Patterning of PZT thin films

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Received November 26, 2009

A wet chemical etching process for lead zirconate titanate ($PbZr_xTi_{1-x}O_3$ or PZT) thin films is reported. The influences of the etchant compositions, temperatures, and concentrations on the etching rate are studied, and the patterning of PZT thin films is successfully attained using the wet chemical etching process. The relationship between the etching ratio and the ratio of lateral to thickness of less than 1:1.07 is obtained. Furthermore, there is no residue on the pattern. The selectivity of etchant for the photosensitive resist mask and Pt electrode is shown to be good. This process is suitable for the patterning of PZT thin film, of which line width reaches the micrometer range.

OCIS codes: 310.0310, 160.0160.

doi: 10.3788/COL201008S1.0210.

Lead zirconate titanate ($PbZr_xTi_{1-x}O_3$ or PZT) ceramics are ferroelectric materials, which are currently used and widely studied. PZT materials with perovskite-type structure have many excellent features, such as pyroelectric, piezoelectric, photoelectric, ferroelectric, and dielectric characteristics[1]. PZT is also an important material for infrared thermal imaging detectors, ferroelectric random access memory devices, and uncooled infrared focal plane arrays. It has many important or potential applications in the fields of microelectronics, integrated optics, and micromechanics.

Ferroelectric microelectromechanical system devices can be manufactured by using the ferroelectric thin film with silicon microprocessing technology. The patterning of ferroelectric materials is a very important step in the process of manufacturing the microstructure of ferroelectric materials. Currently, patterning is done using two main methods of dry etching and wet etching. Dry etching methods, such as reactive ion etching, electron cyclotron resonance etching, and so on, are limited because of the expensive equipment, the slow etching rate, and the pollution resulting from the etching process. In contrast, the wet etching method is simple, easy to operate, and can maintain the accurate chemistry ratio. In this letter, the wet etching method is used to complete the patterning of PZT thin films.

PZT is composed of mainly the oxides of titanium, zirconium, and lead. The titanium may be dissolved in HCl, H_2SO_4, HF, H_3PO_4, and so on. However, the titanium compounds must be etched with an oxidizing acid. Zirconium is only etched with HF and aqua regia. Lead is only etched with HF, aqua regia, concentrated H_2SO_4, and a mixture of HF and HNO_3[2,3]. Baude *et al.* etched the PZT thin film with HCl-HF. The etching rate of PZT films was 5 μm/min, the surface of the film was coarse, and the side etching was very serious[4]. Mancha *et al.* found that using the mixture composed of BOE, which is the oxidant buffer solution made of $NH_4F(40\%)$:HF(49%) = 6:1 and HCl, showed better results[5]. Lin *et al.* also obtained similar results[3]. Qin *et al.* used the BHF/HNO_3 solution with a volume ratio of BHF:HNO_3:H_2O = 1:1:5000000 to etch the PZT thin film, and the etching rate was 2400 nm/min at the room temperature[6]. Ezhilvalavan *et al.* used mixture BOE + CH_3COOH + HNO_3+ HCl + NH_4Cl + EDTA ($C_{10}H_{18}N_2O_{10}Na_2$) + H_2O as the etching solution[7] with the etching rate of 200 nm/min, and the side etching ratio was 1.5:1.

Different etching solutions, solution concentrations, and temperatures are crucial factors that influence the manufacturing precision and electrical performance of the ferroelectric thin film etching patterns. In order to obtain good linearity, small side etching ratio, suitable etching rate, and non-residuum on the surface of PZT films must be achieved. In this letter, the influences of the different etching conditions on the etching rate, side etching ratio, and the graph depicting the manufacturing precision of the PZT thin film are studied, and good etching results are obtained.

The photoetching pattern was firstly imprinted onto the PZT thin film. The width ($d1$) of the photoetching pattern was measured using the microscope. Then, the pattern was etched onto the PZT thin films. Finally, the photosensitive resist was dissolved, and the new width ($d2$) of the PZT pattern was measured using the microscope. The horizontal etching rate can be calculated using $v = (d2-d1)/2t1$, here $t1$ is the etching time. Before etching, the thickness ($h1$) of the PZT thin films was measured by using the interferometer. After etching, the new thickness ($h2$) of the PZT thin films was measured by using the interferometer. The vertical etching rate can be calculated using $v = (h2 - h1)/t2$, here $t2$ is the etching time.

HCl + HF solution was selected as the basic solution for etching the PZT thin film in this letter.

