Room-temperature weak ferromagnetism of amorphous $HfAlO_x$ thin films deposited by pulsed laser deposition

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The room-temperature weak ferromagnetism of amorphous $HfAlO_x$ thin films deposited by pulsed laser deposition on various substrates in oxygen-defective ambient is demonstrated. The magnetization is independent of film thickness, but depends on substrates and deposition temperatures. A magnetic moment of $\sim 0.26\mu_B$ per $HfAlO_x$ f.u. is recorded for $HfAlO_x$ films deposited under optimized conditions [deposited at 600 °C on (001) sapphire in high vacuum]. It is argued that interfacial defects are one of the possible sources of the weak ferromagnetism. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2405883]

HfO_2, as one of acceptable high-k dielectric candidates, has been widely studied in recent years.[1–4] According to magnetism theory, HfO_2 is nonmagnetic because of either full or empty d and f shells of Hf^{4+} and O^{2-} ions. However, it was recently reported that laser ablated crystalline HfO_2 thin films without magnetic doping exhibit weak ferromagnetism with a Curie temperature above 500 K.[5] Moreover, the magnetization does not scale with film thickness and shows remarkable anisotropy.[6] Such unexpected ferromagnetic behavior is much different from traditional ferromagnetism, and is named as "d^0 ferromagnetism."[7] Besides HfO_2, d^0 ferromagnetism was also observed in irradiated graphite,[8] hexaborides,[9–13] and other dilute ferromagnetic oxides and nitrides.[14–20] It poses a challenge to our understanding of magnetism in solid insulators because parasitic ferromagnetic impurity phase in the films is not a general explanation. Coey *et al.* contributed d^0 ferromagnetism to oxygen vacancies (V_O),[6] while it was demonstrated that intrinsic point defects in HfO_2 films, such as Hf vacancy sites (V_{Hf}), are most likely the source.[21] Though the origin is still an unresolved problem, the d^0 ferromagnetism makes HfO_2 films more attractive due to its possible applications in spintronics.

$HfAlO_x$, a HfO_2-based pseudobinary alloy, seems to be even superior to HfO_2 as high-k dielectric candidate due to its high crystalline temperature above 900 °C and good electric performances.[22] It would be interesting to investigate its possible ferromagnetism at room temperature (RT). Our previous experiments indicated that for amorphous $HfAlO_x$ thin films prepared at deposition temperature or after rapid thermal annealing (RTA) $T_s > 600$ °C, HfO_x clusters precipitating from the amorphous matrix were identified.[23] These HfO_x clusters are nonstoichiometric and heavily oxygen defective. In this letter, we prepare $HfAlO_x$ films by pulsed laser deposition (PLD) under high temperatures ($T_s > 600$ °C) and heavily oxygen-defective conditions (a vacuum as high as $\sim 10^{-5}$ Pa). The results demonstrate that the as-prepared $HfAlO_x$ thin films do have RT weak ferromagnetism. Moreover, the magnetic moment M is independent of film thickness but varies with the types of substrates and value of T_s.

The Hf-aluminate ceramic target used for film deposition was obtained by sintering a cold-pressed mixed powder pellet (1:1 mole ratio of HfO_2 and Al_2O_3) at 1500 °C for 6 h. Three kinds of single crystal substrates, (001) sapphire, (001) MgO, and (100) Si, with dimension of $5 \times 5 \times 0.5$ mm^3 were used. The (001) sapphire was ultrasonically cleaned in acetone and de-ionized water, while (001) MgO was only ultrasonically cleaned in absolute alcohol in order to prevent it from deliquescing in water. Ultrasonically cleaned (100) Si wafers were etched in diluted hydrofluoric solution (1:25 $HF:H_2O$) for 2 min to remove the native SiO_2 cover layer and leave a H-terminated surface. $HfAlO_x$ films were deposited in high vacuum ($\sim 10^{-5}$ Pa) by using a similar procedure of deposition as reported earlier.[23] The thickness of $HfAlO_x$ films was measured by using an optical step technique, and x-ray diffraction (XRD) was used to investigate its crystallization behaviors. The magnetization was measured at RT using Quantum Design MPMS XL superconducting quantum interference device magnetometer with magnetic field H in parallel to the surface of substrates.

