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Oxidized titanium nitride thin films *in situ* grown by pulsed laser deposition for diluted magnetic semiconductor

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Abstract

Different oxidation states of titanium nitride thin films, including pure TiN(*h*00), $TiN_{1-x}O_x$(*h*00), Ti_2O_3(00*l*) and pure anatase TiO_2(00*l*), were prepared by pulsed laser deposition with various oxygen pressures (P_{O2}) using a TiN target. We found that the Ti_2O_3(00*l*) film, which was prepared at oxygen pressures $P_{O2} = 10^{-4}$ 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. This results also indicate a new way to fabricate the materials of diluted magnetic semiconductor (DMS).

1. Introduction

Recently, transition metal-doped and oxygen-deficient TiO_2 films have been demonstrated to exhibit room temperatureferromagnetic (RTFM) behaviour and thus have attracted extensive interest. In particular, the observation of RTFM in the undoped TiO_2 films has been termed as d^0-magnetism, or magnetism without unpaired *d*-electrons andis due mostly to defects and/or oxygen vacancies [1].Numerous experimental and theoretical works have been reported ever since to explore the origins of the RTFM in these films. Recently, there were proofs supporting the notion that the existence of local ionic magnetic moment(Ti^{3+}/Ti^{2+} or doped magnetic elements) accompanied by oxygen vacancies might be the origin for the observed magnetic order [1], albeit controversial results are not rare and the genuine mechanism responsible for the observed RTFM is still in extensive debate. Therefore, it is crucial to prepare films with various oxygen vacancy concentrations to systematically delineate the effect of oxygen vacancy on the RTFM manifested in the transition meal-free TiO_2 films.

2. Experiments

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*00) films was grown at T_s = 700 ◦C and without introducing oxygen (P_{O2} = 0 Torr) into the chamber during PLD. When the PO2 was increased slightly (from 2×10^{-6} to 5×10^{-5} Torr), it can be seen that the TiN(200) diffraction peak starts to shift to higher diffraction angles and the peak width becomes broader with increasing P_{O2} , 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 oxynitride $TiN_{1-x}O_x$. However, the ionic radius of oxygen is smaller than that of nitrogen ion, which in turn might lead to the local lattice constant reduction. Consequently, although the diffraction peak appears to remain the same as that of pure TiN(200), the peak evidently shifts to larger diffraction angles with increasing P_{O2}. The surface morphology in these films, as demonstrated in AFM images (the 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 films are indeed remaining as single-phased TiN-TiO solid solution at this stage. As we further increased the P_{O2} from 5×10^{-5} to 1×10^{-4} Torr, it is evident that the peak of $TiN_{1-x}O_x$/TiO(200) disappears gradually and a small, new peak at $2\theta \sim 39.6^\circ$ starts to emerge. This new peak can be indexed to the diffraction peak of Ti_2O_3(006) (corundum structure). It is noted that the appearance of the Ti_2O_3(006) peak was also observed by Xu et al [2], when using PLD to prepare the anatase TiO_2 films with a Ti target under various P_{O2}'s [2]. The relatively faint intensity and broadening appearance of this peak indicates that the obtained Ti_2O_3 films should have rather defective and disordered microstructure. However, as will be shown later, this film is, in fact, possessing the most pronounced RTFM among all the samples investigated in this study. This implies that the electronic state of the Ti ions and the large amount of oxygen vacancies in this film may have offered the most favourable environment to give rise to RTFM. When P_{O2} was further increased to 1×10^{-3} Torr, we found that a diffraction peak corresponding to the metastable anatase TiO_2(00l) structure appeared, which then evolved into a high intensity and sharp XRD peak corresponding to pure anatase TiO_2(004) diffraction at P_{O2} = 1×10^{-2} Torr. By further increasing P_{O2} to 2.5×10^{-1} Torr, the films became amorphous TiO_2. As revealed by AFM images (figure 1(b)), when the growth orientation of the

films changes from (*h*00) to (00*l*) within the P_{O2} = 1 × 10^{-4} ~ 1 × 10^{-2} Torr range, the surface morphology of the films also changes to become more granular with high-density of precipitations over the surface, presumably due to the formation of Ti_2O_3 and anatase TiO_2. The particulates on the surface then disappear at even higher P_{O2}, reflecting the formation of amorphous TiO_2. All of these surface morphology observations revealed by AFM are quite consistent with the XRD results described above.

