Observation of ferromagnetism in highly oxygen-deficient HfO_2 films*

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Abstract: Ferromagnetism in undoped and cobalt-doped high-k HfO_2 films was investigated. No ferromagnetism was observed in stoichiometric HfO_2 films, but we observed weak ferromagnetism in highly oxygen-deficient HfO_2 films. Undoped and cobalt doped films were treated by alternate annealing in vacuum and oxygen atmospheres. From the experiments, both the lack of oxygen vacancies and the increase of oxygen species in bulk (e.g. interstitial oxygen) will degrade the magnetic ordering. Additionally, it is believed that cobalt doping has no obvious relationship with the observed intrinsic d^0 magnetism.

Key words: sputtering; dielectrics; high k; d^0 magnetism; oxygen vacancy
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1. Introduction

Recently, a scientific controversy based on the intriguing observation of unexpected ferromagnetism in a high-k dielectric oxide HfO_2 has greatly attracted people's attention[1]. According to magnetism theory, HfO_2 should be nonmagnetic because of either full or empty d and f shells of the Hf^{4+} and O^{2-} ions, while the reports of Coey *et al.*[1,2] and Hong *et al.*[3] have made us aware of the phenomenon of so-called d^0 magnetism. Such an unexpected ferromagnetic discovery poses a challenge to our understanding of magnetism in solid insulators[4]. Undoubtedly, the d^0 ferromagnetism in a transparent oxide HfO_2 has great significance for advances in the spintronic field[2,5]. It also makes HfO_2 films more attractive, since HfO_2 has been widely studied in recent years as gate dielectrics for next generation devices in semiconductor technology[6–9]. The combination of ferromagnetism with the good dielectric characteristics of HfO_2 films should enable the integration of complementary metal-oxide semiconductors (CMOS) with spintronic technology[10,11]. Moreover, this d^0 ferromagnetism could help us to understand the underlying mechanism of diluted magnetic semiconductor (DMS) behavior which has been actively researched in recent years[12–15].

However, recent reports about ferromagnetism in HfO_2 films are aboil with controversy. For instance, there are some contrasting reports which believe that ferromagnetism in undoped HfO_2 films does not exist[10], or attribute it to possible tweezer contamination[16]. Moreover, even for the groups who confirm the existence of d^0 magnetism, a great divide is also present in the explanation of this ferromagnetism's source. Coey *et al.* contributed d^0 ferromagnetism to oxygen vacancies (V_O), and discussed the idea that there should be some mechanism by which oxygen vacancies could produce oxygen holes, and that it is more likely that this kind of lattice defect should be the source of magnetism in HfO_2[2]. Meanwhile, Pemmaraju *et al.* demonstrated that intrinsic point defects at Hf sites in HfO_2 films are most likely the source, which could form high-spin defect states, and therefore they could be ferromagnetic ally coupled with a rather short-range magnetic interaction resulting in a ferromagnetic ground state[17]. From the above reports, it can be concluded that the controversy is basically focused on (1) the existence of this so-called d^0 ferromagnetism and (2) the origin of this special ferromagnetism, if it exists. In addition, although there are no further reports, one could easily imagine a third focus in the future if d^0 ferromagnetism does indeed exist, that is, (3) the relationship of this special ferromagnetism with the widely researched DMS behavior.

In this work we explore the possibility of the occurrence of ferromagnetism in undoped HfO_2 films grown by sputtering. Like recent reports[10,16], we do not observe ferromagnetism in stoichiometric HfO_2 films. However, for highly oxygen-deficient films, ferromagnetism is observed, though it is relatively weak. We also observed enhanced ferromagnetism in Co-doped HfO_2 films which is believed to be from both intrinsic defects and extrinsic cobalt incorporation. From the experiments, it is concluded that more oxygen, whether it is located in the lattice or in interstitial sites, could degrade the magnetic ordering. Therefore, defects at oxygen sites (oxygen vacancy or interstitial oxygen) may directly work as the source of d^0 magnetism. Meanwhile, there is also the other possibility that the role of the oxygen species is to prevent the emergence of d^0 magnetism which comes just from defects at Hf sites, and then as the oxygen species decrease to a certain extent, weak ferromagnetism appears. In the latter instance, the incompatible explanations for the d^0 magnetism source made in previous reports both seem feasible. Additionally, extrinsic cobalt doping has no obvious relationship with the observed intrinsic d^0 magnetism, but doping may lead to a slight lattice aberration, and a small amount of oxygen vacancies might be introduced

