



## InGaZnO<sub>4</sub>-Based Thin Film Transistors Using Room-Temperature Grown Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> Gate Insulator

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This study reports the dielectric and leakage current properties of Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> thin films deposited at room temperature by radio-frequency magnetron sputtering. Polycrystalline Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> thin films showed a reasonably high dielectric constant ( $\epsilon_r = 22$ ) and greatly enhanced leakage current characteristics ( $< 2 \times 10^{-7}$  A/cm<sup>2</sup>) compared to the leakage current ( $\sim 2 \times 10^{-5}$  A/cm<sup>2</sup>) of HfO<sub>2</sub> thin films at 0.4 MV/cm. A bandedge spectroscopic analysis revealed lower conduction bandedge defect states and a greater p-type-like Fermi energy level of Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> compared to the HfO<sub>2</sub> thin films. The suitability of Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> films as gate insulators for low voltage operating InGaZnO<sub>4</sub> thin film transistors (TFTs) was investigated. All room-temperature processed InGaZnO<sub>4</sub> TFTs on plastic substrates exhibited a high field effect mobility of 27.32 cm<sup>2</sup>/Vs and a current on/off ratio of  $4.01 \times 10^6$ . The threshold voltage and subthreshold swing were 2 V and 440 mV/dec, respectively. The fabrication and compositional manipulation method of the Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> films described in this work is simple and versatile, providing fascinating opportunities for new high-*k* gate dielectrics.

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Recently, intensive studies have been carried out on the development of high-*k* gate insulators suitable for use with flexible and transparent thin film transistors (TFTs). For these types of applications, the gate insulators should be fabricated at a low temperature with high optical transparency. In addition, they should possess a high dielectric constant for lower power consumption in battery-powered devices and other electronic devices.<sup>1-3</sup>

Among various gate insulators, HfO<sub>2</sub> has been widely researched as a high permittivity dielectric oxide for use in thin-film capacitors and TFTs due to its high dielectric constant ( $\sim 25$ ), high heat of formation (271 kcal/mol), and large bandgap (5.68 eV).<sup>4,6</sup> Although HfO<sub>2</sub> thin films are one of the prospective candidates for gate insulators, they contain a larger number of trap sites or fixed charges relative to that found in conventional SiO<sub>2</sub> films, resulting in a shift of the threshold voltage, high leakage current, and poor long-term reliability.<sup>7,8</sup> To improve the device properties of TFTs utilizing HfO<sub>2</sub>-based gate insulators, silicon, nitrogen, or aluminum-doped HfO<sub>2</sub> thin films have been proposed.<sup>9-12</sup> However, studies of MgO–HfO<sub>2</sub> composite gate insulators that can produce InGaZnO<sub>4</sub> TFTs that operate at a low voltage are rare or nonexistent. In a previous work, the authors showed that the leakage current characteristics of Ba<sub>0.6</sub>Sr<sub>0.4</sub>TiO<sub>3</sub> could be markedly improved by adding MgO, which is a large bandgap insulator with a high breakdown strength.<sup>3</sup> In an effort to improve the dielectric and electrical characteristics of HfO<sub>2</sub> thin films further, in this work, MgO-incorporated HfO<sub>2</sub> films, i.e., novel Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> thin films, are fabricated by radio-frequency (rf) sputtering at room temperature using MgO–HfO<sub>2</sub> composite ceramic targets. The dielectric and leakage current properties of the Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> thin films are characterized and compared with these properties in pure HfO<sub>2</sub> thin films. The physical origin of the differences in the leakage current characteristics between Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> and HfO<sub>2</sub> was identified by the spectroscopically resolved bandedge defect states and the Fermi energy ( $E_f$ ) levels using spectroscopic ellipsometry (SE) and X-ray photoelectron spectroscopy (XPS). The potential suitability of a Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> thin film as a gate insulator for producing high performance InGaZnO<sub>4</sub> TFTs on a plastic substrate is discussed.

