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Microstructure and magnetic properties of oxidized titanium nitride thin films in situ grown by pulsed laser deposition


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Abstract
Different oxidation states of titanium nitride thin films, including pure TiN(0 0 0), TiN_{1-x}O_x(0 0 0), Ti_2O_3(0 0 1) and pure anatase TiO_2(0 0 1), were prepared by pulsed laser deposition with various oxygen pressures (P_O_2) using a TiN target. Elaborative evolutions of the crystal and electronic structures of the obtained films were examined systematically by x-ray diffraction and x-ray absorption spectroscopy. We found that the Ti_2O_3(0 0 1) film, which was prepared at oxygen pressures P_{O_2} = 10^{-4} Torr, exhibited the maximum room temperature ferromagnetism (RTFM) behaviour. The bound magnetic polaron model is used to clarify the origin of RTFM in these films.

1. Introduction
Titanium dioxide (TiO_2) thin films have been studied and used extensively [1–6] since they possess remarkable optical, electronic, chemical and mechanical properties such as excellent optical transmittance (>85%) in the visible and near infrared wavelength ranges, high index of refraction (n ≈ 2.35 at 550 nm), large dielectric constant (ε_r ≈ 105 at 4.2 K) and low loss tangent (tan δ ≈ 10^{-7} at 4.2 K) [7, 8], high chemical stability and mechanical durability. The widespread applications of TiO_2 films include (a) anti-reflecting and protective coating on optical elements; (b) capacitors or gates in microelectronic devices; (c) photocatalyst and catalytic devices; (d) optical waveguide in integrated optics and (e) suitable template layers for growing high-Tc superconducting YBa_2Cu_3O_7 (YBCO) films, CrO_2 and LaSrMnO_3 films for microwave, biepitaxial junctions and spintronics applications [9–11].

Recently, transition metal-doped and oxygen-deficient TiO_2 films have been prepared with several in situ methods, include (1) in situ growth of TiO_2 thin films by pulsed laser deposition (PLD) using the synthesized TiO_2 target under various oxygen partial pressures during deposition [16–18]; (2) in situ growth of...
TiO$_2$N$_x$ thin films by direct-current (dc) magnetron sputtering using a metallic Ti target under various pressure ratios of oxygen and nitrogen [19]; (3) \textit{ex situ} nitridation of TiO$_2$ films, i.e. incorporating nitrogen into the anatase or rutile phase of TiO$_2$ [20]; (4) \textit{ex situ} oxidation of TiN films, i.e. incorporating oxygen into TiN [21–24]; (5) \textit{ex situ} introducing structural disorder, defects and/or columnar amorphization into TiO$_2$ films by swift heavy ion irradiation [25]. However, no systematic investigations on the magnetic properties of these films have been carried out.

Previously, epitaxial single-phase rutile or anatase TiO$_2$ thin films were successfully prepared on (1 0 0)-SrTiO$_3$ (STO) substrates with \textit{in situ} PLD by our group [26]. It was found that, for films deposited on STO(1 0 0) substrates directly using a rutile TiO$_2$ single crystal target, pure anatase TiO$_2$(0 0 1) films were obtained even when the substrate temperature ($T_s$) was higher than 1000°C. On the other hand, pure rutile TiO$_2$(1 1 0) films were obtained by \textit{ex situ} oxidation of TiN films immediately after they were obtained by PLD. The oxidation temperature was higher than 700°C with the oxygen pressures ($P_{O_2}$) being kept at 5 Torr. It is apparent that the specific phases and the preferred orientation of the films obtained under various conditions were mainly determined by the subtle compatibility between the surface and crystalline structures of the substrate (STO), TiN and TiO$_2$ [26]. In this work, in order to manipulate the oxygen vacancies in titanium oxy-nitride (TiN$_x$O$_{1-x}$) films, we have deliberately varied the oxygen partial pressure to deposit different TiN$_x$O$_{1-x}$ films, including pure TiN(h 0 0), TiN$_{1-x}$O$_x$(h 0 0), TiO$_2$(0 0 1) and pure anatase TiO$_2$(0 0 1) on the STO(1 0 0) substrate by \textit{in situ} PLD using a TiN target. The evolution of crystalline and electronic structures has been systematically studied by x-ray diffraction (XRD) and x-ray absorption spectroscopy (XAS) measurements. Moreover, the observed changes in film crystalline and electronic structures exhibit intimate correlations with the manifested magnetic properties of these films. We found that the corundum structure of Ti$_2$O$_3$(0 0 1) films exhibited the most pronounced room temperature ferromagnetism (RTFM). We infer that formation of the transit structure (Ti$_2$O$_3$) may have generated significant amount of oxygen vacancies needed to trigger RTFM. The interactions between the magnetic ions of Ti$^{3+}$ and electrons bound by oxygen vacancies are the fundamental ingredients for forming bound magnetic polaron (BMP) and the percolation of the BMPs at high enough densities would lead to RTFM.

