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Bottom electrode etching effect on the electrical properties of lead strontium titanate thin film

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Abstract $(Pb_{0.4}Sr_{0.6})TiO_3$ thin films were prepared by a modified sol-gel method on $Pt/Ti/SiO_2/Si$ substrates, where lower figure of merit of about 16% was observed in spite of higher tunability above 58%. The electrode surface was etched with different CF_4 and Ar gas ratios to modify the surface roughness. The electrical properties of PST thin films were investigated as a function of etching condition and film thickness. With changing $CF_4/(Ar+CF_4)$ gas composition, the dielectric loss and the figure of merit were apparently affected which can be explained in terms of the surface roughness of Pt bottom electrode. When the Pt electrode surface was etched by using $CF_4/(Ar+CF_4) = 20\%$ gas mixture, the improvement above 25–27% in dielectric loss and figure of merit was observed, according to the decreased rms value of Pt surface of ~30%, from 1.8 to 1.2 nm. The etching effect was found to be dominant for the dielectric loss and the thinner films.

Keywords Surface roughness · Dielectric properties · Pt bottom electrode · Dry etching · Tunable device

Introduction

The $(Pb_{(1-x)}Sr_x)TiO_3$ (PST) system offers good control over many of the desired room temperature dielectric and piezoelectric properties as reported in the studies based on bulk ceramics [1] and thin films [2, 3]. Especially Somiya et al. [4] have suggested these PST ceramics for promising tunable device application. In case of the PST based thin films, there is a trade off between dielectric tunability and material loss tangent, practically for microwave tunable device application. The formation of $(Pb_{(1-x)}Sr_x)TiO_3$ heterostructure film has been reported, achieving optimum figure of merit (FOM, tunability/loss tangent) while maintaining the high tunability [5]. In case of the microelectronic devices, it has been well known that the rough morphology of surface and interface and the presence of material defects altered their operational conditions [6]. Indeed, it has been found, through a large number of experiments, that the surface/interface morphology has a great influence on the electrical properties of dielectrics. Pontes et al. [7] have reported that the film surface roughness is extremely important for device performance since the dielectric properties depend not only on the well-defined microstructures but also on the quality of electrode-film interface. In particular, lower dielectric loss implying higher FOM, can be obtained by improving the interfacial property between electrode and dielectric film. Thus in this study, $(Pb_{0.4}Sr_{0.6})TiO_3$ composition with relatively higher tunability of ~58% but lower FOM of ~16 was selected. The surface of Pt bottom electrode was etched by using CF_4 and Ar gas in order to improve the electrical properties of PST films and the adhesion at the electrode-dielectric film interface by decreasing the surface roughness. The dielectric properties of PST thin film caused by changes in the surface morphology and the roughness for both Pt bottom electrode and PST thin

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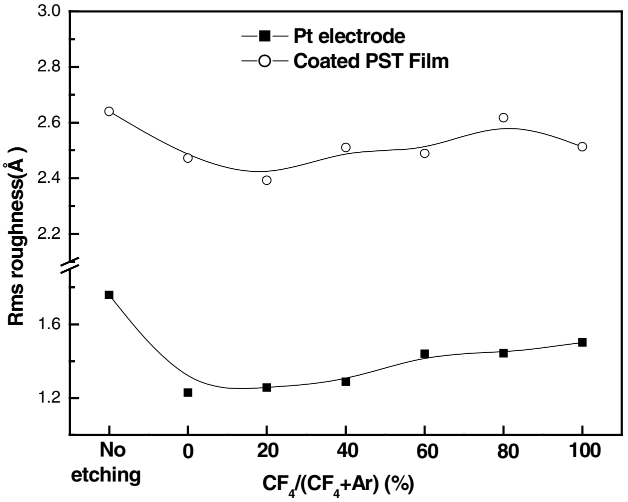

Fig. 1 Rms roughness value of Pt electrode and deposited PST film on the etched Pt electrode as a function of $CF_4/(CF_4 + Ar)$ gas mixing ratio

film were investigated in terms of Pt etching condition and thickness of the PST dielectric thin films.

