Ferroelectrics, 380:1, 97-101, 2009
Reprints available directly from the publisher
DOI: 10.1080/00150190902873295
URL: http://dx.doi.org/10.1080/00150190902873295

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ISSN: 0015-0193 print / 1563-5112 online

Chemical Reactions During Wet-Etching Process of LSMO/PZT/LSMO-Structured Device Fabrication

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Etching behavior of Lanthanum Strontium Manganate electrode and ferroelectric PZT in wet-etching processes for large area ferroelectric thin film devices using LSMO/PZT/LSMO pattern was investigated using various etching solutions. The results show that PZT and LSMO oxide thin films of the LSMO/PZT/LSMO micro-sensing structures can be protected by the Pt hard etching mask during the wet etching process. The etching mechanism of PZT ferroelectric thin film was attributed to the double replacement reaction etching model. The difference of etching rates of PZT and LSMO using wet etching may cause damage of upper electrodes resulting in device failure. A careful design of the mask pattern of PZT and a well control of etching time are suggested to prevent the problem.

Keywords: wet etching, PZT, ferroelectric thin film, chemical reaction

Introduction

Micro-electromechanical systems (MEMS) containing active electro-ceramic components are of great importance in the field of sensors, actuators and transducers [1-3]. The most commonly used piezoelectric material is PZT. For application in micro-sensors and micro-actuators, the etching technique of PZT thin films is an essential step in device fabrication process and has attracted considerable attention [4]. The common used structure of the Si wafer is deposited with a layer of thermally oxidized silicon dioxide (SiO_2), a thin adhesive enhancing titanium (Ti) layer, and a platinum (Pt) layer as the common bottom electrode due to its inertness [5]. Various dry etching processes, including ion beam etching and reactive ion etching, have been reported to define patterns of ferroelectric materials. However, it is difficult to obtain satisfactory PZT patterns because of the different sputtering rates of Pb, Zr and Ti and the poor selectivity of PZT over the photoresist and Pt bottom electrode. Moreover, chemical contaminations during the RIE process are likely to deteriorate the surface roughness and degrade the properties of etched PZT films. Compared to dry etching, wet

Received August 3, 2008; in final form December 31, 2008.
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etching is an effective technique in MEMS due to its high etching rate, low cost and high selectivity. In recent years, many researchers have studied Pt/PZT film fabrication using wet-etching technique [6-8]. However, significant undercutting was observed in the pattern. The selection of electrode structure, type of etchant and its concentration are found to play major role in getting defect free films. Here, we present the chemical reactions taking place during wet etching process of Pt/LSMO/PZT pattern and the effect of chemical reaction on the property was discussed on the basis of proposed model.

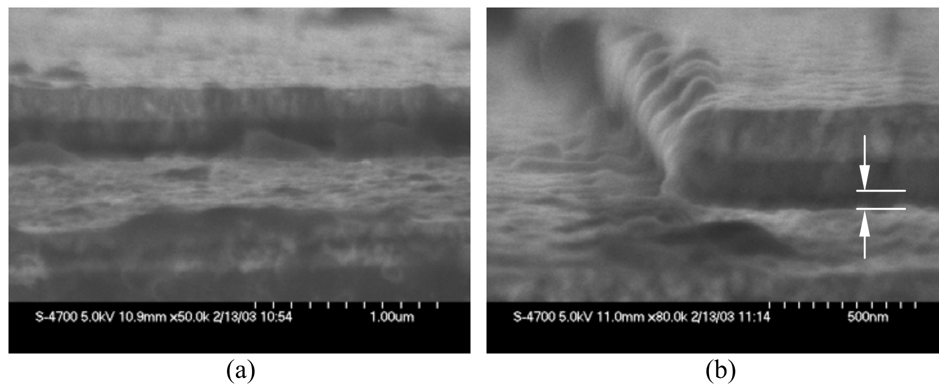
Experimental

PZT thin films were prepared by the modified sol-gel method and spin coating process on Pt/Ti/SiO_2/Si substrates. These films were annealed at 650°C for 30 min to form perovskite phase without pyrochlore. LSMO and Pt were sputtered and the multilayer of Pt/LSMO is used as top electrode. Mixed solutions of NH_4F with HNO_3 and HCl in concentrated and diluted form were used as etchants to etch LSMO/PZT/LSMO structure. The etching time was fixed for 30 sec. NH_4F was selected due to its controlling ability of F^- ion concentration in the etching solution and to act as buffer agent. Among these, HF is a necessary composition because only HF can etch ZrO_2 effectively. HCl and HNO_3 were used as other components because their etching rates on PbO and TiO_2 matches with that of HF on ZrO_2 and TiO_2. The microstructure of the PZT thin films was recorded using SEM-EDS (JEOL JSM-6500F, Japan). For the characterization of ferroelectric property, Precision Work Station 2000 was used.

