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# Structure and magnetic properties of pure and Gd-doped HfO<sub>2</sub> thin films

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Pure HfO<sub>2</sub> and Gd-doped HfO<sub>2</sub> thin films have been grown on different single crystal substrates (silicon, R-Al<sub>2</sub>O<sub>3</sub>, and LaAlO<sub>3</sub>) by pulsed laser deposition. X-ray diffraction (XRD) patterns show that the pure HfO<sub>2</sub> thin films are of single monoclinic phase. Gd-doped HfO<sub>2</sub> films have the same XRD pattern except that their diffraction peaks have a shift toward lower angles, which indicates that Gd dissolves in HfO<sub>2</sub>. Transmission electron microscopy images show a columnar growth of the films. Very weak ferromagnetism is observed in pure and Gd-doped HfO<sub>2</sub> films on different substrates at 300 and 5 K, which is attributed to either impure target materials or signals from the substrates. The magnetic properties do not change significantly with postdeposition annealing of the HfO<sub>2</sub> films. In addition to the films, HfO<sub>2</sub> powders were annealed in pure hydrogen flow, and a ferromagnetic signal was not observed. © 2006 American Institute of Physics.

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## I. INTRODUCTION

Dilute magnetic semiconductors have attracted much attention recently because of their combined magnetic and transport properties. In such materials, the current carriers are either strongly coupled to local moments of the magnetic atoms or directly participated in the magnetism themselves. Many groups have demonstrated room temperature ferromagnetism in a variety of wide band gap doped semiconductors, such as TiO<sub>2</sub>,<sup>1-3</sup> ZnO,<sup>4,5</sup> SnO<sub>2</sub>,<sup>6</sup> ZnGeP<sub>2</sub>,<sup>7</sup> CdGeP<sub>2</sub>,<sup>8</sup> AlN,<sup>9,10</sup> and GaN.<sup>10,11</sup> Recently, Venkatesan *et al.*<sup>12</sup> and Coey *et al.*<sup>13</sup> have found unexpected ferromagnetism in dielectric oxide HfO<sub>2</sub> films, where neither Hf<sup>4+</sup> nor O<sup>2-</sup> is magnetic. Thereafter, theoretical calculation suggests that this unexpected ferromagnetism may arise from the cation vacancy in the HfO<sub>2</sub> films.<sup>14</sup> In this paper, we report the structure and magnetic properties of pure and Gd-doped HfO<sub>2</sub> thin films deposited on different substrates by pulsed laser deposition (PLD) and the effects on the magnetic properties by annealing.

## II. EXPERIMENTS

Pure HfO<sub>2</sub> and Gd-doped (3 at. %) HfO<sub>2</sub> thin films were deposited on single crystal silicon (400), R-Al<sub>2</sub>O<sub>3</sub> (012), and LaAlO<sub>3</sub> (100) substrates using a KrF excimer laser. The laser was operated at 10 Hz and was focused through a 30 cm focal length lens onto a rotating target at 45° angle of incidence. The energy density of the laser beam at the target surface was maintained at 1–2 J/cm<sup>2</sup>. The target-to-

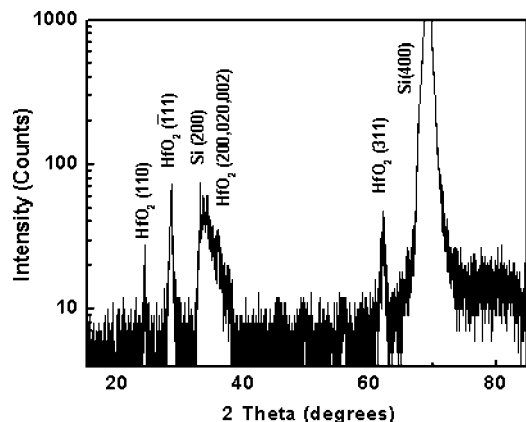
substrate distance was about 3 cm. Pure and Gd-doped HfO<sub>2</sub> targets were prepared by standard ceramic techniques using 99.995% pure HfO<sub>2</sub> and 99.99% pure Gd<sub>2</sub>O<sub>3</sub> powders. Before the deposition, the substrates were cleaned in strong acid (HCl:HNO<sub>3</sub>~3:1) for 20 h, because it was found that the as purchased substrates had weak ferromagnetic signal (about 10<sup>-5</sup> emu) and acid wash could remove it. Films were deposited at a substrate temperature of (700±20) °C, and some at room temperature, with a base pressure of 5 × 10<sup>-7</sup> Torr at a growth rate of about 0.15 Å/s. Some film samples were annealed afterward in air at 700, 900, and 1100 °C. The crystal structure of the films was investigated by x-ray diffraction (XRD) with Cu Kα radiation and high resolution transmission electron microscopy (HRTEM) with energy dispersive spectroscopy (EDS). The magnetic properties were studied with a superconducting quantum interference device (SQUID) magnetometer.

