Microwave characterization of (Pb,La)TiO_3 thin films integrated on $ZrO_2/SiO_2/Si$ wafers by sol-gel techniques

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Polycrystalline perovskite lead lanthanum titanate (PLT) thin films were prepared by a sol-gel method on $ZrO_2/SiO_2/Si$ substrates. The structure of the films was studied by x-ray diffraction and scanning electron microscopy, and the microwave dielectric properties characterized on a network analyzer. A strong dependence of the dielectric constant of PLT films and, correspondingly, the resonance frequency of PLT-based interdigital capacitor on the sample preparation conditions were observed. They resulted from the structural transformation of PLT from a layered structure to a uniform film as the annealing temperature was raised from 550 to 700 °C, suggesting a possible way to modify the device performance by controlling the layered structure of the ferroelectric film. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1823038]

While many of the ferroelectric/piezoelectric thin film-based devices may work at relatively low frequencies (usually at megahertz or lower), in recent years ferroelectric and piezoelectric devices working at higher frequencies [up to gigahertz (GHz)] have also attracted strong interest. Typical examples of such devices include microwave phase shifters and piezoelectric film-based biosensors for DNA and protein tests.[1–6] Around the GHz range, the ferroelectric domains usually cannot switch fast enough to keep up with the external ac field; consequently, the dielectric behaviors of the ferroelectrics are dramatically different from their low frequency dielectric properties. The microwave characterization of ferroelectric thin films is of significance both for fundamental understandings and practical applications. Technically, the high frequency dielectric measurement of ferroelectric films remains a challenge despite continued research efforts in the last few decades on the development of various testing techniques and theoretical models for solving the technical problems. This may be the reason for the lack of microwave characterization of many typical ferroelectric thin films, even though barium strontium titanate films, as a candidate for tunable microwave devices, have been extensively studied in the last decade.[7–9]

In this letter, the dielectric properties of lanthanum-doped lead titanate [nominal composition as $(Pb_{0.85}La_{0.10})TiO_3$ (PLT)] thin films integrated on buffered silicon were investigated at high frequencies up to the GHz range. PLT is a very useful ferroelectric material that can be used for infrared micro-sensors, ferroelectric memories, electro-optical devices, and piezoelectric micro-sensors (for biological applications).[10–15] The structural development and control, ferroelectric behavior, pyroelectric performance, and piezoelectric properties of PLT have been extensively studied in the literature.

The samples for tests have a layered structure: PLT film/$ZrO_2/SiO_2/Si$. Both ZrO_2 and SiO_2 are the buffer layers. The sample preparation was basically a multistep microfabrication process. On a (100)-oriented silicon wafer with a 5.46 μm thermally grown SiO_2 layer, ZrO_2 film (200 nm thick) was deposited by sol-gel and spin coating techniques followed by pyrolysis at 600 °C for 1 h in O_2. On ZrO_2, the PLT film was similarly coated layer by layer. By each spinning and drying, a ~50-nm-thick layer was formed. After 20 layers were coated and dried, the whole stack was annealed in O_2 at different temperatures (550, 600, 650, and 700 °C, all for 1 *h*). Details of the sample preparation have been described elsewhere.[15]

X-ray diffraction (XRD) revealed that the PLT film has a pure perovskite phase and is randomly oriented, as shown in Fig. 1. With increase of annealed temperature, the intensity of (100) peak had increasing trend. The microstructure of the samples was observed under scanning electron microscopy (SEM). It was found that the film is very dense, smooth, and free of cracks. The average grain size of PLT is about 50 nm in diameter. The cross-sectional micrographs of two samples (one annealed at 550 °C and another at 700 °C) are shown in Fig. 2. Apart from amorphous SiO_2 and columnar-structured ZrO_2, a layered structure is observed in the PLT layer of the 550 °C-annealed sample [the parallel lines shown in Fig. 2(a)]. Quite obviously the layered structure was formed because the final annealing temperature (550 °C) was lower than the hydrolysis temperature (600 °C) so that sufficient diffusion could not occur to eliminate the boundaries between the adjacent layers in PLT. For

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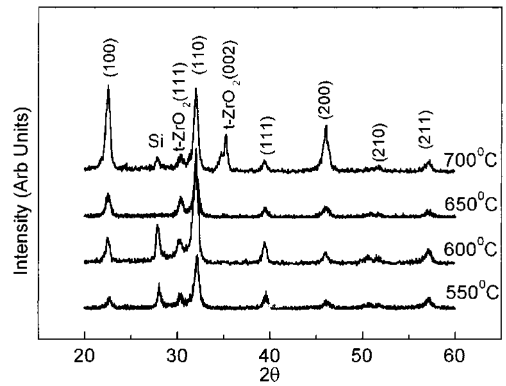

FIG. 1. X-ray diffraction of PLT integrated on $ZrO_2/SiO_2/Si$ and annealed at different temperatures.

the same reason, such layered structure was also observed in the 600 °C-annealed sample (SEM picture not shown). For the sample annealed at 650 and 700 °C, the layer boundaries disappeared and the whole PLT became a uniform single layer [Fig. 2(b)]. As will be demonstrated later in this letter, the structural evolution has led to very different dielectric properties in the samples.

