Effects of high-temperature postannealing on magnetic properties of Co-doped anatase TiO_2 thin films

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The origin of ferromagnetism in cobalt-doped anatase TiO_2 ($Co:TiO_2$) has been quite controversial due to the possible formation of Co nanoparticles. Recently, Shinde *et al.* claimed that high-temperature postannealing (i.e., at 900 °C) should incorporate Co ions into the TiO_2 matrix even from Co-clustered samples, thus proposing a new method to obtain intrinsic diluted magnetic semiconductors using $Co:TiO_2$ [Phys. Rev. B **67**, 115211 (2003)]. In order to verify this intriguing possibility, we investigated the effects of high-temperature annealing on the magnetic and structural properties of two kinds of Co-doped anatase TiO_2 samples, one prepared by Co ion implantation and another by pulsed laser deposition with a Co-doped polycrystalline target. After postannealing under oxygen pressure of 1.0×10^{-6} Torr at 900 °C, we observed drastic changes in the magnetic properties of both kinds of films. Although the Co nanoclusters, formed during the implantation, seemed to disappear inside the film, we found the formation of large clusters composed of metallic Co on the surface of the film using transmission electron microscopy. After annealing the samples prepared by pulsed laser deposition, similar large Co clusters were found at the interface. The results from x-ray-absorption near-edge spectroscopy and x-ray magnetic circular dichroism measurements on the postannealed film also demonstrated that the observed ferromagnetism in our films should come from Co metal.

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I. INTRODUCTION

Since the observation of ferromagnetism (FM) by Matsumoto *et al.* in cobalt-doped anatase TiO_2 ($Co:TiO_2$) with a Curie temperature higher than room temperature,[1] this phenomenon has attracted much attention as well as controversy.[2–12] We grew epitaxial anatase $Co:TiO_2$ thin films by pulsed laser deposition (PLD) and found that Co clusters could be easily created and that they seemed to make a major contribution to the FM observed in our films.[3] X-ray magnetic circular dichroism (XMCD) measurements on the films, reported by Kim *et al.*, also confirmed that the FM signals coincide with those of Co metal.[4] However, there are still discrepancies in the properties of $Co:TiO_2$ samples grown by different growth methods, which include PLD,[1,3–6] oxygen plasma-assisted molecular-beam epitaxy,[7,8] reactive cosputtering,[9] sol gel process,[10] and so on.[11,12] The origin of the FM in the $Co:TiO_2$ films remains controversial. The main fact underlying such controversies is that the solid solution of Co and TiO_2 is not thermodynamically stable.

Recently, Shinde *et al.* proposed that anatase $Co:TiO_2$ thin films postannealed in a pure argon ambience at 900 °C could have FM even without Co nanoclusters.[5] They actually observed segregation of metallic Co in their anatase $Co:TiO_2$ thin films grown by PLD. However, after the postannealing at 900 °C, most of the Co nanoclusters seemed to disappear. Based on x-ray diffraction and temperature-dependent mag-

netization results, they argued that the Co should be incorporated into the anatase TiO_2 matrix. If this is true, it suggests that there might be a thermodynamically stable solid solution phase of Co and TiO_2 at 900 °C, which could be metastable and ferromagnetic at room temperature. In that case, the anatase Co:TiO_2 could be a good candidate material for spintronics.

More recently, we observed superparamagnetic behaviors in Co ion-implanted TiO_2 thin films,[13] which were composed of Co nanoclusters much smaller than those of the films prepared by PLD with a Co-doped polycrystalline TiO_2 target.[3] We believe that these samples prepared by the two methods can be used to check the feasibility of stabilizing the Co:TiO_2 solid solution using high-temperature postannealing. In this paper, we report on the drastic changes in magnetic and structural properties of Co ion-implanted epitaxial anatase TiO_2 thin films as well as those prepared by PLD after postannealing at 900 °C under an oxygen partial pressure (P_{O_2}) of 10^{-6} Torr. Throughout this paper, the former and the latter will be referred to as ion-implanted and PLD grown films, respectively. At first sight, the Co nanoclusters seemed to disappear inside the bulk. However, after careful analysis, we found that the Co clusters diffused to the surface or interface of the films and formed vary large metallic Co particles on the surface or at the interface. Under these circumstances, we concluded that the ferromagnetism on our films originates from metallic Co.

