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Magnetism of TiO and TiO₂ nanoclusters

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Nanoclusters of rocksalt TiO, anatase TiO₂, and rutile TiO₂ were produced by cluster deposition and examined with transmission-electron microscopy, x-ray diffraction, and magnetization measurements. The clusters are all magnetic at room temperature, but the magnetization is structure-dependent. The hysteresis loops show coercivities that are of the order of 100 Oe and all films show a preferential in-plane magnetization direction. The size dependence of the magnetization was investigated for rutile clusters with average sizes from about 15 to 40 nm. The analysis of the measurements indicates that the magnetism is predominantly located near the surface of the clusters and characterized by a nominal value of 7.6 μ_B/nm^2 . © 2009 American Institute of Physics.

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I. INTRODUCTION

The discovery of room-temperature ferromagnetism in Co-doped anatase TiO₂ (Ref. 1) has led to intense experimental and theoretical research in the field of doped titanium oxides.²⁻⁵ This interest has been reinforced by the observation of room-temperature ferromagnetism in *undoped* TiO₂.^{6,7} Doped and undoped TiO_x ($x \sim 1-2$) are of interest in various areas of technology, from optics and spin electronics to multiferroics. Among open or frequently discussed questions are the physical origin^{8,9} of the moments (oxygen defects versus magnetism caused by Ti³⁺ or even Ti²⁺ ions), the mechanism responsible for ferromagnetic coupling and room-temperature magnetic order,⁸ the spatial location of the moment (surface or bulk),⁸ and the preferential magnetization direction.¹⁰ In the literature, there is a general consensus that oxygen vacancies play a crucial role.

Our emphasis is on nanoparticles of TiO_{2-x} ($0 \leq x \leq 1$), motivated by three considerations. First, past work has focused on thin films, as compared to nanoclusters with regular size and shape. Second, undoped Ti-O is much less studied than Co-doped Ti-O, where the presence of Co may obscure the roles of Ti and oxygen. Third, the magnetism of nanoparticles with compositions close to TiO has not been investigated. This is likely due to the difficult fabrication of Ti oxides with well-defined stoichiometry, and previous fabrication methods of TiO have resulted in nonstoichiometric TiO_x,^{11,12} with x ranging from 0.70 to 1.25.

In this paper, we use cluster deposition to produce nanoparticles of rocksalt TiO, anatase TiO₂ (A-TiO₂), and rutile TiO₂ (R-TiO₂), and investigate their magnetism as a function of oxygen content and particle size.

II. EXPERIMENTAL METHODS

A cluster-deposition system¹³ has been used to synthesize rocksalt TiO, A-TiO₂, and R-TiO₂ clusters. The Ti clus-

ters have been produced by combining dc magnetron sputtering of a high-purity Ti target using argon and helium as sputtering gases with the gas-aggregation tube held at room temperature. The R-TiO₂ clusters were then prepared by postdeposition oxidation of Ti clusters with rapid thermal annealing in an oxygen atmosphere. The TiO and A-TiO₂ clusters have been produced via *in situ* oxidation of Ti clusters by feeding oxygen into the gas-aggregation chamber, and the oxygen partial pressure has been varied from 0.6% to 8.5% to obtain TiO and A-TiO₂ clusters, respectively. X-ray diffraction (XRD) was used to determine the composition and phases of the cluster films, and transmission-electron microscopy (TEM) images were used to determine the cluster sizes. Magnetic properties were investigated using a superconducting quantum interference device (SQUID).

III. RESULTS AND DISCUSSION

Figure 1(a) shows the Cu $K\alpha$ XRD spectra of bare Ti clusters, and Fig. 1(b) indicates the formation of rocksalt structure TiO upon *in situ* oxidation at low oxygen partial

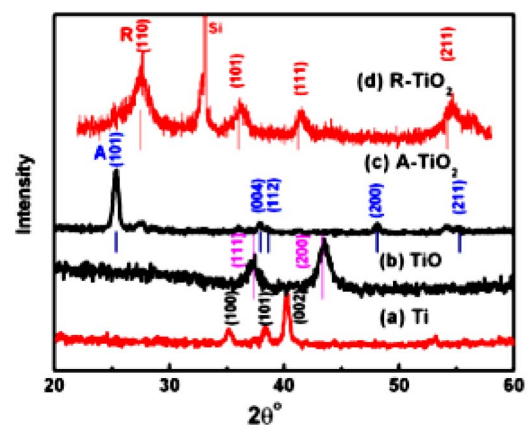


FIG. 1. (Color online) Cu $K\alpha$ XRD of (a) Ti, (b) TiO, (c) A-TiO₂, and (d) R-TiO₂ clusters films.

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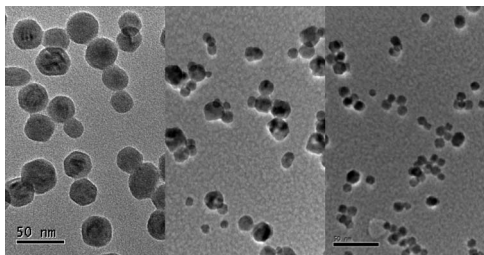


FIG. 2. TEM images for (a) Ti, (b) TiO, and (c) A-TiO₂ clusters. All three images are of the same scale, and the black bar is 50 nm.

pressure. Figure 1(c) shows the predominant A-TiO₂ phase formation with a minor rutile phase at high oxygen partial pressure. The postdeposition thermal annealing of Ti clusters results in the formation of R-TiO₂ [Fig. 1(d)]. Figure 2 shows representative TEM images of as-produced (a) Ti clusters before the postdeposition annealing, (b) TiO, and (c) A-TiO₂ clusters. The estimated average sizes of the Ti, TiO, A-TiO₂ clusters are 23, 16, and 13 nm, respectively.