The dielectric characterization was conducted at room temperature on the $Au/PLT/ZrO_2/SiO_2/Si$ coplanar capacitors. On the PLT film, a gold layer was sputtered by magnetron sputtering and then patterned by photolithography and wet chemical etching to form the interdigital electrodes (IDEs). The finger width of the IDEs is 3 μm, the separation between two adjacent fingers is 5 μm, and the finger length is 25 μm. The total number of fingers is 21 (refer to Ref. 15 for the electrode configuration). The measurement of these interdigital capacitors (IDCs) was carried out on a vector network analyzer 8720ES (Agilent, USA) together with a micoprobe station RF-1 (Cascade, USA). Before the measurement, the test system was carefully calibrated following the operation instruction. Then the reflection parameter S_{11} of the IDCs was determined and from S_{11} the impedance was obtained. The dielectric constant of PLT was extracted from

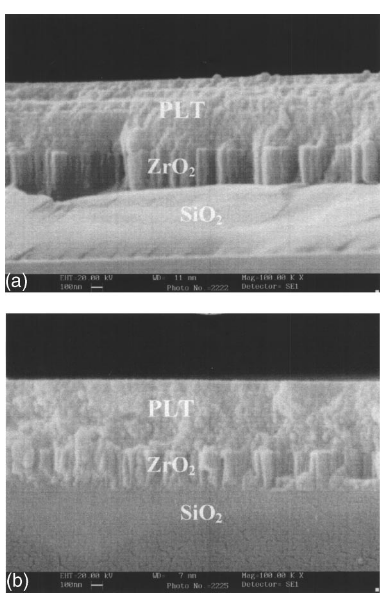

FIG. 2. Cross-sectional observation under SEM of $PLT/ZrO_2/SiO_2/Si$: (a) layered structure in PLT in the sample annealed at 550 °C, and (b) uniform PLT layer in the sample annealed at 700 °C.

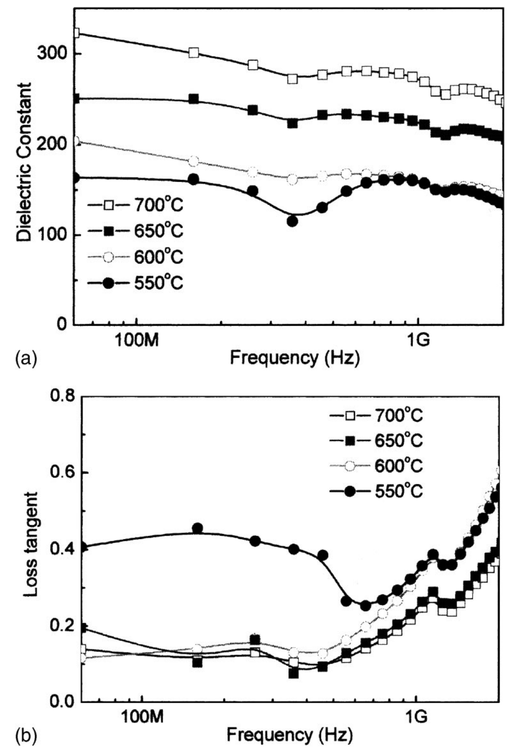

FIG. 3. Frequency dependence of (a) the in-plane dielectric constant, and (b) the loss tangent of PLT films.

the impedance by using a program that we developed based on the Gevorgian's model.[8,16,17]

Figure 3 shows the frequency dependence of the dielectric constant of the PLT films annealed at different temperatures. In the whole frequency range, the sample annealed at a higher temperature has a larger dielectric constant than the sample annealed at a lower temperature, as shown in Fig. 3(a). At $f=1$ GHz, for example, the dielectric constant of the samples annealed at 550, 600, 650, and 700 °C was found to be 157, 158, 222, and 269, respectively. It is interesting to note that the dielectric constant of the 550 °C-annealed sample is only about 40% of the dielectric constant of the 700 °C-annealed sample (the difference is even larger at lower frequencies), while the XRD and SEM observation did not show significant difference in the two samples on the crystallinity and grain size. Thus we propose that the critical factor that causes the difference is the layered structure of PLT. Just like many other interface layers in ferroelectric heterostructures, the interfaces inside the PLT films have smaller dielectric constant, leading to the lowering of the dielectric constant of the whole PLT layer in the 550 °C-annealed sample (and similarly in the 600 °C-annealed one). For the sample annealed at 700 °C, the dielectric constant is larger because it dose not have such interfaces. For the same reason, the loss tangent of the samples decreases as the annealing temperature increases, as shown in Fig. 3(b).

