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Low-temperature fabrication of $Ba_{1-x}Sr_xTiO_3$ thin films with good dielectric properties on platinized silicon substrates

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Abstract

$Ba_{0.7}Sr_{0.3}TiO_3$ (BST) thin films 500 nm in thickness were prepared on technologically desirable $Pt/TiO_2/SiO_2/Si(1\,0\,0)$ substrates by ion beam sputtering (IBS) and post-deposition annealing method. The effect of annealing temperature on the structural and dielectric properties of BST thin films was systematically investigated. A sharp transition in their tunable dielectric behaviours was observed in good agreement with the evolution of crystal structure from amorphous to crystalline phase. It was demonstrated that the perovskite phase could crystallize in BST films at a very low temperature, around 450 °C. The lowering of perovskite crystallization temperature in the BST films was explained in terms of the high energetic process nature of IBS technique. A high dielectric tunability of 42% at E (electric field intensity) = 500 kV/cm and a low loss tangent of 0.013 at zero bias were both obtained in the 450 °C-annealed film, thereby resulting in the highest figure-of-merit factor among all the different temperature annealed films. Moreover, the 450 °C-annealed film showed superior leakage current characteristics with a low leakage current density of about 10^{-4} A/cm^2 at E = 800 kV/cm.

Keywords: $Ba_{1-x}Sr_xTiO_3$; Dielectric properties; Ion beam sputtering; Thin films; Annealing temperature

1. Introduction

Recently, barium strontium titanate ($Ba_{1-x}Sr_xTiO_3$, hereafter represented as BST) thin films have been intensively investigated for applications in tunable microwave/RF components, such as frequency-agile filters, voltage-controlled oscillators, phase shifters and antennas, because of their large electric field-dependent tunability and relatively low dielectric loss.[1–4] Compared to mechanically and magnetically tuning techniques, the tunable devices based on ferroelectric films are fast, small and lightweight and, because they work using an electric field, have low power consumption. Since silicon wafer plays a dominant role in the integrated electronics industry, the integration of BST thin films with conventional silicon microelectronic technology is of great significance. However, a rather high processing temperature, around 600–800 °C,[1–6] is generally required to achieve sufficient crystallinity and, thus, good physical properties of BST thin films, which limits inevitably the applicability of these thin films in integrated circuits (IC), especially in the issues of above-IC technologies.

In this work, we report on the fabrication of $Ba_{0.7}Sr_{0.3}TiO_3$ thin films on technologically desirable platinized silicon substrates by ion beam sputtering (IBS) and post-deposition annealing method. The effect of annealing temperature on the structural and electrical properties of the BST films was systematically investigated. This particular composition of BST (70/30) was chosen to meet the requirements of room temperature tunable device applications. It is noteworthy that the best overall dielectric properties have been obtained in the film with post-annealing temperature as low as 450 °C, i.e., a low processing temperature compatible with the above-IC technologies.

2. Experimental

BST thin films with thickness of 500 nm were deposited on $Pt/TiO_2/SiO_2/Si(1\,0\,0)$ substrates by ion beam sputtering from a single stoichiometric $Ba_{0.7}Sr_{0.3}TiO_3$ target in an Oxford 500 apparatus. When compared to conventional sputtering methods,

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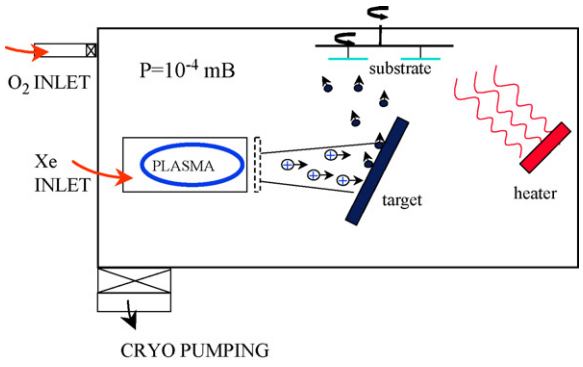

Fig. 1. Schematic illustration of ion beam sputtering deposition system.

