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Investigation of Magnetic and Electrical Properties of $GdFeO_3/Fe_{97}Si_3$ Bilayer Thin Films

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Abstract
Bilayer thin films of $GdFeO_3/Fe_{97}Si_3$ have been synthesized by RF–magnetron sputtering at different thicknesses of $GdFeO_3$. A pure phase polycrystalline growth of $GdFeO_3$ and $Fe_{97}Si_3$ has been confirmed by XRD measurements. Stress-induced room-temperature magnetocrystalline anisotropy has been confirmed in all the bilayer thin films. A high magnetic moment has been induced in antiferromagnetic $GdFeO_3$ thin films resulting in the ferromagnetic character of all the samples. The ferromagnetic moment was found to be enhanced with increasing thickness of the $GdFeO_3$ layer. The maximum value of the room- temperature magnetic moment has been observed as M_s ~ 9.3 emu/ml in 170-nm-thick $GdFeO_3$ film. Dielectric measurements confirmed the induced magnetocapacitance due to grain boundary accumulation of charge carriers. Magnetic field control of capacitance and current–voltage measurements of these thin films represents a strong potential for the existence of magnetoelectric coupling in $GdFeO_3/Fe_{97}Si_3$ films. A maximum 30% rise in magnetocapacitance and a 95.6% increase in tunneling current in an applied 1-kOe magnetic field was obtained for 170-nm-thick GFO thin film. These thin films possess applications in spintronic devices due to the presence of room- temperature magnetocrystalline anisotropy and magnetic control of the electric properties.

Keywords Multiferroic · antiferromagnetic · magnetic anisotropy · ferromagnetism · magnetocapacitance

Introduction

The current scenario of artificial intelligence and machine learning has led to increased demand for data storage and energy-efficient computing. The current existing technology of complementary metal oxide semiconductors (CMOS) seems to be incapable of fulfilling this demand, evidenced in the form of the recent global semiconductor chip crisis.[1] In this regard, there is a dire need of alternative multifunctional materials which could replace existing CMOS devices. Multiferroic materials are the most appropriate alternative materials for semiconducting chip design, due to their potential applications in data storage and spintronic devices. Multiferroic materials exhibit coexisting ferroelectric and magnetic order parameters so that one parameter can be controlled by another, resulting in magnetoelectric coupling.[2] In the quest of a novel room-temperature magnetoelectric device, multiferroic thin films have attracted extensive research activities in the last few years. Among the potential room-temperature multiferroic materials, rare-earth orthoferrite, $GdFeO_3$, has attracted the focus of the scientific community due to the presence of intrinsic coupling between ferroelectric and magnetic order parameters.[3] The structure of $GdFeO_3$ is derived from distorted cubic perovskite where Fe^{3+} spins form an antiferromagnetic order along the *a*-axis below Neel's transition temperature, T_N (Fe) ~ 661 K.[3] A weak ferromagnetic component is generated along the *c*-axis of the cube due to spin canting in the *ac* plane.[4] On the other hand, Gd^{3+} spins are arranged in *G*-type antiferromagnetic order along the *a*-axis below T_N (Gd) ~ 2.5 K.[3] The ferroelectric polarization results from spin exchange interaction between Fe^{3+} and Gd^{3+} spins so that Gd^{3+} ions

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displace along the *c*-axis inducing polarization along the *c*-axis.[3] The magnetoelectric interaction in bulk $GdFeO_3$ exists only at low temperatures, but thin films of $GdFeO_3$ can give rise to room-temperature magnetoelectric effects. However, very few reports have been published on the study of room-temperature magnetic and electrical properties of $GdFeO_3$ thin films.[5–7] In this work, thin films of $GdFeO_3$ have been synthesized on an $Fe_{97}Si_3$ buffer layer by RF–magnetron sputtering. The application of a bottom $Fe_{97}Si_3$ layer serves as a bottom electrode while it primarily alters the magnetic behavior of $GdFeO_3$. The pinning of the Fe atom of the $Fe_{97}Si_3$ layer to the Fe atom of the $GdFeO_3$ layer give rise to induced ferromagnetism in antiferromagnetic $GdFeO_3$. The pure phase of $GdFeO_3$ has been successfully deposited, and stress-induced ferromagnetism with in-plane magnetic anisotropy has been confirmed. The dielectric and ferromagnetic properties of bilayer thin films have been studied in detail at different thicknesses of $GdFeO_3$. A room-temperature magnetocapacitance has also been obtained which can lead to the application of these samples towards magnetoelectric devices.