II. EXPERIMENTAL TECHNIQUES

To prepare the ion-implanted films, Co^+ ions were implanted into epitaxial anatase TiO_2 thin films on $SrTiO_3$ (001) (STO). The films were grown by our PLD and monitored with *in situ* reflection high-energy electron diffraction.[3] The thickness of the films was measured and found to be about 600 nm. The Co^+ ions were implanted at a dose of $(3 \text{ or } 5)\times 10^{16}\,\text{cm}^{-2}$ and an energy of 250 keV, which produced incorporation depths of about 2000 Å and a peak Co ion concentration of either 3 or 5 at.%. A precise description of the conditions of our sample preparation and Co implantation can be found in our previous report.[13] The samples were postannealed for 30 min after implantation at a temperature of 900 °C under various P_{O_2} between 1.0×10^{-6} and 1.0×10^{-1} Torr.

The PLD grown films were prepared on STO (001) substrates with the same PLD system described above. A sintered polycrystalline $Ti_{0.96}Co_{0.04}O_2$ target was ablated by a KrF excimer laser (wavelength 248 nm) with a fluence of $1.5\ \text{J/cm}^2$ at 2 Hz. The substrate temperature was maintained at 600 °C. P_{O_2} was 3.3×10^{-7} Torr. The growth rate was controlled so as to be extremely slow, less than 0.2 nm/min, which was reported to be necessary to reduce the Co inhomogeneity.[7] The thickness of the films used in this study was about 1000 Å. The postannealing conditions for the PLD grown films are identical to those of ion-implanted films.

To explore the structural, magnetic, and chemical properties of the films, we employed several characterization techniques. Their structural properties were analyzed by conventional and high-resolution x-ray-diffraction (XRD) methods.

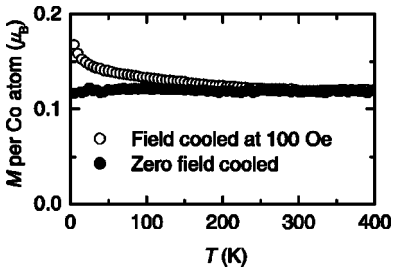

FIG. 1. Magnetization vs temperature curves of the Co ion-implanted TiO_2 film after postannealing at 900 °C with an oxygen pressure of 10^{-6} Torr for 30 min. The filled and empty circles are measured in ZFC and FC conditions at 100 Oe, respectively.

The XRD measurements showed that the Co:TiO_2 films remained in the anatase phase after the ion implantation and the postannealing. For microstructural analysis, cross-sectional and plane-view transmission electron microscopy (TEM) and energy-dispersive spectroscopy (EDS) were used. The magnetic properties were measured by using a superconducting quantum interference device (SQUID) magnetometer. Co *K*-shell x-ray-absorption near-edge spectroscopy (XANES) was used to measure the chemical states of the dopant, for which we used the synchrotron source of the Pohang Accelerator Laboratory (PAL). To elucidate the origin of the FM directly,[14] XMCD measurements were carried out at the Dragon beamline at the National Synchrotron Radiation Research Center as well as at PAL.

