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Ferroelectric, electrical and magnetic properties of Cr, Mn, Co, Ni, Cu added polycrystalline $BiFeO_3$ films

Hiroshi Naganuma,[a] Jun Miura, and Soichiro Okamura
Department of Applied Physics, Tokyo University of Science, 1-3, Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan

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Cr, Mn, Co, Ni, and Cu were added to polycrystalline $BiFeO_3$ films, and their influence on the ferroelectric, electrical, and magnetic properties was investigated. All the additives except Ni reduced the leakage current density in the high electric field region. The addition of Cu and Co decreased the coercive field without reducing remanent polarization. The addition of Co caused spontaneous magnetization at room temperature, which exhibited a large coercive field of 16 kOe at 10 K. It was revealed that Co addition suppressed the leakage current density, decreased the electric coercive field, and induced spontaneous magnetization and large magnetic coercivity. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2965799]

$BiFeO_3$ films have attracted considerable attention because their multiferroic properties are such that the films simulatneously exhibit ferroelectricity and magnetic ordering above room temperature. In particular, by first principles calculation, the spontaneous polarization of these films is predicted to be $90-100\ \mu C/cm^2$.[1] In fact, a significantly high remanent polarization has been experimentally reported in the $BiFeO_3$; however, $BiFeO_3$ films generally have a high leakage current density at room temperature.[2] Therefore, considerable effort has been made to reduce the leakage current density of $BiFeO_3$ films. One effective method for reducing the leakage current density is to add small amount of additives such as La,[3,4] Sc,[5] Mn,[6,7] Cr,[8,9] and Ti.[10,11] Although some of these additives drastically reduce the leakage current density, the degree of improvement differs in each study even for the same additives; therefore, it is difficult to judge which additive is the most effective in improving the insulating properties of $BiFeO_3$ films. $BiFeO_3$ films possess a high electric coercive field due to their high Curie temperature (T_C) of ~1100 K. This implies that switching the polarization of these films requires a strong electric field. We anticipate that additives such as La (Ref. 4) can reduce the strength of the switching field in $BiFeO_3$ films. On the other hand, $BiFeO_3$ shows a small spontaneous magnetization due to its antiferromagnetic spin configuration, which hinders its multiferroic properties. In this study, we propose that magnetic moment and anisotropy are increased by substituting other 3*d* transition atoms for the iron atoms at *B* sites of $BiFeO_3$, due to the differences in the magnetic moments among the *B* sites, which has a possibility to induce a local ferrimagnetic spin configuration, a complex chiral spin structure, or a change in the gradient of spin canting. Thus, both the ferroelectric and magnetic properties of the films are expected to improve with the addition of additives, for example, reduction in the electric coercive field, reduction in the leakage current density, and induction of spontaneous magnetization. Our aim in the present study is a systematic investigation of the effects of the 3*d* transition metal additives on the ferroelectric, electric, and magnetic properties of polycrystalline $BiFeO_3$ films.

Cr, Mn, Co, Ni, and Cu added $BiFeO_3$ films ($t \approx 200$ nm) were fabricated by chemical solution deposition onto 111-textured $Pt/Ti/SiO_2/Si(100)$ substrates followed by postdeposition annealing at 923 K for 10 min in air. The film structure was confirmed by a conventional $\theta/2\theta$ x-ray diffraction (XRD) pattern. The ferroelectric properties were measured using the ferroelectric testers (TOYO Corporation: FCE-1A and aixACCT: TF-2000). The leakage current was measured by a picoampere meter and the response forms of a positive-up-negative-down (PUND) measurement. The magnetic properties were measured by a vibrating sample magnetometer (VSM Tamakawa) at room temperature and by a superconducting quantum interface device (SQUID MPMS-5) at 10 K.

Figure 1(a) shows the XRD patterns of Cr, Mn, Co, Ni, and Cu of 5 at. % added $BiFeO_3$ films [$Bi(M_{0.05}Fe_{0.95})O_3$]. Many diffraction peaks due to the $BiFeO_3$ structure was observed, indicating the formation of a polycrystalline structure. The (012) diffraction peak of the Co added $BiFeO_3$ film was stronger than those of other additives; this implies the formation of a 012-textured structure. In Cr addition, not

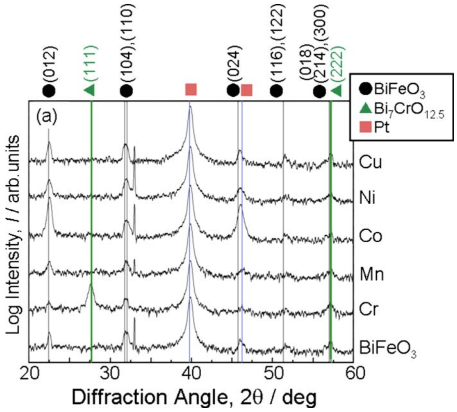

FIG. 1. (Color online) XRD patterns for $Bi(M_{0.05}Fe_{0.95})O_3$ [M=Cr, Mn, Co, Ni, and Cu] films.

