Laser ablated Ni-doped HfO_2 thin films: Room temperature ferromagnets

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Laser ablated Ni-doped HfO_2 thin films fabricated under a wide range of growth conditions all showed ferromagnetism above room temperature. However, the films deposited at 800 °C under an oxygen partial pressure of 10^{-6} Torr have the largest magnetic moment of $2.7\mu_B$/Ni. Ni-doped HfO_2 films also well demonstrate a large anisotropy. Magnetic force microscopy measurements confirmed that Ni-doped HfO_2 films are real room temperature ferromagnets with a domain structure, and that the size of magnetic domains is larger than 10 μm. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1949723]

HfO_2 is known as an insulating oxide that can be used as a dielectric layer for nanometer-scale electronic devices.[1] Its high dielectric constant makes it a potential candidate to reduce the leakage current, so that it can be substituted for SiO_2 to be a gate dielectric material.[2] On the other hand, HfO_2 is an attractive oxide due to its superior electrical performance.[3] Except only a recent report on magnetism in HfO_2 thin films, which most probably results from some specific growth conditions,[1] basically HfO_2 is known to be nonmagnetic.

In general, ferromagnetic insulators (FI) are rare since in insulating compounds, most probably, spins tend to couple with each other antiferromagnetically. With the light shed from the resulting research on introducing room temperature ferromagnetism by doping transition metals into semiconducting oxides such as ZnO, TiO_2, or SnO_2, (Refs. 4–6), in this work, we undertook an investigation of doping Ni in HfO_2 in the thin-film form to verify if such a doping can result in some kind of insulating ferromagnets. It was expected that Ni might play a role as an intermediate to help the isolated spins in HfO_2 to interact with one another ferromagnetically through the Ruderman-Kittel-Kasuya-Yoshida (RKKY) interaction.

Ni-doped HfO_2 thin films were fabricated from a $Hf_{0.95}Ni_{0.05}O_2$ ceramic target by pulsed laser deposition (PLD) technique (KrF-248 nm, 5 Hz, 1.8 J/cm^2) on (100) yttrium stabilized zirconia (YSZ) substrates. Various growth conditions with the substrate temperature from 750 to 850 °C and the oxygen partial pressure (P_{O2}) from 10^{-4} to 10^{-6} Torr had been used.

Our Ni-doped films are about 186–216-nm thick [note that the thickness was determined precisely from Rutherford backscattering spectroscopy (RBS) measurements], colorless, highly transparent, and insulating (at room temperature the resistance of the films is in the range of GΩ). X-ray diffraction (XRD) data have shown that films are formed as a monoclinic structure, *c*-axis oriented, with only (200) and (400) reflections appearing in the spectra (see Fig. 1).

Figure 2(a) showed the *M-H* curves taken at 300 K for films fabricated at a fixed temperature (850 °C) with the P_{O2} changed from 10^{-4} to 10^{-6} Torr. It is found that the film deposited at a P_{O2} of 10^{-6} Torr is more strongly ferromagnetic than the others. Similarly, the *M-H* curves for films fabricated at a fixed P_{O2} of 10^{-6} Torr, but at various temperatures (750–850 °C), are shown in Fig. 2(b). It is found that the film fabricated at 800 °C has the largest magnetic moment (as of about $2.7\mu_B$/Ni, by using the number of Ni atoms determined by Rutherford backscattering measurements, and supposing that all the Ni atoms in the films contribute to the magnetism). This observed magnetic moment is too large to be due to any precipitation of grains of pure Ni, so that it more likely comes from the doped matrix.

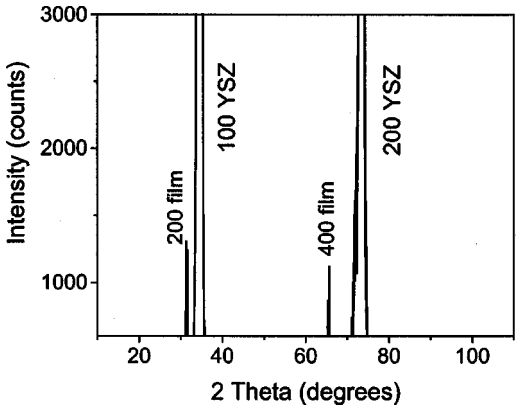

FIG. 1. XRD pattern for a film of Ni-doped HfO_2 thin film fabricated at 800 °C under an oxygen partial pressure of 10^{-6} Torr.