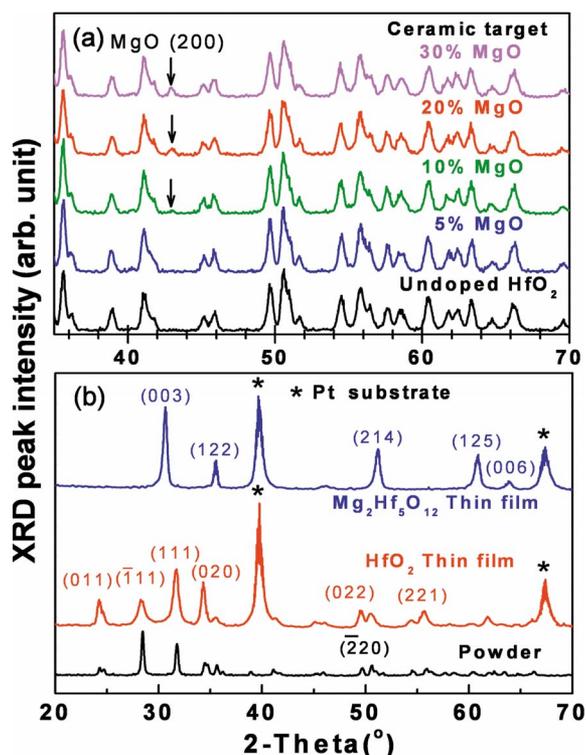
### Experimental

HfO<sub>2</sub> and (MgO)<sub>0.3</sub>(HfO<sub>2</sub>)<sub>0.7</sub> sputtering targets with 2 in. diameters were prepared by a conventional mixed oxide method. To prepare the (MgO)<sub>0.3</sub>(HfO<sub>2</sub>)<sub>0.7</sub> ceramic targets, a mixture of HfO<sub>2</sub> and MgO powders with a MgO content of 30 mol % was calcined at 1200°C for 3 h. Sintering was conducted at 1400°C under an air atmosphere for 5 h. Details of this fabrication process for an InGaZnO<sub>4</sub> target are available in the literature.<sup>3</sup> HfO<sub>2</sub> and Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> thin films were deposited using rf sputtering at an rf power of 80 W and a working pressure of 60 mTorr in a pure Ar atmosphere. The chamber was pumped down to a low base pressure of  $10^{-6}$  Torr. All films were deposited at room temperature without any intentional heating. The film thicknesses of the HfO<sub>2</sub> and Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> thin films were fixed at 300 nm. Structural identification was characterized by an X-ray diffractometer (XRD, Rigaku D/MAX-RC, with Cu K $\alpha$  radiation,  $\lambda = 1.5406$  Å). The morphology and microstructure were investigated using a transmission electron microscope (TEM, Tecnai F20) operating at 200 keV. An atomic force microscope (AFM, Seiko, SPA400) was used to investigate the surface roughness of the HfO<sub>2</sub> and Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> thin films. The optical transmittance of 100 nm thick HfO<sub>2</sub> and Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> thin films was measured using a UV-3101 PC spectrophotometer (Shimadzu). The real and imaginary parts of the complex dielectric function,  $\epsilon_c = \epsilon_1 + i\epsilon_2$ , for the thin films were determined by using visible-UV SE in a rotating compensator configuration spectrometer. XPS was carried out using a VG Scientific Escalab 220i-XL spectrometer with a monochromatic Al K $\alpha$  radiation source.

A metal–insulator–metal (MIM) capacitor structure was fabricated on a 100 nm thick Pt-coated Si substrate to determine the leakage current and dielectric characteristics of the HfO<sub>2</sub> and Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> thin films. For the top electrode, 100 nm thick Pt was deposited through a shadow mask on top of sputter-deposited HfO<sub>2</sub> and Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> thin films by dc magnetron sputtering. The dielectric properties were measured at 100 kHz with an applied electric field ranging from  $-0.4$  to  $0.4$  MV/cm using an HP4192A impedance analyzer. An HP4145B semiconductor analyzer was used to measure the leakage current characteristics.

To evaluate the potential suitability of Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> thin films as a gate insulator, InGaZnO<sub>4</sub> TFTs were fabricated on a poly(ethylene terephthalate) (PET) substrate. For the fabrication of InGaZnO<sub>4</sub>

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**Figure 1.** (Color online) XRD patterns of (a) ceramic targets: Undoped, 5, 10, 20, and 30 mol % MgO added HfO<sub>2</sub> ceramic targets sintered at 1400°C. (b) Bare HfO<sub>2</sub> powder or thin films: HfO<sub>2</sub> powder, HfO<sub>2</sub> thin film, and Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> thin film deposited at room temperature on Pt substrates.

TFTs, a 100 nm thick Cr gate electrode was deposited by rf magnetron sputtering on a PET substrate. A sputter-deposited Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> gate insulator and InGaZnO<sub>4</sub> channel layer were subsequently grown on the Cr gate electrode. Al top contacts for source and drain electrodes were deposited by evaporation to obtain channel lengths of 100 μm with widths of 2000 μm. For comparison, an InGaZnO<sub>4</sub> TFT was also fabricated using pure HfO<sub>2</sub> gate insulators. The performance levels and characteristics measurements of the TFTs were characterized with an HP 4145B semiconductor parameter analyzer.