In order to resolve the surface roughness when etching the PZT thin film using HCl + HF, CH_3COOH was added into the basic solution because it can remove PbO effectively. A solution of 5 ml HCl + 5 ml HAc + 20 ml H_2O + 1 ml HF was used to etch the PZT thin film at the room temperature, and the etching time was 15 s. The etching result is shown in Fig. 1. The edge of the pattern was not straight, which means that the side etching was serious. Adding CH_3COOH into the basic solution can

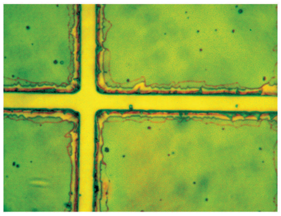

Fig. 1. Etching effects after the addition of the CH_3COOH.

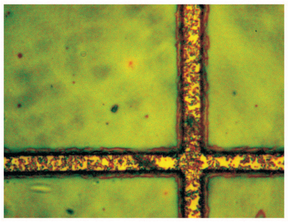

Fig. 2. Etching effects after the addition of 0.5-g NH_4F.

remove the PbO residue because no residuum was seen.

To solve the mentioned serious side etching phenomenon, 0.5-g NH_4F was operated added into the etching solution. Etching was operated under the same condition above, but with 10-s etching time. The results are shown in Fig. 2. Using this solution, the horizontal undercutting phenomenon was suppressed, but there was no residue present.

The etching solution was divided into two parts and labeled as Nos. 1 and 2. 2-ml H_2O_2 was added into etching solution No. 1, which was subsequently labeled as No. 3. As shown in Fig. 3, there are compact residua in left, the edge is clear and straight after etching for 15 s. The addition of H_2O_2 accelerated the hydrolysis and oxidation of Ti^{4+}, the titanium acid radical ion TiO^{2+} was formed. Alternatively, 0.8-ml HNO_3 (69%) was added into etching solution No. 2, which was subsequently labeled as No. 4. After etching for 15 s, there were some residua, and the edge was clear but not straight. This shows that HNO_3 can remove the residue effectively, and that Ti^{4+} is unstable and can easily form TiO^{2+}. The appropriate oxidized environment and stable ion transformational environment can therefore be obtained by adding H_2O_2 and HNO_3 into the etching solution.

In order to prevent residue and the small undercutting etching pattern, 0.5-g ethylenediamine tetraacetic acid (EDTA) was added into etching solutions Nos. 3 and 4, and etching time was 15 s. For No. 3, there was a little residue observed, but the edge was clear and no undercutting. For No. 4, there was no residue, and the undercutting was small. This is mainly because EDTA forms a stable, complex compound with the majority of metallic ions to the chelating agent[7−9]. Owing to the EDTA chelating agent, it does not form promptly with the hydrolysis of TiO^{2+} and H_2O_2. Therefore, it can form a stable complex ion $[TiO(H_2O_2)Y]^{2-}$ and make F^- ineffective. Thus, it reduces Ti^{4+} and Zr^{4+} during hydrolysis and causes the non-uniform etching or the existence of residues. This means that EDTA may make the etching result in better edge quality. Based on this and through optimizing the proportion of the etching solution, better etching effects were obtained, as shown in Fig. 5.

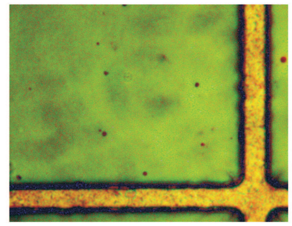

Fig. 3. Etching effects after the addition of H_2O_2 in No. 1.

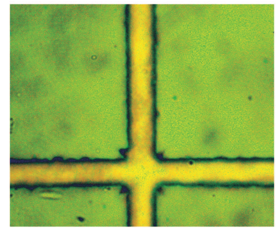

Fig. 4. Etching effects after the addition of HNO_3 in No. 2.

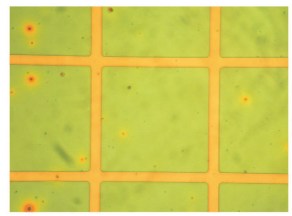

Fig. 5. Etching effect after using the original etching solution.

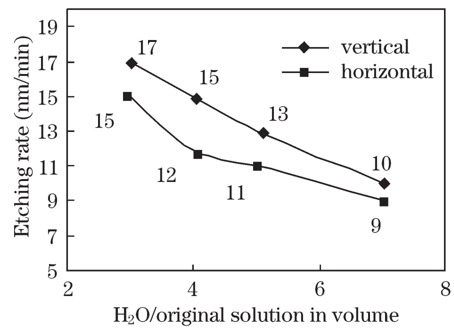

Fig. 6. Vertical and horizontal etching rates at different solution concentrations.