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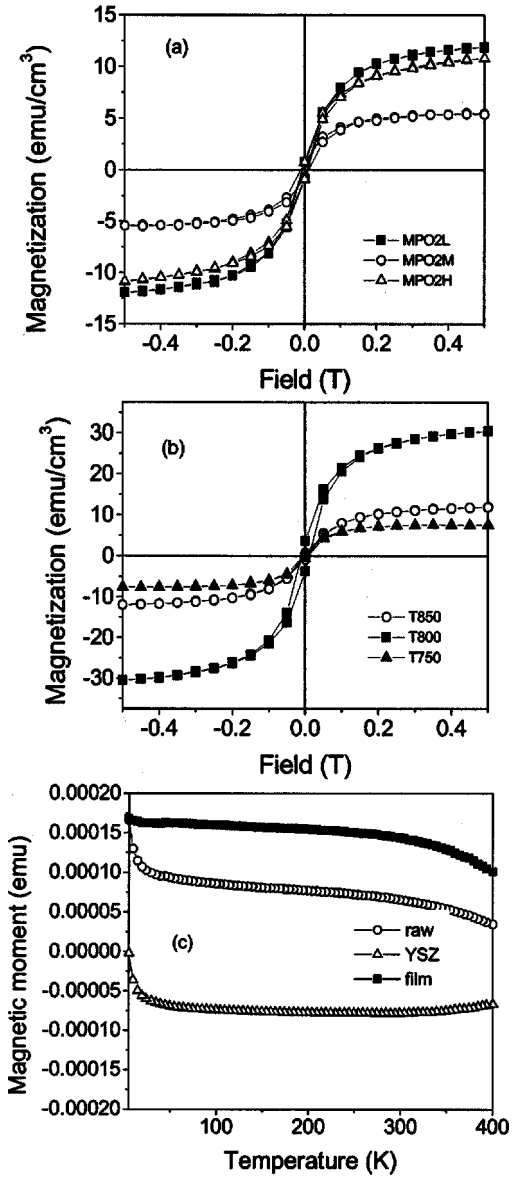

FIG. 2. Magnetization vs (a) magnetic field at 300 K for Ni-doped HfO_2 film fabricated at 850 °C under various oxygen partial pressures, (b) magnetic field at 300 K for Ni-doped HfO_2 films fabricated under an oxygen partial pressure of 10^{-6} Torr at various temperature, and (c) temperature under 0.5 T for the Ni-HfO_2 film fabricated under the optimal condition, for the film plus the YSZ substrate, and for the bare YSZ substrate, with the same size.

Figure 2(c) shows the magnetization versus temperature for the best film. One can see that the film is room temperature ferromagnetic with T_C much higher than 400 K. The *M-H* curves of the film, of the film and the substrate (raw data), and of the YSZ substrate alone were put altogether to compare. It is obvious that the ferromagnetic signal indeed comes from the Ni-doped film, and it could not be mistaken for any "contamination" of the substrate, because as one can see clearly, YSZ the substrate gives a certain evidence for its being diamagnetic.

As seen from Fig. 3, there is a huge anisotropy in magnetization, which is 1.7 times larger when the magnetic field is applied parallel to the film plane than when it is applied in the perpendicular direction. In transition-metal-doped ZnO thin films, it was found that in every case except Co, the magnetic moment was larger when the field was applied perpendicular to the film plane (also similar to the case of HfO_2 film), and it was claimed to be anisotropic d^0 ferromagnetism. Our case is different, and it is similar to that of Co-doped ZnO thin films.[4] Note that the Ni concentration is low, and films are oriented, so that the huge anisotropy and the large magnetic moment, which were observed, are very irregular. They are likely in agreement to support the assumption for a new source of magnetism, which might be due to lattice defects, such as oxygen vacancies or the similarities that could be induced by the Ni doping.[4]

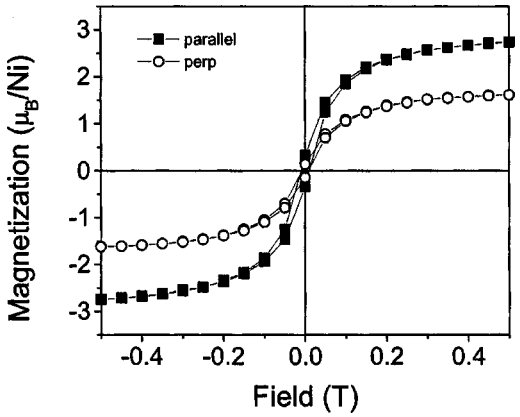

FIG. 3. Magnetization vs magnetic field at 300 K for the film of Ni-doped HfO_2 thin film fabricated at 800 °C under an oxygen partial pressure of 10^{-6} Torr measured in two different configurations: field parallel and field perpendicular to the film plane.

Magnetic force microscopy (MFM) measurements were performed under zero field at room temperature. The magnetic probe is a standard cantilever coated by a magnetic layer of CoCr. The most important point in these kind of measurements is how to separate the magnetic image from the topography one. In order to solve that, magnetic measurements were executed by a two-pass method. During the first pass, the topography image was taken by using a noncontact mode. In the second pass, the cantilever was lifted to a selected height for each scan line after the topography measurement. The distance between the tip and the sample (i.e., lift height) must be large enough to eliminate the Van der Waals' forces, but not too large to be sensitive to the magnetic ones. During the second step, the cantilever resonance oscillations can be used to detect the magnetic force signals. Thus, it is possible to record the magnetic signals, which are proportional to the second derivative of the stray field.

