Directly patterning ferroelectric films by nanoimprint lithography with low temperature and low pressure

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In this article, the authors demonstrate an imprint method for patterning ferroelectric films. In contrast to conventional nanoimprint lithography, the patterned mold is directly imprinted in a ferroelectric film or a metal/ferroelectric film bilayer structure. In general, direct imprint in a ferroelectric or metal film needs ultrahigh pressure or temperature to form patterns. In this article, the authors improve the direct imprint processes by using a sharp mold and an underlying soft gel film for the reduction of the imprint pressure and temperature. The imprint pressure can be reduced to be compatible with the conventional nanoimprint instrument. The authors also successfully use the metal/ferroelectric bilayer structure to overcome the pattern flattened problem in a gel film. The cover metal layer can also be the upper conductive layer in the ferroelectric application. For direct contact of the metal film with mold, no surfactant should be coated on the surface of mold. It also indicates that no mold-rework processes are necessary for this direct imprint ferroelectric film method. © *2006 American Vacuum Society.* [DOI: 10.1116/1.2395958]

I. INTRODUCTION

Ferroelectric films have been investigated for applications as sensor, actuator, nonvolatile memory, and optoelectronic devices due to their high piezoelectric and ferroelectric properties. Patterning varied profiles of ferroelectric films with submicrometer scale is important for the microelectromechanical systems and optoelectronic applications. Many kinds of ferroelectric films, such as $Pb(Zr,Ti)O_3$ (PZT), are not easy to pattern by conventional semiconductor processes. In general, ferroelectric materials are patterned by lift-off, focused ion beam, and wet-etching or dry-etching processes that are generally complicated and should process with strict conditions.[1–3] Recently, Wang *et al.*[4] introduced a two-step etching process, using buffered HF acid in the first step and $HCl:H_2O$ in the second step, to etch PZT thin film. However, significant undercutting and brim damage are observed in the achieved PZT pattern. Similar results are also found in the research by Ezhilvalavan and Samper in 2005.[5]

Nanoimprint lithography (NIL), a potential candidate for the next generation lithography technology, has performed rapid, large-area, and low-cost technology for the polymer structures. The standard NIL technique is used in a thermoplastic resist as shown in Fig. 1(a).[6] The NIL defines patterns by physical deformation of deformable polymer materials (resist) by adding temperature above their glass transition temperate (T_g). After the removal of the mold, the pattern is transferred to underlying substrates by etching processes. Directly patterning underlying materials without etching processes is desired for rapid processes. This concept can be carried out in a silicon substrate by laser-assisted directly imprint.[7] Using this technique, it needs high power excimer laser (XeCl, 1.6 J cm^{-2}) to melt silicon for embossing and applies external pressure at the same time. However, it is not easy to execute in the common procedure and equipment.

Recently, a process for direct imprint of metal films was reported.[8] This experiment needs to be carried out with ultrahigh pressure (several hundreds of megapascals) by using an oil press imprint instrument. But such processes with ultrahigh pressure are not desirable since they would damage the underlying substrates or devices. Furthermore, the ceramic films such as ferroelectric films are harder than metal films and they should apply higher pressure by a direct imprint process. In this article, we demonstrate a direct imprint method for patterning ferroelectric films with low pressure ($\leqslant$20 MPa) and low temperature. As shown in Fig. 1(b), we improve the direct imprint processes by using a sharp mold and soft gel film for the reduction of the imprint pressure. The imprint pressure of our method is only about 10% as compared with the previous direct imprint method.[8,9]

The ferroelectric properties are generally caused by applying external electric field. As shown in Fig. 1(c), we also demonstrate the direct imprint in a metal/ferroelectric film bilayer structure. The top metal film of the bilayer metal/ferroelectric structure can be as the upper electrode. Otherwise, the issue during conventional NIL process is that the mold is stuck on the imprinted films, and one needs to coat suitable surfactant on the surface of mold to isolate the sticky film. Therefore, we demonstrate that the metal/ferroelectric film bilayer changes the surface properties between the mold and gel layer and tunes the separate condition between the