Our SQUID measurements indicate that though TiO, A-TiO₂, and R-TiO₂ cluster films are all magnetically ordered at room temperature, they have different magnetic properties. The corresponding saturation magnetizations of the samples shown in Figs. 1(b)–1(d) are 0.14, 0.12, and 12.32 emu/cm³. While TiO and A-TiO₂, respectively, have lower magnetizations, they have higher coercivities of 100 and 150 Oe, respectively, compared to that of 50 Oe for R-TiO₂. At the same time, TiO and A-TiO₂ have relatively large hysteresis loop squarenesses with M_r/M_s ratios of about 46% and 56%, respectively, much higher than that of the R-clusters, which is 11%.

An interesting feature noticed for doped and undoped dilute magnetic oxides is the anisotropy of magnetization,¹⁰ which is different from conventional ferromagnets. The anisotropy of our samples was also investigated. Figure 3 shows the room-temperature hysteresis loops in the in-plane as well as the perpendicular directions for the TiO cluster film. The cluster film is more easily magnetized in the in-plane direction. A preferential in-plane magnetization direction was also found for A-TiO₂ and R-TiO₂ cluster films. Similar anisotropy was reported in Fe-doped TiO₂ films¹⁴ and V-doped SnO₂,¹⁵ and this anisotropy was attributed to texture and spin-orbit coupling. However, the details of the origin of the moment anisotropy in magnetic oxide cluster films is only partially understood.

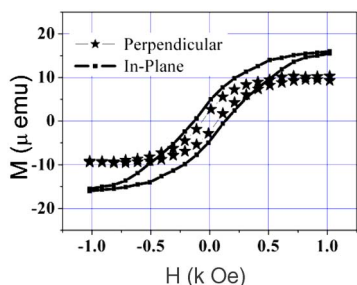


FIG. 3. (Color online) Room temperature film hysteresis loops in the in-plane (line) and perpendicular (star) directions for a TiO film with a normal cluster size of 16 nm.

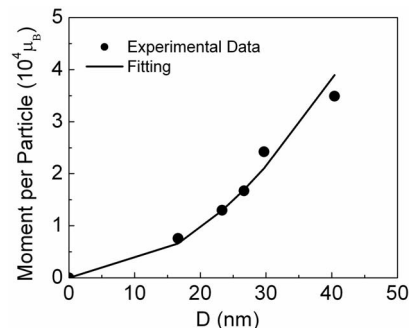


FIG. 4. Moment vs particle size: experimental (circles) and theoretical fitting (solid line).

To investigate the spatial origin of the moment, R-TiO₂ clusters of average sizes ranging from 15 to 40 nm were used. We have fitted the experimental magnetization data under the assumption of surface magnetism. To determine the surface area per particle and the corresponding average radii, a large number of particles on TEM images were modeled as ensembles of nearly spherical particles. In Fig. 4, magnetization is plotted as a function of surface averaged particle size. The theoretical predictions (solid lines) are least-square fit assuming that the moment per particle is proportional to the surface per particle. The surface moment obtained from the fit is 7.6 μ_B/nm^2 , corresponding to 0.7 μ_B per formula-unit cross section area or Ti surface atom. Attempts to fit the experimental data to homogeneous bulk magnetism yield much poorer results. This finding is consistent with the creation of oxygen defects created by diffusion at the surface.

During the investigation of magnetism in TiO_{2- δ} thin films, an oxygen-deficient environment and reduced film thickness were found to enhance both the magnetism and the conductivity, which was explained by Yoon *et al.*⁷ by the generation of anion defects with associated Ti³⁺ and/or Ti²⁺ cations. Reducing the oxygen content involves oxygen diffusion and affects the surface of the Ti–O films or nanoparticles first. Thus the magnetism of the particles would have the character of a surface magnetization that decays with increasing distance from the surface. That is probably why ferromagnetism has been observed only in systems with reduced dimensions, whereas bulk samples are insulating and nonmagnetic. An alternative model for the source of the magnetic moment is oxygen vacancies themselves.^{8,9} Irrespective of the origin of the moment, the oxygen 2*p* electron plays an important role in the realization of exchange interaction and magnetic order.^{5,8,9} The large overlap between neighboring oxygen 2*p* orbitals² ensures an extended effective interaction range¹⁶ and a relatively high ordering temperature, in spite of the low net moment.

IV. CONCLUSIONS

In summary, we have fabricated and investigated the magnetism of titanium-oxide cluster films of different stoichiometries and structures. The investigated TiO and TiO₂ clusters are all ferromagnetic, but the moment is structure dependent. Compared to the R-TiO₂ cluster films, as-produced TiO and A-TiO₂ cluster films have much lower

saturation magnetizations but exhibit larger loop squareness and higher coercivities. Our investigation of the moment of $R\text{-TiO}_2$ clusters as a function of cluster size indicates that moments are located near the surface of the clusters. This is consistent with the creation of oxygen defects and magnetic moment by oxygen diffusion at the cluster surfaces.

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