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4.0-nm-thick amorphous Nb–Ni film as a conducting diffusion barrier layer for integrating ferroelectric capacitor on Si

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ABSTRACT

We have successfully integrated $La_{0.5}Sr_{0.5}CoO_3/PbZr_{0.4}Ti_{0.6}O_3/La_{0.5}Sr_{0.5}CoO_3$ (LSCO/PZT/LSCO) capacitors on silicon substrate using a ~4.0-nm-thick amorphous Nb–Ni film as the conducting diffusion barrier layer. Transmission electron microscopy technique confirms that the Nb–Ni film is still amorphous after fabrication of the capacitors, and the interfaces related to Nb–Ni are clean and sharp without any findable interdiffusion/reaction. The LSCO/PZT/LSCO capacitor, measured at 5 V, possesses very good properties, such as large remanent polarization of ~22.1 μC/cm^2, small coercive voltage of ~1.27 V, good fatigue-resistance, and small pulse width dependence, implying that ultrathin amorphous Nb–Ni film is ideal as the conducting diffusion barrier layer to fabricate high-density silicon-based ferroelectric random access memories.

1. Introduction

Ferroelectric random access memory (FRAM) has been attracting much attention due to its fast-speed, high density, and nonvolatile property [1–3]. Because of its excellent properties, *e.g.* low coercive voltage, large remnant polarization and piezoelectric constant, $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) has been investigated extensively for the applications of FRAM [4–6], field effect devices [7], and other electric devices [8–11]. PZT ferroelectric capacitors are regarded as the core element in ferroelectric random access memory. In order to realize the large-scale applications of the FRAM, PZT capacitors must be compatible with the modern silicon transistor technology so that we can integrate ferroelectric capacitors with silicon to yield the one-transistor–one-capacitor (1T–1C) memory architecture. It is reported that Pt electrode can induce PZT capacitors fatigue, resulting from several reasons such as formation of oxygen vacancy or of Pb_XPt_{1-X} phase [12,13]. This can be overcome by using a complex oxide electrode, such as $La_{0.5}Sr_{0.5}CoO_3$ (LSCO), $LaNiO_3$ (LNO). In order to fabricate a 1T–1C memory cell, the drain must be electrically in contact with the bottom oxide electrode of the capacitor. However, high temperature and oxygen atmosphere are needed to grow high quality of oxide electrode and PZT film, chemical reaction and interdiffusion may happen [14]. If PZT ferroelectric capacitor stack is directly integrated on Si, a nonconducting layer can be generated at the interface of the bottom electrode and silicon, leading the failure of the fabrication of the memory cell. To solve this problem, a diffusion barrier layer has to be inserted between the capacitor bottom electrode and the silicon substrate in order to separate them from each other. Besides the high electrical conductivity, the barrier layer should possess high thermal and chemical stability, and strong oxidation resistance. Traditional barrier materials, which are related to Pt or Ir [15,16], has been limited due to the high cost, ion etching problem, and the formation of Pt hillock structure. Therefore, it is pressing to find some inexpensive and simple materials to be the alternative materials suitable for the fabrication of FRAM. Some materials, such as Ti–Al, Ni–Al, and Ni–Ti have been reported as the conducting barrier layer for integrating silicon based PZT ferroelectric capacitors with very good structural and physical properties [14,17].

The glass forming ability (GFA) of Ni–Nb binary alloys has been studied, and it is found that some of the alloys can be prepared into bulk metallic glasses by a conventional Cu-mold casting [18]. The authors further investigated the glass formation mechanism for binary Ni–Nb alloys from the thermodynamic point of view and proposed the GFA parameter (g^*) to describe the ability of glass formation against crystallization. Amorphous alloys have attracted

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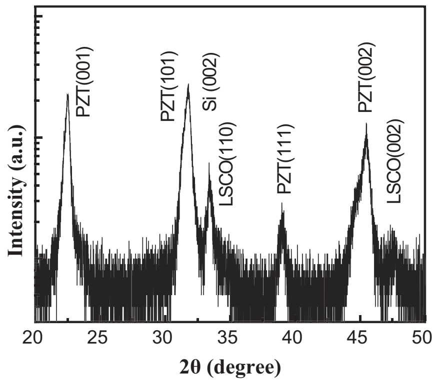

Fig. 1. XRD spectrum of the LSCO/PZT/LSCO/Nb–Ni/Si heterostructure.

great interest because of the appearance of high mechanical strength, useful physical properties, and good chemical properties resulting from their new alloy compositions and new atomic configurations [19]. Based on the ideal properties of high thermal, chemical stability, and oxidation resistance, amorphous Nb–Ni film has been investigated as the barrier layer for integrating Si-based ferroelectric capacitors in our experiments. In this letter, we report that ~4-nm-thick ultrathin amorphous Nb–Ni film (A-Nb–Ni) is used as the barrier layer to integrate PZT ferroelectric capacitors on silicon substrate to fabricate the LSCO/PZT/LSCO/A-Nb–Ni/Si heterostructure, and the microstructure of the heterostructure, and the physical properties of the LSCO/PZT/LSCO capacitors have been systematically investigated.

