Microstructure and magnetoelectric properties in Pb(Zr$_x$Ti$_{1-x}$)O$_3$–Ni composite ferroic films

Xiaofang Bi[a)]
MSE, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213 and MSE, Beijing University of Aeronautics and Astronautics, Beijing 100083, China

Shaoyan Chu
MSE, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213

Jian-Gang Zhu
ECE, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213 and MSE, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213

David E. Laughlin
MSE, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213 and ECE, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213

Ferroic composite thin films consisting of Pb(Zr$_x$Ti$_{1-x}$)O$_3$ and Ni were prepared using rf magnetron sputtering at room temperature in an argon atmosphere. The film structure depends strongly on the Ni content. After annealing the ferroic composite films grown on SiO$_2$/Si substrates at 650 °C, a perovskite structure was obtained when the Ni content was in the range of 17–27.5 at. %. It has been found that the role of Ni in obtaining the perovskite is attributed to the formation of NiO, which acts as a nucleation site for the crystallization of the perovskite structure. The coercivity was evaluated at 10 and 293 K by superconducting quantum interference device magnetometry to estimate magnetoelectric effect for the films with and without the perovskite structure. © *2006 American Institute of Physics.* [DOI: 10.1063/1.2162091]

I. INTRODUCTION

Composite ferroic materials have become increasingly interesting from both fundamental and practical perspectives, due to their unique coupling between different fields such as magnetic, electric, and stress.[1,2] They possess great potential for applications in devices such as energy converters, sensors, and actuators. Composite ferroic materials contain two individual phases with each of the phase responding directly to the different fields. This contrasts with the multiferroic materials which are single phase.[3,4] In the magnetoelectric composites, one phase is a piezoelectric material and the other a magnetostrictive material. The coupling is through elastic interactions between the two ferroic phases. There has recently been a report of magnetoelectric effect in the self-assembled composites of the BaTiO$_3$ ferroelectric and CoFe$_2$O$_4$ magnetostrictive materials.[1] It is well known that Pb(Zr$_x$Ti$_{1-x}$)O$_3$ exhibits excellent piezoelectric properties, a high Curie temperature, and in addition a high electromechanical coupling coefficient. On the other hand, Ni is known as a magnetostrictive material with the largest magnetostriction coefficient among the magnetic elements. A magnetoelectric effect, therefore, could be realized in very simple lead zirconic titanate-(PZT) Ni composite systems. Previous study on PZT films has revealed that their properties depend largely on parameters such as composition, substrate orientation, and temperature, as a result of the variation of its structure and texture. It is of great importance, there-fore, to obtain an insight into the effect of the Ni content on the microstructural evolution of the PZT, which is crucial to obtain a PZT-Ni ferroic composite films showing a magnetoelectric effect.

In this work, we investigated the structural features as a function of Ni content, with the aim of obtaining PZT-Ni ferroic composite films with a simple constitution. The films have been deposited on Si wafers with a native amorphous oxide SiO$_2$. The magnetoelectric effect has been examined by superconducting quantum interference device (SQUID) magnetometer measurements.

II. EXPERIMENTAL

The PZT-Ni composite films were prepared by rf magnetron sputtering. The composition of the commercial PZT target used in this work was Pb(Zr$_{48}$Ti$_{52}$)O$_3$. The content of Ni was controlled by changing the number of Ni chips placed on the target. Sputtering was performed in a pure argon gas at the pressure of 5 mT. Substrates were not heated during deposition. The composite films were deposited directly on Si substrates with native SiO$_2$. The as-deposited films were then subjected to a postannealing at 650 °C in an argon atmosphere. The composition of Ni for the films was determined by electron dispersive spectroscopy (EDS) and the film structure was characterized by x-ray diffraction.. Transmission electron microscopy (TEM) was utilized to observe the microstructure of films with various Ni contents. The magnetoelectric effect was investigated by measuring

a)Electronic mail: bixf@163bj.com
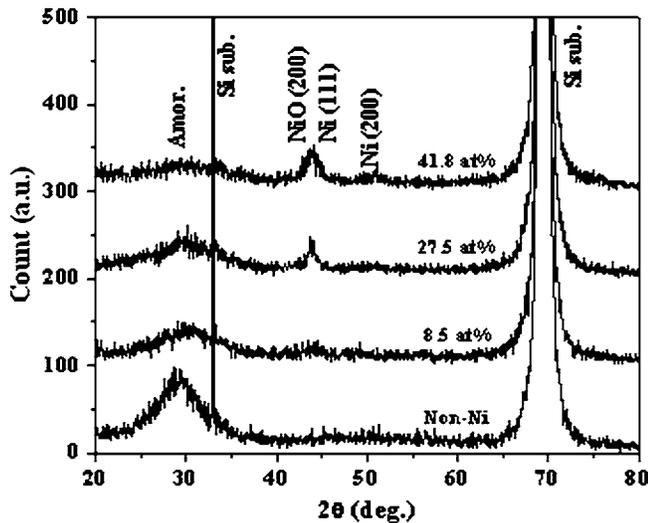
FIG. 1. X-ray-diffraction patterns for the as-deposited films containing different Ni contents, along with the one without Ni.

