Electronic and structural properties of ferroelectric $SrBi_2Ta_2O_9$ thin films and its Schottky junction by photoelectron spectroscopies

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Electronic and structural properties such as Fermi level, density-of-states and chemical bonds of ferroelectric $SrBi_2Ta_2O_9$ (SBT) thin films have been characterized by UV-photoyield spectroscopy (PYS) and X-ray photoelectron spectroscopy (XPS), and band diagrams of its Schottky junction have been studied.

Electronic structure of ferroelectric thin film is very important to obtain good ferroelectricity and high insulation which are closely related to polarization switching phenomena in 1T1C FeRAM capacitor and also memory retention characteristics in ferroelectric gate FET memory. SBT thin film is used widely for the memory application, and so its electronic structure has been investigated. XPS spectra of Au and SBT film show that band bending of 0.5 eV happens at their junction. UV-PYS spectrum of the SBT film shows that its work function is 5.90 eV after the deposition and decreases to 5.56 eV by O_2 annealing. This change increases the hole barrier height from 1.80 to 2.14 eV, so induces reduction of the current through metal-SBT junction, and coincides well that leakage current of SBT film capacitor was reduced after the O_2 annealing. Moreover, this reduction improves the memory retention time of capacitance of the MFIS structure, which is hopeful to realize ferroelectric gate FET memory. Ar^+ bombardment effect on electronic structure of the SBT film has been studied by XPS to clarify mechanism of the improvement of the barrier height and the current conduction. The Bi4f XPS signal mainly shows oxide state on the surface, but after Ar^+ bombardment reduces contribution of the oxide and enhances contribution of the metallic. On the other hand, ratio of the oxide contribution to the metallic changes little in the signal of Ta4d and Sr3d. The density of states corresponding to $(Bi_2O_2)^{2+}$ layer decreases with Ar^+ bombardment time. These results suggest that Bi_2O_2 layer is easily damaged and deoxidized by the Ar^+ bombardment. Therefore, the O_2 annealing is considered to improve insufficient oxidation of $(Bi_2O_2)^{2+}$ layer which might exist in the as-deposited SBT film.

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Low temperature processing of PZT-based thin films

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The usually reported crystallization temperatures of the perovskite phase for lead zirconate titanate (PZT) thin films prepared by chemical solution deposition (CSD) method are around 600 °C. It is a continuous challenge to lower the crystallization temperature in order to decrease the possibility of either interface reaction of PbO with the substrate or PbO evaporation and to be able to use substrates and/or electrodes that are stable below 500 °C.

It is generally accepted that the activation energy for nucleation of the perovskite phase is considerably higher than that for growth. Further, the crystallization temperature of PZT solid solution decreases with decreasing Zr/Ti ratio.

By careful control of solution chemistry and annealing conditions, Ti-rich PZT and PLZT films were successfully processed at temperatures as low as 400 °C. The crystallization of these films is characterized by rapid nucleation and rapid growth. The microstructure and corresponding ferroelectric properties are controlled by thermal treatment. Films with thickness below 100 nm can be processed as well. The maximum value of $Pr = 33\,\mu C/cm^2$ and $Ec = 99\,kV/cm$ of PZT30/70 films were obtained.

The Zr-rich PZT and PLZT compositions require a lead titanate (PT) seeding layer for further crystallization at a temperature of 400 °C. The growth of the perovskite phase is diffusion controlled and, as a consequence, slow. The step of conversion of amorphous to crystalline phase depends on the amount of PbO excess in starting composition. The results are discussed in terms of sublimation of PbO as well as incorporation of lead on to B sites of perovskite lattice.

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Composition–structure–properties studies on bismuth layered ferroelectric thin films

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By both alternating the structure of layered ferroelectrics $A_{m-3}Bi_4Ti_mO_{3m+3}$ (m = 3, 4, 5, 6, and $SBTi_m$) and partially substituting A site of perovskite cell by lanthanide elements, the composition–structure–property relationship of these ferroelectrics were studied. The thin films were prepared by pulse laser deposition (PLD). With the capacitor structures of $Pt/SBTi_m/Pt/TiO_2/SiO_2/Si$, these films show excellent fatigue properties ($>10^{11}$). The feasibility of the family in optimizing ferroelectric properties was established. Epitaxial heterostructures of $SBTi_m/SrTiO_3$ were investigated by high-resolution transmission electron microscope (HRTEM), showing epitaxy relation of [110]//[100], [1$\bar{1}$0]//[010], and (001)//(001) of $SBTi_m$//$SrTiO_3$. The dielectric properties of these films were analyzed by near field microwave microscope. The possibility of manipulating their polarization and dielectric constant was proposed. By A-site substitution, the polarization nature of the film was changed substantially.

