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Search for ferromagnetism in undoped and cobalt-doped $HfO_{2-\delta}$

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We report on the search for ferromagnetism in undoped and cobalt-doped high-k dielectric HfO_2 films. Over a broad range of growth conditions, we do not observe ferromagnetism in undoped HfO_2 films. On the other hand, we do observe room temperature ferromagnetism in dilutely Co-doped HfO_2 films, but the origin of the same appears extrinsic (a Co rich surface layer) at least for the regime of growth conditions explored. © *2006 American Institute of Physics*.
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A recent intriguing report of the observation of unexpected and highly anisotropic ferromagnetism in a high-k dielectric oxide HfO_2[1] has stirred the scientific community. If validated, this discovery of d^0 ferromagnetism in a transparent oxide undoubtedly represents a major advance for the field of spintronics.[2,3] Interestingly, the high-k dielectric oxides such as HfO_2 (hafnia) are already under active consideration as gate dielectrics for next generation devices in semiconductor technology in view of the material compatibility with silicon.[4–6] Introducing a magnetic response in such dielectrics should enable an integration of complementary metal-oxide semiconductor (CMOS) with spintronic technology.[7] Moreover, in the wake of recent spur in research activity in DMS systems,[8–15] this work could throw light on the understanding of the underlying mechanism of the intriguing DMS behavior.

In this work we have explored the possibility of occurrence of ferromagnetism in undoped and dilutely Co-doped HfO_2 films, grown under various conditions by pulsed laser deposition (PLD), using a variety of characterization techniques. Contrary to the recent report,[1] however, we do not observe ferromagnetism in undoped HfO_2 films. On the other hand, we do observe ferromagnetism in Co-doped HfO_2 films grown under a rather narrow temperature and oxygen partial pressure (O_2pp) parameter space. However, evidence suggests that the origin of this ferromagnetism is extrinsic emanating from a thin cobalt-rich layer formed on the surface.

HfO_2 (Hafnia) is a wide band gap ($E_g \sim 4.5$ eV) oxide high-k ($\varepsilon \sim 25$) dielectric material. High thermal stability and low leakage current of ultrathin hafnia films make it a potential replacement for next generation SiO_2 gates in MOS devices.[16] In general, hafnia (Hf:$[Xe4f^{14}]5d^36s^1$; O$[1s^2]2s^22p^4$) can exist in three crystallographic forms, viz., cubic fluorite phase (>2800 K; space group: $Fm3m$), tetragonal phase [>2000 K; space group: $P4_2/nmc$], and monoclinic phase (at room and low temperatures; space group: $P2_1/c$).[17] The oxygen vacancy and defect-stoichiometry issues influence the performance of HfO_2-based devices.[18] Moreover, vacancies can be generated in thin films and bulk hafnia depending on the growth, deposition, and doping parameters.

In this Letter, we present the data on $Hf_{1-x}Co_xO_2$ ($0<x<0.05$) films grown on (100) yttria stabilized ZrO_2 (YSZ) substrates by pulsed laser deposition. A wide processing parameter space, namely, variation in the substrate temperature [600–850 °C] and oxygen partial pressure (1×10^{-1}–1×10^{-6} torr) during growth, was explored. The samples were characterized by various techniques such as four-circle x-ray diffraction (XRD), Z-contrast high-resolution scanning transmission electron microscopy (HR-STEM, FEI Tecnai F20 UT microscope operated at 200 kV) in combination with electron energy loss spectroscopy (EELS), secondary ion mass spectrometry (SIMS), x-ray photoelectron spectroscopy (XPS), Rutherford backscatter-

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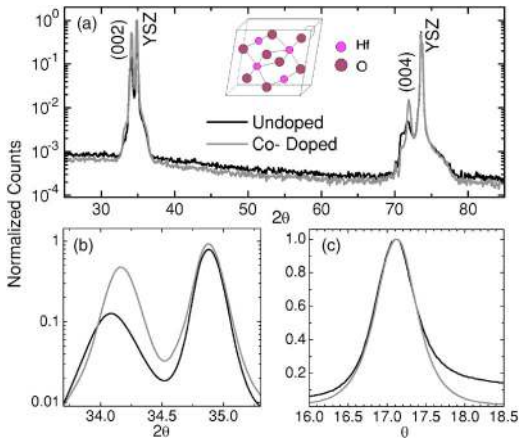

