Co distribution in ferromagnetic rutile Co-doped TiO_2 thin films grown by laser ablation on silicon substrates

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Pure rutile Co-doped TiO_2 films were fabricated by the pulsed-laser-deposition technique on silicon substrates from a ceramic target. Under the right fabrication conditions, Co concentration in the films could be almost the same as in the target, and films under various conditions all are ferromagnetic well above room temperature. Even though Rutherford backscattering spectroscopy measurements show that Co atoms mostly localize near the surface of the films and exist less in deeper levels, other experimental evidence shows that the ferromagnetism does not come from Co segregations, but from the Co-doped TiO_2 matrix. Rutile $Ti_{1-x}Co_xO_2$ thin films grown by a very simple technique on low-cost silicon substrates showing a Curie temperature (T_C) above 400 K appear to be very attractive to applications. © *2003 American Institute of Physics.*
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Since the discovery by Matsumoto *et al.*[1] about two years ago, Co-doped TiO_2 ($Ti_{1-x}Co_xO_2$) thin films have attracted many research groups due to their exhibition of ferromagnetism well above room temperature. Growth of this diluted magnetic semiconductor by thin-film techniques, such as molecular-beam epitaxy (MBE) or pulsed laser deposition (PLD), provides excellent control of the dopant concentration and the ability to grow single-layered films. However, there are certain issues in this research field at the moment: how to control the concentration of dopant more easily, how to improve the ferromagnetism, and how to clarify the nature of magnetism in those films. So far, Co-doped TiO_2 films have been deposited from two targets—Ti and Co or TiO_2 and Co-doped TiO_2—with a very high concentration of Co in order to get a very low percentage of Co incorporated in the films, by using very sophisticated methods, such as combinatorial laser ablation (using the rotation of combinatorial masks), MBE laser ablation, oxygen-plasma-assisted MBE, or co-sputtering.[1–4] Some research reported about films that were ablated from a ceramic target, but it was said that Co did not get into the structure, but remained as Co metal.[5] The average magnetic moments per Co atom reported so far are still very modest (0.32 μ_B for laser ablated films[1] and about 1.1 to 1.3 μ_B for films grown by oxygen-plasma-assisted MBE[3,4]), and the nature of ferromagnetism was claimed to be caused by Co or cobalt oxide clusters.[4–7] In order to look ahead to solving some of those problems, in this work we have tried to fabricate Co-doped TiO_2 films from a ceramic target on silicon substrates by using a conventional PLD system. It is believed that if we use a well-made target, and control the growth conditions correctly, the films whose dopant concentrations are almost the same as they are in the fixed target with ferromagnetism above room temperature can be obtained.

A polycrystalline target of Co-doped TiO_2 with Ti:Co ratio as 0.88:0.12 was synthesized by an organic gel-assisted citrate process. The 230 nm-thick films were deposited by PLD technique (248-nm KrF excimer laser, pulses of 5 Hz) on unetched (100) Si substrates. We applied various conditions: the oxygen partial pressure (P_{O_2}) was kept as 1×10^{-6} or 1×10^{-5} Torr, and the energy density was 1.5 or 3 J/cm^2. Hereafter, four main conditions will be marked as LL (low P_{O_2}, low energy density), LH (low P_{O_2}, high energy density), HL (high P_{O_2}, low energy density), and HH (high P_{O_2}, high energy density). The temperature on the substrates was kept at 700 °C. After deposition, all films were cooled down slowly to room temperature under an oxygen pressure of 20 mTorr. The crystalline structure was studied by x-ray diffraction (XRD) with Cu K_α radiation ($\lambda=1.5406$ Å), using a Seifert for the $\Theta-2\Theta$ scan and an X'Pert™ Philips MRD for the in-plane measurements (Φ-scans). The magnetization measurements were performed by a Quantum Design superconducting quantum interference device system from 0 to 0.5 T in the range of temperature from 400 K down to 5 K. The film morphology was checked by a scanning electron microscope (SEM), and the chemical composition was determined by both energy dispersive x-ray (EDX) and Rutherford backscattering spectroscopy (RBS) methods. The RBS measure-