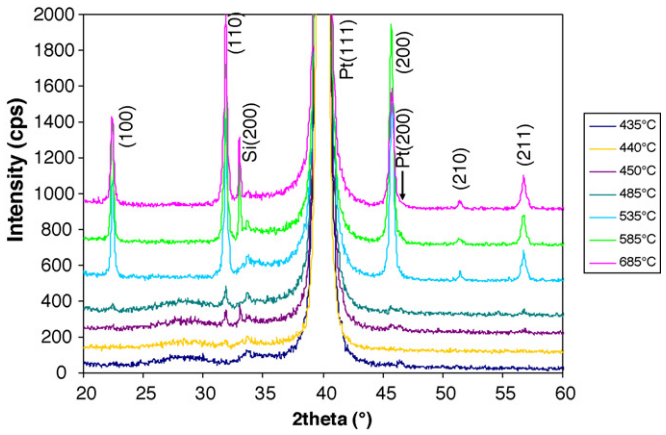

Fig. 2. XRD θ–2θ scans of the BST thin films 500 nm in thickness that were deposited on Pt(111)/TiO_2/SiO_2/Si substrates and post-annealed at different temperatures ranging from 435 to 685 °C.

the IBS technique exhibits several very attractive advantages: (i) The plasma is isolated from the substrate, thereby avoiding plasma damage to the deposited films. (ii) Very high kinetic energy ion beam leads to excellent adhesion and high density for film deposition. The sputtered material impacts on the substrate with a kinetic energy which may be several orders of magnitude higher than in conventional sputter deposition techniques. (iii) The IBS process can be precisely controlled and easily automated so that films can be deposited with extremely high accuracy and repeatability. Fig. 1 presents a schematic illustration of our IBS system. Xe ions rather than Ar ions are used in order to achieve a better stoichiometry of the BST films, particularly for precise Ba and Sr composition in the films, because the atomic mass of Xe is comparatively closer to that of Ba and Sr elements. In this system, substrates can be heated up to 150 °C by IR lamps, and they are continuously rotated during the deposition for good film thickness uniformity. More details about this IBS deposition system can be found elsewhere.[7] In the present work, the ion beam voltage and ion beam current were set at 500 V and 30 mA, respectively. The substrates were not heated during the deposition and their temperature was only dependent on ion bombardment. After deposition, the films were post-annealed at a wide range of temperatures, ranging from 300 to 700 °C, for 30 min in a conventional furnace in air ambient.

The structural, dielectric and electrical properties of the BST films were characterized. Their crystallographic structures were analyzed by X-ray diffraction (XRD) with a Siemens D5000 diffractometer using CuK_α radiation. In order to measure the dielectric and electrical properties of the films, circular top platinum electrodes with 110 μm in diameter were patterned by photolithography and lift-off process. The dielectric properties of the BST films were measured with a Hewlett-Packard 4275A multi-frequency LCR meter. The leakage current–voltage measurements were performed by using an HP4140B pA meter/DC voltage source.

3. Results and discussion

Fig. 2 shows θ–2θ XRD scans of the BST thin films that were annealed at different temperatures in the range of 435–685 °C. Judging from the major diffraction peaks (1 0 0), (1 1 0) and (2 0 0), especially from peak (1 1 0), one can see a gradual evolution in the perovskite crystallization with increasing the annealing temperature. For the 435 °C-annealed film, it is still amorphous. However, the BST film starts to nucleate and grow in the perovskite phase when the annealing temperature is raised to 440 °C. Accordingly, a weak (1 1 0) diffraction peak can be visible. Then, a further increase in the annealing temperature results in an enhancement of peak intensity and, thus, an improvement in the BST film crystallinity. As a result, the perovskite phase can be clearly evidenced in the 450 °C-annealed film. Such a low crystallization temperature is promising for the integration of these thin-film materials into silicon integrated circuits. The dramatic lowering of the crystallization temperature in our case is believed to originate from the high energetic process nature of IBS technique, which is helpful in enhancing the reactive activation of sputtered atoms and effectively overcomes the energy barrier for perovskite crystallization in films.

