Point and Extended Defects in $Ba_{1-x}Sr_xTiO_3$ Thin Films Grown by Pulsed Laser Deposition

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Point and extended defects in $Ba_{1-x}Sr_xTiO_3$ (BST) are believed to be partially responsible for lowering the dielectric constant of these materials in film form compared to that of bulk BST of the same composition. We have performed a study of the electrical and structural properties of BST films grown by PLD on MgO and on $0.29(LaAlO_3):0.35(Sr_2TaAlO_6)$ (LSAT) substrates. We have compared the in-plane dielectric constant and the defects in BST films before and after annealing of samples grown on both substrates. The in-plane dielectric constant, ε_{11}, was obtained using interdigital electrodes on as-grown and annealed samples and, as shown in Fig. 1, it shows very similar values and behavior regardless of what the substrate is. The effect of point defects (namely, oxygen vacancies) was studied by annealing, under different ambients, two samples that were grown under identical conditions. The two samples were prepared by cutting a sample in two halves. One half was annealed in O_2 and the other half in N_2. Both samples were annealed at 950 °C for 14 hours. Figure 2 shows the dielectric constant ε_{11} as a function of voltage at 1 MHz for both samples before (dotted curve) and after annealing (dashed curve). This figure shows that both samples had approximately the same increase in ε_{11} upon annealing regardless of the atmosphere. The same result was obtained from films grown on MgO and LSAT substrates. This result suggests that oxygen vacancies do not give rise to a measurable improvement in the recovery process of the dielectric properties of BST films upon annealing. To exclude the possibility that N_2 may have reacted with the BST films a second annealing experiment, this time with O_2 for 14 hours at 950 °C, was performed on both samples. Again, both samples showed further increase in ε_{11} (solid curves in Fig. 2).

The role of dislocations and planar defects on the dielectric properties of BST films was studied by comparing plan view and cross sectional TEM images of BST films grown on MgO and LSAT substrates. The lattice mismatch of BST (x=0.5) on MgO and on LSAT is very high (~ - 2.44% on LSAT and ~ +5.88% on MgO). On either substrate the critical thickness for strain relaxation is very small and the films relax the strain by generating misfit dislocations at the film/substrate interface. Figure 3 shows cross sectional dark field images of BST films grown on (a) LSAT and (b) MgO showing strain contrast due to misfit dislocations at the film/substrate interface. Figure 4 shows plan view images of BST films grown on LSAT substrates (a) as grown and (b) after annealing. The as grown sample has a density of $2.2\times10^{11}/cm^2$ of threading dislocations which decreases by a factor of ~35% upon annealing. We believe that the high density of dislocations in the films grown on LSAT (even after annealing for 14 hours) is responsible for the low dielectric constant of the films compared to bulk.

Plan view images of the BST films grown on MgO did not show such as high a density of threading dislocations as the films grown on LSAT substrates. Instead, these images showed the presence of antiphase domain boundaries (ADB) as can be seen in Fig. 5. The size of the domains is estimated to be ~40 nm in the as grown samples and increases to ~120 nm after annealing. Figure 6 shows an atomic resolution image of one of the domain boundaries showing a shift of ½[110] between the two domains. This boundary corresponds to a Ba/SrO double layer.

First Principles Calculations at zero temperature have shown that the presence of antiphase domain boundaries lowers the dielectric constant of $SrTiO_3$ along the direction normal to the ADB.