## III. RESULTS AND DISCUSSION

Figure 1 is the XRD pattern of a pure HfO<sub>2</sub> thin film deposited on Si (400) substrate. Beside Si peaks, all peaks match those of the simple monoclinic phase of HfO<sub>2</sub>. Similar XRD patterns have been obtained for HfO<sub>2</sub> films deposited on Al<sub>2</sub>O<sub>3</sub> and LaAlO<sub>3</sub> substrates. Gd-doped HfO<sub>2</sub> thin films have the same XRD pattern except that their diffraction peaks have a small shift toward lower angles. For example, (111) peak is shifted by 0.18° from 28.29° to 28.11°, which means that the lattice parameter increases after the Gd doping. The ionic radii of Gd<sup>3+</sup> are 0.1078 (six coordinate) and 0.1193 nm (eight coordinate), whereas the ionic radii of Hf<sup>4+</sup> are 0.085 and 0.097 nm for the corresponding coordinates.

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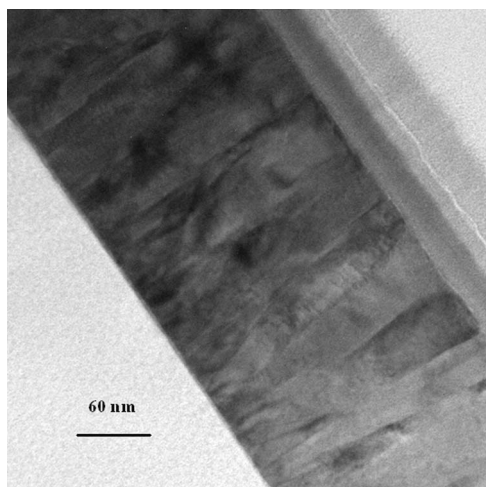
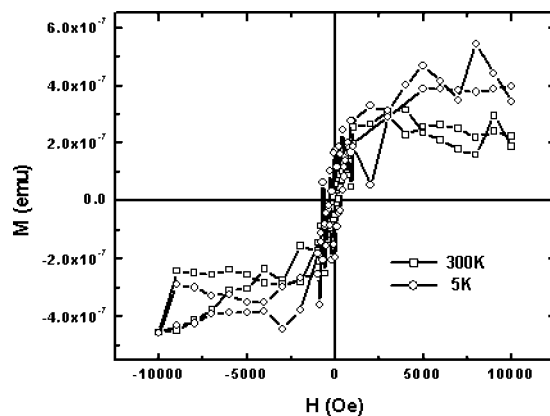
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FIG. 1. XRD pattern of a pure HfO<sub>2</sub> thin film.

Since the radii of Gd<sup>3+</sup> are larger than those of Hf<sup>4+</sup>, our XRD result implies that Gd dissolves in HfO<sub>2</sub>. High resolution transmission electron microscopy images (Fig. 2) exhibit a columnar structure in the HfO<sub>2</sub> films, and the film thickness is typically in the range of 200 nm. The thickness is also confirmed by Rutherford backscattering spectrometry (RBS). RBS results showed, in addition, that there was no other impurity in the films, which was also confirmed via EDS analysis.