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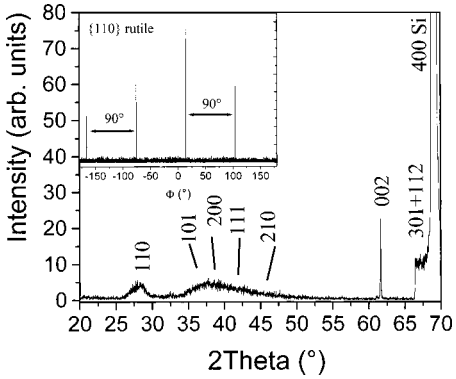

FIG. 1. XRD pattern for a $Ti_{0.908}Co_{0.092}O_2$ thin film deposited on a Si substrate under an oxygen pressure of 1×10^{-6} Torr and a fluence of 3 J/cm^2. The bump around $2\Theta=40°$ results from various diffraction peaks arising from different out-of-plane orientations of the TiO_2 phase. Only diffraction peaks corresponding to the rutile phase were observed. The inset depicts the Φ-scan recorded for the (110) reflection of the rutile TiO_2.

ments were performed with an incident energy of He^+ at 3.049 MeV, a scattering angle of 170°, and an accumulation charge for each measurement as of 2 μC).

X-ray measurements confirmed that all film are single-phased rutile, with only rutile peaks appearing in the spectra (for an example, see Fig. 1 for x-ray patterns of the HL film). The films are highly epitaxial, with the *c*-axis of the rutile (around 2.96 Å) perpendicular to the substrate plane. Neither Co nor cobalt oxide phase was found in the spectra. Films on Si substrate are mostly *c*-axis oriented, but other diffraction peaks, indexing on the basis of the rutile phase, are present, indicating that the film grows with several orientations (probably due to the large lattice mismatch). However, the Φ-scan recorded around the 110 reflection [see the inset of Fig. 1(a)] shows 90° separated peaks that gives an evidence of in-plane texture of the rutile phase. Similar scans taken on the 220 reflection of Si revealed that the TiO_2 rutile layer grows epitaxially, cube-on-cube on Si substrates. In fact, from SEM images, the HL sample, whose x-ray pattern are shown, is the one which has the worst morphology, with the presence of some alien parts that are thought to be due to Co segregations, however, we found no peaks of cobalt or cobalt oxide, and the film is pure rutile. For other better films, the same results are obtained: only rutile peaks appear in the spectra. It is not possible to say very positively that there is no segregation of Co in the films if it is below the detection limit, but it is certain that the Co-doped films on Si are well established as rutile. Although rutile Co-doped films on Si substrates have been already fabricated by co-sputtering from Co and Ti targets,[8] in the present study they are done by a PLD from one ceramic target.

All films with our chosen growth conditions showed ferromagnetic behaviors at room temperature. The magnetization loops are quite similar, except the difference in magnitude of saturated magnetization (M_s) and coercivity (H_C). The highest M_s achieved in our films was 0.31 μ_B/Co, almost the same as that of the $Co_xTi_{1-x}O_2$ film with $x=7\%$ on a $SrTiO_3$ substrate reported by Matsumoto *et al.*[1] Figure 2(a) shows the magnetization as a function of magnetic field taken at 300 K for the LL film. Hysteresis was observed, showing that the film is ferromagnetic even at room temperature. The $M(T)$ curve taken at 0.2 T in Fig. 2(b) shows that

