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Highly oriented ferroelectric CaBi$_2$Nb$_2$O$_9$ thin films deposited on Si(100) by pulsed laser deposition

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We report the successful deposition of highly $c$-axis oriented CaBi$_2$Nb$_2$O$_9$ (CBN) thin films directly on $p$-type Si(100) substrates by pulsed laser deposition. The CBN thin films exhibited good structural, dielectric, and CBN/Si interface characteristics. The electrical measurements were conducted on CBN thin films in a metal–ferroelectric–semiconductor (MFS) capacitor configuration. The typical measured small signal dielectric constant and the dissipation factor at a frequency of 100 kHz were 80 and 0.051, respectively. The leakage current of the MFS capacitor structure was governed by the Schottky barrier conduction mechanism and the leakage current density was lower than $10^{-7}$ A/cm$^2$ at an applied electric field of 100 kV/cm. The capacitance–voltage measurements on MFS capacitors established good ferroelectric polarization switching characteristics. © 1997 American Institute of Physics. [S0003-6951(97)00711-0]

Ferroelectric thin films have been widely investigated for their use in a variety of devices exploiting their unique piezoelectric, pyroelectric, polarization switching, and electro-optic properties. Integration of these films directly with Si or poly-Si will open a new era for practical applications in both active and passive electronic devices. Recently, there has been a surge in research activity on ferroelectric thin films for nonvolatile random access memory (NVRAM) applications. Ferroelectric thin films with large remanent polarization, low coercive field, low fatigue rate, and good retention characteristics have the potential for use as memory elements in high density 1T-1C nonvolatile memories. The ferroelectric gate insulator field effect transistor is the desired configuration for a one transistor high density memory array. Metal–ferroelectric–semiconductor field effect transistors (MFSFETs) have attracted considerable attention as promising devices for applications to nonvolatile memories. MFSFET exploits the ferroelectric field effect, which is the modulation of conductivity by the electrostatic charges induced by ferroelectric polarization, and thus requires the direct deposition of ferroelectric thin film on Si wafer. For use in MFSFET, the ferroelectric film need not have a high remanent polarization; it should have just sufficient polarization to cause modulation of the FET channel conductivity. Additionally, it is necessary that the film maintains its ferroelectric properties on the semiconductor surface and the interface state density at the ferroelectric film/Si interface be small enough for the normal MOSFET operation. Thin films of various ferroelectric materials have been investigated for MFSFET devices. Thin films of these materials usually exhibit good ferroelectric properties on metal electrodes such as platinum. However, it is difficult to preserve ferroelectricity on Si due to existence of interfacial traps and/or interdiffusion of the constituent elements. Therefore, there are a few reports of good MFS devices. In the present letter, we report the fabrication of highly oriented CaBi$_2$Nb$_2$O$_9$ (CBN) thin films directly on Si by pulsed laser deposition technique. The Pt/CBN/Si capacitors exhibited the desired polarization switching behavior; establishing good CBN/Si interface characteristics.

CBN is a layered perovskite ferroelectric oxide, whose lattice constants are: $a = 0.5435$ nm, $b = 0.54658$ nm, and $c = 2.4970$ nm. The CBN material was selected because of its good lattice matching with Si substrate, reasonably high dielectric constant, and low intrinsic defect density of layered perovskite structure. The CBN thin films are very likely to grow on Si(100) with a highly preferred (001) orientation since they have a very good lattice matching along $a$- and $b$-axis with Si(100). For device applications, a single crystalline film has an edge over a polycrystalline film in obtaining stable and desirable properties. In this letter, we report the structural and electrical characteristics of highly $c$-axis oriented CaBi$_2$Nb$_2$O$_9$ (CBN) thin films deposited on Si by pulsed laser deposition (PLD) technique. The CaBi$_2$Nb$_2$O$_9$ thin films were deposited on $p$-type ($p \approx 30$ $\Omega$ cm) Si(100) substrates by a pulsed laser ablation technique. A Lambda Physik (LPX) 300 excimer laser utilizing KrF radiation (248 nm) was used at a pulse rate of 4 Hz and a laser energy of 700 mJ. The film growth rate was 0.17 nm/s. The target having the stoichiometric composition was prepared by a conventional ceramic process. The calculation and sintering were conducted in air at temperatures of 900 and 1120 °C for 3 h, respectively. The substrates were cleaned by a room temperature technique called spin etching, to remove the native silicon oxide and make the substrate surface hydrogen terminated. Substrates were placed parallel to the target at a distance of 60 mm. During deposition, the chamber pressure was maintained at 200 mTorr with oxygen gas, and the target and the substrates were rotated at a speed of 11 and 4 rpm, respectively. The crystallographic structure of the as-deposited films was investigated by x-ray diffraction (XRD) utilizing Cu$K_\alpha$ radiation. Surface and cross-sectional morphologies of the films were observed by atomic force microscopy (AFM) and scanning electron microscopy (SEM). The thickness of the films was measured by spectroscopic ellipsometry and cross-sectional SEM. Several platinum electrodes (contact area $= 5.6 \times 10^{-4}$ cm$^2$) were sputter deposited through a mask on the top surface of the films to form metal–ferroelectric–semiconductor (MFS) capacitors. The capacitance–voltage ($C-V$) measurements were conducted...
on MFS capacitors at room temperature with a HP 4192A impedance analyzer.