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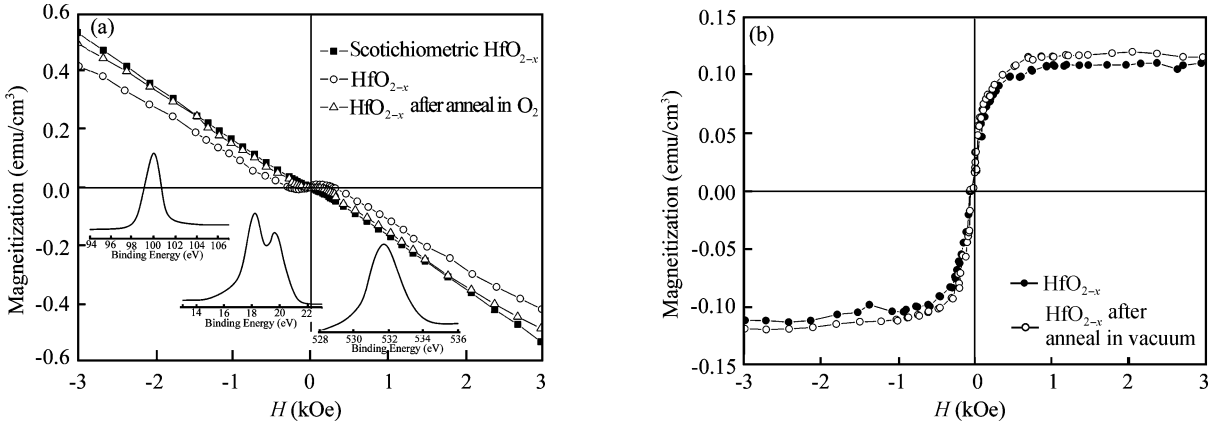

Fig. 1. (a) *M–H* curves obtained at room temperature of the as-deposited and oxygen-annealed highly oxygen-deficient HfO_2 films which show the occurrence of ferromagnetism. The solid symbol denotes the *M–H* curve of the stoichiometric film for comparison. The inset shows Si2p, Hf4f, and O1s XPS results for the highly oxygen-deficient films. (b) *M–H* curves for the highly oxygen-deficient HfO_2 film after subtracting the diamagnetic background from the substrate. Both the as-deposited and the vacuum-annealed films are shown.

in this process.

2. Experimental

HfO_2 films were prepared by standard reactive sputtering on (100) sapphire substrates. Hf target (99.99% purity) was employed to deposit the HfO_2 films with Ar/O_2 mixture in plasma. In our experiments, highly oxygen-deficient and the stoichiometric samples were obtained when 3% and 35% oxygen was applied in plasma, respectively. The total flow rate was kept constant at 40 sccm. The distance of target and substrate was constant at 8.0 cm during deposition. In order to ensure that the reaction proceeded sufficiently, the substrate was heated constantly at 800 °C. The base pressure of the sputtering chamber before deposition was 3.5×10^{-5} Pa and the working pressure was kept at 4×10^{-2} Pa. The deposition power was kept at 60 W. An annealing furnace was connected to the sputtering system. After deposition, films were treated by different heating processes. The film thickness was determined by ellipsometry measurements and the typical thickness of the Co-doped HfO_2 films was 220 nm. The chemical states of the films were investigated using a high-resolution X-ray photoelectron spectroscope (XPS) with an Al Kα source. A vibration sample magneto meter (VSM) (Lake shore 7304) was used to measure the magnetization of the films. Room temperature photoluminescence (PL) spectra were measured by a spectrofluorophotometer (RF-540) by using the 325 nm line of a He–Cd laser as the excitation source.