III. RESULTS AND DISCUSSION

A. Properties of the ion-implanted Co:TiO_2 films

The Co ion-implanted TiO_2 films showed superparamagnetic behaviors both with and without postannealing below 600 °C under P_{O_2} of 10^{-6} Torr. Although detailed data have already been published,[13] we will state here some important facts for comparison. The films showed paramagnetism at room temperature, and an FM-like behavior at 5 K. For the films just after ion implantation, the saturation magnetization and the coercive field at 5 K were $1.1\mu_B$ per Co and 600 Oe, respectively. For the films after the 600 °C postannealing, the saturation magnetization and the low-temperature coercive field became $1.5\mu_B$ per Co and 650 Oe, respectively.

We observed that the magnetic properties of the Co ion-implanted TiO_2 films altered drastically after postannealing at 900 °C under P_{O_2} of 10^{-6} Torr. Figure 1 shows magnetization versus temperature $[M(T)]$ curves for the postannealed film. The zero-field-cooled (ZFC) curve shows an almost constant value from 0 to 400 K and the field-cooled (FC) curve exhibits only a slight deviation from the ZFC curve at low temperatures. This indicates that the film can be ferromagnetic at room temperature. The drastic change in $M(T)$ curves might be related to a corresponding change in the origin of FM, as reported by Shinde *et al.*[5] They annealed their PLD grown samples with metallic Co clusters at about 900 °C in ambient argon. After being subjected to the high-temperature anneal, their sample showed almost full matrix incorporation of Co resulting in carrier-mediated intrinsic

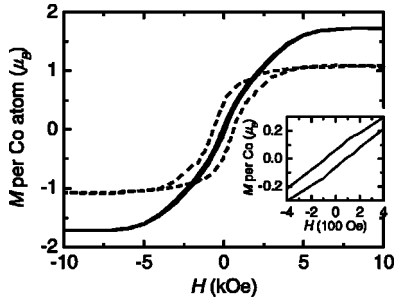

FIG. 2. Magnetization vs magnetic field curves of the Co ion-implanted TiO_2 film before and after the 900 °C postannealing are shown in the dashed and solid lines, respectively. The $M(H)$ loops are measured at 5 K. The inset shows an extended view near $H=0$ Oe for the annealed film.

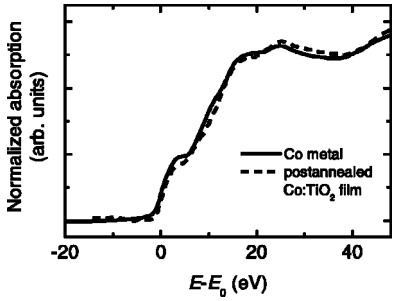

FIG. 3. Normalized Co K-edge absorption vs effective photon energy $(E-E_0)$ curve after the 900 °C postannealing of the ion-implanted TiO_2 film is shown in the dashed line. The solid line is obtained from a reference of Co metal. E_0 corresponds to 7708.8 eV.

FM. When annealing in Ar at 1 atm, it is only residual oxygen in the Ar that would reoxidize the bulk of the film. If the Ar is sufficiently pure, no reoxidation is expected. Annealing in vacuum is analogous to annealing in high-purity Ar.

The magnetization versus magnetic field $[M(H)]$ curves after the 900 °C postannealing of the ion-implanted films also show magnetic behaviors different from those of the film just after the implantation. The solid line in Fig. 2 shows the $M(H)$ curve measured at 5 K for the for the 900 °C postannealed film, exhibiting ferromagnetic behavior. The dashed line is the $M(H)$ curve of the film just after the Co implantation. After the postannealing, the value of the saturation magnetization increased to about $1.7\mu_B$ per Co atom, which is very close to the bulk Co value, i.e., $1.72\mu_B$ per Co atom. However, it has a very small coercive field value, i.e., about 100 Oe. The inset shows the enlarged $M(H)$ curve near $H=0$ Oe. Note that the coercive field of the film after Co ion implantation is about 600 Oe at 5 K.[13] The $M(H)$ curve measured at 300 K does not exhibit much difference from that at 5 K, but there is a slight decrease in the coercive field to about 70 Oe. These profound changes in the magnetic properties imply that high-temperature postannealing could result in changes in the Co nanoclusters, which provide the superparamagnetism for the as-implanted samples.