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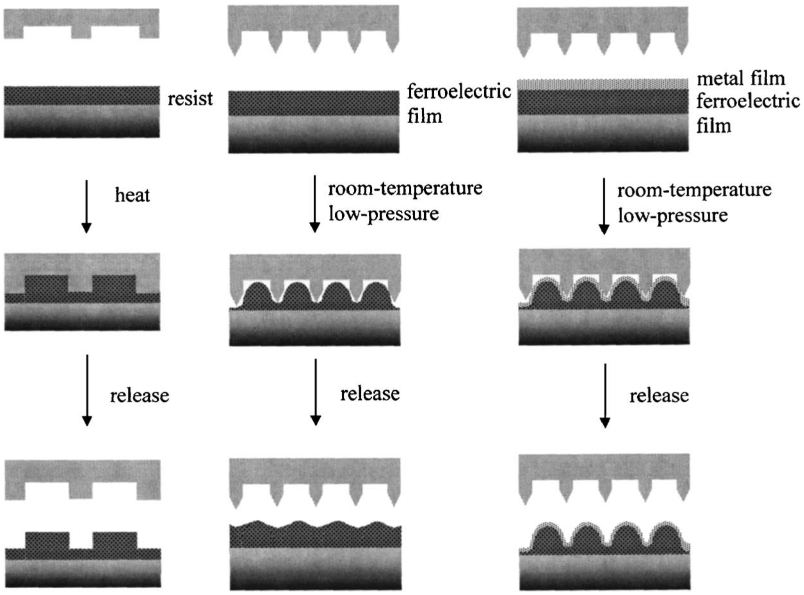

FIG. 1. Schematic diagrams of imprint technologies: (a) conventional nanoimprint lithography, (b) direct imprint on a ferroelectric film, and (c) direct imprint on a metal/ ferroelectric film bilayer structure.

imprinted film and mold. We find that no mold-rework processes are necessary for this bilayer NIL method.

II. EXPERIMENT

We fabricated patterned ferroelectric PZT films by imprint gel films, which were prepared by metal organic decomposition (MOD) solution. The composition of PZT film is Pb1.1($Zr_{0.52}$,$Ti_{0.48}$)O_3 and the 10% excess of Pb is used as the compensation for PZT loss during high temperature annealing. MOD precursor used in our article was a commercial solution (Kojundo, Japan) and fabricated by dissolving stoichiometric amounts of Pb-ethylhexanoate, Ti-isopropoxide, and Zr-*n*-propoxide in ethyl-hexanoic acid and xylene. The PZT films were deposited on silicon and fused silica substrates by spin coating (500 rpm for 10 s, 2000 rpm for 20 s) with the thickness of about 200 nm. After the deposition process, the films from MOD-based precursor were dried for 5 min at 50 °C to remove organic solvent and formed the PZT gel films. Silicon molds used in our experiments were fabricated by using electron beam lithography (Leica, Weprint-200) followed by the reactive-ion-etching process. The high-density-plasma reactive-ion-etching (HDP-RIE) system (Duratek, Multiplex Cluster) with inductively coupled plasma (ICP) sourced was used to fabricate the hexagonal pyramid molds.[10,11] The imprint pressure applied was about 10–20 MPa at room temperature during imprint processes. After imprint, the patterned gel films were first dried at 120 °C for 30 min and pyrolyzed at 450 °C for 30 min in air. Finally, the samples were annealed at 650–800 °C for 60 min in oven to obtain the perovskite phase. The structures could be identified by low-angle x-ray analysis (PANalytical X'Pert Pro, Cu $K\alpha$). The images and surface profiles of patterned metal films were observed by scanning electron microscope (JEOL, JSM6500F) and atomic field microscope (NT-MDT, P-47), respectively. The hardness was measured by the nanoindenter (CSIRO, UMIS II) with a Berkovich-type diamond tip. At each test, the loading speed was adjusted to keep 30 s loading time, 2 s delay at peak load with 1 mN, and 30 s unloading time. The hardness was obtained through dividing the load by the area of the residual indents.

III. RESULTS AND DISCUSSION

Figure 2 shows the x-ray diffraction spectra of PZT films. The PZT films did not form the complete perovskite phase after the pyrolysis process (450 °C). When we increase the temperature, the diffraction peaks of perovskite phase of the PZT films appeared. The PZT films begin to be crystallized at 600 °C. At higher temperature, the PZT films become denser and form the more complete perovskite phase. The better ferroelectric properties can be induced from the perovskite phase.[12,13]

In order to reduce the requirement of imprint pressure, the sharp mold is used to increase the tip pressure. Figure 3(a) shows the silicon mold used in our experiments that is fab-