Figure 1 shows the XPD patterns of (a) simulated CBN, (b) bulk CBN (target), and (c) as-deposited CBN thin film. The simulated pattern was generated, based on an orthorhombic crystallographic structure, by XPOW/PLOT software developed by Gibbs et al. The space group used was Cmc2₁ (an international type), which was transformed from the A2₁am reported by Newnham et al. with a proper transforming matrix. The XRD pattern of the target [Fig. 1(b)] matched quite well with the simulated pattern [Fig. 1(a)] except for the intensity of the (002) peak, which implied that the target used was a single phase of CBN and the simulated pattern was an acceptable result. Since there are no reports on the XRD patterns of CBN, these might be used as standard data. Figure 1(c) shows a typical XRD pattern of the highly c-axis oriented CBN thin films, where most of the peaks are in the (001) family. The pole figure measurement also revealed that the films had a highly (001) preferred orientation. The ω-scan measurement showed that the full-width at half-maximum of the (0010) peak was 4.00°. The (001) preferred orientation of the CBN thin films on Si(100) is believed to be due to good lattice matching between CBN and Si.

Figure 2 shows the typical AFM micrographs of the highly oriented CBN thin films. Figure 2(a) is a normal height image obtained in a tapping mode AFM where the oscillation amplitude is used as a feedback signal, and Fig. 2(c) shows a relationship between the height and the color of the grains. The film consisted of large grains of about 300 nm in diameter and small grains of about 50 nm in diameter. The size of the large grains was slightly larger than the film thickness, implying that the growth behavior of each large

on MFS capacitors at room temperature with a HP 4192A impedance analyzer.

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highly oriented CaBi₂Nb₂O₉ thin films.

This mode of switching is charge compensation on the Si surface is induced by the polarization present in the film. This mode of switching is characteristic of a ferroelectric film on voltage response. A clockwise rotation in the round trip direction of the hysteresis loop of the capacitance-potential switching behavior can be established by the injection type on/off switching behavior or the ferroelectric thin film. As the applied voltage was increased and became positive, a depletion layer was formed inside silicon near the interface. A further increase in voltage caused inversion of the surface. The capacitance approached a minimum value \( C_{\text{min}} \) in the inversion region. The measured minimum capacitance \( C_{\text{min}} \) was 4.79 pF. The depletion capacitance \( C_D \) calculated from relation (1) using experimental values of \( C_{\text{max}} \) and \( C_{\text{min}} \) was 4.94 pF, and the theoretical value of \( C_D \) calculated from relation (2), was 5.13 pF.

\[
1/C_{\text{min}} = 1/C_{\text{max}} + 1/C_D \quad (1)
\]

and

\[
C_D = \varepsilon \varepsilon_0 A/W_m \quad (2)
\]

where \( \varepsilon_0 \) is the permittivity of silicon, \( A \) is the area of electrodes, and \( W_m \) is the maximum depletion width which was estimated to be 1.10 nm from the semiconductor data. The measured depletion capacitance was very close to the theoretical value, indicating that the film capacitance was not masked by any possible interface capacitance present in series with the film capacitance.

In summary, highly \( c \)-axis oriented CaB₂Nb₂O₉ thin films were successfully deposited directly on Si(100) by a pulsed laser deposition technique, and their MFS capacitor structure exhibited reasonable dielectric constant, low leakage current density, and a good ferroelectric polarization property which is the desired mode for memory devices.

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