3. Results and discussion

Figure 1(a) shows room-temperature curves of the magnetization versus magnetic field (*M–H*) for a (100) sapphire substrate plus a highly oxygen-deficient HfO_2 film. The *M–H* curve of a stoichiometric film is also shown for comparison, and its magnetization behavior is linearly diamagnetic. The inset shows XPS spectra for the highly oxygen-deficient films. It is known that the $Hf4f_{7/2}$ binding energy of stoichiometric HfO_2 is 16.5–17.0 eV[18, 19]. One can observe that the binding energy of the main $Hf4f_{7/2}$ peak is located at about 18.1 eV. This difference corresponds to the transition from stoichiometric HfO_2 to oxygen-deficient $HfO_{x<2}$[19]. It is confirmed by the Si2p core-level spectra, where we can see that the peak at the binding energy of ~103 eV representing the Si–O bond has almost completely vanished. This means that the HfO_2 film extracts oxygen from SiO_2, which indicates a high oxygen deficiency in the HfO_2 film. Moreover, the O1s BE position is also far from the reported value for the stoichiometric case (~530.6 eV)[19, 20]. The XPS measurements strongly reflect the fact that the samples are far from full stoichiometry and that they are in the vicinity of a greatly oxygen-deficient case[19].

From Fig. 1(a), weak ferromagnetic signals are observed for the highly oxygen-deficient films, which are overlapped on the linear diamagnetic background. Meanwhile, the film became diamagnetic after oxygen annealing, which could be evidence for the oxygen vacancy mechanism supposed by Coey *et al.*[1, 2], since filling up the oxygen vacancies does destroy the ferromagnetic ordering in the highly oxygen-deficient sample. Nevertheless, it seems not yet precise enough to say that oxygen vacancies are responsible for ferromagnetism alone, since they might just be a necessary condition for the ferromagnetism appearing. After subtracting the background, the *M–H* curve for the highly oxygen-deficient film shows typical ferromagnetism behavior as shown in Fig. 1(b). One can see that after heating in vacuum, the magnetic moment of the films is enhanced slightly. The effect of vacuum annealing could possibly be to remove oxygen from the samples, as mentioned in recent work[21]. However, the oxygen atoms in the lattice, which is so well located by bonds to the neighboring cations, should be not easily removed just via vacuum annealing. The removed oxygen could be interstitial oxygen atoms, which are comparatively immune to the restriction of the lattice and inevitably formed in tempestuous sputtering even for highly oxygen-deficient films. If this assumption is valid, the enhanced ferromagnetism after vacuum annealing is not ascribed to the increase of oxygen vacancies, because whether or not the interstitial oxygen atoms fill up the oxygen