Experimental

Bilayer thin films of $GdFeO_3/Fe_{97}Si_3$ (GFO/Fe-Si) were deposited on a single-crystalline MgO (100) substrate. A metallic target of the ferromagnetic alloy, $Fe_{97}Si_3$, was used to deposit Fe-Si thin films while a ceramic $GdFeO_3$ target was used for GFO film deposition. For bilayer thin-film preparation, first, a 50-nm Pt layer was deposited on a single-crystalline MgO (100) substrate. Subsequently, a 20-nm thin film of Fe-Si was deposited on the Pt/MgO substrate, and, finally, GFO thin films at three different thicknesses, 50 nm, 110 nm, and 170 nm, were deposited on Fe-Si/Pt/MgO heterostructures. The deposition of the Fe-Si thin films was carried out at 0.6×10^{-3} Pa with a base pressure of pure Ar gas, while the base pressure of the vacuum chamber was maintained at 3.99×10^5 kPa. The temperature of the MgO substrate was kept at 450°C for Fe-Si thin film deposition. $GdFeO_3$ film was deposited at 2.6×10^{-3} Pa pressure of Ar + O_2 (4:1), while the temperature of the buffer Fe-Si layer was maintained at 550°C. A top Pt electrode of 0.1-μm diameter was then deposited on the $GdFeO_3$ layer. X-ray diffraction (XRD) measurements were performed by x-ray spectrometer (Phillip's X-pert pro) with CuK_α radiation ($\lambda = 0.154$ nm). Magnetic measurements were carried out using a vibrating sample magnetometer (Lakeshore—7304). atomic force microscopic (AFM) images were explored using a Nanoscope-V microscope. Dielectric measurements were performed by an LCR meter (Wynekerr 6500B).

Results and Discussion

The XRD patterns of the $Fe_{97}Si_3$ thin film on the MgO substrate and the $GdFeO_3/Fe_{97}Si_3$/MgO thin film heterostructure are shown in Fig. 1. The XRD spectra depict pure phase polycrystalline growth of $GdFeO_3$, while (110) plane-oriented growth of Fe-Si can be observed in Fig. 1. The XRD peaks of $GdFeO_3$ confirmed the orthorhombic structure of $GdFeO_3$ having space group $^{P}_{nma}$ with reference to the JCPDS card No. 78-0451.[8] In-plane lattice mismatch of $Fe_{97}Si_3$ and $GdFeO_3$ was calculated by, $\frac{a_{Fe}-a_{Gd}}{a_{Gd}} \times 100\%$, where a_{Fe} is the lattice parameter (a) of $Fe_{97}Si_3$ having the BCC structure and a_{Gd} is a lattice parameter (a) of $GdFeO_3$ having an orthorhombic structure. A high compressive strain of 48.89% was calculated in the structural growth of $GdFeO_3$, which may lead to interfacial strain-induced anisotropy in antiferromagnetic $GdFeO_3$. The thickness of the samples was measured by a stylus-based surface profilometer (Nanomap 500 ES) with an error of ± 5 nm. The thickness plots of the samples are presented in Fig. 2.

The surface morphology and grain growth of the thin films were analyzed by AFM images, as shown in Fig. 3. The grain growth of the pure Fe-Si thin film on the MgO substrate is presented in Fig. 3a where a metallic texture and the agglomeration of small grains to form metallic islands can be seen. The surface morphology of the $GdFeO_3$ thin films at different thicknesses can be seen from Fig. 3b–d). Increasing the thickness of the $GdFeO_3$ thin films clearly results in increased crystallinity and increased grain size on the films' surface. The average grain size of the Fe-Si thin films was calculated as S_a ~ 45 nm, and the average surface roughness was calculated as R_a ~ 2.288 nm. The

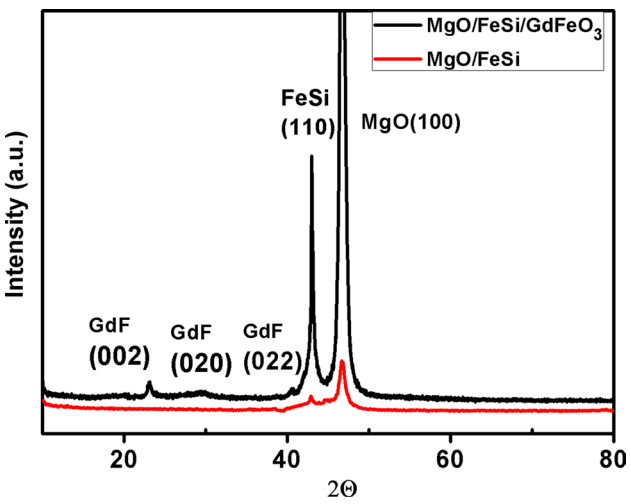

Fig. 1 XRD patterns of $Fe_{97}Si_3$ single layer (*red*) and $GdFeO_3/Fe_{97}Si_3$ bilayer (*black*) thin films on the MgO substrate (Color figure online).