2. Experiments and discussion

2.1. Sample preparation

A KrF excimer laser operating at a repetition rate of 5 Hz with an energy density of 4 J cm$^{-2}$ was used. The target was a hot-pressed TiN (99.9%, purity) pellet. The distance between the target and substrate is 5 cm. The $T_s$ was monitored by a thermocouple attached to the substrate holder and was kept at 700°C during all deposition processes. The background pressure in the chamber was 2 × 10$^{-7}$ Torr at room temperature. As we reported previously [26], the best TiN films were obtained under the background pressure and at $T_s = 700$ °C, and pure rutile TiO$_2$ films could be obtained by oxidizing the TiN films at $P_{O_2} > 3.0 \times 10^{-1}$ Torr after deposition. Therefore, in order to systematically investigate the evolution of both the crystalline and electronic structures of the TiN$_x$O$_{1-x}$ films deposited \textit{in situ}, the system was operated at $T_s = 700$ °C with $P_{O_2}$ being varied in the range 0–0.25 Torr. The thickness of each sample was ∼120 nm as determined by an alpha-step profilometer. The areas of all samples are the same as that of the ∼0.5 × 0.5 cm$^2$ STO substrates used for deposition. The crystalline structure of the films was measured by XRD, using Cu Kα radiation. The surface morphology of the films was examined by means of atomic force microscopy (AFM). The electronic structure of the TiN$_x$O$_{1-x}$ films was investigated by XAS, using the 6 m high-energy spherical grating monochromatic (6 m-HSGM) beam line at National Synchrotron Radiation Research Center (NSRRC), Taiwan, Republic of China. Moreover, the magnetic property of these samples was measured by a Quantum Design® superconducting quantum interference device (SQUID).

2.2. Crystalline structure

Figures 1(a) and (b) show the results of XRD and AFM measurements for samples prepared at various oxygen pressures, respectively. As shown in figure 1(a), epitaxial TiN(h 0 0) films was grown at $T_s = 700$ °C and without introducing oxygen ($P_{O_2} = 0$ Torr) into the chamber during PLD. The 2θ ≈ 42.60° diffraction peak assigned to TiN(2 0 0) in figure 1(a) corresponds very well to the lattice parameter of 4.24 Å of TiN [26]. When the $P_{O_2}$ was increased slightly (from 2 × 10$^{-6}$ to 5 × 10$^{-5}$ Torr), it can be seen that the TiN(2 0 0) diffraction peak starts to shift to higher diffraction angles and the peak width becomes broader with increasing $P_{O_2}$, as well. This can be understood as follows. With the presence of oxygen during deposition, the nitrogen in pure TiN will be replaced by oxygen due to the higher activity of oxygen. Since the crystal structure of TiN and TiO is the same (B1, rock-salt structure), it is quite natural to conceive that the films are basically consisting of TiN–TiO solid solution, i.e. titanium oxy-nitride TiN$_{1-x}$O$_x$. However, the ionic radius of oxygen is smaller than that of nitrogen ion, which in turn might
lead to the local lattice constant reduction [27]. Consequently, although the diffraction peak appears to remain the same as that of pure TiN(2 0 0), the peak evidently shifts to larger diffraction angles with increasing \( P_{O_2} \). The surface morphology in these films, as demonstrated in AFM images (top two images of the left column of figure 1(b)), shows the atomically smooth surface with sparsely distributed particulates distributed over the entire image. The root mean square (rms) roughness of the surface was estimated to be about 2 nm, suggesting that the entire image. The surface morphology observations revealed by AFM are quite consistent with the XRD results described above.