The curves of the vertical and horizontal etching rates at the different volumes of H_2O/original etching solution are shown in Fig. 6. The etching temperature was 25 °C, and the etching time was 10 s. From Fig. 6, we can see that the vertical and horizontal etching rates slowly decrease as the solution concentration decreases. This is mainly due to the decrease in reactive ions in the etching solution after decreasing the solution concentration, which leads to the reduction of the reaction rate.

The original etching solution composed of 5 ml HCl + 5 ml HAc + 20 ml H_2O + 1 ml HF + 0.5 g NH_4F + 2 ml H_2O_2 + 1 ml HNO_3 + 0.5 g EDTA was used to study the dependence of the etching rate on the different temperatures with the etching time of 30 s. The vertical and horizontal etching rates at the different solution temperatures are shown in Fig. 7. It shows that the vertical and horizontal etching rates increase with the increase of the solution temperature. This is mainly due to the increase in the expansion of ions when the solution temperature increases.

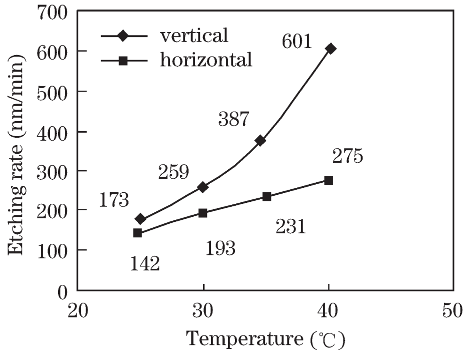

Fig. 7. Vertical and horizontal etching rates at different solution temperatures.

The original etching solution was used to measure the vertical etching rate at the room temperature. The results are shown in Table 1. It was found that the vertical etching rate increases with the addition of the etching time. This may be due to the pollution on the surface of PZT thin film. At the same time, the PZT thin film was etched nearly thoroughly after 35 s.

The original etching solution was used to measure the horizontal etching rate at the room temperature. The results are listed in Table 2. It was found that the horizontal etching rate increases with the addition of the etching time. Moreover, the horizontal etching rate was less than 262.5 nm/min. This is because that the PZT thin film was almost etched thoroughly after 35 s.

Table 1. Effects of Different Etching Time on the Vertical Etching Average Rate

Etching Time (s)	Thickness before Etching (nm)	Thickness after Etching (nm)				Average Etching Rate (nm/min)
6	166.45	164.8	164.7	164.8	164.6	17.25
10	166.45	163.6	163.7	162.9	163.4	18.3
15	166.45	161.7	162.0	161.0	161.8	19.3
25	166.45	150.6	149.6	148.8	149.8	40.2
30	166.45	79.0	79.2	79.9	80.0	173.85
35	166.45	3.219	3.314	2.75	3.08	280.04

Table 2. Effects of Different Etching Time on the Horizontal Etching Average Rate

Etching Time (s)	Photosensitive Resist Pattern Width (μm)	PZT Pattern Width (μm)	Etching Rate (nm/min)
40	5.2	5.6 5.5 5.5 5.6	262.5
45	5.2	5.8 5.7 5.9 5.7	400
60	5.2	6.1 6.2 6.0 6.1	450
120	5.2	7.2 7.0 7.8 7.2	525

As shown in Tables 1 and 2, the side etching ratio of PZT thin film (average rate of horizontal etching: average rate of vertical etching) was less than 262.5/280.04 = 1:1.07. According to this side etching ratio, the error of the film etched was merely 200 nm. This is because that the thickness of the PZT thin film deposited is approximately 200 nm in the PZT devices, which is very small compared with the unit size.

In conclusion, through optimizing the basic etching solution, HCl + HF, the etching solution composed of 5 ml HCl + 5 ml HAc + 20 ml H_2O + 1ml HF + 0.5 g NH_4F + 2 ml H_2O_2 + 1 ml HNO_3 + 0.5 g EDTA is successfully obtained for the patterning of PZT ferroelectric thin film, and the influence of the solution composition on the patterning is studied. The selection ratio of the obtained etching solution is better than that for the Pt electrode and the photosensitive resist mask. On this basis, the influences of the concentration, the temperatures of the etching solution, and the different etching time on a fixed etching rate of PZT thin film are studied, and the curves of the horizontal and vertical etching rates are obtained. The optimum side etching ratio obtained is less than 1:1.07. Furthermore, there is no residuum on the surface of the figure and the edge linearity is good.

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