Results and Discussion

Figure-1 shows the SEM image of Pt/Ti/LSMO/Pt pattern etched using diluted HNO_3 for 4 min. The thickness of Pt and Ti layers were around 1350A° and 1680A°. LSMO residuals were found after etching. The result reveals that the sputtered Ti/LSMO electrode on PZT device pattern might be the better electrode in order to enhance the adhesion.

The SEM cross sectional image of the Pt/LSMO/PZT/Pt/Ti/SiO2/Si device pattern before etching is shown in figure-2. The thickness of each layer is around 0.2 μm. The cross sectional image shows uniform thickness and well dense microstructural features. The interface between the adjacent layers and adhesion between them are found better.



(a) (b)

Figure-1 SEM images of Pt/Ti/LSMO/Pt substrate after etching with diluted HNO_3

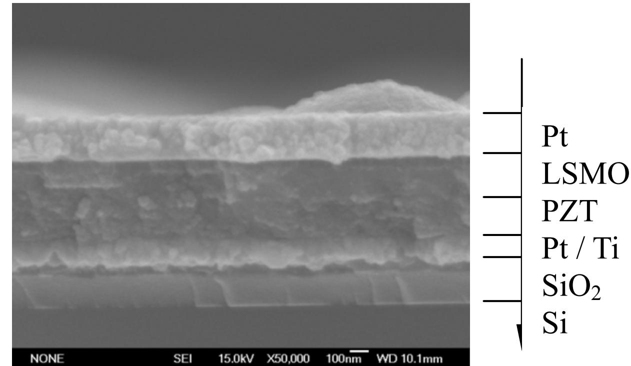
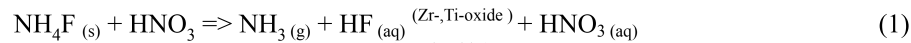


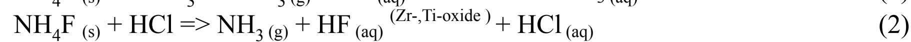
Figure 2 SEM image of Pt/LSMO/PZT/Pt/Ti/SiO2/Si pattern

Figure-3 shows the microstructural features of Pt/LSMO on etched PZT/Pt/Ti/SiO_2/Si pattern. NH_4F mixed with HNO_3 and HCl were used as two different etching solutions. The etching rates were fixed on the basis of etching solution. In order to etch LSMO and PZT using NH_4F+HNO_3 solution, the etching rates of 46.47 nm/sec and 38.33 nm/sec were fixed. The microstructural features indicate the better etching of PZT and LSMO. Higher etching is observed in the case of LSMO compared to PZT. Moreover, the interface is found good. In the case of NH_4F + HCl etching solution the etching rate of 43.88 nm/sec was taken for both LSMO and PZT. The effect of etching solution is found severe and a bending of Pt layer toward PZT surface was observed. This caused short circuit and destroyed the pattern. In order to explain the effect of concentrated etching solution on the surface morphology and appearance of final products on the surface of Pt, double replacement reaction etching model was proposed.

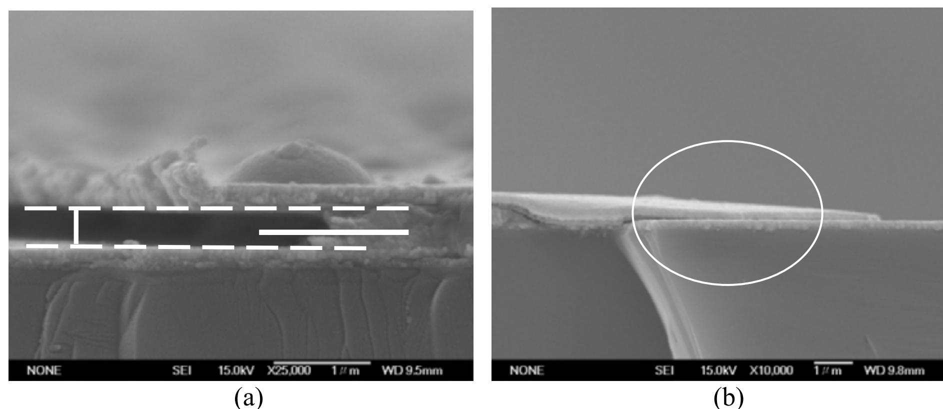
The chemical reaction occur between the two solutions in an etchant can be written as follows:



$$NH_4F_{(s)} + HNO_3 \Rightarrow NH_{3\,(g)} + HF_{(aq)}{}^{(Zr\text{-},Ti\text{-}oxide)} + HNO_{3\,(aq)} \quad (1)$$



$$NH_4F_{(s)} + HCl \Rightarrow NH_{3\,(g)} + HF_{(aq)}{}^{(Zr\text{-},Ti\text{-}oxide)} + HCl_{(aq)} \quad (2)$$

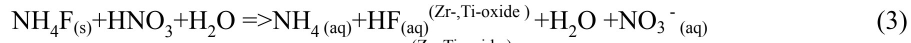


(a) (b)