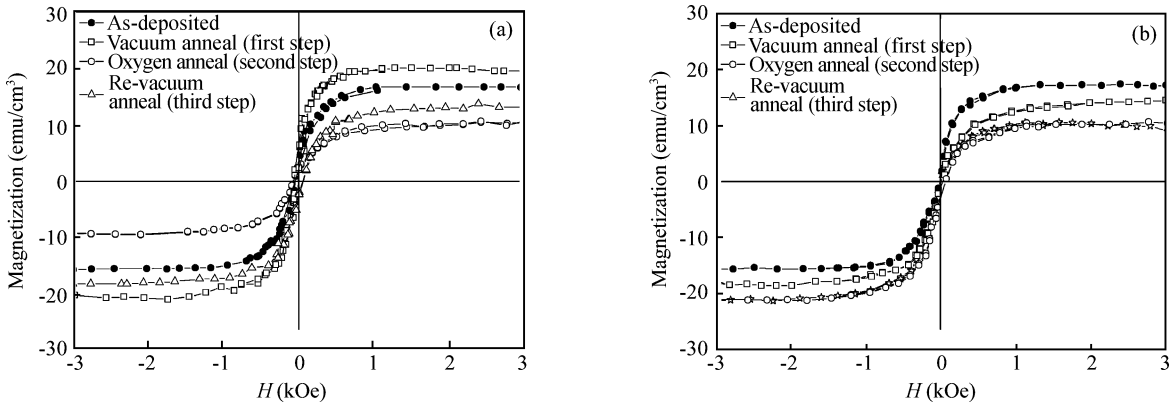

Fig. 2. Room temperature M–H curves of highly oxygen-deficient HfO_2 films with cobalt doping. The sample in (a) is annealed in vacuum, then in oxygen and finally in vacuum; the sample in (b) is annealed in oxygen, then in vacuum and finally in oxygen. All oxygen anneals were kept to 1 h while the vacuum anneals were kept to 24 h to ensure they were sufficient. The anneals were all undertaken at 600 °C . The paramagnetic component has been subtracted to clearly show the ferromagnetic phase.

vacancies during the transfer in the vacuum annealing, the oxygen vacancies in the lattice do not increase. Therefore, the decrease of the amount of the interstitial oxygen atoms could also be assumed to help with the ferromagnetism in HfO_2 films. This does not conflict with the assumption that the increase of the amount of oxygen vacancies could be the reason for the ferromagnetism, since both assumptions come down to the reduction of the oxygen species in HfO_2 films. Therefore, the degradation of ferromagnetism after oxygen annealing in Fig. 1(a), could also be ascribed to an increase of interstitial oxygen as well as a decrease in the amount of oxygen vacancies in the lattice.

It should be noted that the ferromagnetism of the highly oxygen-deficient HfO_2 films is quite small, about two orders of magnitude lower than Hong *et al.*'s report for pure HfO_2 films[21]. Actually, the ferromagnetism at this level in highly oxygen-deficient HfO_2 films is not especially obvious. However, the magnetism can be greatly enhanced by incorporating a magnetic transition metal, like cobalt doping. The M–H curves of Co-doped HfO_2 films are shown in Fig. 2. Ferromagnetism at room temperature with a saturated magnetization (M_s) of ~ 20 emu/cm^3 can be seen, which is about two orders of magnitude larger than that for the undoped highly oxygen-deficient films. According to this fact, the above-mentioned contamination from tweezers[16,22] possibly does make the intrinsic inconspicuous ferromagnetism more evident, which further confirms the conclusion in Ref. [10] that the magnetic metal possibly works in the surface region.

In order to check the conclusion obtained in Fig. 1, a so-called "three step annealing" process was introduced to the Co-doped HfO_2 films. The as-deposited films were firstly annealed in vacuum, then annealed in oxygen, and finally annealed in vacuum as shown in Fig. 2(a). After each single step, the magnetic properties of the films were checked by the magnetometer. One can find that the magnetism is enhanced and degraded by vacuum annealing and oxygen annealing, respectively. It is must be pointed out that though the final vacuum anneal was kept at 24 h, no full recovery of ferromagnetism could be obtained. The degradation caused by oxygen annealing seems not to be reversible by vacuum annealing, which is strong evidence for our assumption that vacuum annealing could only remove interstitial oxygen. If the vacuum anneal was strong enough to remove the oxygen located in the lattice as well as the interstitial atoms, then the ferromagnetism could be restored to the original level. In contrast, oxygen annealing (second step) has drastically counteracted the influence of the vacuum anneal (first step), and further led to more degradation. This confirms that oxygen annealing could not only fill up the oxygen vacancies but also add new interstitial oxygen species in highly oxygen-deficient HfO_2 films. The function of oxygen annealing thus could be described as to increase the amount of oxygen species in films, while vacuum annealing could only partially remove the oxygen species (interstitial atoms). In Fig. 2(b), the heat treatments applied for the Co-doped films are seemingly opposite to those we used for the films mentioned in Fig. 2(a), since the first annealing was applied in oxygen. Similarly, the vacuum heating performed after the oxygen annealing partially recovered the ferromagnetism, while the final oxygen anneal could easily bring the ferromagnetism back again.