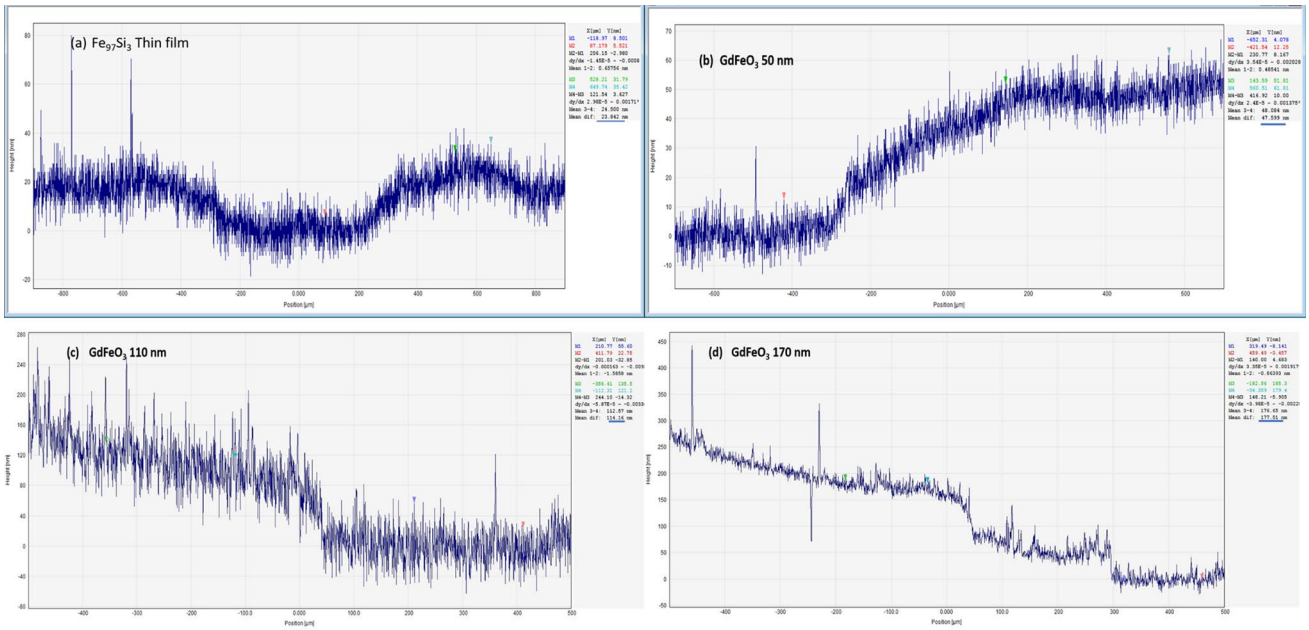

Fig. 2 Thickness profiles of (a) $Fe_{97}Si_3$ (20 nm) and $GdFeO_3$ at (b) 50-nm, (c) 110nm, and (d) 170-nm thicknesses.

grain size of the $GdFeO_3$ thin films was calculated as S_a ~ 8 nm for 50-nm thin films, S_a ~ 24 nm for 110-nm thin films, and S_a ~ 37 nm for 170-nm thin films. The average surface roughness was calculated as R_a ~ 1.324 nm for 50-nm thin films, R_a ~ 1.0036 nm for 110-nm thin films, and R_a ~ 0.8586 nm for 170-nm $GdFeO_3$ thin films. To analyze the interface quality of the bilayer thin films, cross-sectional SEM images of $GdFeO_3$ (170 nm)/$Fe_{97}Si_3$ (20 nm)/MgO are presented in Fig. 4. Polycrystalline growth of GFO and Fe-Si thin films with a well-defined interface can be observed from the images.