The first XTEM studies showed that the Co nanoclusters inside the ion-implanted Co:TiO_2 films actually disappeared. To check whether the Co ions have been completely incorporated into the TiO_2 matrix, as claimed by Shinde *et al.*,[5] we examined the oxidation state of Co in the ion-implanted films after the high-temperature postannealing with XANES. Note that the Co ions incorporated into the Ti site should have an oxidation state of $+2$ or $+3$.[4,7] Figure 3 shows the XANES spectra of the Co K shell of the film. The absorption spectrum of the film is nearly the same as that of the reference Co metal. The spectrum indicates that the Co in our high-temperature postannealed film is in a metallic state and not in an oxidized state, which is in contrast to the earlier claim.[5]

In order to understand the origin of the observed FM in the 900 °C postannealed sample, we performed Co $L_{2,3}$-edge XMCD measurements. As we demonstrated in our earlier works,[4] this technique is quite powerful, since it provides spectral features only from elements which exhibit FM. The energy resolution of the incident light was set to be 0.5 eV and the polarization of the light was chosen to be 85% circular. The XMCD spectra were obtained in a total electron yield mode with an about 100 Å probing depth. Just after implantation, the film was introduced into a UHV analysis chamber without any postannealing process. The detailed parameters of the measurements can be found in our previous report.[4]

Figure 4(a) shows the spectra for the spin directions that are parallel (ρ_+) and antiparallel (ρ_-) to the photon helicity vector. Their intensities were normalized by the photon flux. The first set of spectra is from the film just after implantation. The second set of spectra were taken after annealing the film inside the analysis chamber at 900 °C under P_{O_2} of 10^{-6} Torr for 30 min. The shapes of the x-ray-absorption spectra of the film after implantation and after postannealing

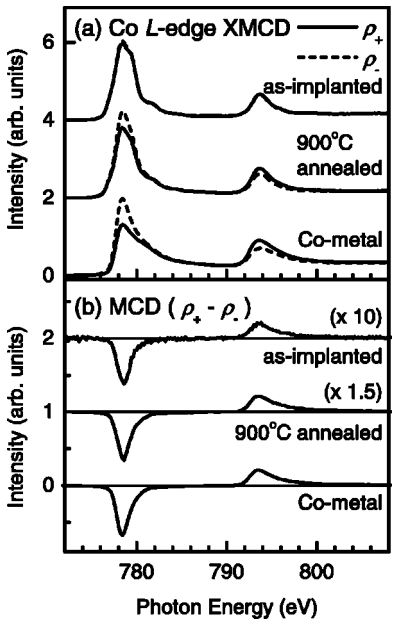

FIG. 4. XMCD spectra of the Co ion-implanted TiO_2 thin films before and after the postannealing in comparison to those of Co metal. The temperature, the oxygen pressure, and the duration of the postannealing are 900 °C, 10^{-6} Torr, and 30 min, respectively. (a) Co $L_{2,3}$-edge XMCD spectra and (b) MCD signal; $\rho_+-\rho_-$.

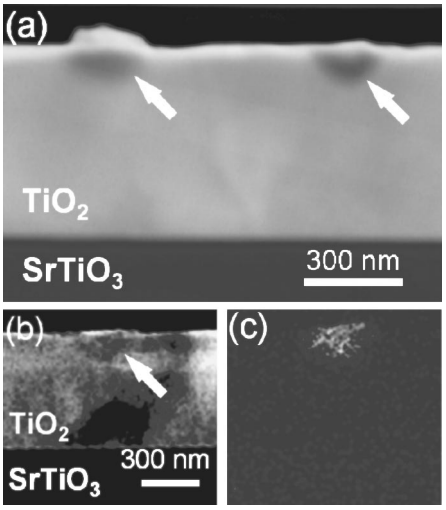

FIG. 5. (a) An XTEM image of the 900 °C postannealed film, (b) another image with a cluster, and (c) the corresponding EDS mapping of elemental Co. The white arrows indicate clusters on the surface formed after the 900 °C postannealing.