The dielectric properties of the BST films were investigated systematically as a function of the annealing temperature. Fig. 3 shows the annealing temperature dependence of the relative dielectric constant (ε_r) at zero bias, percent tunability ($=[\varepsilon(0) - \varepsilon(E)]/\varepsilon(0) \times 100\%$) with a dc bias field of 500 kV/cm, loss tangent ($\tan\delta$) at zero bias, and figure of merit (FOM), all of which were measured at room temperature and at a frequency of 100 kHz. The figure of merit, defined as tunability/$(\tan\delta)_{0\,kV/cm}$, is commonly used to evaluate the overall dielectric performance of the materials for tunable microwave devices.[8] As shown in the figure, the dielectric constant and tunability display a sharp transition to high values at 435–440 °C where the BST films undergo a structural transition from amorphous to crystalline phase. Also interesting to note that the tunability for the BST films annealed at low temperatures (440 and 450 °C), roughly 42%, is comparable to those results obtained in high temperature annealed films, although the crystallinity is much inferior in the films annealed at low temperatures. This unexpected but exciting result could be understood as follows. The incompletely crystallized films, which were annealed at low temperatures, can be considered as crystalline/amorphous composite.[9] The big contrast in the values of dielectric permittivity of the amorphous and crystalline regions affects the redistribution of the electric field around the amorphous regions. Therefore, the dielectric per-

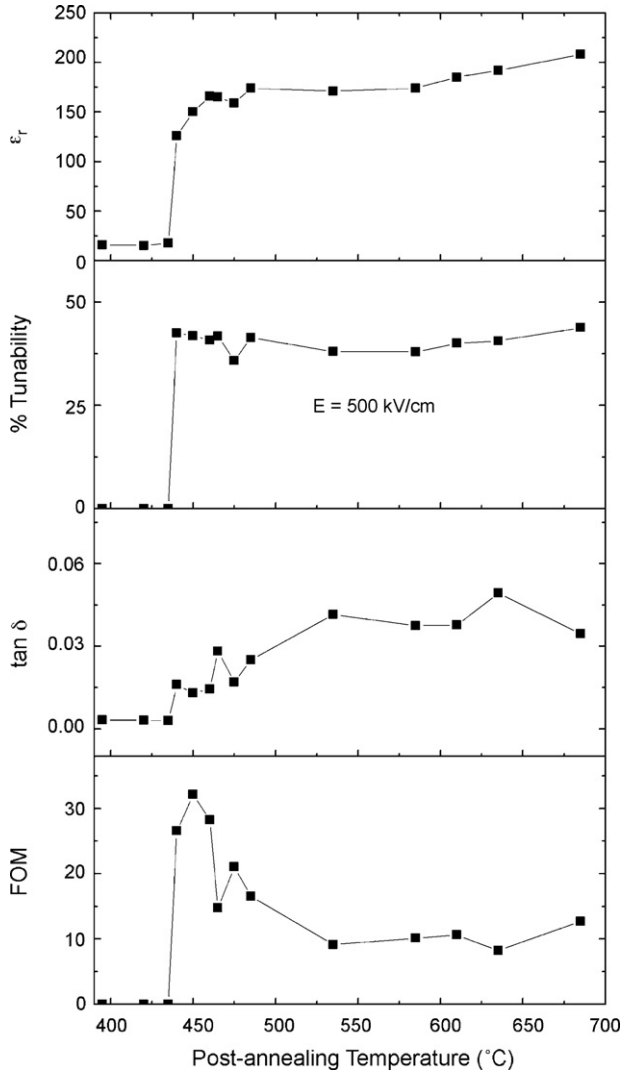

Fig. 3. Post-annealing temperature dependence of the relative dielectric constant at zero bias, percent tunability with a dc bias field of 500 kV/cm, loss tangent at zero bias, and figure of merit, measured at 300 K and 100 kHz.

mittivity of the crystallites under applied electric field becomes inhomogeneously distributed over the volume of the crystallites. The redistribution of the electric field surrounding the amorphous regions can enhance the local tuning ability of the crystallites, which can effectively compensate for the suppression of the tunability caused by a reduced total volume of crystallites.[10]

It is worth mentioning that the BST films annealed at low temperatures not only show high tunability but also relatively lower dielectric loss. As shown in Fig. 3, a fairly low tan δ, 0.013 in value, is achieved in the 450 °C-annealed film, leading to the highest figure-of-merit factor in this film. High-performance BST thin films by such a low-temperature process (450 °C) can ensure their applicability in above-IC technologies, and at the same time, benefit from a low thermal budget.