2.3. Magnetic property

Figure 2 shows the magnetization \( (M) \) versus applied magnetic field \( (H) \) curves measured by SQUID at room temperature (300 K) for all samples. The substrate STO and the samples deposited at \( P_{O_2} \) values ranging from 0 to \( 5 \times 10^{-5} \) Torr (i.e. TiN\(_{1-x}\)O\(_x\) films) display essentially diamagnetic behaviour (figure 2(a)). On the other hand, as shown in figure 2(b), for the film deposited at \( P_{O_2} = 10^{-5} \) Torr, which comprises mainly the corundum Ti\(_2\)O\(_3\)(0 0 6) structure, a well-defined ferromagnetic hysteresis loop is clearly demonstrated, indicating the existence of pronounced RTFM. The RTFM property, nevertheless, diminishes gradually with further increasing \( P_{O_2} \) and disappears completely when \( P_{O_2} \) reaches up to \( 1 \times 10^{-1} \) Torr at which the TiO\(_2\) films becomes amorphous. These observations strongly suggest that the manifestation of RTFM in these \( d^0 \) oxides must be intimately related to the detailed crystaline and electronic structures of the material.

2.4. Electronic structure

The advantage of XAS is its sensitivity to chemical properties and electronic structure of the samples under study. More specifically, analysis of the obtained XAS spectra allows one to discern the unique information on the crystal field strength and symmetry, hybridization, as well as the valence of the specific ion of interest, in this case Ti ions. Thus, in order to elucidate the correlations between the observed magnetic properties and the variation of electronic structures in these Ti\(_n\)O\(_y\) films deposited under different oxidizing atmospheres, we have systematically measured the O K-edge, Ti L\(_{2,3}\)-edge, and N K-edge XAS spectra of all the samples.

Figures 3(a) and (b) show the O K-edge and Ti L\(_{2,3}\)-edge XAS spectra taken in total electron yield (TEY) mode for the as-deposited TiN\(_{1-x}\)O\(_x\) thin films, respectively. The O K-edge XAS spectra reflect the partial density of unoccupied O p states and map, via hybridization, bands of primary Ti character [29]. The spectra of region I (530–536 eV) are attributed to O 2p states hybridized to Ti 3d states. The characteristic XAS peaks for the standard TiO\(_2\) powder are shown in figure 3(c) for comparison. The degenerate Ti 3d band splits into \( t_{2g} \) (corresponds to 530.3 eV peak) and \( e_g \) (532.9 eV peak) bands due to crystal field effects [30]. This

![Figure 2. M–H curves measured by SQUID at room temperature (300 K) for the STO substrate and the samples deposited at \( P_{O_2} \) (a) from 0 to \( 5 \times 10^{-5} \) Torr, (b) from \( 1 \times 10^{-4} \) to \( 2.5 \times 10^{-1} \) Torr.](image)
Figure 3. The XAS spectra of (a) O K-edge, (b) Ti L\(_{2,3}\)-edge for the samples prepared at various oxygen pressures. The characteristic XAS peaks of (c) O K-edge, (d) Ti L\(_{2,3}\)-edge for standard TiO\(_2\) powder. The incident direction of x-ray is along the normal line of the sample surface. Details explained in the text.