The magnetic properties of bilayer thin films of GFO/Fe-Si at different thicknesses were analyzed by a vibrating sample magnetometer. Room-temperature M-H hysteresis loops of pure Fe-Si and GFO/Fe-Si bilayer thin films are presented in Fig. 5a. The room-temperature M-H loop of pure $GdFeO_3$ thin film of 50-nm thickness after subtracting the diamagnetic contribution of the MgO substrate is shown in Fig. 5b. The $GdFeO_3$ thin film represents an antiferromagnetic character at higher magnetic fields, whereas the weak induced ferromagnetism at a low magnetic field indicates uncompensated Fe spins atthe MgO/$GdFeO_3$ interface. A detailed analysis of the optimization of room-temperature magnetic anisotropy in pure Fe-Si thin films was carried out in our earlier work.[9] In-plane magnetic anisotropy with a high magnetic moment of 60 emu/ml was obtained in pure 20-nm Fe-Si thin films deposited on MgO substrates. A small induced in-plane ferromagnetic magnetic moment, M_s ~ 2.4 emu/ml. was obtained in 50-nm GFO/Fe-Si thin film after subtracting the diamagnetic contribution of the MgO substrate. The magnetic moment of the $GdFeO_3$ film was observed to be enhanced with increasing thickness of the film. The magnetic moment, M_s ~ 3.1 emu/ml, was obtained for 110-nm-thick $GdFeO_3$ thin film, while M_s ~ 9.3 emu/ml was obtained for 170-nm-thick film. The coercivity of the bilayer thin film was also enhanced with increasing the thickness of the $GdFeO_3$ layer. Multiferroic $GdFeO_3$ is a G-type antiferromagnetic, and the small induced magnetic moment in bilayer thin films is assigned to uncompensated spin moments at the GFO/Fe-Si bilayer interface.[10] The magnetic anisotropy in bilayer thin films may be interpreted as a fingerprint of stress at the GFO/Fe-Si interface, which has also been confirmed from XRD calculations. The enhanced magnetic moment with increasing thickness of $GdFeO_3$ film may be due to ferromagnetic alignment of Fe^{3+} ions that results in enhanced spin exchange interaction between Fe^{3+} ions.

Frequency-dependent variation of capacitance (C) and magnetocapacitance/magnetoloss (ΔC/ΔD) is shown in Fig. 6. These measurements were carried out at an applied magnetic field of 1 kOe to the thin films in the longitudinal direction to estimate the maximum change in magnetocapacitance. Here, magnetocapacitance is defined as: $\Delta C = \frac{C_{H=1000Oe} - C_{H=0Oe}}{C_{H=0Oe}}$ and magnetoloss is given as: $\Delta D = \frac{D_{H=1000Oe} - D_{H=0Oe}}{D_{H=0Oe}}$. It can be clearly observed from Fig. 6a and b that capacitance of GFO/Fe-Si bilayer thin films is increased with the applied magnetic field over the frequency range 100 Hz to 10 MHz. The maximum change in the lower frequency range (100 Hz–1 KHz) observed in bilayer thin