FIG. 2. X-ray-diffraction patterns for films after annealing at 650 °C in an argon atmosphere. The Ni contents are 8.5, 14.0, 17.1, 27.5, and 41.8 at. %, respectively, along with the one without Ni.

the coercivities at 10 and 293 K, which were obtained from hysteresis loops using SQUID magnetometer with a field of 4 kOe.

III. RESULTS AND DISCUSSION

Figure 1 shows the x-ray diffraction (XRD) patterns of the PZT-Ni ferroic films before annealings. For the as-deposited film without Ni, only the amorphous structure is observed (strong broad peak around 30°). In contrast to this, for the composite films containing Ni, a peak with 2θ at about 44° appeared. The large full width at half maximum (FWHM) of the peak indicates coexistence of the NiO(200) and Ni(111) peaks. Increasing the Ni content caused the intensity of the peak to increase while the amorphous peak became weaker. However, the as-deposited films with the addition of Ni revealed a very similar structure comprised of amorphous phase, Ni and NiO crystalline, regardless of varying Ni contents in the present range. It was observed, however, that the structure evolution during annealing for the films on the Si substrates is very sensitive to the Ni contents as shown in Fig. 2. When Ni was less than 14 at. %, no perovskite structure was obtained for the films. As the Ni content increased to 17 at. %, the films began to have a perovoskite phase present with a (100)/(101) mixed orientation together with Ni and NiO. With further increase of the Ni content to 41 at. %, however, a pyroclore phase and an unidentified phase were observed in addition to the Ni and NiO. The above results show that a certain amount of Ni added in the PZT films is favorable for the formation of the perovskite structure for the films grown directly on the Si substrates. To further investigate the effect of Ni on the microstructural evolution for the composite films, TEM observations were performed.

Figure 3 shows TEM micrographs for the films containing 27.5 at. % Ni before and after annealing. Their corresponding diffraction patterns are also displayed. For the as-deposited film with 27.5 at. % Ni shown in Fig. 3(a), in addition to an amorphous halo, Ni(111), Ni(200), NiO(200),
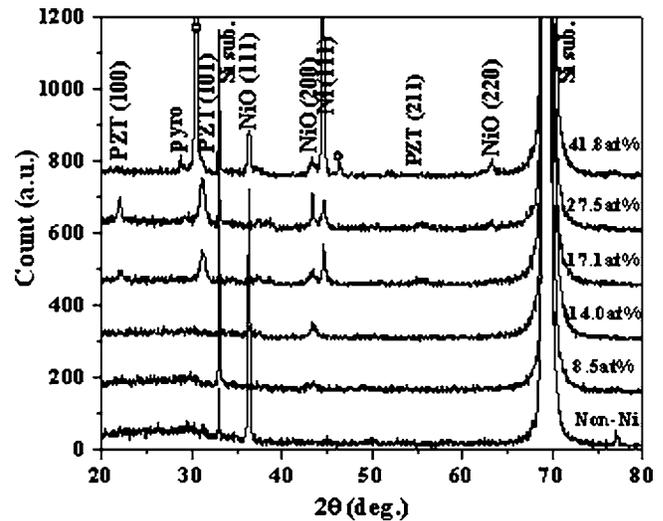
and (220) rings are observed. In combination with its bright field image, it can be seen that very fine grains of less than 5 nm are Ni and NiO, and are embedded in an amorphous like matrix.