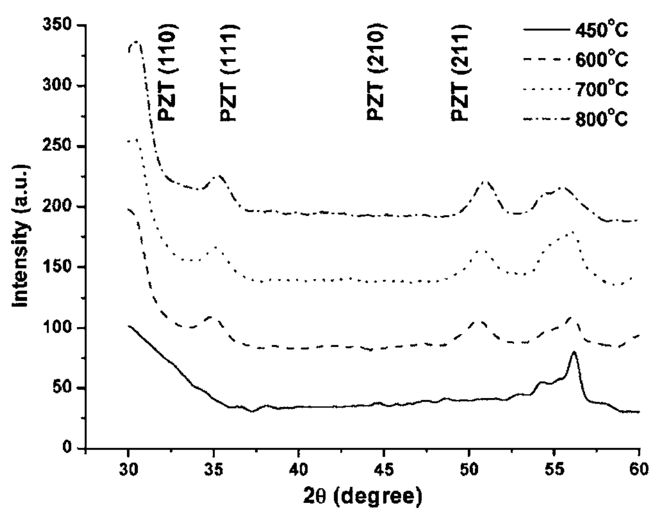

FIG. 2. XRD spectra of PZT films at different temperatures.

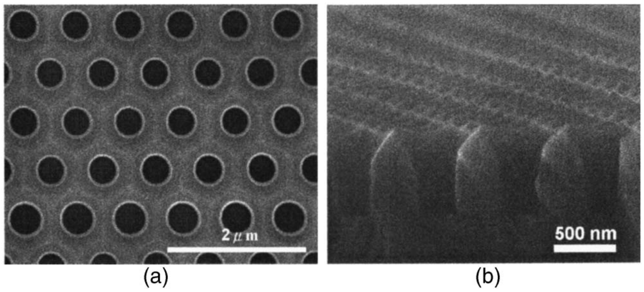

FIG. 3. SEM images of hexagonal pyramid mold: (a) top view and (b) cross section.

ricated by using the electron beam lithography followed by HDP-RIE process. Figure 3(b) shows the cross section of the sharp mold fabricated by the optimized etching process. The HDP-RIE system with ICP source has a chamber surrounded by rf coils and a rf bias provided for the substrates. For the fabrication of sharp mold, we use the 400 W rf-bias power that would increase ion bombardment on the surface of the mold.

During the imprint process, the imprint pressure is dependent on the relative properties between molds and ferroelectric thin films. The most important characteristic is the hardness of molds and imprinted films. Figure 4 shows a comparison of hardness between molds and the ferroelectric films after different temperature treatments. At room temperature (25 °C), the PZT thin film contains much organic solvent and the films formed wet-gel films. When the hardness of the wet-gel film with little viscosity was measured, the tip of the nanoindentation system would directly contact to the underlying silicon substrate. As the baking temperature rises to 120 °C, much solvent of PZT wet-gel films is evaporated. The PZT gel film with little solvent would cause the plastic deformation during the tip contact with the PZT film that would decrease the hardness. As temperature gradually increases, the ferroelectric films gradually form ceramic

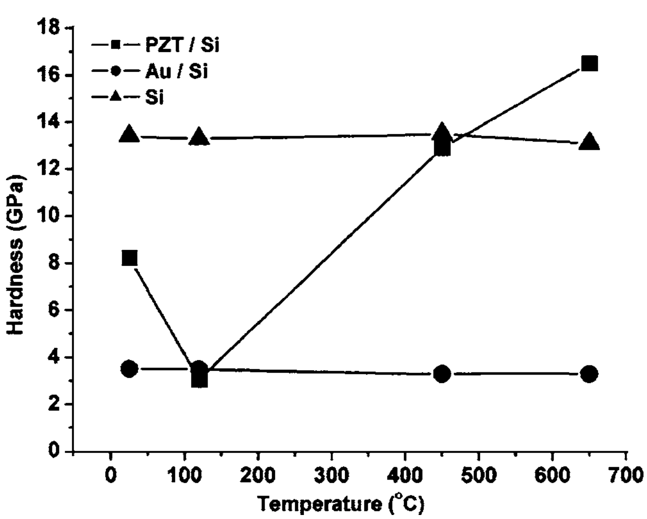

FIG. 4. Hardness of different material structures at different temperatures. (–■–) PZT/Si, (–●–) Au/Si, and (–▲–) Si.