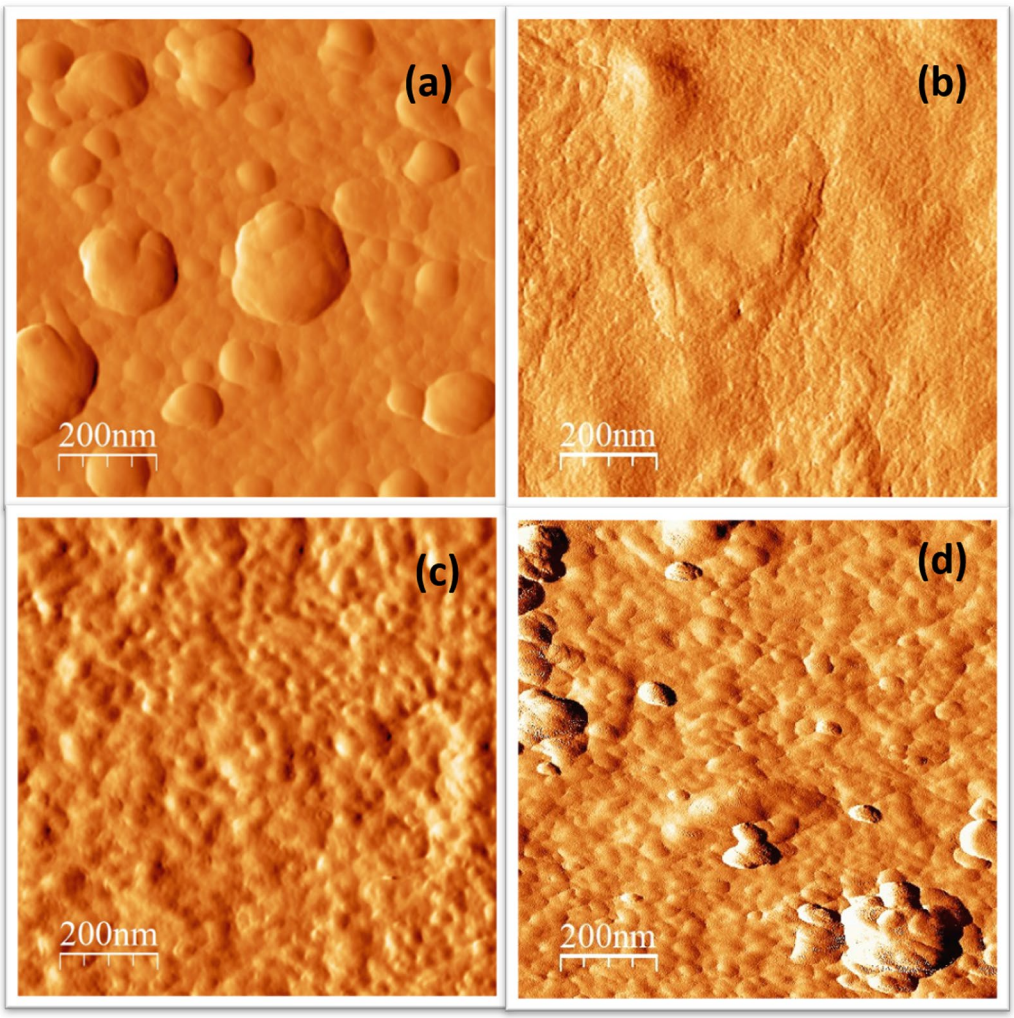

Fig. 3 AFM images showing the surface morphology of (a) $Fe_{97}Si_3$ single-layer and $GdFeO_3/Fe_{97}Si_3$ bilayer films at $GdFeO_3$, (b) 50-nm, (c) 110-nm, and (d) 170-nm thicknesses.

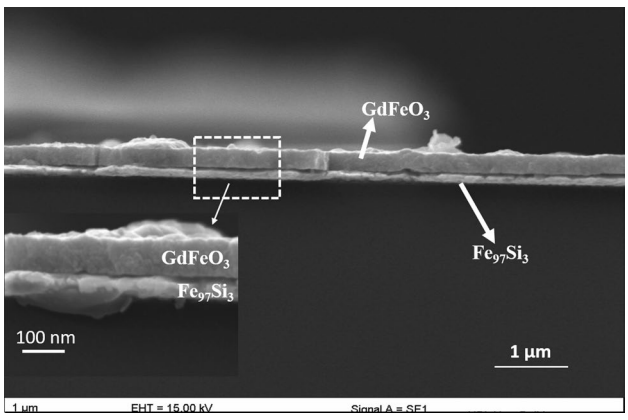

Fig. 4 Cross-sectional SEM image of the $GdFeO_3/Fe_{97}Si_3$ bilayer film on an MgO substrate.

films is attributed to Maxwell–Wagner space charge polarization.[10] However, the intrinsic contribution of grain boundary charge to magnetocapacitance can be clearly observed from Fig. 6b and d, where a sharp peak at 100 KHz represents the grain boundary magnetocapacitance. It can also be observed from Fig. 6d that the magnetocapacitance is increased with increasing thickness of the GFO thin film. A maximum 30% increase in magnetocapacitance was obtained for 170-nm-thick $GdFeO_3$ thin film. This can be due to the larger grain size for the 170-nm-thick film resulting in higher orientational polarization across the grain boundary.[11] The magnetocapacitance measurements could not be carried out for the 50-nm-thin GFO film due to the high leakage current. $GdFeO_3$ films thinner than 50 nm were not used for this work due to the high leakage current and weak electrical properties. The conclusions of the dielectric measurements were further confirmed by magnetic field-dependent current–voltage (I/V) measurements. The current was measured across