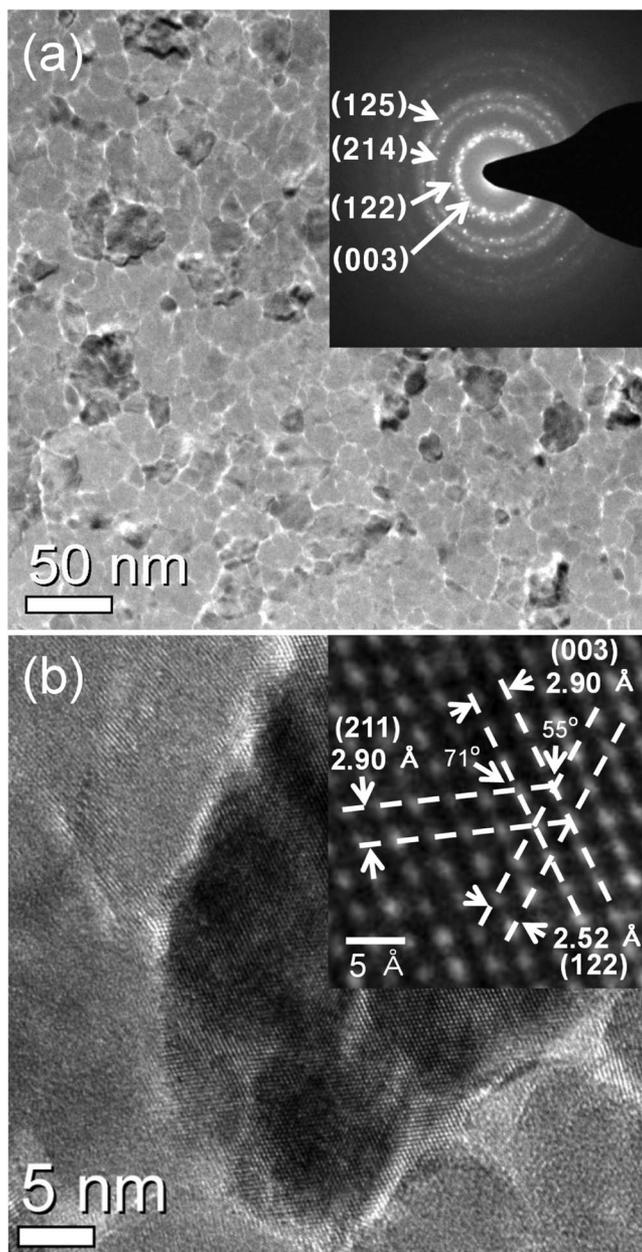
### Results and Discussion

**Material characteristics of Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> thin films.**— The structural identification of the MgO–HfO<sub>2</sub> composite ceramic targets, HfO<sub>2</sub> powder, HfO<sub>2</sub> thin film, and (MgO)<sub>0.3</sub>–(HfO<sub>2</sub>)<sub>0.7</sub> composite thin film was carried out using XRD, as shown in Fig. 1. Five ceramic targets, consisting of pure MgO, (MgO)<sub>0.05</sub>–(HfO<sub>2</sub>)<sub>0.95</sub>, (MgO)<sub>0.1</sub>–(HfO<sub>2</sub>)<sub>0.9</sub>, (MgO)<sub>0.2</sub>–(HfO<sub>2</sub>)<sub>0.8</sub>, and (MgO)<sub>0.3</sub>–(HfO<sub>2</sub>)<sub>0.7</sub> composites, were fabricated to ascertain the mixing behaviors of MgO with HfO<sub>2</sub>. It was concluded that the solubility limit of MgO to HfO<sub>2</sub> ranged from 5 to 10 mol %, as shown in Fig. 1a. The XRD peaks of the 5 mol % MgO–HfO<sub>2</sub> target were identical to those of the HfO<sub>2</sub> target. However, for the HfO<sub>2</sub> composite targets with 10, 20, and 30 mol % of MgO added, the MgO peaks appeared at 43°, while the peaks of HfO<sub>2</sub> were maintained. As the MgO content in the composite targets increased, the intensity of the (200) MgO peak increased, indicating further precipitation of the MgO phases. Based on the scanning electron microscopy (SEM) analysis, the pure HfO<sub>2</sub> target exhibited a homogeneous yellow color. However, the MgO–HfO<sub>2</sub> composite ceramic targets showed two distinct phases uniformly distributed with each other in terms of image contrast. Based on the SEM energy-dispersive X-ray spectroscopy mapping analyses, there were dark regions (MgO-rich) and white regions