Figure 3 shows the magnetization curves measured at 300 and 5 K for the pure HfO<sub>2</sub> film on Si substrate. An extremely weak ferromagnetic signal of about  $5 \times 10^{-7}$  emu was observed. We did not observe similar anisotropy as reported in Ref. 12, although reorientating the sample relative to the magnetic field direction did change the magnitude of the signal due to the particular configuration of the sample holder. If we assume that the measured signal is attributed to the HfO<sub>2</sub> films, the moment of the film is approximately equivalent to 0.0003 Bohr magneton per Hf ion, an extremely small value. Moreover, considering the contribution from either the impurities in the target material or the residual on the substrates, we feel that our HfO<sub>2</sub> films are not ferromagnetic.

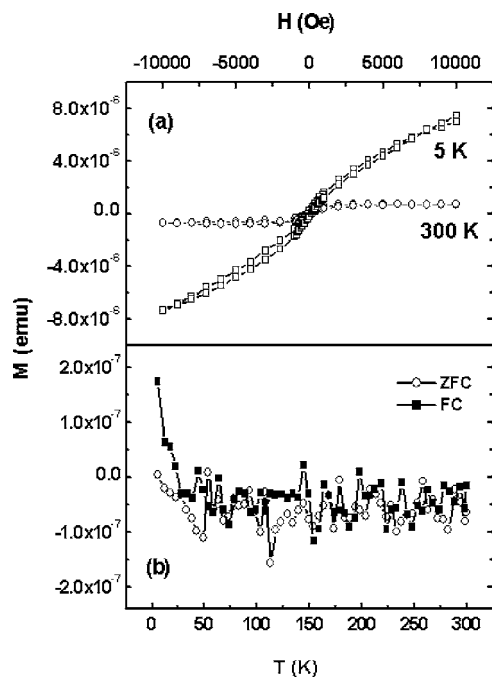
In order to alter the interface structure between the film and substrate, we have also deposited HfO<sub>2</sub> films on Al<sub>2</sub>O<sub>3</sub>

FIG. 2. TEM image of the pure HfO<sub>2</sub> thin film.FIG. 3. Magnetization curves at 300 and 5 K for the pure HfO<sub>2</sub> film grown on Si substrate.

(012) and LaAlO<sub>3</sub> (100) substrates in addition to Si. Different substrates should result in different interfaces and defect structures, which may be the source of the ferromagnetism.<sup>13,15</sup> Our experiments suggest that there is no obvious difference in the magnetic properties of the HfO<sub>2</sub> films deposited on three different substrates.

Some films were annealed in air at 700, 900, and 1000 °C in hoping that annealing may change the defects in the HfO<sub>2</sub> films and may influence their magnetic behavior. In otherwise nonmagnetic compound such as CaB<sub>6</sub> (Ref. 16) and CaO,<sup>17</sup> like HfO<sub>2</sub>, the magnetism is considered to be driven by intrinsic point defects. However, the magnetic signal does not change with annealing and with increasing annealing temperature.

HfO<sub>2</sub> films were also deposited at room temperature to vary the defect density in the films. The films were found to be amorphous by XRD measurements. The magnetic signal is again extremely weak.

FIG. 4. (a) The magnetization curves at 300 and 5 K and (b) ZFC-FC curves ( $H=100$  Oe) for 3 at % Gd-doped HfO<sub>2</sub> thin film.

In addition to the films, pure HfO<sub>2</sub> powders were annealed at different temperatures (700, 900, and 1100 °C) in pure hydrogen flow. XRD measurement indicates that there is no phase change for the HfO<sub>2</sub> powders after annealing. Magnetic measurement shows that both the original powders and annealed ones are not ferromagnetic. Apparently the defects introduced by hydrogen reduction carried out here did not affect the magnetic behavior of the powders.

We have recently observed *4f-5d* coupling in HfO<sub>2</sub> films from photoemission experiments.<sup>18</sup> It is interesting to see how Gd, with *4f* electrons, would change the magnetic properties of HfO<sub>2</sub>. Figure 4(a) shows the magnetization curves at 300 and 5 K for a Gd-doped (3 at. %) HfO<sub>2</sub> film. At room temperature, its magnetization is about  $7 \times 10^{-7}$  emu, which is similar to that of the pure HfO<sub>2</sub> films. At low temperatures, the sample exhibits a strong paramagnetic signal due to Gd. Zero-field-cooled and field-cooled (ZFC/FC) curves [Fig. 4(b)] do not show a ferromagnetic behavior.

#### ACKNOWLEDGMENTS

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