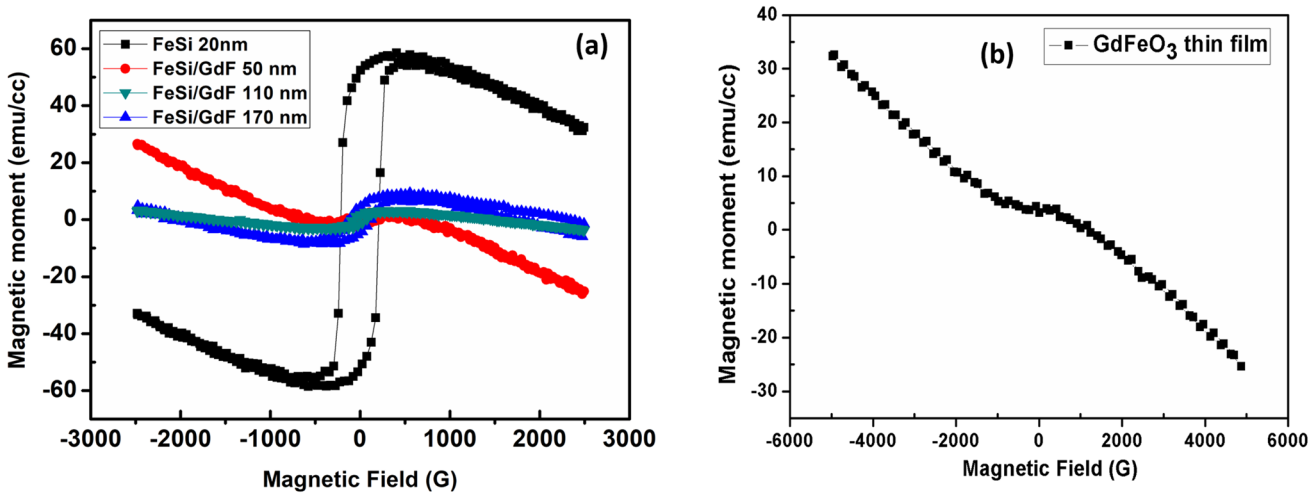

Fig. 5 (a) Magnetization versus magnetic field (M-H) plots of pure $Fe_{97}Si_3$ and $GdFeO_3/Fe_{97}Si_3$ bilayer films, (b) M-H plot of $GdFeO_3$ (50-nm)/MgO thin film.

