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Synthesis and ferromagnetism of Co-doped $\text{TiO}_{2-\delta}$ nanobelts by metallorganic chemical vapor deposition

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$\text{Ti}_{1-x}\text{Co}_x\text{O}_{2-\delta}$ nanobelts were synthesized without using any metal catalysts by metallorganic chemical vapor deposition. The nanobelts consisted of ~ 10 – 20 nm nanocrystallites, which were dominantly rutile structure. The $\text{Ti}_{0.986}\text{Co}_{0.014}\text{O}_{2-\delta}$ nanobelt sample showed a magnetic anisotropy with a high coercive field value (~ 500 Oe) at room temperature, significantly affected by intrinsic effect. In contrast, the $\text{Ti}_{0.982}\text{Co}_{0.018}\text{O}_{2-\delta}$ nanobelt sample revealed isotropic magnetic characteristics due to enhanced Co clustering. A few or several Co clusters per nanobelt were typically observed even in the lightly Co-doped $\text{Ti}_{0.986}\text{Co}_{0.014}\text{O}_{2-\delta}$ nanobelts because of the very thin thickness (~ 20 nm) and high specific surface area of nanobelts. © 2008 American Institute of Physics. [DOI: 10.1063/1.2904648]

One-dimensional (1D) diluted magnetic semiconductor (DMS) nanostructures are of intense interest for fundamental research and promising spintronic device applications.^{1–3} DMS materials with the Curie temperature T_C beyond room temperature (RT) have been extensively studied in realizing the integration of practical spintronic and electronic devices.^{4–10} Among potential DMS materials, transition metal-doped TiO_2 has been extensively studied as one of the most promising candidates^{5–10} since cobalt (Co)-doped TiO_2 ($\text{Ti}_{1-x}\text{Co}_x\text{O}_2$) was shown to be ferromagnetic with T_C up to 400 K.⁵ However, little information is available on the synthesis and characteristics of $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ 1D nanostructures. Synthesis methods of $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ 1D nanostructures have been limited to template-assisted fabrication^{2,3} and solution-based techniques such as hydrothermal treatment¹ so far. Synthesis of $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ 1D nanostructures by chemical vapor deposition (CVD) represents a challenging issue which has not been reported thus far. CVD has several advantages over other reported approaches for compatibility with silicon technology and mass production on large-scale wafers. Another key issue is the origin of the RT ferromagnetism (RTFM) of $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$, whether it is due to an intrinsic or an extrinsic effect (Co clusters).^{5–10} Most of these studies have been focused on thin films, but very few investigations of $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ 1D nanostructures have been reported. Moreover, the Co concentrations of the studied $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ nanotubes were more than 4 at. %.^{1,2} Such a Co concentration can be high enough to form Co clusters. Co clustering has been reported in rutile $\text{Ti}_{0.98}\text{Co}_{0.02}\text{O}_{2-\delta}$ thin films.⁸ Our recent study also shows that the solubility of Co in anatase $\text{Ti}_{1-x}\text{Co}_x\text{O}_{2-\delta}$ thin films was significantly low (<3 at. %).⁹ The high specific surface area of 1D nanostructures can enhance Co clustering because Co atoms strongly tend to segregate onto the surface. In this letter, we report the self-catalytic growth of $\text{Ti}_{1-x}\text{Co}_x\text{O}_{2-\delta}$ nanobelts via metallorganic

CVD (MOCVD) without using any metal catalysts. The Co clustering and RTFM characteristics of very lightly Co-doped $\text{Ti}_{1-x}\text{Co}_x\text{O}_{2-\delta}$ ($x < 2$ at. %) nanobelts have been thoroughly investigated.

$\text{Ti}_{1-x}\text{Co}_x\text{O}_{2-\delta}$ nanobelts were grown on bare sapphire (0001) substrate by MOCVD using $(\text{C}_{11}\text{H}_{19}\text{O}_2)_2(\text{C}_3\text{H}_7\text{O})_2\text{Ti}$ and $\text{Co}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3$. The growth temperature and the pressure were fixed at 510°C and 10 Torr, respectively. The Ti and the Co precursors were bubbled with an argon (Ar) gas flow of 150 and 50 SCCM (SCCM denotes cubic centimeter per minute at STP), respectively. The total flow rate was fixed at 300 SCCM. We noted that all $\text{Ti}_{1-x}\text{Co}_x\text{O}_{2-\delta}$ nanobelt samples studied here were grown by supplying Ar gas only. As a result, the $\text{Ti}_{1-x}\text{Co}_x\text{O}_{2-\delta}$ nanobelt samples were highly reduced and showed a very low resistivity (a few $\Omega\text{ cm}$). The bubbling temperature of the Ti precursor was fixed at 200°C . The Co doping concentration could be controlled by varying Co bubbling temperature. The slope ($-\Delta H$) of the Clausius–Clapeyron equation was gentle enough that Co vapor pressure could be controlled reliably for such a low doping amount used here. The average Co doping concentrations were found to be 1.4 and 1.8 at. % for 180 and 185°C of the Co bubbling temperatures, respectively, as analyzed by an electron probe microanalyzer. The $\text{Ti}_{1-x}\text{Co}_x\text{O}_{2-\delta}$ nanobelts were characterized by vibrating sample magnetometer (Lake Shore 7400 series), field-emission scanning electron microscopy (SEM) (Jeol JSM 7000F), transmission electron microscopy (TEM), and photoluminescence (PL) spectroscopy. To investigate Co clustering, we carried out high angle annular dark field (HAADF) scanning TEM (STEM) study using FEI Tecnai F20 UT.