Figure 1 shows XRD spectra of $HfAlO_x$ films deposited at $T_s = 800$ °C on (001) sapphire and then RTA processed at 900 and 1000 °C for 5 min, respectively. It is observed that $HfAlO_x$ films remain amorphous even after RTA at 900 °C, but amorphous HfO_x clusters can be identified if either deposition or RTA was done at $T_s = 600$–900 °C. Monoclinic HfO_2 (201) and (111) peaks cannot be identified until a deposition or RTA at $T_s = 1000$ °C. This indicates that the HfO_x clusters begin to crystallize at $T_s > 900$ °C to form monoclinic HfO_2 crystals. We emphasize on the RT weak ferromagnetism of amorphous HfO_x clusters embedded in $HfAlO_x$ matrix, so the deposition and RTA are undertaken at $T_s \leqslant 900$ °C.

Figure 2(a) shows the RT M-H curves for a (001) sapphire substrate plus a 30 nm thick $HfAlO_x$ film deposited at $T_s = 600$ °C, and a bare substrate endured the same thermal

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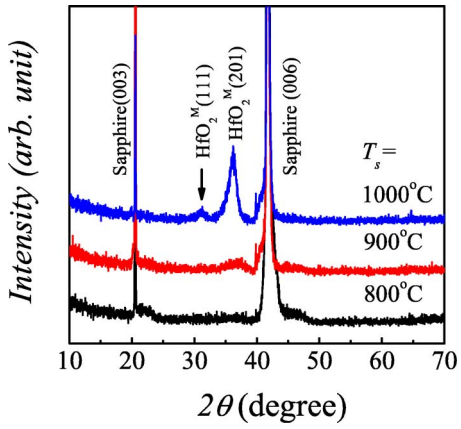

FIG. 1. (Color online) XRD spectra of $HfAlO_x$ film deposited on (001) sapphire substrates at T_s=800 °C and rapidly thermally annealed at 900 and 1000 °C for 5 min, respectively.

cycle as the deposition process. For the bare substrate, the magnetization behavior is linearly diamagnetic with a mass susceptibility of -2.45×10^{-9} m^3/kg, which is bigger than that of bulk Al_2O_3(-3.6×10^{-10} m^3/kg) and HfO_3 (-1.1×10^{-10} m^3/kg).[24] Moreover, the mass of substrate is four orders of magnitude larger than that of the $HfAlO_x$ film, so the diamagnetic signal from substrates is much stronger than that from films. Therefore, the diamagnetic signal from the films is negligible and only the diamagnetic backgrounds from substrates should be removed. As shown in Fig. 2(a), visible ferromagnetic (FM) signals are observed, which are overlapped on the linear diamagnetic background. After subtracting the background, the *M-H* curve for the film is shown in Fig. 2(b), indicating a typical FM behavior similar to a soft magnet. The saturation field is about 0.15 T, as shown in the inset of Fig. 2(b). It is then demonstrated that the as-prepared amorphous $HfAlO_x$ thin films with HfO_x clusters have RT weak ferromagnetism.

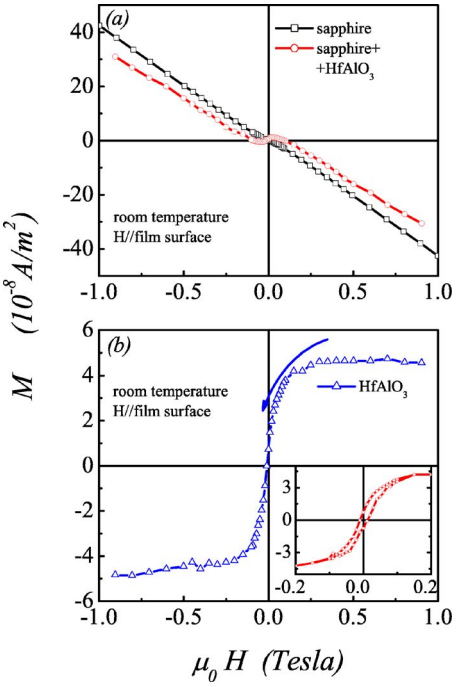

FIG. 2. (Color online) Room-temperature *M-H* curves for (a) a bare sapphire substrate and the sapphire substrate plus a 30 nm thick $HfAlO_3$ film deposited at 600 °C in a vacuum of $\sim10^{-5}$ Pa, and for (b) the 30 nm thick $HfAlO_x$ film after subtracting the diamagnetic background from the sapphire substrate. The inset in (b) is the amplified *M-H* hysteresis constructed from the *M-H* curve in (b).