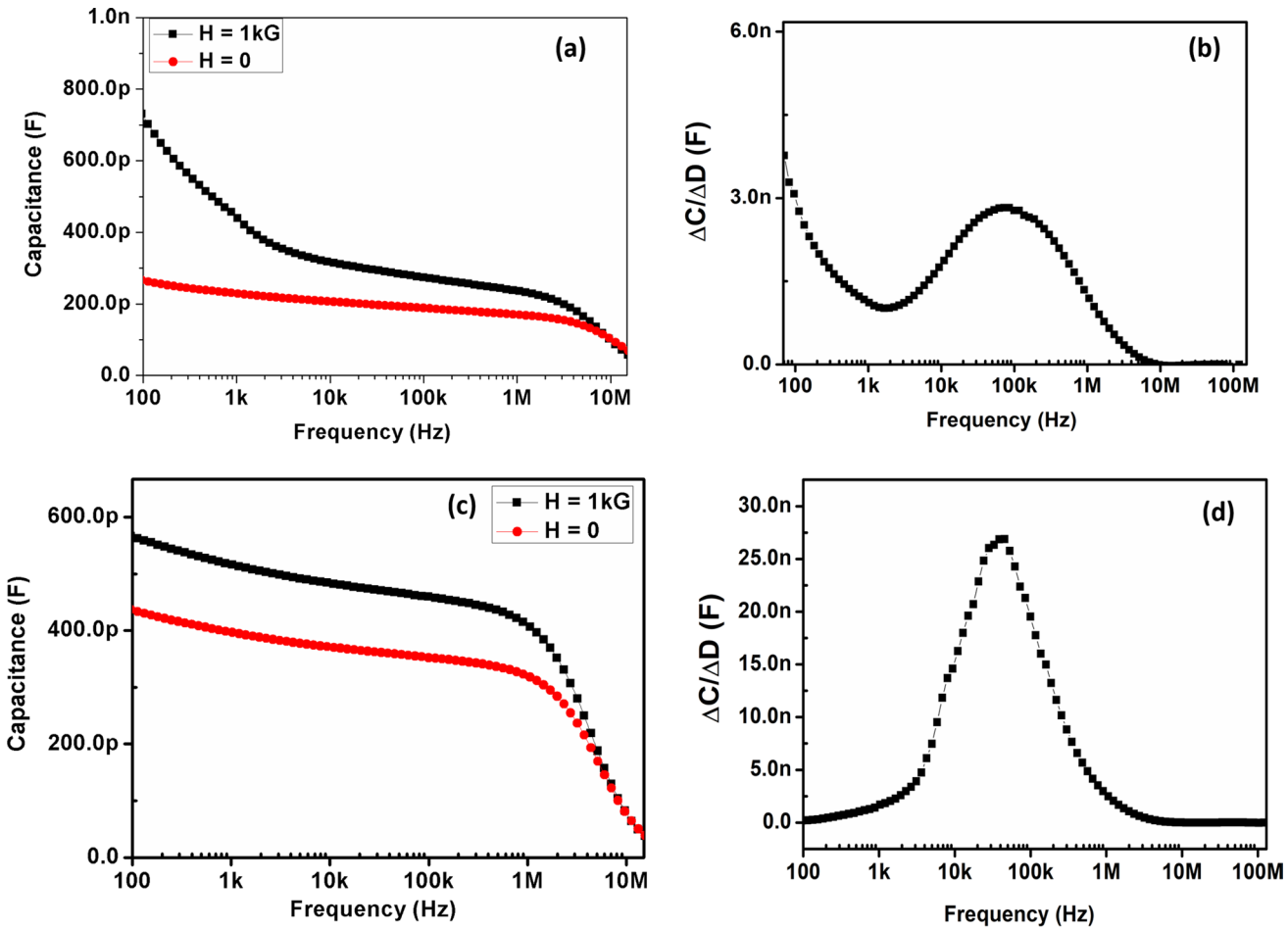

Fig. 6 Frequency dependence of capacitance (*red*) and magnetocapacitance (*black*) plots for $GdFeO_3/Fe_{97}Si_3$ bilayer films at 110-nm (a, b) and 170-nm (c, d) $GdFeO_3$ film thicknesses (Color figure online).

the interface while the magnetic field was applied along the longitudinal direction of the sample. The *I*/*V* plots and variations in magnetoresistance with applied voltage for the GFO/Fe-Si thin films are shown in Fig. 7. The measurements were taken at room temperature at a fixed applied magnetic field of 1 kOe. A non-ohmic space charge-limited conduction mechanism was obtained in the bilayer thin film samples and the leakage current was observed to be reduced with increasing thickness of the $GdFeO_3$ film. The *I*/*V* plots indicate grain boundary charge transport in GFO/Fe-Si bilayer thin films as also confirmed from dielectric plots. A clear increase in current across the interface with an applied magnetic field of 1$kOe can be observed from Fig. 7a and c, which indicates the presence of magnetoresistance in the bilayer thin film samples. The increase in current flowing across the bilayer interface can be assigned to the alignment of randomly oriented interface spin magnetic moments leading to enhanced charge transport through the grains of the sample. The effect of higher exchange coupling with increasing thickness of $GdFeO_3$ film on magnetoresistance is distinctly visible in Fig. 7b and d, where a sharp increase in magnetoresistance/voltage plot is observed for the 170-nm-thick $GdFeO_3$ thin film, while a scattered plot is observed for the 100-nm-thick $GdFeO_3$ film. A maximum 95.6 % increase in the tunneling current at an applied voltage of 1.5 V was obtained for the 170-nm-thick GFO thin film. The obtained magnetoresistance is attributed to interface-controlled low field tunneling through the grain boundary due to the alignment of magnetic moments of the disordered grain boundary interface.[12] It can also be observed from Fig. 5a that saturation magnetization of GFO thin films is nearly equal to the applied magnetic field (1 kOe). The low field magnetoresistance in GFO thin films is also enhanced by spin-dependent scattering through magnetic inhomogeneities (Si atoms) present at the Fe-Si bilayer interface. GFO/Fe-Si bilayer thin films represent potential for room-temperature spin filtering devices.