were very similar to those for metallic Co, which coincides with the results of XANES. Figure 4(b) shows the dichroism spectra $(\rho_+ - \rho_-)$, where a degree of circular polarization was taken into account. The XMCD signal of the film just after implantation was very weak, but it increased drastically after the heat treatment. Although there is a huge difference in their intensities, the shapes of the XMCD spectra are very similar to each other and coincide with those of bulk metallic Co. Note that the MCD spectra of the as-grown film, in Fig. 4(b), is magnified 10 times. The MCD spectra show that the ferromagnetism of the film originates from metallic Co, which is consistent with our previous results.

As we mentioned earlier, our first XTEM studies showed that the Co nanoclusters inside the ion-implanted Co:TiO_2 films disappeared. Where does the Co metal go? To find the answer, we carefully performed the XTEM studies again. Figure 5(a) shows an XTEM image after the postannealing of the ion-implanted film, which shows the formation of large particles on the film surface. The size of the particles is typically greater than 100 nm. From EDS mapping for elemental Co, shown in Fig. 5(c), the density of Co was found to be very high at the segregation sites. Combined with the results from XANES and XMCD studies, it is quite evident that, during the 900 °C postannealing, the Co nanoclusters originally inside the TiO_2 matrix moved to the film surface and formed large Co particles. The high density of defects, generated by the ion implantation near the surface, might help the diffusion of the Co dopant to form the large clusters on the surface. These Co particles are the origin of the observed FM in our heat-treated samples.

The formation of large Co particles on the surface can also explain the changes in the magnetic properties of our films, shown in Fig. 2. Note that the saturation magnetization after the high-temperature postannealing is nearly the same as that of the bulk value. In addition, the decrease in the coercive field also complies with this picture: namely, the particle size becomes large enough to allow domain-wall motion inside the Co particles at the surface.

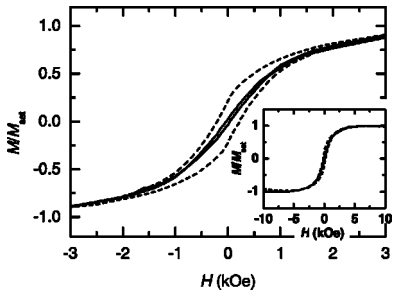

FIG. 6. Magnetization vs magnetic field curves of the Co:TiO_2 films prepared by PLD before and after the 900 °C postannealing are shown in the dashed and solid lines, respectively. The $M(H)$ loops are measured at 5 K. The inset shows saturation behaviors under a high magnetic field.

B. Properties of the PLD grown Co:TiO_2 films

To investigate the effect of high-temperature postannealing on the PLD grown films, we postannealed the Co:TiO_2 thin film just after the PLD. One would expect almost the same outcomes after postannealing the ion-implanted and PLD grown Co:TiO_2 films; the high-temperature postannealing puts the samples in thermodynamic equilibrium, and should not depend on initial conditions. However, we cannot completely exclude the possibility of different results: There are some differences between these samples, such as the densities of defects and oxygen vacancies, that can affect the diffusion process of the Co ions.

After the high-temperature postannealing, measurements of magnetization revealed that the PLD grown Co:TiO_2 film showed similar changes in magnetic properties to those of ion-implanted ones. $M(H)$ curves for the PLD grown film before and after the high-temperature postannealing are shown in the dashed and the solid lines in Fig. 6, respectively. The curves were measured at room temperature. The inset shows their behavior under a high magnetic field. The values of the saturation magnetization of both films were found to be about $1.7\mu_B$ per Co atom, which is similar to that of bulk Co. Note the decrease of the coercive field after the high-temperature postannealing. It is highly likely that the high-temperature postannealing exerts a similar influence on the magnetic properties of both the ion-implanted and the PLD grown films.