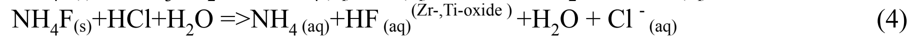
Figure-3 Cross sectional SEM image of LSMO/PZT pattern (a) etched using NH_4F + HNO_3 (b) etched using NH_4F + HCl

The reaction between high concentrated solutions resulted in the formation of HF and NH_3 due to existence of high concentrated F^- ions. HF is the common etching solution used for wet etching of oxides. But there is a need to control the higher activity of F^- ions and to control the over-etching. In addition the H^- ions formed by mixing the solutions will again produce HNO_3. The F^- ions easily react with Zr_xO_y and Ti_xO_y type compounds to etch very fast. It is also possible to etch Pb_xO_y, but the etching rate is smaller. Pb rich compounds are found to form easily on the electrode surface and these compounds can be removed easily with high concentrated etching solutions due to double replacement reaction. HNO_3 and HCl solutions make Pb-rich compounds soft and decrease their strength. Hence it is possible to remove Pb rich compounds from the Pt electrode surface after etching with high concentrated solutions.

The formation of Pb-rich compounds on the surface of Pt electrode can be reduced by decreasing the concentration of the etching solution. This is possible by adding H2O to the concentrated solutions. SEM-EDS analysis revealed the formation of reaction products on the surface of Pt. This can be explained on the basis of single replacement reaction etching model. The reactions that occur in this process can be written as:



$$NH_4F_{(s)}+HNO_3+H_2O \Rightarrow NH_{4\,(aq)}+HF_{(aq)}^{(Zr\text{-},Ti\text{-}oxide)}+H_2O+NO_3^{-}{}_{(aq)} \quad (3)$$



$$NH_4F_{(s)}+HCl+H_2O \Rightarrow NH_{4\,(aq)}+HF_{(aq)}^{(Zr\text{-},Ti\text{-}oxide)}+H_2O+Cl^{-}{}_{(aq)} \quad (4)$$

NH_4 has a characteristic property to dissolve easily in water. Hence the concentration of HNO_3 and HCl reduces and HF will become the major etching solution. HF will etch Zr_xO_y and Ti_xO_y of PZT. SEM-EDS analysis has shown Ti existence on the surface of Pt after etching using NH_4F +HCl + H_2O solution (Table-1). This is because of NO_3^- ion which can react with Ti and etch Ti_xO_y easily. The etching rate of Ti_xO_y by NO_3^- is easier than Cl^-. Since, the concentration of etching solution was reduced by adding water, the structure of Pb rich compounds (PbF_2, $PbCl_2$, PbFCl) formed on the surface is not easy to soluble and not easy to remove from Pt electrode surface in the case of diluted etching solutions. High melting point compounds such as TiF_3, TiF_4, $TiCl_3$, $TiCl_4$ are easy to form [9]. The overall results reveal that the use of H_2O is not appropriate. Another possible solution need to be used to decrease the concentration of etching solution by controlling the PH value and to restrain the Pb-rich compounds formed on the surface of Pt electrode. The work in this direction is in progress.

Table-1 SEM-EDS analysis of PZT/LSMO/Pt pattern

Etchant wt %	Pb	Zr	Ti	O	F	Cl	Pt
Original	50.38	24.55	6.75	18.5			
$NH_4F+H_2O+HNO_3$	42.48			3.86	12.33		41.33
NH_4F+H_2O+HCl	36.43		1.97	5.98	5.88	6.22	43.52

Figure-4 shows the hysteresis loops of PZT thin films with Pt/LSMO top electrode before and after etching. The remanent polarization decreased from 23.66 C/cm^2 to 20.79 C/cm^2 after etching with NH_4F+HNO_3 solution. This indicates the effect of Pr-rich compounds existence on the surface of the electrode by hard etching process.

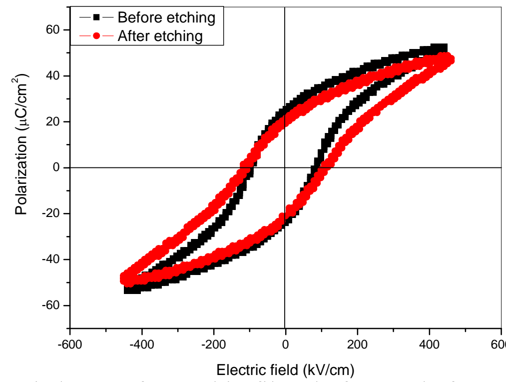


Figure-4 Hysteresis loops of PZT thin films before and after etching

Conclusions

Wet etching process for novel LSMO/PZT/LSMO thin films using NH_4F + HNO_3 and NH_4F + HCl etchants is proposed. LSMO/PZT patterns with better undercutting and uniform thickness etching were achieved. NH_4F is found better agent in controlling the replacement reaction and the concentration of F^- ions. This study indicates the possible use of Pt/LSMO/PZT pattern for the device application in the MEMS field.

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