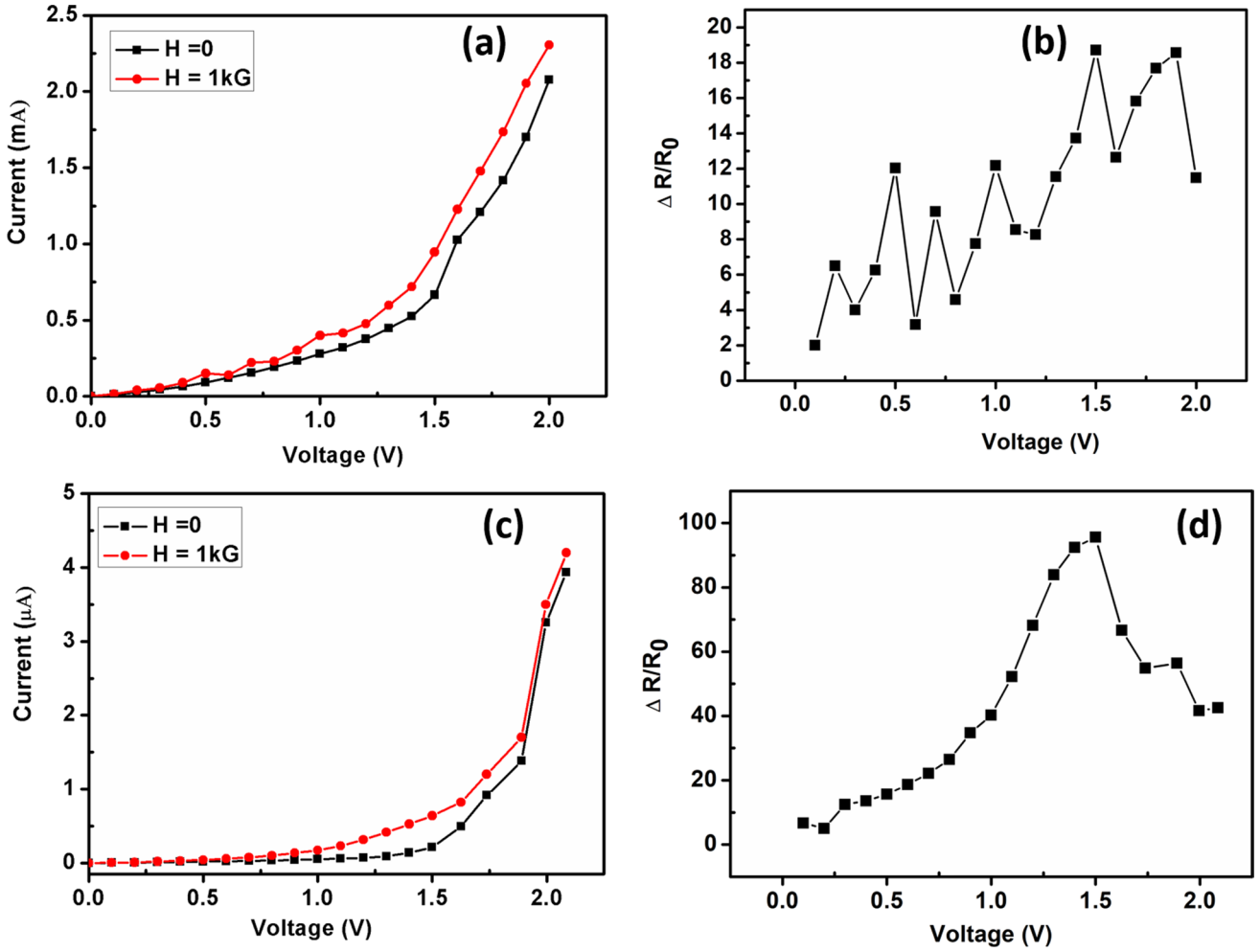

Fig. 7 Current–voltage (*I*/*V*) and voltage dependence of magnetoresistance plots for $GdFeO_3/Fe_{97}Si_3$ bilayer films at 110-nm (a, b) and 170-nm (c, d) $GdFeO_3$ film thicknesses.

Conclusions

Bilayer thin films of GdFeO3/$Fe_{97}Si_3$ were investigated at different thicknesses of $GdFeO_3$ thin films to investigate the effect of thickness on the magnetic, magnetodielectric, and magnetoresistive properties of the samples. Room-temperature in-plane magnetic anisotropy with the high magnetic moment of ~ 9.3 emu/ml was obtained at the 170-nm thickness of $GdFeO_3$ film. Disordered magnetic spins of grain boundaries in polycrystalline bilayer GFO/Fe-Si thin films led to high grain boundary magnetocapacitance and magnetoresistance. A maximum 30% rise in magnetocapacitance and a95.6% increase in tunneling current in an applied 1-kOe magnetic field was obtained for 170-nm-thick GFO thin film. The spin alignment at disordered grain boundaries with an applied magnetic field gave rise to an enhanced tunneling current which in turn induced room-temperature magnetoresistive and magnetocapacitive properties in GFO/Fe-Si bilayer thin films. The observed properties in the GFO/Fe-Si thin films are applicable for room-temperature spintronic and magnetoresistive devices.

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Conflict of interest The authors declare that they have no conflict of interest.

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