(HfO<sub>2</sub>-rich) (not shown here). The peaks of the HfO<sub>2</sub> target and the HfO<sub>2</sub> thin films were well matched with the monoclinic structure, although the HfO<sub>2</sub> thin film was deposited at room temperature (see Fig. 1b). The structural properties of HfO<sub>2</sub> thin films are largely governed by processing techniques.<sup>13,14</sup> Room-temperature sputtering growth often provides a nanocrystalline structure, whereas HfO<sub>2</sub> films grown by electron-beam evaporation or atomic layer deposition are preferentially amorphous. Figure 1b also shows the XRD pattern of a (MgO)<sub>0.3</sub>–(HfO<sub>2</sub>)<sub>0.7</sub> thin film deposited at room temperature. Similar to HfO<sub>2</sub>, the (MgO)<sub>0.3</sub>–(HfO<sub>2</sub>)<sub>0.7</sub> thin film showed a polycrystalline structure, identified as rhombohedral Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> according to JCPDS card no. 33-0862. The XRD peaks of the bulk (MgO)<sub>0.3</sub>–(HfO<sub>2</sub>)<sub>0.7</sub> composite target were wholly different from those of the Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> thin film. This can be attributed to the rearrangement of the Mg<sup>2+</sup>, Hf<sup>4+</sup> ions or clusters detached from the (MgO)<sub>0.3</sub>–(HfO<sub>2</sub>)<sub>0.7</sub> composite target, and the formation of a new phase during the sputtering deposition process. To investigate the microstructure of the Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> thin films, high resolution transmission electron microscopy (HRTEM) measurements were carried out.

Figure 2a shows a plane-view TEM image of a Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> thin film deposited at room temperature. This image indicates that Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> thin films grown at room temperature have a polycrystalline structure with a crystallite size distribution of ~20 nm. The average crystallite size was also calculated by the Scherrer equation,  $D = (0.94\lambda/B \cdot \cos \theta)$ , where  $D$  is the mean grain size,  $\lambda$  is the wavelength of the X-ray radiation ( $\lambda = 0.154$  nm for Cu K $\alpha$  radiation), and  $B$  is the full width at half-maximum of the diffraction peak at  $\theta$ . This resulted in  $D \approx 20$  nm as the average grain size of the Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> thin films. This value agrees with direct measurements obtained using TEM. The selected area electron diffraction pattern of the Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> thin films (upper right inset in Fig. 2a) shows the characteristic diffraction rings, which correspond to reflections (003), (122), (214), and (125) of the rhombohedral structure. The d-spacings calculated from each ring are 2.90, 2.52, 1.78, and 1.52 Å, respectively, as reported in JCPDS card no. 33-0862. Figure 2b shows an HRTEM image of the Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> thin films. The inset in Fig. 2b emphasizes a magnified view of the Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> crystallite. The lattice fringes are clearly visible. In general, a rhombohedral system is grouped into a larger hexagonal system. The interplanar spacings were measured as 2.90, 2.90, and 2.52 Å, corresponding to the (003), (211), and (122) planes of Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub>. The angle between the (003) and (211) planes was 71° and that between the (003) and (122) planes was 55°. These measured values agree well with the theoretical values, i.e., 70.5 and 54.8°, respectively, for Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub>. From the phase diagram of the MgO–HfO<sub>2</sub> system,<sup>15</sup> the Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> phase forms at a temperature in excess of 1600°C. This indicates that a very high sintering temperature is required to fabricate a single Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> target from MgO–HfO<sub>2</sub> composites. However, here, it was possible to achieve nanocrystalline Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> thin films utilizing a (MgO)<sub>0.3</sub>–(HfO<sub>2</sub>)<sub>0.7</sub> composite target fabricated at a low sintering temperature of 1400°C.