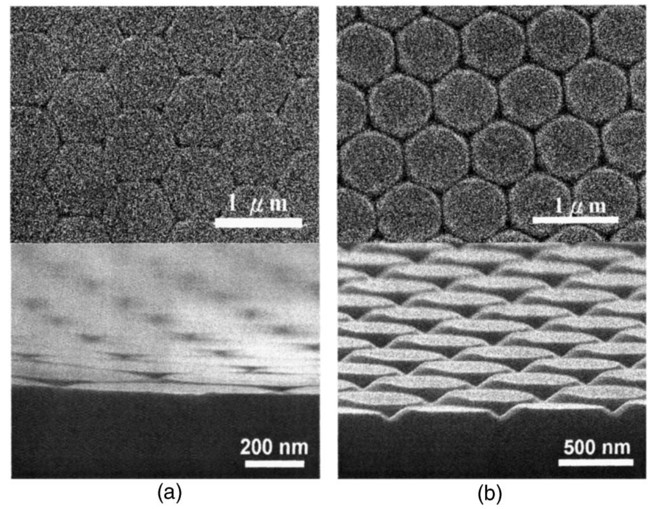

FIG. 5. SEM images of PZT gel films imprinted by hexagonal pyramid mold under (a) 14 MPa and (b) 20 MPa pressures.

films with large hardness. We find that the largest hardness difference between the silicon mold and PZT film is achieved after baking at 120 °C. Therefore, we directly pattern ferroelectric films after baking at 120 °C for the reduction of imprint pressure.

Generally a metal layer should be coated on a ferroelectric film for applying external electric field to get ferroelectric properties. Therefore, the direct imprint Au/PZT bilayer structure was also demonstrated in this article. As shown in Fig. 4, the hardness of gold film is lower than a silicon mold and it may be patterned after imprinting processes.

Figure 5 shows the patterned ferroelectric cells obtained by imprinting a single-layer PZT gel film with a hexagonal pyramid silicon mold. As shown in Fig. 5(a), the PZT film does not deform markedly the profile by applying the imprint pressure of 14 MPa. Because of the characteristics of a gel film, the imprinted profiles become flattened as the mold leave from the surface of PZT film. As the applied pressure is increased to 20 MPa, the patterns become clear and the depth is only about 60 nm as shown in Fig. 5(b). For the flattened effect of a gel film, the imprint depth is much smaller than the step height of the mode.

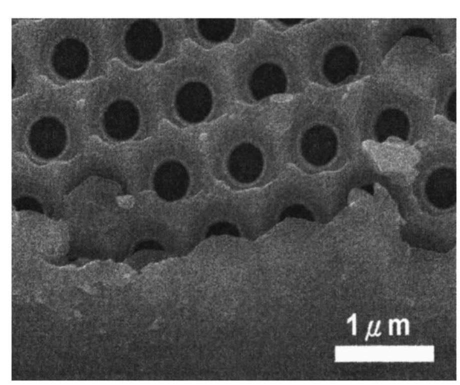

FIG. 6. SEM image of the mold after the imprint PZT gel film process.

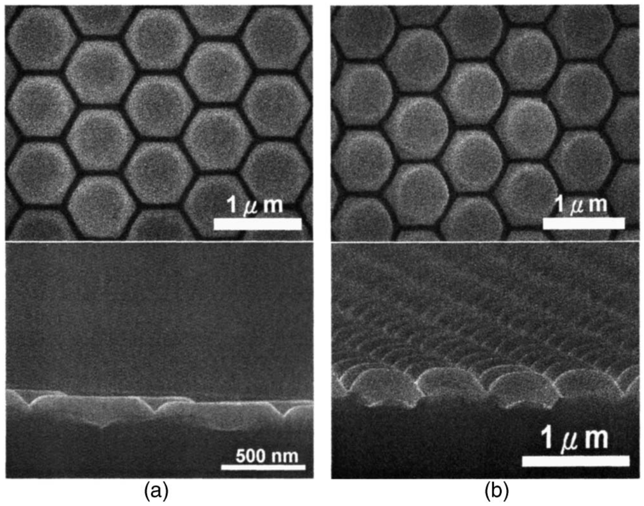

FIG. 7. SEM images of Au/PZT structures imprinted by hexagonal pyramid mold under (a) 14 MPa and (b) 20 MPa pressures.

As shown in Fig. 6, the PZT gel film is adhered on the silicon mold after imprint processes. Some of the patterns are destroyed and it is difficult to remove these patterns from the mold especially for the ceramic gel film. Therefore, changing the surface properties between the mold and gel layer, such as adding a surfactant layer, to tune the separate condition is essential.