Figure 1 is a SEM image of $\text{Ti}_{0.986}\text{Co}_{0.014}\text{O}_{2-\delta}$ nanobelts grown on a sapphire (0001) substrate for 10 min. The image shows that nanobelts were formed at a high density and a bunch of several nanobelts were branched at the same place. The nanobelts are $\sim 2\text{ }\mu\text{m}$ in length and the width and the thickness are ~ 100 – 150 and ~ 20 nm, respectively. Figure 2(a) shows a typical bright-field TEM image of a single

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FIG. 1. SEM image of $\text{Ti}_{0.986}\text{Co}_{0.014}\text{O}_{2-\delta}$ nanobelts on sapphire substrate.

$\text{Ti}_{0.986}\text{Co}_{0.014}\text{O}_{2-\delta}$ nanobelt. The TEM image reveals that nanobelts consisted of $\sim 10\text{--}20$ nm size nanocrystallites. Moreover, the high-resolution lattice image [Fig. 2(b)] shows that the nanocrystallites are well aligned with one another. The inset of Fig. 2(b) shows the corresponding digital diffractogram pattern, indicating that nanocrystallites of nanobelts are oriented along the $[211]$ zone-axis rutile phase.

The magnetic properties of the $\text{Ti}_{1-x}\text{Co}_x\text{O}_{2-\delta}$ nanobelt samples were investigated with the magnetic field along in plane ($H_{\parallel}$) and out of plane ($H_{\perp}$) at RT. The diamagnetic background of the substrate was subtracted from the data. As seen in Fig. 3, the $\text{Ti}_{0.986}\text{Co}_{0.014}\text{O}_{2-\delta}$ nanobelt sample reveals the magnetization hysteresis loops with the coercive field (H_C) of ~ 500 Oe, indicating RTFM. Moreover, the sample shows anisotropic magnetic characteristics that the saturation magnetization (M_S) value (~ 40 memu/g) at $H_{\parallel}$ is slightly larger than that (~ 30 memu/g) at $H_{\perp}$. The anisotropic magnetic characteristics may indicate the possibility of the intrinsic DMS characteristics. It was reported that FM by Co clusters in $\text{Ti}_{1-x}\text{Co}_x\text{O}_{2-\delta}$ thin films did not show any significant magnetic anisotropy.⁷ With increased Co doping level to 1.8 at. %, isotropic magnetic characteristics with a significantly increased M_S value (~ 200 memu/g) were observed (the inset in Fig. 3).

To further investigate the origin of the RTFM characteristics of $\text{Ti}_{1-x}\text{Co}_x\text{O}_{2-\delta}$ nanobelt samples, HADDF STEM study was carried out. Figure 4 shows a typical HADDF STEM image of a single nanobelt of the $\text{Ti}_{0.986}\text{Co}_{0.014}\text{O}_{2-\delta}$ sample. The bright spots in the nanobelt tip region reveal the high concentration of Co element, indicating Co clusters

FIG. 2. Typical TEM images of a $\text{Ti}_{0.986}\text{Co}_{0.014}\text{O}_{2-\delta}$ nanobelt. (a) A low-magnification TEM image. (b) A HRTEM image and its digital diffractogram pattern (inset).

FIG. 3. Magnetization curves of the $\text{Ti}_{0.986}\text{Co}_{0.014}\text{O}_{2-\delta}$ and $\text{Ti}_{0.986}\text{Co}_{0.018}\text{O}_{2-\delta}$ nanobelt samples with the magnetic field along in plane and out of plane at RT.