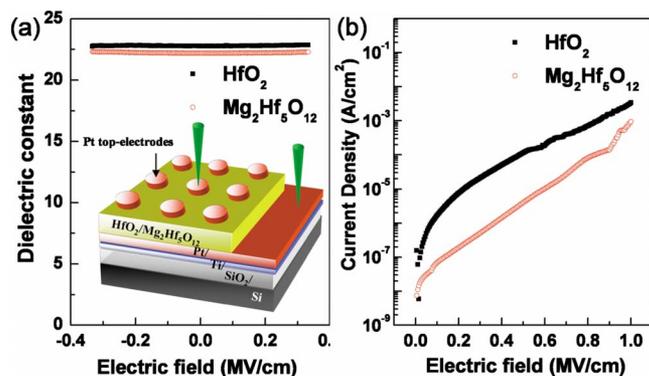
**Dielectric performance and electronic band characteristics of Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> thin films.**— Figure 3a shows the dielectric behaviors of HfO<sub>2</sub> and Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> thin films with a thickness of 300 nm as a function of the electric field. The inset in Fig. 3a illustrates a schematic configuration of Pt–HfO<sub>2</sub>–Pt and Pt–Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub>–Pt MIM capacitors. The pure HfO<sub>2</sub> thin film exhibited a relatively high dielectric constant of 23 at 100 kHz. The dielectric constant of the Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> thin film showed a value similar ( $\epsilon_r = 22.5$ ) to that of HfO<sub>2</sub>. Considering the diphasic mixture of the homogeneously distributed individual thin films, i.e., MgO and HfO<sub>2</sub>, the dielectric constant should be much lower than 22.5 due to the lower dielectric constant (~9.96)<sup>16</sup> of MgO based on the effective medium approximation using the Bruggeman expression.<sup>17</sup> Assuming a series connection capacitance of the MgO and HfO<sub>2</sub> phases, the dielectric constant should be 16. In this case, MgO combined with HfO<sub>2</sub> and



**Figure 2.** (a) Plane-view of the TEM image of the  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$  thin film. The inset is a selected area diffraction pattern of  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$  thin film. (b) HR-TEM image of  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$  thin film. The inset is a magnified view of  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$  crystallite.

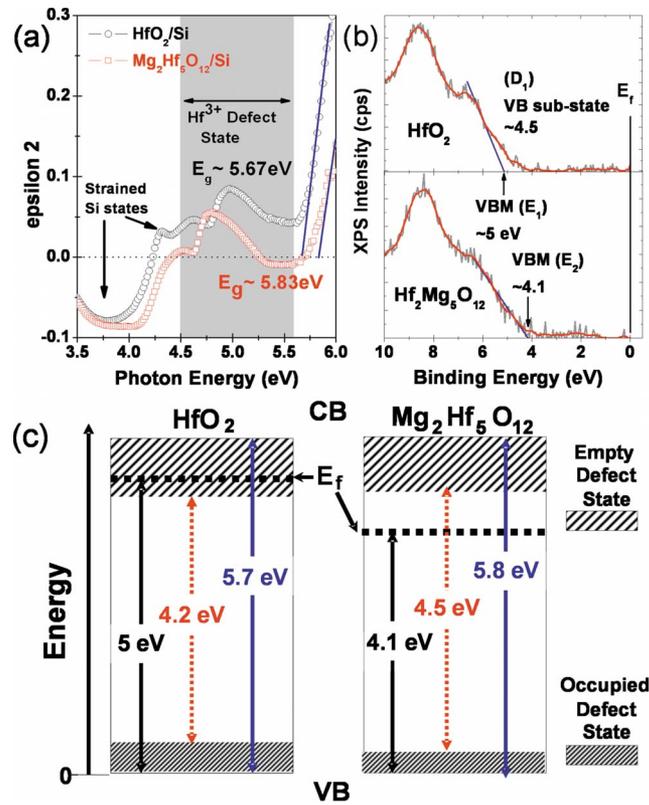
formed a single  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$  phase, resulting in a high- $k$  value of 22.5. Figure 3b shows the current density of  $\text{HfO}_2$  and  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$  thin films as a function of the electric field with the configuration of the MIM structure. The  $\text{HfO}_2$  thin films exhibited a relatively high leakage current of  $2.0 \times 10^{-5}$  A/cm<sup>2</sup> at 0.3 MV/cm. However, the  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$  thin film showed a much lower leakage current of  $4.5 \times 10^{-7}$  A/cm<sup>2</sup> at the same electric field. According to an AFM analysis, the surface morphology was similar (not shown here) and the root-mean-square values of the  $\text{HfO}_2$  and  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$  thin films were 1.04 and 0.99 nm, respectively. Such a large reduction in the leakage current density is likely not related to the surface morphology but to the material characteristics of  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$ .