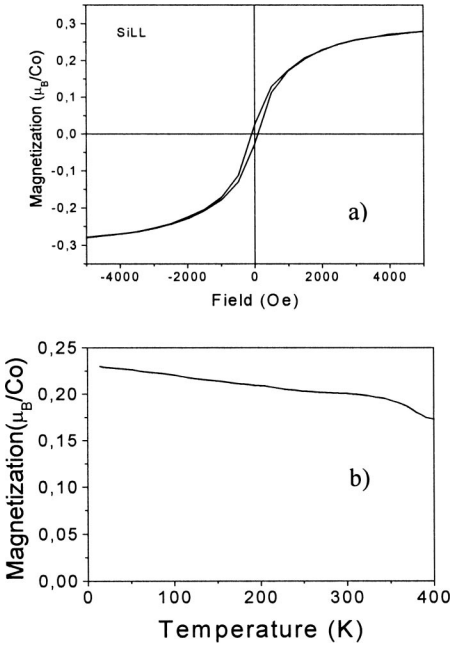

FIG. 2. Magnetization of a $Ti_{0.908}Co_{0.092}O_2$ thin film deposited on a Si substrate under an oxygen pressure of 1×10^{-6} Torr and a fluence of 1.5 J/cm^2 (a) versus magnetic field at 300 K and (b) versus temperature under 0.2 T.

the film has Curie temperature (T_C) higher than 400 K.

As mentioned earlier, an important issue in the field at the moment is how to control the dopant concentration, and to know Co distribution in the films and the nature of ferromagnetism as well. EDX measurements showed that four films with four different conditions have a Co content of 12%, the same as in the synthesized target. SEM images are shown in Fig. 3. The LL and HH films' morphology are similar, rather homogeneous among all, but the films are full of particles. The surface of the LH film seems to be smoothest, even if it has few alien particles on it (white parts). The morphology of the HL film is the worst, with very large white parts that are believed to be excess Co, CoO, or Co_3O_4, since those white parts do not have the spherical shape of normal droplets of thin films, but rather look like

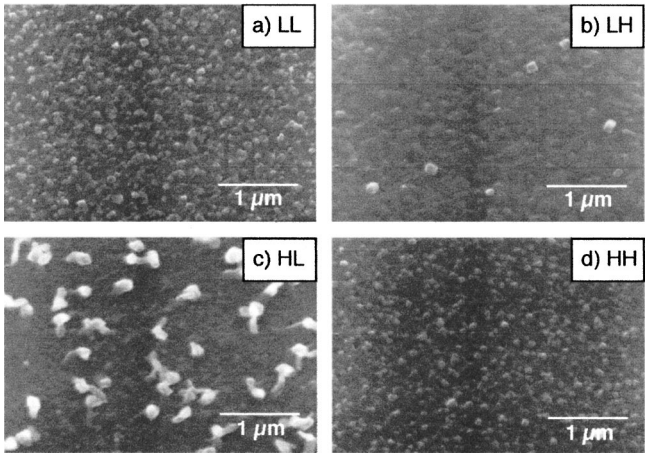

FIG. 3. SEM images of Co-doped TiO_2 films with four different conditions: (a) LL (P_{O_2} of 1×10^{-6} Torr and fluence of 1.5 J/cm^2), (b) LH (1×10^{-6} Torr, 3 J/cm^2), (c) HL (1×10^{-5} Torr, 1.5 J/cm^2), and (d) HH (1×10^{-5} Torr, 3 J/cm^2).

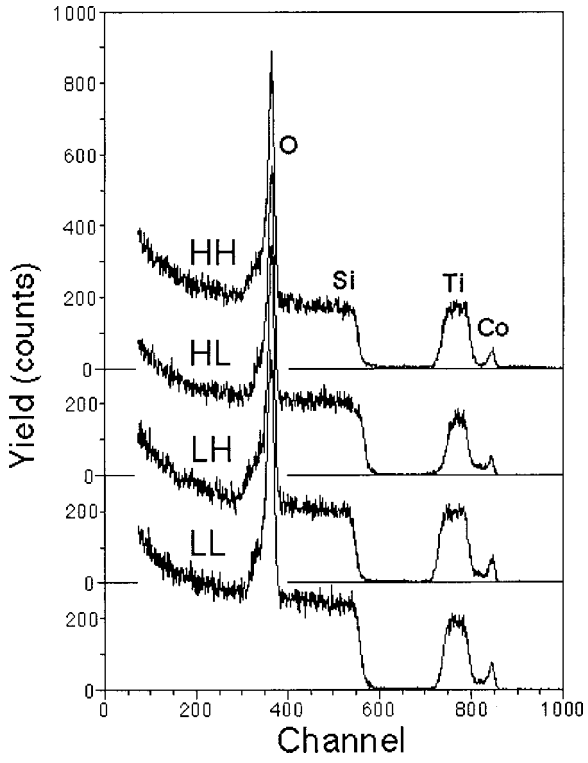

FIG. 4. RBS spectra of Co-doped TiO_2 films with four different conditions: (a) LL, (b) LH, (c) HL, and (d) HH.