Co $L_{2,3}$-edge XMCD measurements were also performed to verify the origin of the ferromagnetism of the PLD grown films after the high-temperature postannealing. Figure 7(a) shows the x-ray-absorption spectra of ρ_+ and ρ_- geometries. The first set of spectra is from the film just after the PLD and is very similar to that of Co metal, shown in Fig. 4(a), which indicates that the ferromagnetism in this sample also originates from clusters of metallic Co, as we previously reported.[3,4] The second set was taken after the high-temperature postannealing. The shape of the x-ray-absorption spectra of the annealed film is very similar to that of the as-grown film. The high-temperature postannealing also decreases the intensity of the x-ray-absorption signal very much. The rather noisy spectra of the high-temperature postannealed film results from the small intensity. Figure 7(b) shows dichroism spectra $(\rho_+ - \rho_-)$ of the PLD grown

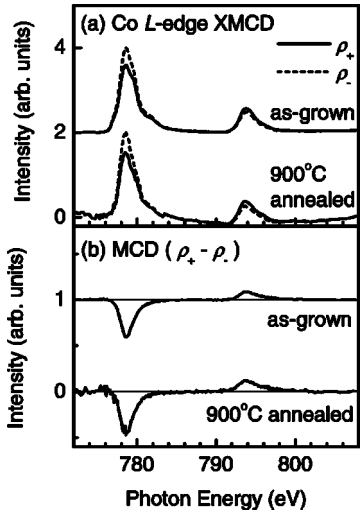

FIG. 7. XMCD spectra of the Co:TiO_2 films prepared by PLD before and after the 900 °C postannealing. (a) Co $L_{2,3}$-edge XMCD spectra and (b) MCD signal; $\rho_+ - \rho_-$.

films, and the shapes of the spectra are very similar to each other and coincide with those of bulk metallic Co. The MCD spectra clearly demonstrate that the ferromagnetism of the PLD grown film after high-temperature postannealing also originates from metallic Co.

To verify the origin of the changes in the magnetic properties, we performed TEM studies on the high-temperature postannealed PLD grown film. Unlike the case of the ion-implanted films, we were able to find large Co clusters mainly at the interface between the TiO_2 film and the STO substrate. Figure 8(a) shows an XTEM image of the PLD grown film after high-temperature postannealing, which shows large clusters marked by arrows. Most of large clusters were found to be located at the interface, with a few small clusters remaining inside the film. The distribution and the size of the clusters can be seen more clearly in a plan-view TEM study. Figure 8(b) shows an annular dark field TEM image of the same sample, which gives a contrast depending on atomic number. Instead of many nanosized clusters distributed all over the sample, there are a reduced number of large-sized clusters. The maximum diameter of the clusters, shown as white spots, is about 170 nm. The EDS mapping image for elemental Co over the same area, as seen in Fig. 8(c), indicates that the clusters should be mainly composed of Co. From a nanobeam diffraction pattern, the clusters were found to be metallic Co. The diffraction pattern, shown in Fig. 8(d), is that of hexagonal Co along the $(1\bar{2}13)$ direction. For the PLD grown films, the large clusters after the postannealing are the origin of the observed ferromagnetism. The reduction of the coercive field in $M(H)$ curves can be explained by the formation of the large-sized clusters, in which a magnetic domain can be formed.

