Conductive LaNiO\textsubscript{3} electrode grown by pulsed laser ablation on Si substrate

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Using the pulsed laser ablation (PLA) technique, conductive LaNiO\textsubscript{3} thin films have been successfully grown on (001) Si substrates. The XRD \(\theta-2\theta\) scan patterns indicate a preferential (110) orientation, and the electron probe microanalyzer (EPMA) investigations show that the three elements La, Ni, and O distribute uniformly in the films. The resistivity of the as-deposited LaNiO\textsubscript{3} films display a metallic character. Polycrystalline PbTiO\textsubscript{3} films are deposited by metalorganic chemical vapor deposition (MOCVD) on these LaNiO\textsubscript{3} electrodes. Ferroelectricity measurements of the PbTiO\textsubscript{3}/LaNiO\textsubscript{3} heterostructure prove LaNiO\textsubscript{3} to be a promising electrode material in the integration of ferroelectrics and Si wafer.

I. INTRODUCTION

Among various oxides, the use of perovskite-type conductive materials as electrodes favors the growth of high quality ferroelectric thin films such as PZT and PLZT due to the similar structure and small lattice mismatch.\textsuperscript{1–4} These heterostructures have shown great promise for use in ferroelectric random access memories (FRAM), infrared (IR) detectors, electro-optic devices, and high-frequency transducers.\textsuperscript{5–7} Integration of ferroelectric thin films with the Si semiconductor technique has stimulated extensive investigations in recent years. The traditional Pt, Ti electrodes directly deposited on Si at the growth temperature of several hundred degrees centigrade will form silicides, preventing the further growth of ferroelectrics.\textsuperscript{8,9} Perovskite cuprate superconducting electrodes such as \(\text{YBa}_2\text{Cu}_3\text{O}_{7-x}\) (YBCO) and \(\text{Bi}_2\text{Sr}_2\text{Cu}_2\text{O}_{8-x}\) (BSCCO) still suffer from poor chemical and thermal stability and rough surfaces.\textsuperscript{10}

As a perovskite Pauli paramagnetic, LaNiO\textsubscript{3} exhibits a metallic property with a resistivity of \(\sim 10^{-5} \ \Omega \cdot \text{m}\) at room temperature. The rhombohedral lattice of LaNiO\textsubscript{3} can be regarded as a pseudocubic structure with the lattice constant of \(a = 3.84\ \text{Å}\). Satyalakshmi and Hegde \textit{et al.}\textsuperscript{11,12} have reported the results of fabrication and characterization of LaNiO\textsubscript{3} thin films on SrTiO\textsubscript{3}, LaAlO\textsubscript{3}, and YSZ substrates. In our paper, we report the use of conductive LaNiO\textsubscript{3} thin films as the electrode for the fabrication of a metal/ferroelectrics/metal/Si capacitor. Our experiment proved the possibility of integration of PbTiO\textsubscript{3} ferroelectric with Si-based semiconductor materials by using a LaNiO\textsubscript{3} electrode.

II. EXPERIMENTAL

The LaNiO\textsubscript{3} pellet used as the PLA target was prepared by the sinter method: one mole of La\textsubscript{2}O\textsubscript{3} powder was ground together with one mole of Ni\textsubscript{2}O\textsubscript{3} powder, the mixture was pressed into pellets and fired for 800 °C for 12 h, and the pellets were then ground, pressed into pellets, and sintered to 1200 °C for 2 h.

The phases of the target were examined by x-ray diffraction. Figure 1(a) shows that a pure LaNiO\textsubscript{3} phase target is obtained.

The PLA process was performed using a Lambda Physik LPX205i KrF excimer laser system with the 248 nm radiation of 30 ns in pulse width and 5 Hz in pulse frequency. The laser beam was focused onto the rotating LaNiO\textsubscript{3} target. The average laser pulse energy density was 200 mJ/mm\textsuperscript{2}. In the experiment, the Si
substrate was mounted on a resistively heated stage. The typical oxygen partial pressure and substrate temperature were 30 Pa and 700 °C, respectively, during the laser ablation process. The deposition time was 30 min. After deposition, the films were kept at 700 °C in $2 \times 10^4$ Pa oxygen for 30 min and then cooled down to room temperature at a rate of 10 °C/min.

The thickness of the as-prepared film was measured to be 5800 Å using a profilemeter at the film edge made by selective deposition through a cover-glass mask. This value is consistent with that from the scanning electron microscope (SEM) cross-section morphology.

III. RESULTS AND DISCUSSION

The SEM surface morphology (Fig. 2) of the LaNiO$_3$ film shows a smooth surface which is very important for the fabrication of a multilayer structure. No droplets can be found on the film surface. The grain size observed from the SEM image is about 500 Å.