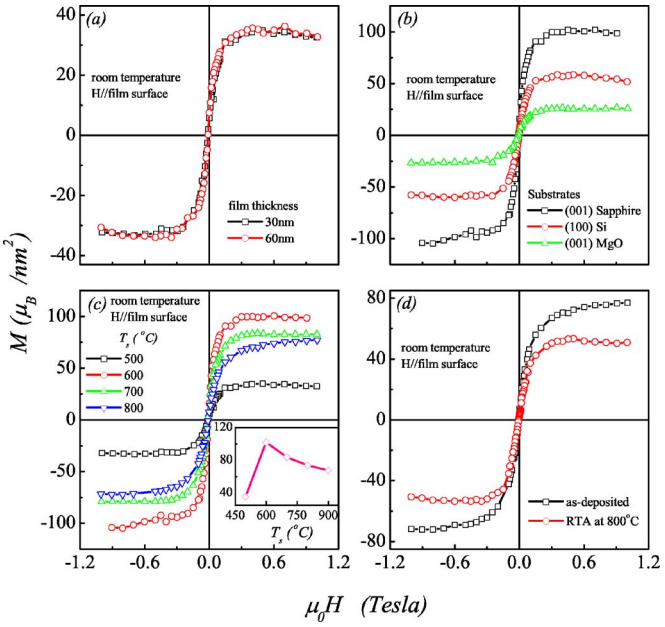

FIG. 3. (Color online) Room-temperature *M-H* curves of (a) 30 and 60 nm $HfAlO_x$ films deposited at 600 °C on (001) sapphire substrates; (b) 30 nm $HfAlO_x$ films deposited at 600 °C on (001) sapphire, MgO (001), and Si(100) substrates, respectively; (c) 30 nm $HfAlO_x$ films deposited on (001) sapphire substrates at 500, 600, 700, and 800 °C, respectively; and (d) 30 nm $HfAlO_x$ film deposited at 600 °C on (001) sapphire substrates before and after RTA at 800 °C in oxygen ambient for 10 min. All the films are deposited in high vacuum of $\sim10^{-5}$ Pa.

Previous experiments[6,25,26] demonstrated that d^0 ferromagnetism in HfO_2 films does not scale with film thickness, which is one of the characters of d^0 ferromagnetism that is different from traditional ferromagnetism. We also investigate the dependence of *M-H* curve on the film thickness *d*, as shown in Fig. 3(a), where the films of d=30 and 60 nm were deposited on (001) sapphire under identical conditions (T_s=600 °C without RTA), indicating clearly no dependence of the *M-H* relation on *d*. This implies that the ferromagnetism of $HfAlO_x$ films is not the outcome of bulk effect but of the film/substrate interfacial configuration and defects. To demonstrate this argument, we measure subsequently the *M-H* curves for films of $d\sim30$ nm deposited respectively on (001) sapphire, (001) MgO, and (100) Si substrates under identical conditions (T_s=600 °C without RTA), as shown in Fig. 3(b). The films deposited on (001) sapphire have the largest magnetic moment, while those on (001) MgO have the weakest one. In the following experiments, we choose (001) sapphire as substrates.

It should be pointed out that $HfAlO_x$ films deposited at T_s=600 °C are amorphous. Different substrates do not impose any texture variations of the films. Therefore, the difference in interface property should be responsible for the fluctuations in ferromagnetism, suggesting again that the RT ferromagnetism comes from the film/substrate interface and defects rather than from the films themselves. The interfacial defects may be the origin of the ferromagnetism.