The high density of large Co clusters near the interface after the high-temperature postannealing can explain the intensity reduction of the x-ray-absorption spectra and the XMCD signal. As shown in Fig. 7, the intensity of XMCD spectra was decreased by 1/3 with high-temperature postannealing, resulting in the noisy spectra. With a limited skin

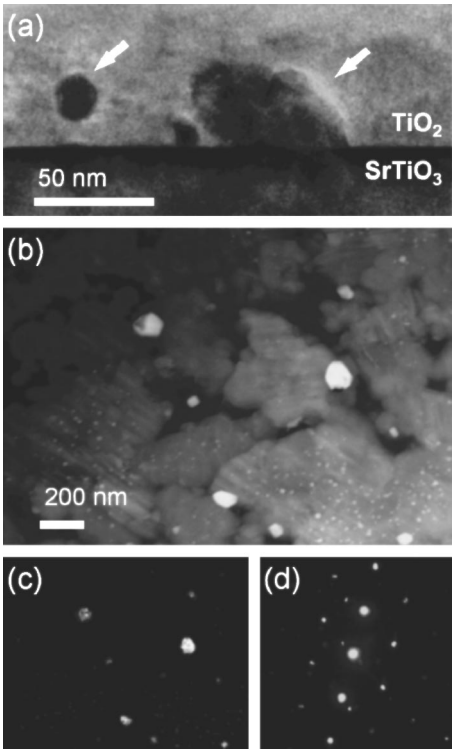

FIG. 8. (a) An XTEM image after the 900 °C postannealing of the Co:TiO_2 film prepared by PLD, (b) a plane-view annular dark field TEM image, (c) the corresponding EDS mapping of elemental Co for the image in (b), and (d) the nanobeam diffraction pattern of the clusters in (b). The white arrows indicate large clusters formed after the 900 °C postannealing.

depth of about 100 Å, XMCD cannot detect the signal of the large Co clusters at the interface through the 1000-Å-thick TiO_2 films. The high density of large clusters at the interface can be explained by its structural instability.[3] For the lattice mismatch of about 3% between anatase TiO_2 and STO, there should be large numbers of defects that can promote diffusion of Co dopant and, eventually, the coalescence of small clusters.

C. Effect of oxygen partial pressure on the results of the high-temperature postannealing

The incorporation of Co inside an anatase matrix should require proper oxidization. P_{O_2} during the annealing, which determines the oxidation state of Co, is very important. To study the effect of P_{O_2}, we annealed the films under precisely controlled P_{O_2}, varying it from 10^{-6} to 10^{-1} Torr. After 900 °C postannealing was done with a high P_{O_2} of 10^{-1} Torr for 30 min, neither the ion-implanted nor the PLD grown films showed FM. This indicates that the ferromagnetism and the diffusion of Co are very sensitive to oxygen pressure during annealing. Oxygen vacancies, which can be easily generated under a low oxygen pressure, can help the process of diffusion, which results in large-sized Co clusters. According to generally accepted theories of DMS, the matrix should contain enough carriers to mediate exchange interaction between the doped magnetic impurities.[15] In our Co:TiO_2 thin

films, the carriers might be generated by oxygen vacancies. However, they can accelerate diffusion of the magnetic dopant, Co, which will eventually result in magnetic clusters. To realize carrier-mediated magnetism in this system, there needs to be some means of introducing magnetic impurities as well as carriers without disturbing the thermodynamic stability.

IV. SUMMARY

We investigated the effects of high-temperature postannealing on the magnetic properties of Co-doped anatase TiO_2 thin films prepared by Co ion implantation into TiO_2 thin films as well as by PLD of a Co-doped polycrystalline target. After postannealing at 900 °C under an oxygen pressure of 10^{-6} Torr for 30 min, both films showed drastic changes in their magnetic properties. In contrast to the earlier work indicating that the high-temperature postannealing should incorporate the Co ions into the TiO_2 matrix, we found that the changes in magnetic properties originated from the formation of large Co particles on the film surface or at the interfaces for the films prepared. Results from x-ray-absorption near-edge spectroscopy, x-ray magnetic circular dichroism measurement, and transmission electron microscopy also support this conclusion. Our investigations demonstrate that it is very important to check whether ferromagnetic secondary phases are formed in oxide-diluted magnetic semiconductors.

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