induced damage in thin films of complex oxide BiFeO₃ APL Mater. 2 222109
[15] Kan D et al 2005 Blue-light emission at room temperature from Ar⁺—irradiated SrTiO₃ Nat. Mater. 4 4816–9
[16] Frey L, Lehrer C and Ryssel H 2003 Nanoscale effects in focused ion beam processing Applied Physcis A 76 1017–23
[17] Kolibał M, Matlocha T, Vystavel T and Sikola T 2011 Low energy focused ion beam milling of silicon and germanium nanostructures Nanotechnology 22 103034
[18] Huh Y, Jung K and Shin K S 2013 Amorphization induced by focused ion beam milling in metallic and electronic materials Microsc. Microanal. 19 33–7
[19] Dai C, Agarwal K and Cho J-H 2018 Ion-induced localized nanoscale polymer reflow for three-dimensional self-assembly ACS Nano 12 10251–61