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[a] Author to whom correspondence should be addressed. Electronic mail: naganuma@mlab.apph.tohoku.ac.jp. Tel.: +81-2-2795-7948. FAX: +81-2-795-7947. Present address: Department of Applied Physics, Tohoku University, 6-6-05 Aoba Aramaki Aoba-ku Sendai, Miyagi 980-8579, Japan.

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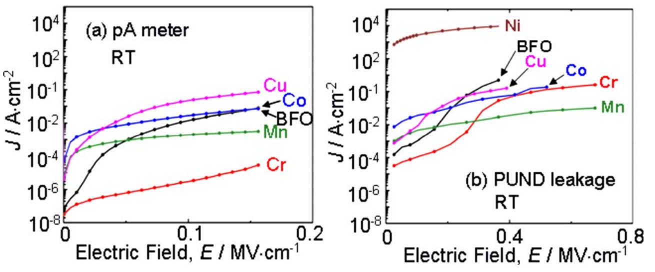

FIG. 2. (Color online) Leakage current density at room temperature measured using a picoampere meter (a) and the response forms of the up pulse in PUND measurements (b).

only $BiFeO_3$ phase but also the secondary phase of $Bi_7CrO_{12.5}$ was formed.

Figure 2 shows the leakage current density of $Bi(M_{0.05}Fe_{0.95})O_3$ films measured by the picoampere meter. The leakage current density of the Ni added $BiFeO_3$ could not be evaluated precisely because of a considerably high leakage current. On increasing the electric field, the leakage current density of pure $BiFeO_3$ film increased more rapidly than those of films with additives. However, even for the added films, it was difficult to measure the leakage current density above 0.2 MV/cm by the picoampere meter due to the occurrence of a dielectric breakdown. To evaluate the leakage current density at higher electric fields, the leakage current density was estimated from the pulse response forms of the PUND measurements. In this way, the leakage current at high electric field can be measured by the reduction in the Joule heat damage.[12,13] An electric field of at least 0.36 MV/cm could be applied, which is higher than that measured by the picoampere meter. Figure 2(b) shows the leakage current density estimated by the response forms of the up pulse. The leakage current density of the Ni added $BiFeO_3$ film could also be measured by this method. It was found to be considerably higher than that of the pure $BiFeO_3$ film. This indicates that the PUND method can be used for materials with a high leakage current density. The addition of Mn, Co, and Cu to the $BiFeO_3$ films effectively reduced the leakage current density in the high electric field region.

Figure 3 shows the ferroelectric hysteresis loops of the $Bi(M_{0.05}Fe_{0.95})O_3$ films measured at room temperature using the ferroelectric tester with a 100 kHz driving system (TOYO Corporation: FCE-1A type) and measured at 90 K using a 2 kHz driving system. Ferroelectric hysteresis loops could not be observed for the Ni added $BiFeO_3$ film. The pure $BiFeO_3$ film showed an expanded hysteresis loops at room temperature, which could be attributed to the leakage current component. The squareness of the ferroelectric hysteresis loops was clearly improved by addition of Mn, Co, and Cu to the $BiFeO_3$ films. This squareness is attributed to the reduction in the leakage current density in the high electric field region. Although the leakage current density is reduced by the addition of Mn, Co, and Cu, it is still difficult to apply a high electric field at room temperature. Therefore, the ferroelectric hysteresis loops were measured at 90 K using the 2 kHz driving system. At 90 K, the leakage current density was considerably lower than the inversion current due to domain switching as inferred from the current response of the PUND measurements. In fact, the ferroelectric hysteresis loops did not expand and showed high squareness at 90 K. E_c versus E plots show that the electric coercive field reduced by the addition of Co and Cu. In contrast, the addition of Mn and Cr to the $BiFeO_3$ films produced a higher electric coercive field compared to the pure $BiFeO_3$ film. In the Co and Cu added films, P_r versus E plots almost overlapped up to 1.3 MV/cm. Thus, Co and Cu addition suppress the reduction in the switching field of polycrystalline $BiFeO_3$ films without reducing remanent polarization, which is suitable for devices such as memory and/or piezoelectric devices.