The dielectric constant and loss tangent for the 450 °C-annealed film are shown as a function of the applied dc bias field in Fig. 4. Compared to the aforementioned tunability of 42% at an electric field intensity of 500 kV/cm, a higher tunability of

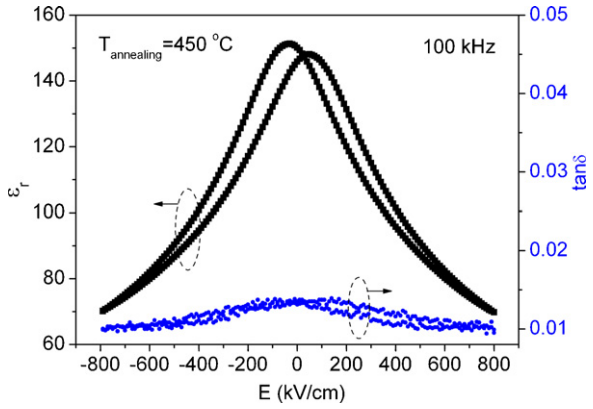

Fig. 4. Dielectric constant and loss tangent as a function of the applied dc electric field for the 450 °C-annealed film, measured at 300 K and 100 kHz.

53% is obtained at 800 kV/cm, indicative of a great potential for the improvement in dielectric tunability upon increasing the applied dc field. Moreover, the loss tangent displays similarly a downward trend with the applied dc electric field, making the dielectric loss fairly low over the entire range of operating voltages. It should be pointed out that the observed butterfly shaped hysteresis effect might be attributed to the presence of space charges, such as oxygen vacancies, trapped at the grain boundaries and/or at the film/electrode interfaces, which give rise to local polar regions in the film.[11,12]

Fig. 5 shows the variations of leakage current density with the applied dc electric field up to 800 kV/cm for the BST films annealed at different temperatures. As can be seen in the figure, the leakage current density for the 450 °C-annealed film remains at a quite low level (10^{-4} A/cm^2) when the dc electric field is increased to 800 kV/cm, which, especially on the positively biased side, is remarkably lower than those obtained in the films annealed at higher temperatures. This is probably because the high temperature thermal treatment promotes the possibilities of interdiffusion between the film and the electrodes. It is noted that the slight asymmetry in the leakage behaviour stems from the different upper electrode/film and film/bottom electrode interfacial qualities.

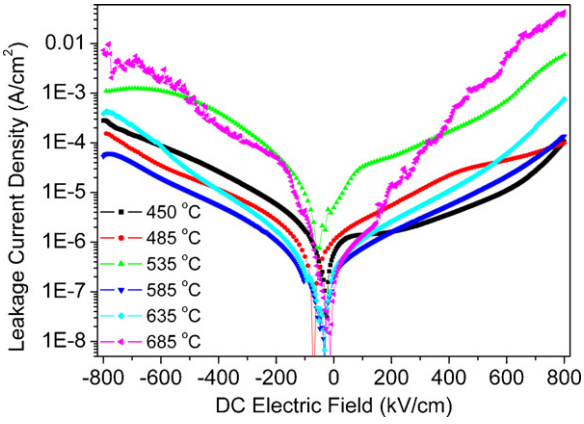

Fig. 5. Variations of leakage current density with the applied dc electric field up to 800 kV/cm for the BST films annealed at different temperatures. All the leakage current measurements were carried out at room temperature.

4. Conclusions

$Ba_{0.7}Sr_{0.3}TiO_3$ thin films with 500 nm thickness were prepared on technologically desirable platinized silicon substrates by ion beam sputtering and post-deposition annealing method. A sharp transition in the tunable dielectric behaviours of BST thin films has been achieved, in good agreement with the evolution of crystal structure from amorphous to crystalline phase. It is demonstrated that the perovskite phase could crystallize in BST films at a very low temperature, around 450 °C. The lowering of perovskite crystallization temperature in the BST films is associated with the high energetic process nature of IBS technique, which is helpful in enhancing the reactive activation of sputtered atoms and effectively overcomes the energy barrier for perovskite crystallization in films. Very importantly, both a high dielectric tunability of 42% at $E = 500$ kV/cm and a low loss tangent of 0.013 at zero bias have been obtained in the 450 °C-annealed film, thereby resulting in the highest figure-of-merit factor among all the different temperature annealed films. Moreover, the 450 °C-annealed film possesses superior leakage current characteristics with a low leakage current density of about 10^{-4} A/cm^2 at $E = 800$ kV/cm. Excellent dielectric and electrical properties obtained by a low-temperature process make the BST thin film a good candidate for above-IC integration in communication applications.

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