Experimental

The precise procedure for preparing the PST precursor solution was presented in previous report [3]. Before coating PST dielectric thin layer, the surface of Pt bottom electrode was etched in a magnetic inductively coupled plasma etcher using various $CF_4/CF_4 + Ar$ gas ratios at the power of 700 W. The $(Pb_{0.4}Sr_{0.6})TiO_3$ 2(PST) thin films were deposited on the no-etched and etched $Pt(111)/Ti/SiO_2/Si(100)$ wafer by spin-coating at 2,200 rpm and 30 s, where the deposition and firing steps were repeated to obtain an appropriate thickness (∼200 nm). After drying at 400°C for 5 min, crystallization of the films was conducted by annealing at 700°C for 10 min. An X-Ray diffractometer (D/MAX 2C, Bruker) and an Atomic force microscopy (SPM-9500J3, Shimadzu) were used to determine the crystal structure, surface morphology and roughness of the films. After Pt top electroding, the electrical properties including C-V and I-V were measured by employing an impedance analyzer (4294A, HP) and a precision pro (Radiant tech. Inc.), and then tunability and FOM values were calculated, which was precisely reported elsewhere [3, 5].

Results and discussion

The application fields of PST thin films have been restricted due to low FOM caused by a large loss tangent despite of its relatively excellent tunability. The crystallographic texture of Pt electrode and the surface morphology were investigated for the Pt bottom electrodes etched using various gas mixtures. Crystallographic direction (111) of the Pt substrate was not changed after dry etching and also the crystallographic direction of as-grown polycrystalline PST film was hardly affected by the etching. Figure 1 shows the rms roughness of Pt substrates and PST thin films deposited on correspondingly etched Pt substrate as a function of $CF_4/(Ar+CF_4)$ etching gas ratio. The roughness of etched Pt substrate drastically jumps down by the etching compared to that of non-etched Pt substrate. Slight increase according to further increase of the CF_4 gas content was associated with reduction of physical bombardment effect by the decrease of Ar concentration in the etching gas [8]. The result of the roughness of Pt surface with etching gas composition is well understood by the decrease of etching rate from 16 Å/sec in a $CF_4/(Ar+CF_4)$ gas composition of 20% to 10 Å/sec in a 100% pure CF_4 etching gas. At the condition of 20% etching gas mixture, the excessive etching time over 15 sec resulted in the increase of rms value. The roughness of PST films also similarly traced the tendency of Pt bottom electrode as shown in Fig. 1. The AFM morphology of the non-etched and etched Pt substrate at $CF_4/(Ar+CF_4) = 20\%$ for 15 sec and PST thin films deposited on correspondingly treated Pt substrate are shown in Fig. 2. It indicates that the surface morphologies of the Pt substrate and PST thin film on Pt were well modified by etching. The dielectric constant and the tunability are relatively constant regardless of etching in the range of less than 40% gas ratio as shown in Fig. 3. Although the increased contact area between the electrode and the dielectric film usually contributes to the increase of capacitance, the relatively large area of electrode used might ignore this effect [6]. On the other hand, as shown in Fig. 4, a great improvement in dielectric loss tangent over 25% compared to the behavior of PST films coated on no-etched Pt substrate was observed. The loss tangent apparently lowered at the 20–40% gas ratio and subsequently the FOM was enhanced up to these gas ratios, which well coincide with the result of the roughness variation as shown in Fig. 1. The poor behavior such as low dielectric constant and tunability and high loss tangent in the mixing gas ratio over 60% might be related to the excessive chemical etching. According to the Wuu et al.'s report [8], the Ar/CF_4 plasma system has been considered much applicable for platinum etch process due to more volatile character of the platinum fluoride compound formed. However the distribution of fluorine in deep inside of the Pt film was detected and also relatively higher concentration of CF_4 addition in Ar/CF_4 etch-gas mixture composition hampered the Pt etch rate due to the lowered physical etching of Ar. Similarly, the slight increase in roughness for the higher CF_4 concentration, e.g. above 60% mixing gas ratio seems to deteriorate the