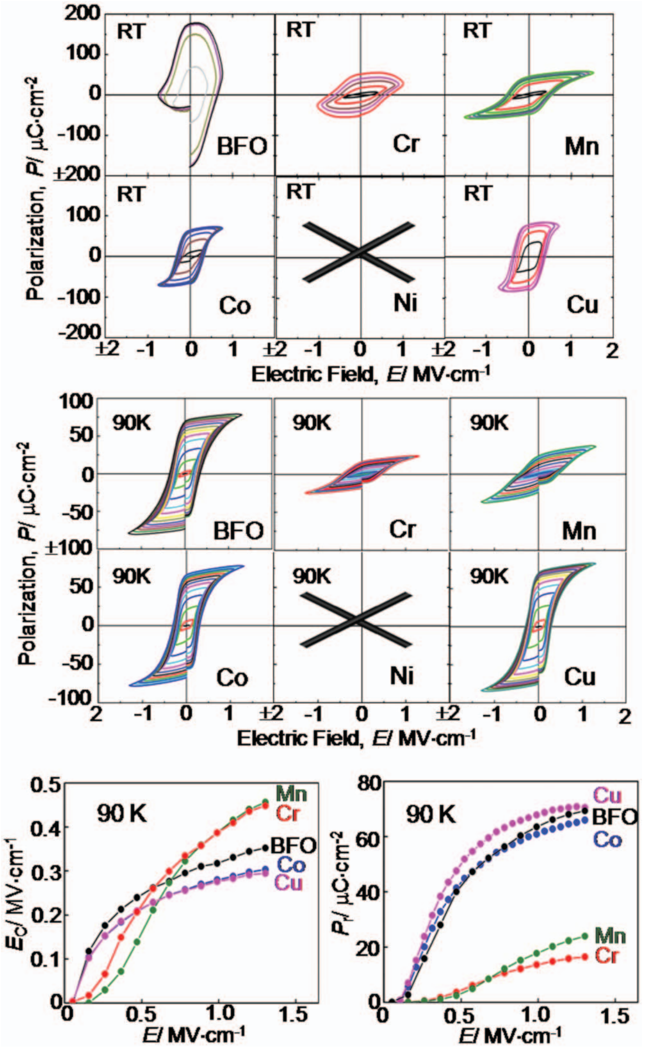

FIG. 3. (Color) Ferroelectric hysteresis loops for $Bi(M_{0.05}Fe_{0.95})O_3$ films measured at room temperature using a ferroelectric tester with a 100 kHz driving system and at 90 K with 2 kHz system. Plots of E_c and P_r vs E measured at 90 K.

Figure 4 shows the magnetization curves of the $Bi(M_{0.04}Fe_{0.96})O_3$ films measured at room temperature. The pure $BiFeO_3$ film showed small saturation magnetization without spontaneous magnetization. The addition of Co, Ni, and Cu caused an increase in the saturation magnetization. Therefore, these additives were substituted into the *B* sites of Fe, although it was not clear whether all the additives were substituted into the *B* sites. In the case of Co addition, saturation magnetization increased in addition to appearance of spontaneous magnetization. The coercive field of the Co added film was 2 kOe at room temperature, which increased to 16 kOe at 10 K. This large magnetic coercive field cannot be explained by the existence of Co-based alloyed nanoparticles; therefore, it can be considered that the large magnetic

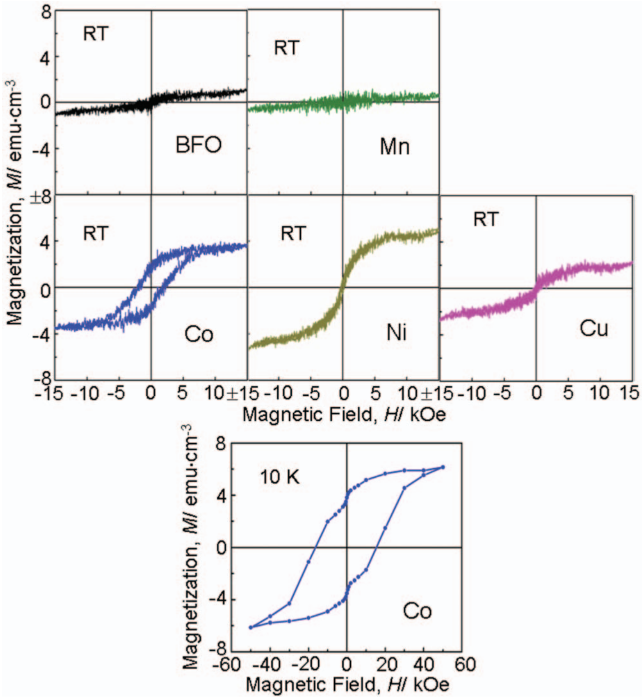

FIG. 4. (Color) Magnetization curves for $Bi(M_{0.04}Fe_{0.96})O_3$ films measured at room temperature and 10 K.

coercive field is attributed to substitution of Co into the *B* sites. Finally, it was concluded that the Co substitution into the *B* sites could improve the leakage current property, reduce the electric coercive field without degrading the remanent polarization, and induce spontaneous magnetization with a large magnetic coercive field.

In summary, the XRD patterns indicated that only the diffraction peaks attributed to the $BiFeO_3$ structure were observed for all the additives except Cr. The addition of Mn, Cu, and Co to the $BiFeO_3$ film could suppress the leakage current density in the high electric field region. From the *P-E* loops at 90 K, it could be observed that the addition of Co and Cu reduced the switching field without reducing the remanent polarization. In the case of Co addition, the saturation magnetization increased and spontaneous magnetization appeared together with the magnetic coercive field of 2 kOe at room temperature. The magnetic coercive field increased to 16 kOe at 10 K, indicating the influence of a strong thermal fluctuation. Finally, it was concluded that Co addition could improve the leakage current property, reduce the electric coercive field without degrading the remanent polarization, and induce spontaneous magnetization with a high coercive field in the polycrystalline $BiFeO_3$ films.

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