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Micro-patterning of PZT thick film by lift-off using ZnO as a sacrificial layer

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Abstract

Micro-pattern of 8.2-μm-thick PZT films was prepared on Pt/Ti/SiO_2/Si (1 0 0) substrate wafer by combining composite sol–gel and a novel lift-off using ZnO as a sacrificial layer. The processes include ZnO sacrificial layer deposition and patterning, PZT film preparation, and final lift-off. The results reveal the micro-pattern was better than that formed by wet etching, the PZT thick films patterned by lift-off possessed similar dielectric characters, better ferroelectric properties, and higher breakdown voltage than those of films patterned by wet etching. The lift-off is suitable for micro-patterning of PZT thick films.

Keywords: D. ZnO; Composite sol–gel; Micro-patterning; Lift-off; PZT thick film

1. Introduction

There is a strong interest in introducing crack-free lead zirconate titanate ($PbZr_xTi_{1-x}O_3$, PZT) films for applications in non-volatile memory, uncooled infrared detectors, microactuators [1,2] and microsensors [3,4] because of their excellent ferroelectric, piezoelectric, pyroelectric properties. Compared with PZT thin films, thick films (>2 μm) have better properties, can yield greater power outputs and supply high resonance frequency applications such as micromachined ultrasonic transducers [5–7].

The PZT thick films have been prepared by different methods including composite sol–gel, screen-printing, electrohydrodynamic atomization deposition, aerosol deposition, electrophoretic deposition [8–12]. The composite sol–gel technique possesses many advantages such as easier of chemical composition control, easier fabrication of large area high quality films, cost-effective, and low annealing temperature [13,14]. The processes include dispersing ceramic powder into sol–gel solution and followed by ball milling to produce uniform, stable slurry which is afterwards coated on substrates and annealed to get the PZT film crystallized.

As a key patterning technique of PZT thick film, reactive ion etching (RIE) needs expensive equipment and can easily lead to properties degradation [15]. On other hand, the current wet etching process has been inevitably accompanied by lateral etching and the etching solution includes HCl, HF which may damage other film, especially Ti electrode [16]. The worst thing is powder residue that often occurs in the two kinds of patterning process mentioned above, because of the fact that the thick films contain much ceramic powder. Lift-off process is an ideal patterning method, whereas PZT thick films cannot be patterned using conventional lift-off processes for failure of resist stripping caused by high deposition temperature of PZT films. This paper describes the preparation of patterned PZT thick films by composite sol–gel method and a novel lift-off [17]. In the novel process, ZnO instead of photoresist employed in a conventional lift-off was used as a sacrificial layer. The reasons why ZnO was selected as the sacrificial materials are as follows: ZnO is easy to be etched thus stripping process can be carried out smoothly. Moreover, ZnO is high temperature resistant, while photoresist can be carbonized during deposition of PZT films, which leads to failure of resist stripping in lift-off.

2. Experimental

The 0.4 M PZT sol with a Zr/Ti-ratio of 52/48 was fabricated using zirconium nitrate, tetrabutyl titanate, and lead acetate as precursors and acetic acid, 2-methoxyethnaol as the

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solvent. Details of the preparation of the sol were described elsewhere [18]. The PZT powder was also synthesised through a sol–gel process. The starting reagents for the preparation of PZT solution were zirconium propoxide, titanium isopropoxide and lead acetate, acetic acid and propanol as the solvent. The PZT sol was first heated at 200 °C for 8 h to make the solvents volatilize. Afterwards the gel was calcined at 400 °C for 2 h followed by grinding to get amorphous powder. Finally, the PZT powder was obtained by crystallizing at 600 °C for 1 h and the second grinding process.

The PZT slurry was then made by mixing the PZT producing sol with PZT powder with diameter around 0.2 mm in the ultrasonic bath to produce a powder loading of 1.5 g/ml. To get uniform and steady slurry for thick film deposition, the slurry was finally ball milled for 24 h. In order to pattern PZT thick films by lift-off using ZnO as a sacrificial layer, a ZnO layer of contrast opposite to the final PZT features was fabricated on $Pt/Ti/SiO_2/Si$ (1 0 0) substrate before the PZT films deposition. The whole processes were schematically represented in Fig. 1. A ZnO sacrificial layer was first deposited via DC magnetron sputtering and patterned using the standard photolithography techniques and wet etching process. Thus, a negative image of the final PZT features was created on ZnO sacrificial layer as shown in Fig. 1(b). Thereafter, The PZT thick film was deposited by spin-coating slurry at 3000 rpm for 40 s on substrate, and the coating substrate with sol and spinning were subsequently repeated nine times to increase the film density. Each layer was subjected to a heat treatment (150 °C/15 min and 350 °C/15 min) designed to remove the organic component and crystallize the sol. After the deposition of one thick and nine thin films, the ten layers were calcined at 550 °C for 10 min. The above processes were repeated two cycles for obtaining the final film thickness of around 8.2 μm as shown in Fig. 1(c). Finally, the films were annealed at 700 °C for 30 min to develop the perovskite structure. The wafer was then immersed in H_3PO_4 solution and the ZnO film under PZT thick film was etched. As a result, the PZT thick films were patterned by the novel lift-off using ZnO as sacrificial layer as shown in Fig. 1(d). In order to compare wet etching and the novel lift-off, the PZT thick film was also patterned by wet etching.