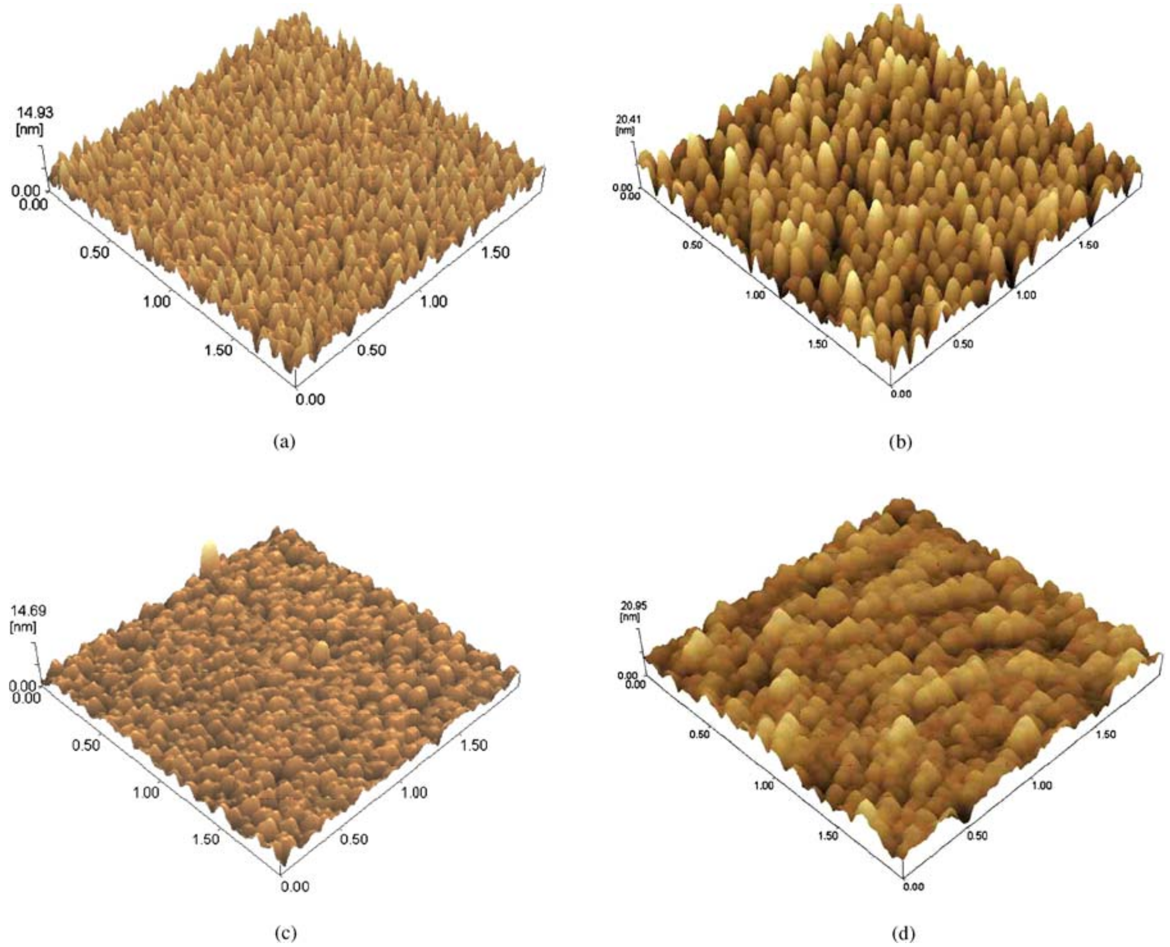

Fig. 2 AFM surface image of no-etched Pt electrode (a) & deposited PST film (b) and etched Pt electrode (c) & deposited PST film (d)

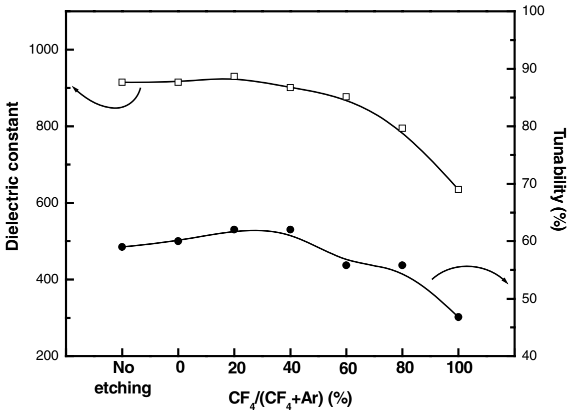

Fig. 3 Dielectric constant, tunability of the $(Pb_{0.4}Sr_{0.6})TiO_3$ thin films deposited on the etched Pt bottom electrode as a function of $CF_4/(CF_4 + Ar)$ gas mixing ratios