To explain the different  $J$ - $E$  (current density-electric field) characteristics in the  $\text{HfO}_2$  and  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$  thin films, band-edge spectroscopic measurements using SE and XPS were made. These re-



**Figure 3.** (Color online) (a) The relationship between the dielectric constant and the electric field in  $\text{HfO}_2$  and  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$  thin films deposited at room temperature. (b) The relationship between the leakage current characteristics and the electric field of  $\text{HfO}_2$  and  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$  thin films.

sults are shown in Fig. 4a and b. In the imaginary dielectric function ( $\epsilon_2$ ) spectra shown in Fig. 4a, the  $\epsilon_2$  states above 4.5 eV correspond to the absorption at the conduction band (CB) edge empty states of the  $\text{HfO}_2$  and  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$  thin films. Below 4.5 eV, both thin films are almost transparent to visible-UV light. Thus, peak states originating from the strained Si surface, which is chemically formed at the Si/dielectric interfaces, are observed at  $<4.2$  eV. The strong absorption onset energy in the  $\epsilon_2$  spectra is usually assigned as the nominal optical bandgap ( $E_g$ ); these values are  $5.67 \pm 0.02$  and  $5.83 \pm 0.02$  eV for  $\text{HfO}_2$  and  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$ , respectively. Therefore, the optical bandgap of  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$  is  $\sim 0.16 \pm 0.02$  eV larger than



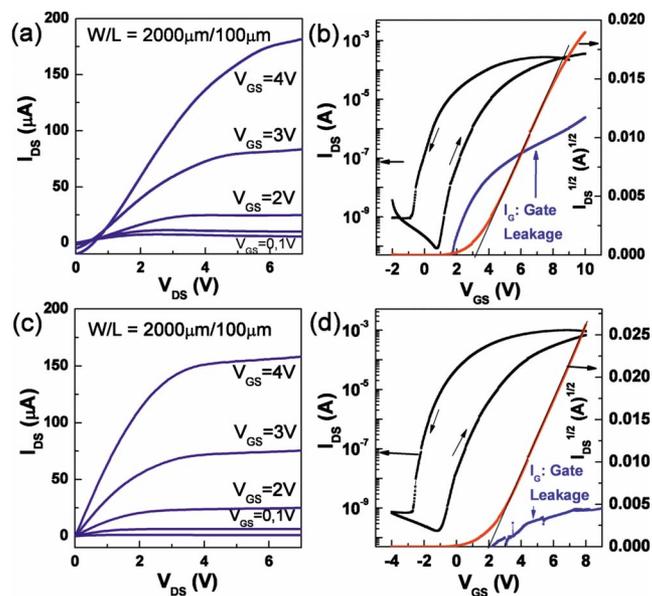
**Figure 4.** (Color online) (a) Imaginary dielectric function ( $\epsilon_2$ ) spectra taken from SE measurements: (b) VB edge XPS spectra and (c) schematic band-edge electronic structure model derived from the SE and XPS spectra of  $\text{HfO}_2$  and  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$ .

that of  $\text{HfO}_2$ . Based on local molecular orbital (MO) theory,<sup>18</sup> the major contribution of the CB onset edge states around the bandgap energy in  $\text{HfO}_2$  stems from the empty  $\text{Hf}^{4+}$  4d state with  $e_g$  bond symmetry mixed with empty O 2p states. This MO state assignment equally holds for the CB onset states in  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$  but suggests that the charge transfer between  $\text{Hf}^{4+}$  4d and  $\text{Mg}^{2+}$  2p states moves the bandgap slightly upward. As the relative density of the Hf 4d states around the bandgap energy is much higher for  $\text{HfO}_2$  than  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$ , a difference in the CB onset state intensity between the two dielectrics is also observed (i.e., a sharp absorption edge at  $\sim 5.7$  eV in  $\text{HfO}_2$  but a weak absorption edge at  $\sim 5.8$  eV in  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$ ).

More importantly, the significant differences in the CB edge defect state between the two dielectrics are clearly noted. The sub-CB edge states at 4.5–5.5 eV are considered to be empty defect states originating from  $\text{Hf}^{3+}$  3d states or oxygen vacancies localized at the grain boundary. This defect state has been commonly observed in the nanocrystalline  $\text{HfO}_2$  or Hf silicates.<sup>18</sup> The relative defect density in the  $\epsilon_2$  spectra of  $\text{HfO}_2$  is higher than that of  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$  over the entire defect state energy range. The charge transport in the nanocrystalline transition-metal oxide including  $\text{HfO}_2$  is mainly due to Poole–Frenkel (P–F) hopping and/or trap-assisted tunneling, where pre-existing defects play a major role. Therefore, the lower defect density of  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$  in the  $\epsilon_2$  spectra provides the good correlation with the lower leakage current level compared to  $\text{HfO}_2$ .