The XRD θ-2θ scan pattern of the LaNiO$_3$ thin film exhibits [Fig. 1(b)] a pure perovskite structure, and a preferential (110) orientation was detected due to the slight lattice mismatch between (110) of LaNiO$_3$ and (002) of the Si substrate. The average grain size was estimated by the full maximum at half width (FMHW) of the diffraction peaks using the Scherrer equation to be ~420 Å. It is consistent with the SEM observation.

The element distribution in the thin film was investigated by a JEOL JXA-8800M electron probe microanalyzer (EPMA). As shown in Fig. 3, only La, Ni, O, and Si were detected using LiF, PET, and STE as spectro-crystals, respectively. Figure 3 displays the element surface distribution in the thin film. The gray scale in the picture represents the relative content of the element; in the examined area of $50 \mu m \times 50 \mu m$, the La, Ni, and O distributed uniformly over the surface. The corresponding random line analyses (Fig. 4) of the three elements showed that the relative content deviation of each element was less than 0.5%.

The resistivity of the as-deposited LaNiO$_3$ thin film as a function of temperature was measured by the four terminal transport method. In Fig. 5, the resistivity versus temperature plot is shown. The film resistivity is measured to be $3.7 \times 10^{-5} \Omega \cdot m$ at room temperature and $3.09 \times 10^{-5} \Omega \cdot m$ at 73 K. The temperature dependence $(d\rho/dT)$ shows a good metallic behavior.
FIG. 3. Element analysis of the LaNiO$_3$ film by an electron probe microanalyzer using LiF, PET, and STE as spectro-crystals; only La, Ni, O, and Si can be detected.

Using the LaNiO$_3$ thin film as the bottom electrode, PbTiO$_3$ ferroelectric thin films were grown by metalorganic chemical vapor deposition (MOCVD). The MOCVD apparatus and typical growth conditions have been described in detail elsewhere.$^{14}$ The SEM cross-section morphology of the heterostructure is shown in Fig. 6. Both the PbTiO$_3$ and LaNiO$_3$ thin films were smooth and dense with abrupt interfaces between each other. The PbTiO$_3$ film thickness was measured to be 5300 Å.

Figure 7 shows the XRD $\theta$-2$\theta$ scan pattern of the heterostructure carried out on a Rigaku Denki/MAX-RA powder diffractometer with nickel-filtered Cu K$_\alpha$ radiation. The as-deposited PbTiO$_3$ thin film has a pure perovskite structure, no pyrochlore phase can be detected, and the spectrum exhibits a typical polycrystalline diffracting pattern. The average grain size is estimated to be 950 Å using the Scherrer equation.$^{11}$ The $c$-axis lattice constant of the film was measured to be 4.126 ± 0.002 Å by using the (004) reflection of the Si substrate as a reference length. This value is less than that of PbTiO$_3$ single crystal (4.150 Å). Unlike the $c$-axis shortening phenomenon found in epitaxial PbTiO$_3$ thin films on other substrates,$^{15-19}$ where the film is under external stress, most of the stress in the polycrystalline film should be released by the grain boundaries. We believe the size-induced ferroelectricity weakening$^{20}$ may cause this $c$-axis deformation when the grain size is down to $\sim$1000 Å and the relaxation of the surface layer cannot be neglected.

The ferroelectric properties of the PbTiO$_3$ thin film were measured with a Sawyer–Tower circuit using a 50 Hz sinusoidal externally applied electric field. A silver pad of 0.7 mm diameter was evaporated onto the surface of the heterostructure to form the top electrode. The bottom LaNiO$_3$ electrode was contacted from the edge of the sample with Ag paint. No poling procedure was taken before the measurement. A typical D-E hysteresis loop of the as-grown PbTiO$_3$ is shown in Fig. 8. The measured remnant polarization $P_r$, spontaneous polarization $P_s$, and coercive field are 26.1 $\mu$C/cm$^2$, 37.4 $\mu$C/cm$^2$, and 13.0 kV/cm, respectively. This shows a smaller $P_s$ and larger $E_c$ as compared with a PbTiO$_3$ single crystal whose $P_s$ is 75 $\mu$C/cm$^2$ and whose $E_c$ is 6.75 kV/cm. The decreasing of $P_s$ seems to be related to the shorte-
FIG. 5. The resistivity versus temperature curve of LaNiO$_3$ thin film.


IV. SUMMARY

PLA LaNiO$_3$ thin films have been deposited as part of a ferroelectric/electrode/substrate heterostructure on a (001) Si wafer. The LaNiO$_3$ film shows a high (110) preferential orientation. Polycrystalline PbTiO$_3$ thin film deposited on the LaNiO$_3$ electrode can produce ferroelectric capacitors with excellent performance. This makes it possible to integrate PbTiO$_3$ ferroelectric thin films with Si-based memory devices.

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REFERENCES