DEPOSITION OF YTTRIUM OR LANTHANUM-SUBSTITUTED BISMUTH TITANATE FILMS BY DIRECT LIQUID INJECTION - METAL ORGANIC CHEMICAL VAPOR DEPOSITION FOR USE IN NON-VOLATILE MEMORIES

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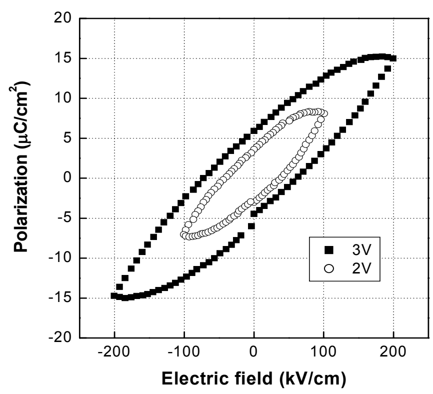
There have been extensive research efforts to enhance the reliability of perovskite-based ferroelectric thin films for use in non-volatile memory. The structure of FRAM is similar to that of conventional dynamic random access memory (DRAM). FRAM is subjected to repetitive polarization switching to read and write data. Ferroelectrics exhibit a decrease in the amount of charge switched each time ('fatigue') after repetitive read/write cycles. To overcome these problems, many researchers started to be interested in BTO with its bulk value of $2P_r$ about $60\mu C/cm^2$. However, BTO, as a thin film shows fatigue and has unexpectedly low value of $2P_r$,(1,2) 4-8 $\mu C/cm^2$. The fatigue in the BTO film is generated because of oxygen vacancies near $(Bi_2O_2)^{2+}$ and $(Bi_2Ti_3O_{10})^{2-}$ perovskite layers. It was shown that the substitution with La ions improved the failure characteristics of BTO (3). But the Curie temperature (T_c) of La-substituted BTO was decreased down to about 400°C (4). Also we used yttrium ions as a substitution element to obtain high T_c ferroelectric films with superior ferroelectric properties.

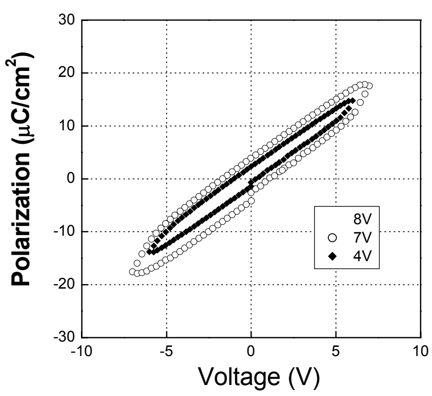
BYT and BLT films were deposited on the $Pt/TiO_2/SiO_2/Si$ substrate using direct liquid injection (DLI)-metal organic chemical vapor deposition (MOCVD) at 400°C (5). Precursors used were $Bi(Ph:phenyl)_3$, $Y(tmhd:tetramethylheptanedionate)_3$-PMDT (pentamethyldiethylenetriamine), $La(tmhd)_3$-PMDT and $Ti(dmae: dimetylamidoethoxide)_4$.

Figure 1(a) shows the hysteresis loop of the BYT capacitor measured at various applied voltage ranging between 4 to 8V. The film was annealed at 750°C in an oxygen atmosphere for 1 hour and its thickness was 100 nm, which was thinner than BLT films already reported. $2P_r$ of the capacitor was measured to be 15 $\mu C/cm^2$ at an applied voltage of 8V. Figure 1(b) shows the hysteresis loop of the BLT capacitor measured at various applied voltage ranging between 1 to 3V. The film was annealed at 650℃ for 60min. The remanent polarization ($2P_r$) of the capacitor is $12\mu C/cm^2$ at an applied voltage of 3V. The ferroelectric capacitor of BLT and BYT films showed practically no significant change of remanent polarization after switching up to 1.0×10^{10} cycles.

The properties, such as polarization, crystallization, lattice constants and leakage current of substituted BTO thin films were affected by the ionic radius of the substituting rare earth element, the bonding strength, and the formation energy of the oxide. The substitution of Bi ions with smaller Y ions reduced the cell volume of ferroelectric crystals. The leakage current density of the film was decreased by two orders of magnitude by the substitution with Y ions.

Figure 1(a) The hysteresis loops for the $Au/BYT/Pt/TiO_2/SiO_2/Si$ film capacitors as a function of the applied voltage at 1MHz. (b) Hysteresis loop for 1000Å thick BLT film after annealing at 650℃.





Conclusions. We describe the preparation and characterization of thin-film capacitors using BYT and BLT. Our BYT and BLT capacitors do not show significant fatigue and furthermore, exhibit low leakage current, higher P_r and higher Curie temperature than any other Bi-based layered perovskite even at film thickness less than 100nm.