As further supporting evidence for the improvement of the leakage current characteristics, the valence band (VB) edge XPS spectra of the  $\text{HfO}_2$  and  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$  thin films are shown in Fig. 4b. While the double edge states ( $E_1$  and  $D_1$  in Fig. 4b) are resolved in  $\text{HfO}_2$ , the single edge state ( $E_2$  in Fig. 4b) is resolved in  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$ . The origin of the double states,  $E_1$  and  $D_1$  in  $\text{HfO}_2$ , is suggested (i) as occupied  $\text{Hf}^{4+}$  4d mixed with O 2p MO states assigned as a VB onset edge or a VB maximum edge ( $E_1$ ) and (ii) as a  $\text{Hf}^{3+}$  occupied MO state stemming from the same physical origin, an oxygen vacancy having the defect state ( $D_1$ ) at the CB edge, respectively. The energy position assignment of the VB edge spectra using linearly fitted extrapolation locates the energy level of the  $D_1$  state at  $\sim 0.5$  eV above the  $E_1$  state. A previous study on VB edge states of  $\text{HfO}_2$  thin films resolved by synchrotron soft XPS measurements reports VB edge state features (defect state lying at 0.5 eV above VB onset edge) similar to those in this study.<sup>19</sup> However, discrete VB edge defect states as those in  $\text{HfO}_2$  were clearly weaker in the  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$ . Therefore, the VB edge spectra reinforce the oxygen vacancy defect suppression in  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$ . In addition, charge transport through the dielectric films at a thickness of  $\sim 400$  nm in this study is not governed only by a pure tunneling process but by a significant P–F hopping process throughout the bulk oxide. Hence, the  $E_f$  position is another crucial reference for bulk charge transport. Following the aforementioned spectral assignments, the  $E_f$  levels (0 of binding energy in Fig. 4b) are positioned at  $4.6 \pm 0.1$  eV from the VB onset edge for  $\text{HfO}_2$  and at  $4.1 \pm 0.1$  eV for  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$ . Therefore, the conductivity of the electrons should be lower for  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$  than  $\text{HfO}_2$ . This lower  $E_f$  level in  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$  also provides the experimentally derived origin of the leakage current suppression.

By combining CB and VB bandedge spectroscopic analyses, a band electronic structure model is proposed, as shown in Fig. 4c. This model, constructed by the experimental results, suggests very plausible origins of the considerable leakage current suppression in  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$  thin film. These include (i) fewer P–F hopping channels with a lower defect density, (ii) a lower CB edge density of state at around the bandgap energy, and (iii) a lower  $E_f$  level (i.e., more p-type-like and correspondingly lower electron conductivity). The correlation between the structural evolution and observed band structure would be a separate interesting topic, but this future study should include theoretical calculations (e.g., ab initio calculations).



**Figure 5.** (Color online) (a) The output characteristics of InGaZnO<sub>4</sub> TFTs using a HfO<sub>2</sub> gate insulator [a channel length ( $L$ ) of 100  $\mu\text{m}$  with a channel width ( $W$ ) of 2000  $\mu\text{m}$ ]. (b) The transfer characteristics of InGaZnO<sub>4</sub> TFTs using a HfO<sub>2</sub> gate insulator. The voltage between the gate and source was swept from  $-2$  to  $10$  V at a  $V_{\text{DS}}$  value of  $5$  V. (c) The output characteristics of InGaZnO<sub>4</sub> TFTs using a  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$  gate insulator [a channel length ( $L$ ) of 100  $\mu\text{m}$  with a channel width ( $W$ ) of 2000  $\mu\text{m}$ ]. (d) The transfer characteristics of InGaZnO<sub>4</sub> TFTs using a  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$  gate insulator. The voltage between the gate and source was swept from  $-4$  to  $8$  V at a  $V_{\text{DS}}$  value of  $5$  V.