splitting is very sensitive to the coordination number and to the extent of the hybridization. Closer inspection reveals that the \(t_{2g}\) and \(e_g\) splitting is slightly smaller for samples deposited at lower \(P_{O_2}\) (\(P_{O_2} < 5 \times 10^{-5}\) Torr), which could be attributed to weaker Ti 3d–O2p interactions caused by the presence of oxygen vacancies and other defects in TiN\(_{1-x}\)O\(_{x}\) and Ti\(_2\)O\(_3\) films. On the other hand, peaks C\(_1\) and D\(_1\) in region II (>537 eV) are attributed to O 2p states hybridized to Ti 4sp bands [31, 32]. This region exhibits larger dispersion effects and is more sensitive to long-range order [29]. Similar to the peaks in region I, the spectra in this region demonstrate that the \(t_{2g}\) and \(e_g\) splitting becomes smaller and the Ti 4sp region is shifted towards lower energies for the samples deposited at lower \(P_{O_2}\) (<5 \times 10^{-5}\) Torr). This indicates that the Ti–O interaction in TiN\(_{1-x}\)O\(_{x}\) is much weaker than that in Ti\(_2\)O\(_3\) and anatase TiO\(_2\) due to lack of long-range order. Finally, we also noted that the O K-edge XAS signals are existent even in the TiN powder and the as-deposited TiN thin films, suggesting that a native oxidation layer may exist at the surface of these TiN samples [29].

The XAS spectra of Ti L\(_{2,3}\)-edge display a considerably more complex structure, which is caused by the combination of atomic interaction and crystal field effects [33, 34]. Figure 3(b) shows the XAS spectra of Ti L\(_{2,3}\)-edge for the TiN\(_{1-x}\)O\(_{x}\) samples and figure 3(d) exhibits the characteristic XAS peaks for the standard TiO\(_2\) powder. The region L\(_3\) and L\(_2\) correspond to O 2p\(_{1/2}\)-Ti 3d and O 2p\(_{3/2}\)-Ti 3d transitions, respectively. For both L\(_2\) and L\(_3\) edges, the crystal field splits the 3d band into \(t_{2g}\) (A\(_2\), C\(_2\)) and \(e_g\)(B\(_2\), D\(_2\)) bands. Since the Ti \(e_g\) orbitals point directly towards the 2p orbitals of the surrounding O atoms, the \(e_g\) band is very sensitive to the local environment. Moreover, the \(e_g\)-related peak of the L\(_1\)-edge further splits into two peaks, labelled as B\(_2\) and B\(_1\) in figure 3(d). Peak B\(_2\), with intensity smaller than that of B\(_2\), is the fingerprint of the anatase TiO\(_2\) [35]. As shown in figure 3(c), when the films deposited at \(P_{O_2} < 5 \times 10^{-5}\) Torr, the XAS spectra of TiN\(_{1-x}\)O\(_{x}\) films exhibit the same features to that of TiN, which indicates that both have the same cubic NaCl crystal structure. Perhaps, the most relevant changes in the spectra are occurring in B\(_2\) peak. The broadening of the peaks and the disappearance of the shoulder B\(_2\) may due to the structure distortions and the chemical changes for the films deposited at \(P_{O_2} < 5 \times 10^{-5}\) Torr. On the other hand, the splitting of (A\(_2\), B\(_2\)) peaks and (C\(_2\), D\(_2\)) peaks due to crystal field effects becomes much more distinguishable and peak B\(_2\) also appears when \(P_{O_2} > 1 \times 10^{-4}\) Torr [36].