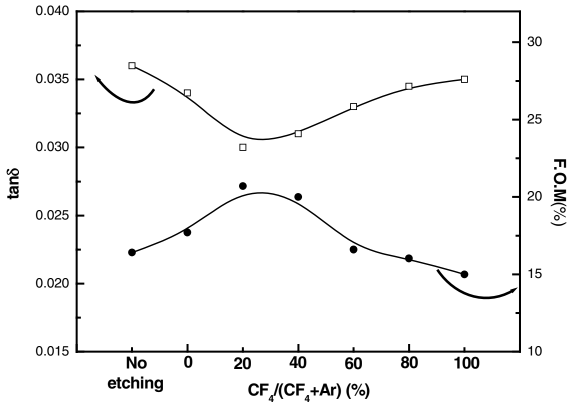

Fig. 4 FOM, tan_ of the $(Pb_{0.4}Sr_{0.6})$ TiO_3 thin films deposited on the etched Pt bottom electrode as a function of $CF_4/(CF_4 + Ar)$ gas mixing ratios

film-electrode interface, resulting in degradation in the dielectric properties as shown in Figs. 3 and 4. It has been well known the importance of quality of the electrode-film interface, as well as a well-defined microstructure for the dielectric film device performance [7]. As presented in Figs. 3 and 4, the dielectric property of PST thin film was observed differently with etching gas composition. Assuming the fact that etched Pt morphology is always identical in the case of a selected etching condition, it can be considered the dependency of the Pt etching effect on dielectric properties with the thickness variation of PST film. Figure 5 shows the effect

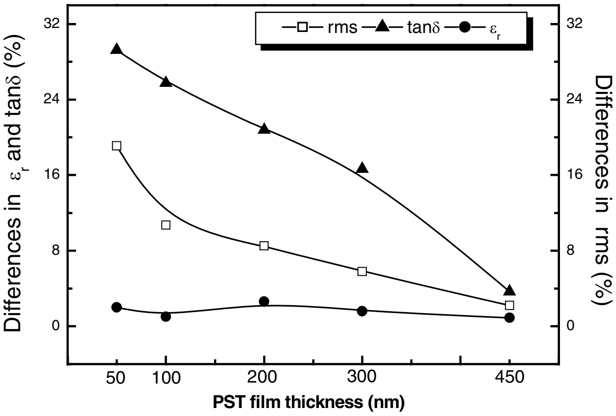

Fig. 5 Degree of differences in rms, tan_ and dielectric constant for the PST films deposited on the non-etched and etched Pt substrate as a function of PST film thickness

of PST film thickness with differences in dielectric properties and roughness for the PST thin films coated on the non-etched and the etched Pt bottom electrodes at the given optimum condition. The difference of rms values of PST thin film deposited on the non-etched and etched Pt substrate gradually decreased with increase in film thickness. Also the loss tangent showed similar tendency, while the difference of dielectric constant maintains relatively constant. It is apparently noticed, from these results, that the lowered surface roughness created by dry-etching improved effectively the loss tangent of PST thin films, especially the thinner films.

Conclusions

The Pt substrate was etched using mixing gases including Ar and CF_4 to improve the adhesion between the substrate and the dielectric PST thin film. The optimal conditions with $CF_4/(Ar+CF_4)$ of 20% and etching time of 15 sec minimized the loss tangent in comparison with the other etching conditions, resulting in the maximum FOM (∼21%). Further excessive etching by duration time and CF_4 concentration degraded its electrical properties. It was therefore clear that the substrate etching is very useful to the application of PST films for microwave devices since the loss tangent can be lowered and the FOM can be enhanced up to a desired level without the expense of decreasing tunability. In particular, the effect of etching was highly improved for the films with thickness in less than 2000 Å because the morphology of substrate directly affected the surface morphology and interface of PST films.

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