FIG. 1. (Color online) (a) X-ray diffraction patterns of undoped (black), 5 mol % Co (gray) hafnia films. (b) A clear shift in the (002) peak of the hafnia phase indicates dopant incorporation. (c) The full width at half maximum (FWHM) curves for undoped and Co-doped HfO_2.

ing (RBS) and channeling, superconducting quantum interference device (SQUID) magnetometry, magneto-optic Kerr effect (MOKE), and magnetic force microscopy (MFM). The HR-STEM enables the study of the thin films with a spatial resolution of 0.14 nm in scanning electron transmission mode with an energy resolution of 0.5 eV, though the spatial resolution in the EELS mode is about 0.4 nm.

All the results presented in this letter pertain to Co-doped hafnia films deposited at 850 °C in an oxygen partial pressure of 1×10^{-6} torr, as the films deposited with the above conditions showed magnetic signature. Figure 1(a) shows the x-ray diffraction data for the undoped, 5 mol % Co-doped HfO_2 films grown at 10^{-6} and 10^{-4} torr. The monoclinic crystal structure is shown in the inset of Fig. 1(a). Interestingly, the Co-doped hafnia films showed a clear shift in the main (002) HfO_2 peak implying a lattice parameter (d) change ($\Delta d\sim0.24\%$) which signifies lattice incorporation of the dopant element [Fig. 1(b)]. The full width at half maximum (FWHM) also showed good crystalline quality [Fig. 1(c)] of hafnium oxide. The tilt angle of the structure was determined as 9.1° from the RBS study, and it conforms to the monoclinic structure.[19] Interestingly, a single tilt variant of the monoclinic structure was seen to dominate (out of the four possible different variants), inviting further work on growth issues which will be pursued subsequently. The RBS data (not shown) indicated uniform depth distribution of Co in the hafnia matrix only up to 2% in all cases.

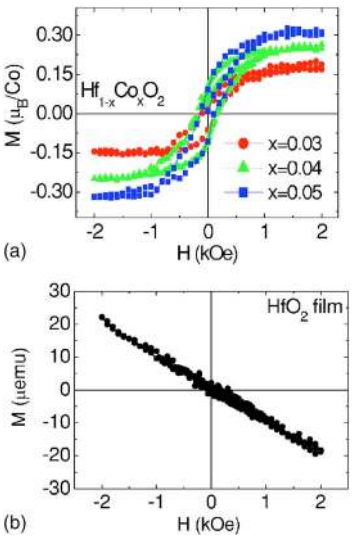

FIG. 2. (Color online) (a) M-H curves obtained at room temperature on $Hf_{1-x}Co_xO_2$ ($0.03<x<0.05$) films grown at 850 °C and 1×10^{-6} torr show the occurrence of ferromagnetism, (b) No ferromagnetic hysteresis is seen in the undoped HfO_2 film deposited under the same conditions as that of above.