Further Reading

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Bismuth layer-structured ferroelectrics with high Curie temperatures

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Bismuth layer-structured ferroelectrics (BLSF) such as Bi_3TiTaO_9 (BTT), Bi_3TiNbO_9 (BTN) and $Na_{0.5}Bi_{2.5}Nb_2O_9$ (NBN) with layer number $m = 2$ have high Curie temperatures T_C which are higher than 700 °C. These ferroelectric ceramics and/or solid solutions with higher T_C usually show unique piezoelectric performances of high mechanical quality factors Q_m and high coerceive field E_C under fully poled conditions. Effects of enhanced poling conditions on their piezoelectric properties are systematically studied for BTT, BTN and NBN-based solid solutions $Sr_{x-1}Bi_{4-x}Ti_{2-x}Ta_xO_9$ (SBTT2(x)) ($1 \le x \le 2$), $Na_{x/2}Bi_{3-x/2}Ti_{1-x}Nb_{1+x}O_9$ (NBTN2(x)) ($0 \le x \le 1$) and La-modified BTT, that is, $Bi_{3-x}La_xTiTa_2O_9$ (BLTT2(x)) ($0 \le x \le 1$).

The T_C of SBTT2 was changed from higher than 900 °C of $x = 1$ (BTT) to about 280 °C of $x = 2$ ($SrBi_2Ta_2O_9$, SBTa) from the measurement of temperature dependence of the dielectric constant. A mechanical quality factor Q_m and electromechanical coupling factor k of the SBTT2 system were enhanced on the poling conditions of applied fields $E_P = 7$–10 kV/mm, poling temperatures $T_P = 200$–300 °C and poling times $t_P = 7$ min, respectively. For example, SBTT2(1.25) with the poling condition of $T_P = 300$ °C shows the maximum Q_m of 13,500 in the planar mode. This value is extremely high in usual piezoelectric ceramics. In the same poling conditions, Q_m of (33) and (15), vibration modes for SBTT2(1.25) were about 8800 and 6000. The T_C of NBTN2 system displays about 900 °C for $x = 0$ (BTN), and becomes gradually lower with increasing the amount of modified NBN ($T_C = 790$ °C). As a poling condition of NBTN2, the poling field $E_P = 7$–10 kV/mm, poling temperature $T_P = 200$ °C and poling time $t_P = 5$ min were chosen, respectively. The largest value (0.15) of k_{33} was obtained for the NBTN2(1.1). However, the k_{33} of NBTN2(1.0) and NBTN2(1.05) are relatively smaller than that of NBTN2(1.1) because it is very hard to pole these ceramics. These BLSF ceramics seem to be a superior candidate for piezoelectric resonator and/or sensor materials with high Q_m and high T_C.

In the measurement of temperature dependence of the dielectric constant the Curie temperatures becomes gradually lower with increasing amount of modified NBN ceramic (T_C = 790 °C). As a poling condition for the piezoelectricity, the poling field $E_p = 7$–10 kV/mm, poling temperature $T_p =$ 200 °C and poling time $t_p = 5$ min were chosen for NBTN2, respectively. The largest value of k_{33} (0.15) was obtained for the NBTN2(1.1) ceramic. However, the k_{33} of NBTN2(1.0) and NBTN2(1.05) ceramics are relatively smaller than that of NBTN2(1.1) ceramic because it is very hard to pole these ceramics. The NBTN2(1.1) ceramic showed the large piezoelectric anisotropy of k_{33}/k_{31} (4.3). These ceramics are seen as a superior candidate for piezoelectric sensor materials with high T_C and large anisotropic characteristics.

Further reading

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