*InGaZnO<sub>4</sub> TFT performance built on PET substrates using a  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$  gate insulator.*—Based on structural, physical, and dielectric analyses,  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$  thin films are expected to show excellent performance as a gate insulator. Thus, InGaZnO<sub>4</sub> TFTs were fabricated using a  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$  thin film to demonstrate the suitability of it as a gate insulator on a PET substrate. The same structure of TFTs was compared using a HfO<sub>2</sub> gate insulator. Figure 5a shows the relationship between the drain-to-source current ( $I_{\text{DS}}$ ) and the drain-to-source voltage ( $V_{\text{DS}}$ ) at various gate-to-source voltages ( $V_{\text{GS}}$ ) in InGaZnO<sub>4</sub> TFTs using the HfO<sub>2</sub> gate insulator. The value of  $I_{\text{DS}}$  is nearly 0 at a 0 gate voltage, indicating that TFTs operate in enhancement mode. The TFTs exhibited an on current of  $180$   $\mu\text{A}$  at a  $V_{\text{GS}}$  value of  $4$  V. Moreover, the output characteristics did not exhibit clear current saturation. However, the TFTs using the  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$  gate insulator showed good drain-to-source current saturation, as shown in Fig. 5c. The on current was  $160$   $\mu\text{A}$  at a  $V_{\text{GS}}$  value of  $4$  V. The poor saturation characteristics of the TFTs using the HfO<sub>2</sub> gate insulator indicate that free electrons were not entirely depleted at the interface between the InGaZnO<sub>4</sub> semiconductor and the HfO<sub>2</sub> gate insulator. Further in-depth study is needed to clarify the correlation between the saturation and interface state. Figure 5b and d shows the transfer characteristics of InGaZnO<sub>4</sub> TFTs using HfO<sub>2</sub> and  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$  gate insulators with drain-to-source voltages ( $V_{\text{DS}}$ ) of  $<5$  V. The gate voltage was swept from  $-2$  to  $10$  V for the TFTs using the HfO<sub>2</sub> gate insulator and from  $-4$  to  $8$  V for the TFTs using the  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$  gate insulator. The on current and off current of the TFTs utilizing the HfO<sub>2</sub> gate insulator were  $3.59 \times 10^{-4}$  and  $8.41 \times 10^{-11}$  A, whereas these values for the  $\text{Mg}_2\text{Hf}_5\text{O}_{12}$  gate insulator were  $6.87 \times 10^{-4}$  and  $1.71 \times 10^{-10}$  A, respectively, with the on/off current ratios calculated as  $4.27 \times 10^6$  and  $4.01 \times 10^6$ , respectively. The field effect mobility and threshold voltage were calculated by a linear fit of the  $\sqrt{I_{\text{DS}}}$  vs  $V_{\text{GS}}$  curve in the saturation region via the equation  $\sqrt{I_{\text{DS}}}$

$= \sqrt{(W/2L)C_i\mu}(V_{GS} - V_{TH})$ , where  $C_i$  is the gate dielectric capacitance per unit area of the gate dielectrics and  $W$  and  $L$  are the width and length of the channel, respectively. The calculated  $V_{TH}$  and  $\mu_{FE}$  values were 3.2 V and 19.01 cm<sup>2</sup>/Vs for the TFTs using the HfO<sub>2</sub> gate insulator, whereas they were 2 V and 27.32 cm<sup>2</sup>/Vs, respectively, for the TFTs using the Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> gate insulator. The relation of high- $k$  gate dielectrics to the channel mobility is not due to the higher- $k$  constant of dielectrics but due to the interface quality (e.g., interface traps) between the gate dielectric and channel surface based on the Si-based metal-oxide-semiconductor gate stack research. In the field of oxide TFT, the use of high- $k$  oxides as gate dielectrics commonly exhibits the higher channel mobility than SiO<sub>2</sub>. In addition to the better oxide interface quality, another possible mechanism of this phenomenon is the channel mobility dependence of the higher density of field-induced electron density at the channel surface (due to the high capacitance in the accumulation mode). Many papers showed the dependence of bulk or field effect mobility on the intrinsic or field-induced electron concentration in an InGaZnO<sub>4</sub> film or channel with high- $k$  gate dielectrics other than SiO<sub>2</sub>.<sup>20,21</sup> Therefore, the higher  $\mu_{FE}$  of TFTs using the Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> gate insulator is ascribed to (i) the better interface quality or less oxide traps and (ii) the higher density of field-induced electron at the channel surface.

The subthreshold swings were 340 and 440 mV/dec for each TFT. Additionally, there was great improvement in terms of the gate leakage for the TFTs using the Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> gate insulator.

### Conclusions

The structural, physical, and dielectric properties of Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> thin film grown at room temperature and its implementation into a flexible InGaZnO<sub>4</sub> TFT as a gate insulator were investigated. The Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> thin film showed a high dielectric constant of 22.5 and showed greatly enhanced leakage current characteristics compared to HfO<sub>2</sub> thin film. The reduced defect density and lower  $E_f$  level against the VB onset edge in Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> are mainly responsible for the greatly reduced leakage current. InGaZnO<sub>4</sub> TFTs with Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> gate insulators exhibited a high field effect mobility of 27.32 cm<sup>2</sup>/Vs, a high on/off ratio of  $4.01 \times 10^6$ , and a low threshold voltage of 2 V with a low operating voltage of less than 4 V.

These results indicate that Mg<sub>2</sub>Hf<sub>5</sub>O<sub>12</sub> thin films show great promise as a high performance gate insulator for the fabrication of highly transparent InGaZnO<sub>4</sub> TFTs on plastic substrates.

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