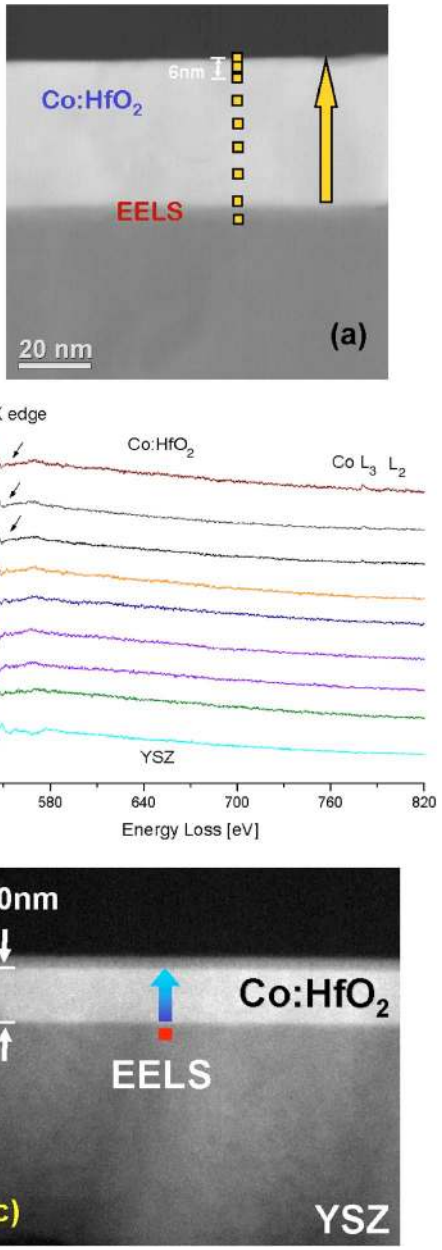

FIG. 3. (Color online) (a) High resolution Z-contrast transmission electron microscopy (TEM) image of Co-doped hafnia film showing epitaxial growth on YSZ. (b) The EELS line scans shown bring out the presence of Co-rich surface layer in top 6 nm. No Co signal detected in the film. (c) establishes more clearly the appearance of a thin layer on the top which is attributed to Co-rich surface layer.

Room temperature magnetization curves of various concentrations of Co-doped HfO_2 films ($Hf_{1-x}Co_xO_2$) grown at 850 °C and 1×10^{-6} torr are presented in Fig. 2(a). Clear magnetic hysteresis loops were obtained for Co concentrations for $x=0.05$, 0.04, and 0.03. The hysteresis loop was barely found for $x=0.02$ of Co-doped HfO_2 films. The films below $x=0.02$ [which includes the $x=0.0$ (undoped hafnia) case, see, for example, Fig. 2(b)] exhibited no magnetic mo-

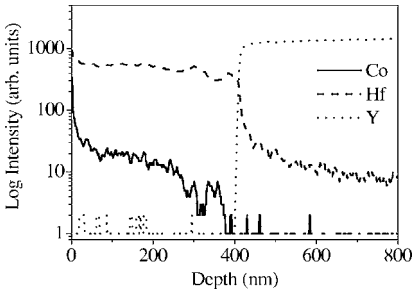

FIG. 4. Secondary ion mass spectroscopy (SIMS) data for Co, Hf, and Y. Note the rapid degradation in intensity for Co in first few nanometer regions suggesting the Co-rich surface layer in Co-doped HfO_2.

ment for a range of growth conditions explored including nominally similar conditions used by Venkatesan *et al.*[1] This result is in clear contradiction with their recent report of observation of magnetism in undoped hafnia.[1] The fact that lattice incorporation of cobalt is seen for $x<0.02$ when no moment is seen suggests that substituted cobalt does not lead to ferromagnetism at least in this low concentration regime.

The films of Co doped were further studied by the HR-STEM analyses (Fig. 3). We will describe a typical case of 40 nm thick 5% Co doped HfO_2 film. The *Z*-contrast images of the film [Fig. 3(a)] show epitaxial growth on YSZ. No dopant clustering or extended defects are observed. The EELS spectra recorded as a function of position on the $Co:HfO_2$ sample [Fig. 3(b)] are virtually the same at all positions with a spatial resolution below 0.4 nm. However, no detectable Co L_2 signal was observed across the film thickness. On careful observation we did see Co L_2 signal in the top ~10 nm layer near the surface. This suggests formation of a Co-rich surface layer and is indicated in Fig. 3(b). However, if 2% of Co is dissolved in the matrix as per the RBS and XRD data then one should see peak structure related to Co L_2 and L_3 edges in EELS scans. It is possible that for growth of a film with cobalt concentration higher than the solubility threshold all the cobalt tends to segregate out. Weak detectivity at low concentration may also be a reason for nonobservation of dilute cobalt signal in the bulk. On studying various films for STEM, we realized that in some films we did observe Co peaks in EELS scan along with a Co-rich surface layer. A typical example of such a STEM image in a somewhat thicker film is shown in Fig. 3(c). From the peaks of the white lines in the EEL spectra, the presence of 2+ valence state for cobalt is suggested, though some +3 admixture cannot be ruled out as confirmed by XPS study.

In order to confirm the formation of Co-rich layer in HfO_2, we grew thicker films (400 nm) for SIMS study. Depth profiles of the samples were obtained using Ion-ToF IV SIMS (Ion-ToF, Germany). Measurements have been done in the dual beam mode: the crater was etched by sputter gun (Ar^+ ions, 3 kV, 25 nA, 45°, 200 mkm area) and the center of the crater was analyzed in noninterlaced mode with pulsed gun (Ga^+, 15 kV, 3 pA, 45°, 100 mkm area). Electron flood gun has been used for charge compensation. As shown in Fig. 4, it is clear that Co signal is strong on the surface and decreases quickly within the first 50 nm. Note that Hf signal is almost constant throughout the thickness in contrast to the Co signal. On etching further across the interface, Y signal gets pronounced, indicating the YSZ substrate contribution. We also performed XPS depth profiling for a 40 nm film. A strong cobalt signal appeared on the surface but dropped down dramatically after removal of ~10 nm surface layer.