outgrowths. Basically, black and white parts are detected from parts that have different electric conductivities, therefore, they are thought to show different compositions. However, we failed to distinguish the difference in compositions of those parts because the detection limit of the EDX technique does not allow us to specifically determine the composition of nanometer-sized particles. Since seeing neither peaks of cobalt nor cobalt oxides in the XRD does not rule out completely the possibility that excess Co or cobalt oxides exist, transmission electron microscopy measurements must be done in the near future.

RBS spectra of Co-doped TiO_2 films are shown in Fig. 4. Based on the obtained data, the Ti:Co ratio for each case can be estimated to be 90.8:9.2 for the LL film, 92.4:7.6 for the LH film, 90.0:10.0 for the HL film, and 93.5:6.5 for the HH film. From RBS data, the highest Co concentration is 10% in the HL film, whose SEM picture shows some outgrowth of excess Co or cobalt oxide. No reasonable explanation can be given for the SEM pictures of the LL film (with 9.2% Co) and of the HH film (6.5% Co) since they are quite the same, and the HH film with lower Co concentration even has some alien particles on it. Thus, it is not very simple to say that when the amount of Co in the target is large, it gives some excess on the film that leads to Co or cobalt oxide particles/clusters. On the other hand, one must say that the way Co atoms distribute in the films depends very much on the growth conditions. As seen in Fig. 4, Co atoms were not distributed uniformly in the films: while Ti peaks have simple rectangular shapes, Co peaks have larger height at the right-hand side (shallower levels, taken from the surface) and smaller height at the left-hand side (deeper levels). Detailed calculations give concrete information: for example, for the LL film, the Ti:Co ratio in the depth from 0 up to 40 nm is 70:30, while in the layer of from 40 to 230 nm thick, it is 94:6, and as a result, the averaged ratio of Ti:Co for the film will be 90.8:9.2 (as mentioned earlier). This means that Co atoms are localized mostly near to the surface of the films, while they exist less in the deeper levels. This RBS result explains why by EDX the Co content was found to be 12% since signals from atoms near the surface are more sensitive in EDX.

It is known that the saturated magnetization of Co metal is 1.7 μ_B/Co. This was confirmed by the experimental evidence of Co-doped TiO_2 films with Co clusters.[5] The value of M_s as 0.31 μ_B/Co in our films shows that the ferromagnetism does not come from Co particles or clusters. This is also confirmed by magnetic force microscopy (MFM) measurements: we found no contrast on the surface of the film with LL conditions, for example; in other words, no particles or clusters were observed and the film is very homogeneous. According to the theory for dopants in Co-doped TiO_2 of Sullivan and Erwin,[9] it seems that our films were grown in the ''rich oxygen condition'' and Co dopants were formed primarily in neutral substitutional form, but not interstitial (''poor oxygen condition'' makes Co concentrations of substitutional and interstitial Co roughly equal, and M_s must be in between 1 and 2 μ_B/Co[4]). It is thought that the magnitude of M_s can be enhanced very much in an appropriate oxygen environment; on the other hand, the homogeneity of the film surely depends strongly on the growth conditions.[10]

In conclusion, we have fabricated room temperature ferromagnetic rutile Co-doped TiO_2 films on silicon substrates by the conventional PLD technique from a ceramic target. Even though the distribution of Co is not uniform, with Co atoms lying mostly near the surface of the films, the ferromagnetism in our Co-TiO_2 films seemingly does not come from Co metals or clusters. Co-TiO_2 films with very high T_C (above 400 K) fabricated by a very simple technique on low-cost silicon substrates are useful for applications. However, the magnitude of saturated magnetization is still modest and a higher homogeneity is still anticipated.

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