We further measure the *M-H* curves for the 30 nm thick films deposited at various T_s, with other deposition conditions identical, as shown in Fig. 3(c). It is very interesting that the strongest RT ferromagnetism is recorded for T_s

=600 °C and either increasing or decreasing of T_s results in decaying of the saturated M. In fact, even for $T_s \gg 900$ °C where the films become well crystallized, the RT ferromagnetism still remains strong, as expected from saturating tendency of the saturated M as a function of T_s, as shown in the inset of Fig. 3(c). The strongest moment recorded at T_s =600 °C is $\sim 0.26\mu_B$ per $HfAlO_x$ f.u. To roughly explain this effect, we refer to our earlier experiments that nonstoichiometric HfO_x clusters begin to precipitate from amorphous $HfAlO_x$ matrix at T_s=600 °C.[23] With increasing T_s for either deposition or RTA, these clusters grow and nucleate to form stoichiometric HfO_2, resulting in the reduction of interfacial defects and eventually causing the decrease of M.

As for the origin of d^0 ferromagnetism, oxygen vacancies were originally suggested as the source of magnetism in HfO_2.[6] However, density functional calculation[21] predicts that oxygen vacancies only form nonmagnetic impurity levels unless p-type codopants are present, and hafnium vacancy sites (V_{Hf}) are more possibly responsible for ferromagnetism in HfO_2 thin films. Moreover, a general theoretical calculation[27] suggests that cation vacancies with certain concentration and interaction in oxide compounds could induce large ($\sim 3\mu_B$) local magnetic moments on neighboring oxygen sites. On the other hand, it is well known that RTA treatment in oxygen ambient can effectively reduce oxygen vacancies but not compensate for hafnium (cation) vacancies. If oxygen vacancies are the main source of d^0 ferromagnetism in amorphous $HfAlO_x$ films, the saturated magnetic moments should heavily decrease after the RTA treatment. On the contrary, if hafnium (cation) vacancies are mainly responsible for d^0 ferromagnetism, the saturated magnetic moments should be invariable. As a test of this assumption, we measure the RT M-H curves for two thin films of the same thickness prepared under identical conditions (T_s =600 °C). One film was RTA treated at T_s=800 °C in oxygen ambient for 10 min and the other was not. The results are plotted in Fig. 3(d). It is observed that the saturated M does decrease, but only decreases slightly upon the RTA. This implies that oxygen vacancies are not the main source of d^0 ferromagnetism. The slight decrease of saturated M is more possibly attributed to the appropriate reduction of interfacial defects after the RTA treatments. This argument is consistent with above experimental results [see Figs. 3(a)–3(c).] Here, it should be pointed out that the RTA treatment in oxygen ambient can reduce but cannot completely eliminate all interfacial defects, so the magnetic moments still remain quite considerable after the RTA treatment of the films.

Unfortunately, our experimental results cannot clarify whether Hf vacancies are also one of the main resources of ferromagnetism or not, because it is too difficult to control Hf vacancies without changing the concentration and distribution of other defects in the films. As predicted theoretically,[27] site substitution of Hf by group 1A element may be a possible approach, helping to clarify the effect of Hf vacancies and other defects in the films.

In summary, we have demonstrated that amorphous $HfAlO_x$ films deposited by PLD under high vacuum conditions have weak room-temperature ferromagnetism. The magnetization is independent of film thickness but depends on the type of substrates and temperature for deposition and RTA. Under the optimized fabricated conditions [deposited on (001) sapphire substrate at 600 °C in high vacuum of 10^{-5} Pa], a large magnetic moment of about $0.26\mu_B$ per $HfAlO_x$ f.u. is obtained. Our experiments suggest that interfacial defects are one of the possible sources of the weak ferromagnetism.