After annealing, as shown in Fig. 3(b), it is observed that the film is composed of grains less than 10 nm and comparatively large grains of about 30 nm. The diffraction pattern shows that the film was crystallized into a PZT perovskite structure, together with Ni and NiO phases. The first ring is discontinuous and indexed as PZT(101). The second and third rings from the center are continuous and both have several spots. They are slightly further away from the center compared to their neighboring rings. Furthermore, several spots are visible on the third ring. From the characterizations of the diffraction pattern, we can determine that the grain sizes of the PZT and Ni grains are larger than those of NiO. Combined with the TEM image, it can be seen that small
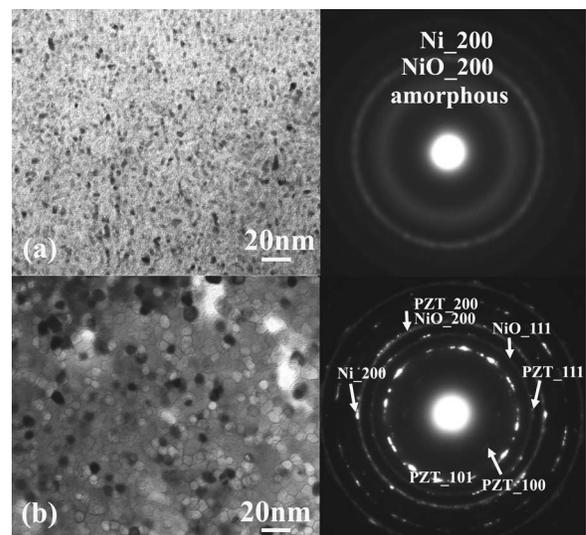
FIG. 3. TEM images of plane view of the PZT-Ni composite films containing 27.5 at. %, along with the corresponding electron-diffraction patterns. (a) As deposited and (b) after annealing.
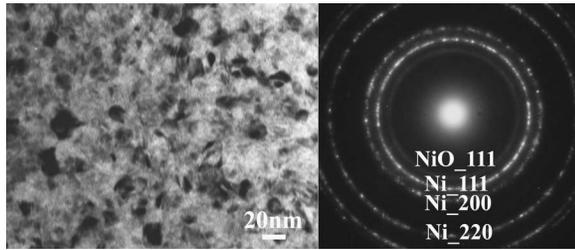
FIG. 4. TEM images of plane view of the PZT-Ni composite films containing 8.5 at. % Ni after annealing, along with its corresponding electron-diffraction pattern.

TABLE I. Coercivity at different temperatures for the PZT-Ni ferroic composite films with perovskite and without perovskite structure.

Temperature (K)	Coercivity (Oe)	
	Perovskite+27.5 at. % Ni film	Nonperovskite+8.5 at. % Ni film
10	422	233
293	147	226

grains of NiO are present around the PZT and Ni grains. There has been a report that the formation of perovskite is associated closely to its nucleation features.[5] A certain buffer layer could change the temperature at which a perovskite phase is produced due to the variation of its nucleation activation energy. Since the lattice constants are almost the same for the PZT and NiO, it is assumed that NiO acts as a nucleation site for the crystallization of perovskite structure from its amorphous state. Consequently, the NiO is expected to exist in between the PZT and Ni. Owing to the presence of NiO, a perovskite structure is obtained even directly on the Si substrate without heating the substrate. On the contrary, with reducing percentage of Ni in the composite film, the number of nucleation sites is decreased. As a result, a perovskite structure is obtained with great difficulty. Figure 4 is the micrograph of the film containing 8.5 at. % Ni, along with its diffraction pattern. A very weak discontinuous ring indexed as NiO is detected. On the other hand, a series of rings showing Ni are observed. The diffraction pattern shows that only a few NiO grains are formed in the films after annealing. Combined with its TEM image, it is seen that the Ni grains exist matrix with a wide distribution of grain size. This result also supports the above assumption that NiO could be a nucleation site for the crystallization of the PZT for the composite film from its amorphous state to the perovskite structure. It is expected that a textured tetragonal structure could be obtained by controlling the orientation of NiO grains.

Table I lists the coercivity of the composite films at 10 and 293 K obtained by using SQUID magnetometry. For both films, the coercivities vary with temperature. This may be partially due to the strong temperature dependence of the magnetic behavior of NiO.[6–8] Furthermore, it can been seen that the change of the coercivity at different temperatures is affected by the structure of the composite films. For the composite film with perovskite, the coercivity decreases almost three times when the temperature increases from 10 K to room temperature. However, the film without perovskite has only a slight decrease in coercivity. It is assumed that the larger change of the coercivity is due not only to the temperature effect but also to the structure change between monoclinic and tetragonal at temperature lower than room one.[9] It is known that piezoelectric effect varies with different structure. Therefore, the change of the structure could vary stresses in the film when the temperature changes, resulting in a large change in the coercivity of the Ni due to magnetostriction. This argument needs to be further investigated by making direct measurements of electrical and magnetic properties.

IV. CONCLUSION

Ferroic composite films of $Pb(Zr_xTi_{1-x})O_3$–Ni were prepared using rf magnetron sputtering at room temperature in an argon atmosphere. The films directly grown on Si substrates have a phase with the perovskite structure after annealing, depending greatly on the Ni content. TEM observation suggests that the NiO acts as nucleation sites for the crystallization of the perovskite structure during annealing process from its amorphous state for the as-deposited films. It was also determined that the coercivity for the composite films with perovskite is dependent largely on the temperature in the range of 10–293 K.

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