To further delineate the substitution of nitrogen by oxygen in all the samples, we also measured the N K-edge XAS in fluorescence yield (FY) mode. Figure 4(a) shows the XAS spectra of N K-edge. The signals in region (397–404 eV) are attributed to N 2p states hybridized to empty Ti 3d bands [37]. The \(t_{2g}\) and \(e_g\) peaks split from Ti 3d caused by crystal field effects for the standard TiN sample. The spectra for the films deposited at \(P_{O_2} < 5 \times 10^{-5}\) Torr exhibit the same features...
except the intensity decreases gradually. This indicates clearly that these TiN$_{1-x}$O$_x$ films present a closed chemical similarity with TiN. The most relevant changes in the spectra occur in the position and magnitude of the $e_g$ peak. The $e_g$ characteristic peak for TiN locates at 400.7 eV, which appears to shift to 401.4 eV for the sample prepared at $P_{O_2} = 1 \times 10^{-4}$ Torr. This peak grows even further and completely dominates the spectrum when $P_{O_2} > 1 \times 10^{-5}$ Torr and has been generally attributed to unbounded nitrogen [38], that is, the nitrogen atoms still remaining and occupying interstitial positions in the TiO$_2$ matrix. For the sample deposited at $P_{O_2} > 1 \times 10^{-2}$ Torr, it is evident that all the $N$ 1s photoelectron spectroscopy (XPS) was performed. Figure 4(b) displays the Ti 2p XPS spectrum of the Ti$_2$O$_3$ film deposited at $P_{O_2} = 1 \times 10^{-4}$ Torr. It is clear that the measured profile is composed of four peaks (labelled as peaks 1–4). The split energy between peaks 2 and 4 is about 5.8 eV, which corresponds very well to the characteristic Ti 2p$_{3/2}$ (458.6 eV) and Ti 2p$_{1/2}$ (464.4 eV) spin doublet of Ti$^{4+}$ and is consistent with the value measured by Murata et al [39]. On the other hand, it is not trivial to precisely distinguish the origin of peaks 1 (457.4 eV) and 3 (463.2 eV). Two of these peaks may correspond to 2p$_{3/2}$ and 2p$_{1/2}$ of Ti$^{3+}$ or Ti$^{2+}$ and/or core level peaks of Ti ions bound to oxygen vacancies [40–43]. It is reasonable to conjecture that both Ti$^{3+}$ ions and oxygen vacancies may exist simultaneously in this unique Ti$_2$O$_3$ films. In this case, the origin of RTFM can be explained by the BMP model [44, 45]. In the undoped Ti oxides, Ti$^{3+}$ and Ti$^{2+}$ ions can provide the local magnetic moment similar to that provided by the 3d transition metals (Mn, Co and Fe, etc) doped in TiO$_2$ [46–49]. Meanwhile, the oxygen vacancies will induce slight lattice distortion in the anatase structure and act as both electron donors and electron traps. Then the localized electrons exhibit exchange interaction with the d-shell of Ti$^{3+}$ or Ti$^{2+}$ ions within a localization radius, leading to the formation of BMP with a large net magnetic moment. If the density of the oxygen vacancy is large enough and the ‘region’ of individual BMP overlaps, the exchange interaction between percolated BMPs would give rise to the ferromagnetic behaviour. It is noted that, within this scenario, for the samples prepared with $P_{O_2} < 5 \times 10^{-5}$ Torr, although there also exist Ti$^{4+}$ or Ti$^{2+}$ in the TiN$_{1-x}$O$_x$ films, the crystalline structure remains the same cubic NaCl structure and no significant vacancy generation is introduced. As a result, no global RTFM was observed. On the other hand, for the samples prepared at $P_{O_2} = 1 \times 10^{-4}$– $1 \times 10^{-2}$ Torr, the films become Ti$_2$O$_3$ and oxygen-deficient

Figure 4. (a) The XAS spectra of N K-edge for samples deposited under different oxygen pressures. (b) The XPS spectrum of Ti$_2$O$_3$($P_{O_2} = 1 \times 10^{-4}$ Torr).