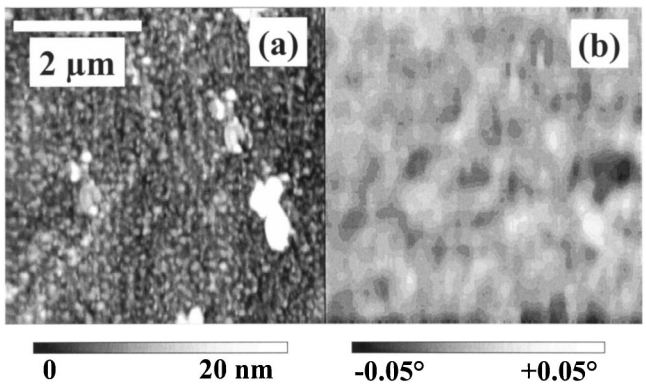

FIG. 4. (a) Topography image and (b) the corresponding MFM image recorded in the area of 5×5 μm^2 for the film of Ni-doped HfO_2 thin film fabricated at 800 °C under an oxygen partial pressure of 10^{-6} Torr. The tip was magnetized perpendicular to the film plane.

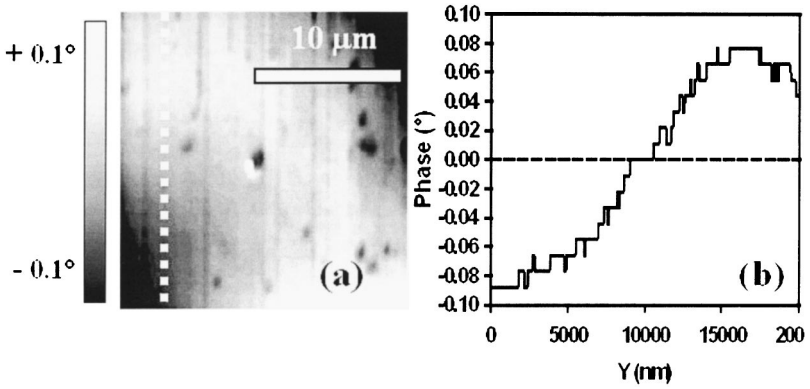

FIG. 5. MFM image (a) recorded in the area of 20 $\times 20$ μm^2 for the Ni-doped HfO_2 thin film fabricated at 800 °C under an oxygen partial pressure of 10^{-6} Torr and the corresponding profile (b) for a vertical cross section (see the dashed line). The tip was magnetized perpendicular to the film plane.

A diluted magnetic structure was observed in Ni:HfO_2 films. The films gave strong magnetic signals at room temperature. Figure 4(a) shows a topography image taken on the area of 5×5 μm^2 and Fig. 4(b) is the corresponding MFM image measured in the same area for the Ni:HfO_2 film fabricated at 800 °C under oxygen partial pressure of 10^{-6} Torr. The topography image taken in this small scale confirms the film's flatness with the local roughness of 1.3 nm. By comparing Figs. 4(a) and 4(b), one can see that the MFM image is completely different from the topography one, thus, the signal detected at room temperature is due to the real magnetic response, not the surface effect. On the other hand, the little difference in brightness of the relative MFM responses (see a small variation in magnetic phase changing only in between very small values of −0.05° and 0.05°) confirms the absence of any magnetic cluster. The MFM image of Ni:HfO_2 film reveals a real diluted magnetic structure with a rather good magnetic homogeneity. Moreover, no domain wall was observed, suggesting that the size of ferromagnetic domains must be larger than the scale that we performed these measurements. In order to determine the domain size of the Ni:HfO_2 ferromagnet, MFM measurements were performed on a larger area as of 20×20 μm^2 [see Fig. 5(a)]. In this large scale, the roughness of the films was averagely determined as of 2 nm [note that thus, there are some contributions of the topography to the MFM image as seen in some small dark spots in Fig. 5(a)]. The difference in absolute values of phase is large (going from −0.1° to 0.1°), confirming the real signals of a strong FM at room temperature. One could see clearly that there are white regions and black regions next to each other, indicating a real domain structure. From the profile of phase sweeping through the cross section vertically (for $x=500$ nm), one can see that the magnetic phase changes from a positive value (highest +0.07°) for the white region to a negative value (lowest −0.1°) for the black region [Fig. 5(b)]. It appears that, in this film, there is a ferromagnetic domain structure where the directions of magnetization of the two nearest-neighbor domains are opposite each other (in the frame of a closure domain structure). The size of those ferromagnetic domains is big, most probably larger than 10 μm. There is a question if there is some difference in the images that were taken when the tip was magnetized parallel or perpendicular to the film plane, which may concern the anisotropy mentioned earlier. We must say that no special discrepancy was found in those two images. However, there is a fact that the measurement in the parallel configuration could be performed even when the lift height was large, while in the perpendicular configuration, signals could be recorded only when the lift height was very small. Thus, it is more likely that the magnetization in the films is "in plane."

In conclusion, we obtained laser ablated Ni-doped HfO_2 thin films on YSZ substrates as room temperature insulating ferromagnets. MFM measurements confirmed the strong ferromagnetism at room temperature of those films, and implied that the Ni-doped HfO_2 films likely have a diluted magnetic structure with the FM originated from the doped matrix rather than any type of magnetic clusters. The size of the ferromagnetic domains is larger than 10 μm.

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