The crystal structure was analyzed using X-ray diffraction (XRD) and the surface profile was examined using a Surface Profiler. A metal-ferroelectric-metal (MFM) structure was made by sputtering Au top electrode onto the PZT thick films for electrical measurement. The WS2000 ferroelectric tester was used to measure the ferroelectric properties, dielectric characters were tested by using the HP4192A impedance analyzer.

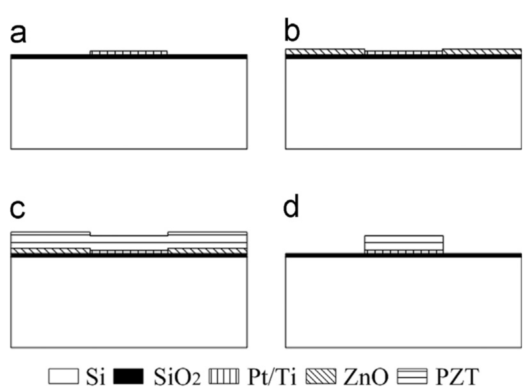

Fig. 1. Novel lift-off processes for PZT thick films.

3. Results and discussion

Fig. 2 shows optical images of PZT patterned by novel lift-off and wet etching, respectively. We can see that the edges of PZT patterned by novel lift-off were neat and straight at the magnification, and the residual PZT powder was not almost found on electrodes and silicon dioxide, which led to that the substrate was smooth after patterning. By contrast, the lateral etching was so serious that some electrodes designed to be covered by PZT were exposed after wet etching, and lots of powder remained on electrodes and dioxide so the substrate became rough as shown in Fig. 2(b). Therefore, the lift-off using ZnO as a sacrificial layer can get better PZT thick film patterns by avoiding lateral etching and powder residue. The successful patterning by lift-off was due mainly to the truth that the ZnO film is easy to be etched and high temperature resistance.

Fig. 3 shows the X-ray diffraction (XRD) pattern of PZT thick films patterned by lift-off. The peaks have been indexed as per the crystal structure of PZT films. The XRD pattern shows perovskite structure except for the Pt (1 1 1) peak. The film was well crystallized with pure perovskite phase and highest (1 1 0) orientation, which means the slurry and anneal processes are appropriate for good phase structures. The surface profiles of the PZT thick films patterned by novel lift-off are shown in Fig. 4. The surface profiles of films with maximum, minimum, average thickness were similar and presented deep wall slope, the sidewalls of PZT film were all regular and steep.

The dielectric constant and loss of PZT thick films with about 8.2 μm thickness were tested by using the HP4192A impedance analyzer in the frequency range from 100 Hz to

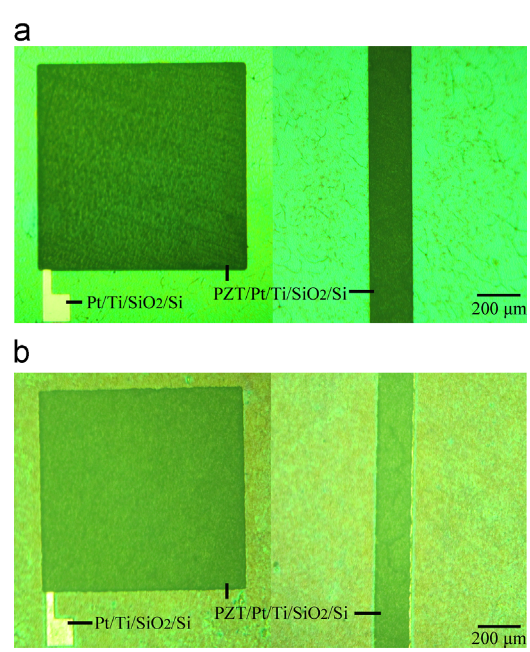

Fig. 2. Optical images of PZT thick films patterned by (a) novel lift-off and (b) wet etching.