The question remaining to be answered is how do such crystalline phases and associated electronic structures correlate with the observed RTFM manifestations? As shown in figure 1(a), the relative faint and broad XRD peak of Ti$_2$O$_3$(0 0 6) indicates that a large amount of oxygen vacancies as well as structural defects may be introduced when the phase transition involves two phases with drastically different crystal structures, such as during the transition between the NaCl structure (TiO) and corundum structure (Ti$_2$O$_3$) with $P_{O_2} \approx 5 \times 10^{-5}–1 \times 10^{-4}$ Torr. Nevertheless, it is also the regime where the most pronounced RTFM was observed. Thus, in order to further explore the possible correlations among the RTFM, amount of oxygen vacancies, and the valance of Ti ions in a particular sample, the Ti 2p x-ray photoelectron spectroscopy (XPS) was performed. Figure 4(b) displays the Ti 2p XPS spectrum of the Ti$_2$O$_3$ film deposited at $P_{O_2} = 1 \times 10^{-4}$ Torr. It is evident that all the N K-edge signals included this peak disappeared completely, indicating that the nitrogen atoms migrate towards the surface and are thermally desorbed.

From what is described above, it is apparent that both the XRD and XAS results gave consistent account on the crystalline phases and the associated electronic structures evolution of the Ti$_2$O$_3$ thin films deposited at various oxygen pressures. Briefly, it can be summarized as follows: (1) for the films deposited at $P_{O_2} < 5 \times 10^{-5}$ Torr, the nitrogen in pure TiN will be replaced by oxygen and form the TiN–TiO solid solution, i.e. titanium oxynitride TiN$_{1-x}$O$_x$. Then the films gradually turns into titanium monoxide (TiO) phase. Since both TiN and TiO are of cubic NaCl structure, the orientation of the films remains the same. (2) For the films deposited at $P_{O_2}$ between $5 \times 10^{-5}$ and $1 \times 10^{-4}$ Torr, the crystal structure changes from the NaCl structure (TiO) to the corundum structure (Ti$_2$O$_3$) with accompanying changes in preferred orientations. (3) When $P_{O_2}$ further increased to $1 \times 10^{-3}$ Torr, the metastable anatase TiO$_2$(0 0 1) structure starts to emerge and an intensive and sharp diffraction peak corresponding to pure anatase TiO$_2$(0 0 4) is observed at $P_{O_2} = 1 \times 10^{-2}$ Torr. Finally, the crystalline phase TiO$_2$ transforms to amorphous by further increasing $P_{O_2}$ up to $2.5 \times 10^{-1}$ Torr.
anatase TiO₂, respectively. In this case, a large amount of oxygen vacancies, structural defects accompanied with Ti³⁺ or Ti²⁺ ions exist in these thin films and macroscopic RTFM is observed. At \( P_{O_2} > 1 \times 10^{-2} \) Torr, stoichiometric TiO₂ films with Ti⁴⁺ are formed and the films become non-magnetic, again.

3. Conclusion

In summary, we have prepared TiN₆O₈ thin films by PLD with various \( P_{O_2} \) using a TiN target. Elaborative evolutions of the crystalline and electronic structures of these films were examined systematically by XRD and XAS measurements. The results indicated that with increasing oxygen partial pressure introduced into the PLD system during deposition, the films evolved sequentially from TiN, TiN–TiO solid solution, TiO, corundum Ti₂O₃, anatase TiO₂, and finally became amorphous at the highest \( P_{O_2} \) (~0.25 Torr) practiced. The magnetic property of these samples measured by SQUID revealed that there exist strong correlation between the RTFM behaviour and the crystalline and electronic structures of the obtained TiN₆O₈ films. We found that only the Ti₂O₃(0 0 1) and oxygen-deficient anatase TiO₂ films, which were prepared with \( P_{O_2} = 1 \times 10^{-4} \) to \( 1 \times 10^{-2} \) Torr, exhibited the RTFM behaviour. The XAS and XPS results suggest that the origin of RTFM behaviour is intimately related to the generation of sufficient oxygen-defects or the absence of Ti³⁺/Ti²⁺ ions, or high pressures (\( P_{O_2} > 1 \times 10^{-2} \) Torr), due to either insufficient oxygen-defects or the absence of Ti³⁺/Ti²⁺ ions, only diamagnetic behaviour was observed.

Acknowledgments

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