2. Experimental details

The samples were prepared using the following procedure. First, a highly doped silicon substrate with a resistivity of $(1–3) \times 10^{-3}\ \Omega$ cm was soaked in HF acid in order to remove the native SiO_2 layer of Si substrate surface. It was then immersed in the de-ionized water to clean HF acid. The wafer was finally cleaned separately by acetone and alcohol in an ultrasonic bath before it was put into the deposition chamber. The background pressure of the chamber was 2.0×10^{-4} Pa. To obtain amorphous Nb–Ni film, the deposition parameters, *e.g.* deposition power density and deposition pressure, were carefully optimized. We found that the sputtering parameters of a radio frequency (R.F.) power of 6.5 W, deposition pressure of 1.9 Pa Ar, and room temperature could make us to obtain the amorphous Nb–Ni film (A-Nb–Ni). ~4-nm-thick A-Nb–Ni was first deposited on silicon substrate to fabricate a A-Nb–Ni/Si heterostructure using magnetron sputtering method at a R.F. of 13.56 MHz from a high-purity NbNi target. Inductively Coupled Plasma (ICP) technique indicates the ratio of Nb and Ni is close to 1:1. Second, LSCO thin film (~55 nm) was *in-situ* deposited on Nb–Ni/Si heterostructure using the same deposition system as for Nb–Ni film deposition. The deposition conditions are as follows: deposition temperature was 400 °C, Ar:O_2 ratio was 3:1, and a power of 50 W. The LSCO/Nb–Ni/Si heterostructure was further post-annealed in a flowing oxygen tube at 550 °C for an hour. Third, $Pb(Zr_{0.4}Ti_{0.6})O_3$ (PZT) film with thickness of 120 nm was coated on LSCO/Nb–Ni/Si heterostructure by the spin coating technique using a modified PZT sol–gel solution, and followed by a 550 °C annealing for an hour. The detailed information about the preparation of PZT by the sol–gel method can be found elsewhere [20]. The well-known properties of PZT films can give us a good reference to evaluate the quality of our samples. Fourth, through a shadow mask, LSCO and Pt depositions were successively performed to obtain the Pt/LSCO/PZT/LSCO/Nb–Ni/Si heterostructure, with 7.85×10^{-5} cm^2 circular pads on the PZT film for capacitive electrical test, and followed by 550 °C annealing. The phase and crystallinity of the PZT/LSCO/Nb–Ni/Si heterostructure were studied using X-ray diffraction (XRD). The interfaces were characterized by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). The ferroelectric properties of the LSCO/PZT/LSCO capacitor were measured vertically from Si substrate to the top electrode using a precision LC unit from Radiant Technologies.

3. Results and discussions

Fig. 1 presents a typical XRD curve of the LSCO/PZT/LSCO/Nb–Ni/Si heterostructure, from which we can see that both LSCO and PZT film are polycrystalline and well crystallized. No obvious peaks of impurities are found in the XRD measurement, implying little reaction happened between the Nb–Ni barrier layer and its adjacent layers during the high temperature fabrication process. It should be noted that no Nb–Ni related peaks can be found from the XRD measurement, indicating that Nb–Ni film is amorphous after high temperature process.

The TEM image of the cross-sectional PZT/LSCO/Nb–Ni/Si heterostructure is shown in Fig. 2(a), from which we can see that the interfaces related to Nb–Ni layer are clean, sharp, and free of interaction and diffusion. To further characterize the interfaces and crystallinity related to Nb–Ni layer, high-resolution TEM was used to obtain information about the interface at atomic scale. As shown in Fig. 2(b), Nb–Ni film is about 4 nm thick, and still amorphous after 550 °C annealing. The stripes of different orientation can be observed in LSCO layer, indicating that LSCO is crystallized, which coincides with the result of the above XRD data. The interfaces between Nb–Ni and its adjacent layer are clean, no signs of reaction or interdiffusion can be found after high temperature process, indicating A-Nb–Ni is a good oxygen diffusion barrier layer for integrating ferroelectric capacitors on Si substrate.

Fig. 3(a) shows the hysteresis loop of a typical LSCO/PZT/LSCO capacitor, which was measured at 5 V. The well-saturated ferroelectric loop confirms the high quality of the LSCO/PZT/LSCO capacitor integrated on Si using the A-Nb–Ni conductive barrier layer, further indicating amorphous Nb–Ni is not fully oxided, and low resistive. The remanent polarization (P_r) and coercive voltage (V_c) were ~22.1 $\mu C/cm^2$ and ~1.27 V, respectively. Fig. 3(b) demonstrates the relation of the switchable polarization [ΔP = switched polarization (P^*) – nonswitched polarization ($P^{\wedge}$)] of the LSCO/PZT/LSCO capacitor with the applied voltage. The switchable polarization of the capacitor is ~28.6 $\mu C/cm^2$ when the measurement voltage is 5 V. Pulse width dependence of

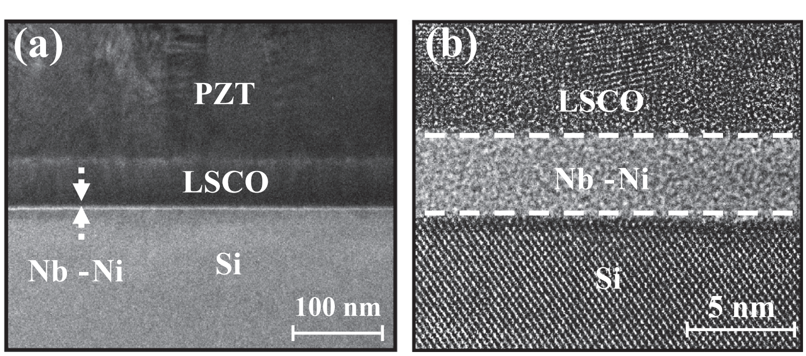

Fig. 2. (a) Cross-sectional image of the PZT/LSCO/Nb–Ni/Si of transmission electron microscopy (TEM); (b) high-resolution TEM cross-sectional image of the interfaces between Nb–Ni layer and its adjacent layer.