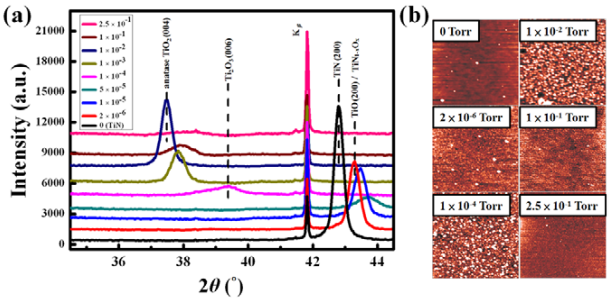

Fig. 1 (a) The XRD pattern of samples deposited with various oxygen pressures. (b) Surface morphologies of samples measured by AFM.

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_{O2} values ranging from 0 to 5 × 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_{O2} = 10^{-4} Torr, which comprises mainly the corundum Ti_2O_3(00l) 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_{O2} and disappears completely when P_{O2} reaches up to 1 × 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 crystalline and electronic structures of the material.

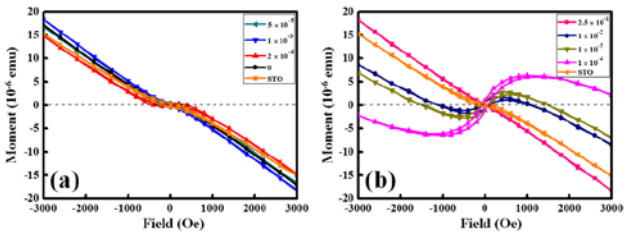

Fig. 2 *M-H* curves measured by SQUID at room temperature (300 K) for the STO substrate and the samples deposited at P_{O2} (a) from 0 to 5×10^{-5} torr, (b) from 1×10^{-4} to 2.5×10^{-1} torr.

Finally, the amount of oxygen vacancies can also be revealed by the photoluminescence (PL) spectrum measured at room temperature. The peak at long wavelength (490 nm-560 nm) is related to the defect level transition caused by the oxygen vacancy. The PL spectrum of the samples in the present work is shown in Figure 3. The intensity in the long wavelength region increases to a maximum level as P_{O2} increases to ~ 10^{-4} torr, then decreases gradually as P_{O2} further increases to 2.5× 10^{-1} torr, which is consistent with our description of the variations of the oxygen vacancy concentrations.[3]

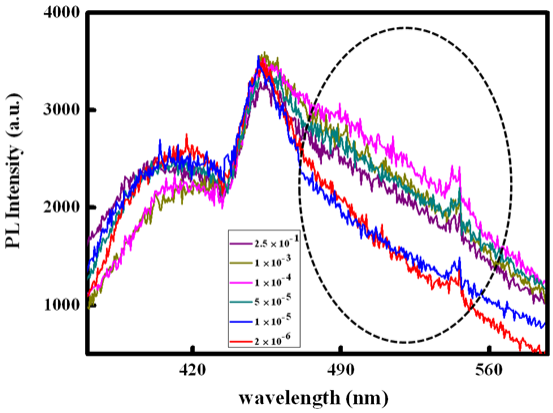

Fig. 3 The photoluminescence spectrum of TiNO samples

3. Conclusions

In summary, we have prepared TiNxOy thin films by PLD with various P_{O2} using a TiN target. Elaborative evolutions of the crystalline of these films were examined systematically by XRD 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 Ti_2O_3, anatase TiO_2 and finally became amorphous at the highest P_{O2} (~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 TiN_xO_y films. We found that only the Ti_2O_3(00*l*) and oxygen-deficient anatase TiO_2 films, which were prepared with P_{O2} = 1 × 10^{-4} to 1 × 10^{-2} Torr, exhibited the RTFM behaviour. This results also indicate a new way to fabricate the materials of diluted magnetic semiconductor (DMS).

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References

[1] C. D. Pammaraju and S. Sanvito, Phys. Rev. Lett. **94** (2005) 217205.

[2] Y. Xu and M. R. Shen, Appl. Phys. A **94** (2009) 275.

[3] Patel S K S and Gajbhiye N S Solid State Commun. **151** (2011) 1500.