When observed over a larger frequency range, an interesting relationship between the dielectric resonance and the sample structure can be established. As shown in Fig. 4, resonance peaks can be clearly identified in the loss tangent versus frequency plot [Fig. 4(b)], which correspond to abrupt decreases of the capacitance in the capacitance versus frequency graph [Fig. 4(a)]. The resonance frequencies f_r of the samples (annealed at 550, 600, 650, and 700 °C) are 6.2, 6.3,

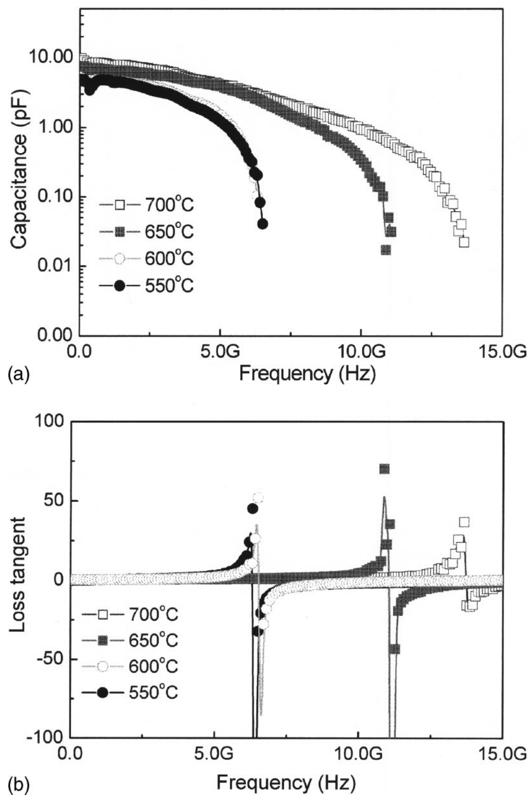

FIG. 4. Dielectric resonance of IDE/PLT/ZrO_2/SiO_2/Si capacitors—the frequency dependence of (a) the capacitance, and (b) loss tangent.

11.1, and 13.3 GHz, respectively. When the frequency dependence of the capacitance increases into the range of resonance, the capacitance of the device rapidly decreases and tends to zero, meanwhile, the loss tangent of the device rapidly increases, then decreases until negative, but the curve of frequency dependence of the capacitance of the device ends the resonance frequency. Therefore, after the resonance frequency, the negative loss tangent of no capacitance had no means. A correlation in the f_r shift and the layered structure of PLT can also be established: A low annealing temperature leads to a layered structure and results in a low f_r and vice versa.[18]

The experimental results indicate a strong dependence of the dielectric performance of the ferroelectric film and device on annealing temperature. Such dependence may have been observed in many other ferroelectric films.[19] Nevertheless, the mechanism of such dependence in the literature is usually related to the grain size, crystallinity, and/or orientation of the ferroelectric film. In our work, however, the dominant factor of the mechanism is the layered structure that exists in some of the samples and disappears in the others. Technically, this result implies that control of the layered structure may be another way to modify the dielectric property of the ferroelectric films and the performance of the devices.

In summary, we have fabricated and characterized the microwave properties of perovskite PLT films on ZrO_2/SiO_2/Si substrate. Depending on the annealing temperature, the in-plane dielectric constant of the PLT film at 1 GHz was found to vary from ~160 to ~260. Correspondingly, the resonance frequency of the interdigital capacitance changed from 6.1 to 13.3 GHz. The strong dependence of the dielectric properties of the films on the annealing conditions was explained as a result of the evolution of PLT from a layered structure to a uniform film as the annealing temperature was raised from 550 to 700 °C.

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[18]At the gigahertz frequency range, these devices cannot be regarded as purely capacitive. Therefore in the equation $f_r = 1/2\pi\sqrt{LC}$, L is not a constant value because the contribution of the devices may change with frequency [if L does not change, then f_r of the high ε material should be smaller than that of the low ε material, opposite to the observation shown in Fig. 4(a)]. The reason for sample A having a smaller f_r value than sample D, for example, can be explained to be a result of, first, the product of L and C of sample A being larger than the latter (in another world, the L value of sample A must be much larger than the L value of sample D). Because of the very complicated device structure and measurement circuit, however, we have not been able to have an equivalent circuit for an accurate and precise description of the behavior of our devices under these measurement conditions. Second, with different annealed temperatures, PLT film having different dielectric property which are different dielectric constant and range of resonance. From Fig. 4, the capacitance trend to zero which the resonant take place at. Therefore, the samples with different temperatures cannot get all data from 60 MHz to 20 GHz, they begin 60 MHz and end of resonant frequency. What are the reasons for the range of resonance, etc.? Further investigation on this issue is still to be undertaken.
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