In conclusion, we have searched for the occurrence of ferromagnetism in an insulating high-*k* dielectric HfO_2 without and with cobalt doping. Contrary to the recent report, no ferromagnetism is observed in undoped HfO_2 at least over the broad range of conditions examined. Ferromagnetism is observed in Co-doped HfO_2 but it is attributed to the formation of a Co-rich surface layer.

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[1] M. Venkatesan, C. B. Fitzgerald, and J. M. D. Coey, Nature (London) **430**, 630 (2004).
[2] J. M. D. Coey, M. Venkatesan, P. Stamenov, C. B. Fitzgerald, and L. S. Dorneles, Phys. Rev. B **72**, 024450 (2005).
[3] I. Zutic, J. Fabian, and S. Das Sarma, Rev. Mod. Phys. **76**, 323 (2004).
[4] M. H. Cho, Y. S. Roh, C. N. Whang, K. Jeong, S. W. Nahm, D. H. Ko, J. H. Lee, N. I. Lee, and K. Fujihara, Appl. Phys. Lett. **81**, 472 (2002).
[5] H. Kim, P. C. McIntyre, and K. C. Saraswat, Appl. Phys. Lett. **82**, 106 (2003).
[6] D. H. Triyoso, R. I. Hegde, S. Zollner, M. E. Ramon, S. Kalpat, R. Gregory, X. D. Wang, J. Jiang, M. Raymond, R. Rai, D. Werho, D. Roan, B. E. White, and P. J. Tobin, J. Appl. Phys. **98**, 054104 (2005).
[7] D. P. DiVincenzo, J. Appl. Phys. **85**, 4785 (1999).
[8] H. Ohno, Science **281**, 951 (1998).
[9] K. Ueda, H. Tabata, and T. Kawai, Appl. Phys. Lett. **79**, 988 (2001).
[10] Y. Matsumoto, M. Murakami, T. Shono, T. Hasegawa, T. Fukumura, M. Kawasaki, P. Ahmet, T. Chikyow, Shin-ya Koshihara, and H. Koinuma, Science **291**, 854 (2001).
[11] S. A. Chambers, S. Thevuthasan, R. F. C. Farrow, R. F. Marks, J. U. Thiele, L. Folks, M. G. Samant, A. J. Kellock, N. Ruzycki, D. L. Ederer, and U. Diebold, Appl. Phys. Lett. **79**, 3467 (2001).
[12] S. R. Shinde, S. B. Ogale, S. D. Sarma, J. R. Simpson, H. D. Drew, S. E. Loafland, C. Lanci, J. P. Biban, N. D. Browning, V. N. Kulkarni, J. Higgins, R. P. Sharma, R. L. Greene, and T. Venkatesan, Phys. Rev. B **67**, 115211 (2003).
[13] D. C. Kundaliya, S. B. Ogale, S. E. Lofland, S. Dhar, C. J. Metting, S. R. Shinde, Z. Ma, B. Varughese, K. V. Ramanujachary, L. Salamanca-Riba, and T. Venkatesan, Nat. Mater. **3**, 709 (2004).
[14] K. R. Kittilstved, N. S. Norberg, and D. R. Gamelin, Phys. Rev. Lett. **94**, 147209 (2005).
[15] A. Punnoose, J. Hays, A. Thurber, M. H. Engelhard, R. K. Kukkadapu, C. Wang, V. Shutthanandan, and S. Thevuthasan, Phys. Rev. B **72**, 054402 (2005).
[16] S. Ramanathan, P. C. Mclyntyre, S. Guha, and E. Guser, Appl. Phys. Lett. **84**, 389 (2004).
[17] X. Zhao and D. Vanderbilt, Phys. Rev. B **65**, 233106 (2002).
[18] A. S. Foster, F. Lopez Gejo, A. L. Shluger, and R. M. Nieminen, Phys. Rev. B **65**, 174117 (2002).
[19] L. C. Feldman, J. W. Mayer, and S. T. Picraux, *Materials Analysis by Ion Channeling-Submicron Crystallography* (Academic, New York, 1982).