As shown in Fig. 1(c), we deposit a gold film on a spin-coated PZT film to form a Au/PZT bilayer structure. Furthermore, we use the same hexagonal pyramid mold to imprint pattern on the bilayer structure with the pressure of 14–20 MPa at room temperature. Figure 7 shows the scanning electron microscope (SEM) images of imprinted Au/PZT bilayer structure under different imprint pressures. Compared with the single-layer PZT gel film, the bilayer PZT profile is much clearer and deeper. Figures 5 and 7 indicate that the depths are markedly different under the same imprinting pressure. The metal film is used for the upper conductive layer to apply the electric field to induce the ferroelectric properties. Moreover, the metal film helps the PZT gel film to be shaped and also helps prevent the pattern from being flattened during imprint processes. We also find that the metal film can solve the problem of the gel film being stuck on the silicon mold. Figure 8 shows the atomic force microscope (AFM) topography of imprinted Au/PZT bilayer structure under different pressures. As shown in Fig. 8(a), we can find that the depth is about 90 nm on the bilayer PZT structure after imprint with 14 MPa pressure. As the imprint pressure is increased to 20 MPa, the depth of the dent is increased to 300 nm, which is almost equal to the thickness of bilayer PZT structure.

IV. CONCLUSION

In this article, we demonstrate an imprint method for patterning ferroelectric films. In contrast to conventional nanoimprint lithography, the patterned mold is directly imprinted in a ferroelectric films or a metal/ferroelectric film bilayer structure. Compared with the single-layer PZT gel film, the bilayer PZT profile is much clearer and deeper. We also improve the direct imprint processes by using a sharp mold or an underlying soft gel film for the reduction of the

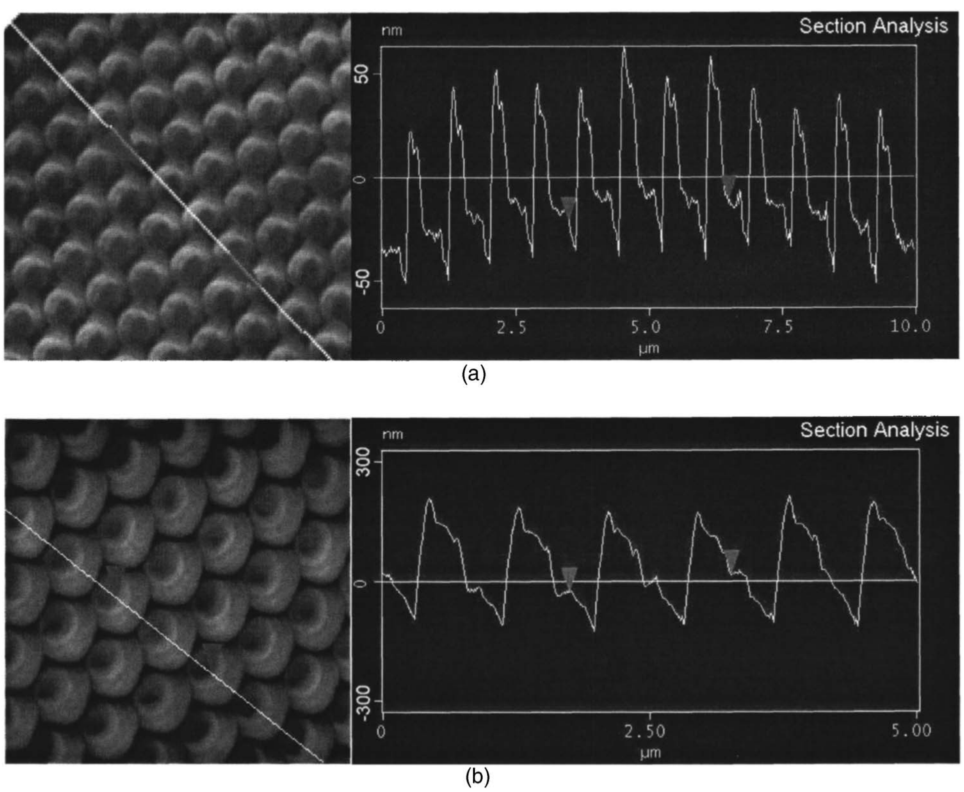

FIG. 8. AFM topography of imprinted Au/PZT structure with hexagonal pyramid mold under (a) 14 MPa and (b) 20 MPa pressures.

imprint pressure under 20 MPa at room temperature. The imprint pressure can be reduced to be compatible with the conventional nanoimprint instrument. The gold cover layer in the bilayer structure can help the PZT gel film to be shaped and overcome the pattern flattening problem in a gel film during imprint processes. The cover metal layer can also be the upper conductive layer in the ferroelectric application. For direct contact of the metal film with mold, no surfactant should be coated on the surface of mold. It also indicates that no mold-rework processes are necessary for this direct imprint ferroelectric film method.

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