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[1] Y.-S. Lin, R. Puthenkovilakam, and J. P. Chang, Appl. Phys. Lett. **81**, 2041 (2002).
[2] S. Ferrari and G. Scarel, J. Appl. Phys. **96**, 144 (2004).
[3] E. P. Gusev, H. Shang, M. Copel, M. Gribelyuk, C. D'Emic, P. Kozlowski, and T. Zabel, Appl. Phys. Lett. **85**, 2334 (2004).
[4] M. S. Akbar, N. Moumen, J. Barnett, J. Sim, and J. C. Lee, Appl. Phys. Lett. **86**, 032906 (2005).
[5] M. Venkatesan, C. B. Fitzgerald, and J. M. D. Coey, Nature (London) **430**, 630 (2004).
[6] J. M. D. Coey, M. Venkatesan, P. Stamenov, C. B. Fitzgerald, and L. S. Dorneles, Phys. Rev. B **72**, 024450 (2005).
[7] J. M. D. Coey, Solid State Sci. **7**, 660 (2005).
[8] T. L. Makarova, B. Sundqvist, R. HoÈhne, P. Esquinazi, Y. Kopelevichk, P. Scharff, V. A. Davydov, L. S. Kashevarova, and A. V. Rakhmanina, Nature (London) **413**, 716 (2001).
[9] D. P. Young, D. Hall, M. E. Torelli, Z. Fisk, J. L. Sarrao, J. D. Thompson, H.-R. Ott, S. B. Oseroff, R. G. Goodrichk, and R. Zysler, Nature (London) **397**, 412 (1999).
[10] P. Vonlanthen, E. Felder, L. Degiorgi, H. R. Ott, D. P. Young, A. D. Bianchi, and Z. Fisk, Phys. Rev. B **62**, 10076 (2000).
[11] T. Moriwaka, T. B. Nishioka, and N. K. Sido, J. Phys. Soc. Jpn. **70**, 341 (2001).
[12] H. R. Ott, J. L. Gavilano, B. Ambrosini, P. Vonlathen, D. P. Young, Z. Fisk, and R. Zysler, Physica B **281-282**, 423 (2000).
[13] L. S. Dorneles, M. Venkatesan, M. Moliner, J. G. Lunney, and J. M. D. Coey, Appl. Phys. Lett. **85**, 6377 (2004).
[14] W. Prellier, A. Fouchet, and B. Mercey, J. Phys.: Condens. Matter **15**, R1583 (2003).
[15] S. J. Pearton, C. R. Abernathy, M. E. Overberg, G. T. Thaler, D. P. Norton, N. Theodoropoulou, A. F. Hebard, Y. D. Park, F. Ren, J. Kim, and L. A. Boatner, J. Appl. Phys. **93**, 1 (2003).
[16] J. M. D. Coey, M. Venkatesan, and C. B. Fitzgerald, Nat. Mater. **4**, 173 (2005).
[17] Y. Matsumoto, M. Murakami, T. Shono, T. Hasegawa, T. Fukumura, M. Kawasaki, P. Ahmet, T. Chikyow, S. Koshihara, and H. Koinuma, Science **291**, 854 (2001).
[18] J. Y. Kim, J. H. Park, B. G. Park, H. J. Noh, S.-J. Oh, J. S. Yang, D.-H. Kim, S. D. Bu, T.-W. Noh, H.-J. Lin, H.-H. Hsieh, and C. T. Chen, Phys. Rev. Lett. **90**, 017401 (2003).
[19] A. Punnoose, M. S. Seehra, W. K. Park, and J. S. Moodera, J. Appl. Phys. **93**, 7867 (2003).
[20] M. Venkatesan, C. B. Fitzgerald, J. G. Lunney, and J. M. D. Coey, Phys. Rev. Lett. **87**, 026601 (2004).
[21] C. D. Pemmaraju and S. Sanvito, Phys. Rev. Lett. **94**, 217205 (2005).
[22] J. Zhu and Z. G. Liu, Appl. Phys. A: Mater. Sci. Process. **80**, 1769 (2005).
[23] X. Y. Qiu, H. W. Liu, F. Fang, M. J. Ha, and J.-M. Liu, Appl. Phys. Lett. **88**, 072906 (2006).
[24] G. V. Samsnov, *The Oxide Handbook*, 2nd ed. (IFI/Plenum, New York, 1982), p. 209.
[25] N. H. Hong, J. Sakai, N. Poirot, and A. Ruyter, Appl. Phys. Lett. **86**, 242505 (2005).
[26] N. H. Hong, J. Sakai, N. T. Huong, and V. Brizé, Appl. Phys. Lett. **87**, 102505 (2005).
[27] G. Bouzerar and T. Ziman, Phys. Rev. Lett. **96**, 207602 (2006).