In order to verify the influence of magnetic metal incorporation on the ferromagnetism of HfO_2 films, XRD measurements have been widely used in previous reports. No, or tiny, differences can be observed in these previously-reported XRD spectra, and the tiny differences were explained to be the corresponding slight lattice distortion in the HfO_2 films after magnetic metal introduction[10,21,25]. Here, different methods, i.e. photoluminescence (PL) measurement, were used instead of XRD measurement to investigate the influence of cobalt doping. Figure 3 shows room temperature PL spectra of Co-doped and undoped HfO_2 films by exciting the samples with a 325 nm He–Cd laser. As shown, the PLs of the doped and undoped highly oxygen-deficient HfO_2 films are dominated by a broad emission peak from 300 to 600 nm, which can be clearly decomposed into two Gaussian bands centered at 385 and 455 nm. The strong 385 nm emission in the HfO_2 film is

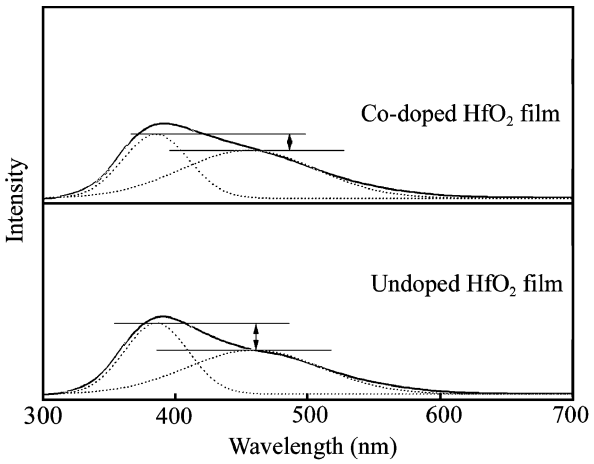

Fig. 3. PL spectra of Co-doped and undoped highly oxygen-deficient HfO_2 films excited with a 325 nm laser. The dotted curves are a simulation of Gaussian distribution.

attributed to oxygen vacancy related states[23], while the latter one at 455 nm is related to Si–O or defect states at the film-substrate interface[24]. It can be seen that the PL subpeak at about 455 nm basically remains constant, which indicates that cobalt does not result in an increase of interface defects, which is also consistent with the report that cobalt mainly keeps to the surface region of films[10]. The slight increase of the 385 nm band for Co-doped film, corresponding to the increase of oxygen vacancies in the lattice, may denote cobalt crashing into the lattice with the result of oxygen vacancy forming. In fact, one oxygen vacancy could most possibly be created for each Co^{2+} that substitutes for Hf^{4+} in the lattice in order to maintain charge neutrality[26]. Though cobalt introduction may lead to a slight increase in the amount of oxygen vacancies, the total amount of oxygen species in the films is not changed. Moreover, in both the previous XRD reports[10, 21, 25] and our PL measurements, the differences are so slight between the undoped and Co-doped films that it is stated here that there is no obvious relationship between cobalt doping and intrinsic ferromagnetism of HfO_2. The great enhancement of ferromagnetism in Co-doped HfO_2 films mainly comes from extrinsic cobalt.

4. Conclusion

In summary, we fabricated highly oxygen-deficient HfO_2 films which show weak room temperature ferromagnetism by sputtering. The obtained ferromagnetism moments were influenced by the amount of oxygen species in the films. Removing oxygen from the films enhances the magnetic moment, increasing the oxygen species reversibly degrades the ferromagnetism, or even completely destroys the ferromagnetic ordering. The oxygen species may be either the source of the ferromagnetism or an obstacle for ferromagnetism due to cation defects. The photoluminescence of Co-doped HfO_2 films is slightly different from that of pure HfO_2 and emission due to oxygen vacancies increases with cobalt doping, indicating that cobalt may have a slight impact on the formation of oxygen vacancies.

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