(~ 10 nm size).⁹ A few or several Co clusters per nanobelt were typically observed. Nevertheless, the possibility of intrinsic RTFM cannot be completely ruled out. The magnetic anisotropy with the high H_C value (~ 500 Oe) cannot be explained by the small number of ~ 10 nm size Co clusters. Shinde *et al.*⁸ reported that $\sim 8\text{--}10$ nm Co clusters in rutile $\text{Ti}_{0.98}\text{Co}_{0.02}\text{O}_{2-\delta}$ thin film showed very small H_C (> 50 Oe) at RT. In contrast, the isotropic magnetic characteristics of the $\text{Ti}_{0.982}\text{Co}_{0.018}\text{O}_{2-\delta}$ nanobelt sample seem to be dominantly affected by Co clusters (the inset of Fig. 3). Co clustering occurred at a lower Co doping concentration (~ 1.4 at. %) than previously reported results.⁷⁻¹⁰ We note that the grown $\text{Ti}_{1-x}\text{Co}_x\text{O}_{2-\delta}$ nanobelts are as thin as just ~ 20 nm. Co atoms have a strong tendency to segregate and form clusters on the surface of $\text{Ti}_{1-x}\text{Co}_x\text{O}_{2-\delta}$ during CVD growth⁹ and annealing process.¹⁰ Compared to bulk or thin film, Co clustering can be significantly enhanced in the nanobelts because of a very thin thickness (~ 20 nm) and high specific surface area. Moreover, oxygen vacancies in nanobelts and oxygen-poor CVD growth conditions can stimulate Co clustering further.

Figure 5 shows the PL spectra of undoped $\text{TiO}_{2-\delta}$, $\text{Ti}_{0.986}\text{Co}_{0.014}\text{O}_{2-\delta}$, and $\text{Ti}_{0.982}\text{Co}_{0.018}\text{O}_{2-\delta}$ nanobelt samples at 4 K. The nanobelt samples yield a strong broad PL peak centered at ~ 530 nm along with a very weak peak at ~ 400 nm. The PL peak at ~ 400 nm is assigned to the recombination of excitons from the band edge of TiO_2 . The visible-light peak at ~ 530 nm can be attributed to the recombination from various defects such as oxygen vacancy and Ti^{3+} . By increasing the Co doping concentration, the PL

FIG. 4. HADDF STEM image of a $\text{Ti}_{0.986}\text{Co}_{0.014}\text{O}_{2-\delta}$ nanobelt.

FIG. 5. PL spectra of undoped $\text{TiO}_{2-\delta}$, $\text{Ti}_{0.986}\text{Co}_{0.014}\text{O}_{2-\delta}$, and $\text{Ti}_{0.982}\text{Co}_{0.018}\text{O}_{2-\delta}$ nanobelt samples at 4 K.

intensity remarkably decreases. It indicates that Co dopants act as nonradiative recombination sites and are effectively distributed to the $\text{TiO}_{2-\delta}$ matrix. We note that the PL peak position of the $\text{Ti}_{0.986}\text{Co}_{0.014}\text{O}_{2-\delta}$ nanobelt sample is slightly blueshifted (~ 20 meV) with respect to that of the undoped $\text{TiO}_{2-\delta}$ nanobelt sample. Meanwhile, the PL peak positions of $\text{Ti}_{0.986}\text{Co}_{0.014}\text{O}_{2-\delta}$ and $\text{Ti}_{0.982}\text{Co}_{0.018}\text{O}_{2-\delta}$ nanobelt samples are almost identical. Guha *et al.*¹¹ reported that the PL peak at ~ 540 nm was blueshifted with increased Co doping amount in epitaxial anatase $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ thin films. The PL peak position was not significantly changed above ~ 2 at. %, that they thought was limited Co solubility. In this study, however, the PL peak position is not further blueshifted with increasing Co doping amount from 1.4 to 1.8 at. %. It may indicate that further doped Co atoms are segregated for Co clusters, which contributes to the observed isotropic magnetic characteristics. With increasing temperature, the PL intensity of the $\text{Ti}_{0.986}\text{Co}_{0.014}\text{O}_{2-\delta}$ nanobelt sample was not significantly changed in the range of 4–50 K. Above 50 K, the PL intensity was exponentially decreased with the activation energy of 43 ± 5 meV, which is attributed to losing holes and electrons into thermally activated nonradiative channels. A very weak PL spectrum centered at ~ 500 nm was still observed at RT.

Finally, we like to mention that a vapor-solid (VS) growth mechanism excluding a liquid phase appears to control the $\text{Ti}_{1-x}\text{Co}_x\text{O}_{2-\delta}$ nanobelt formation.¹² It should be emphasized that ~ 100 nm thick thin film was first grown in the earlier growth stage before the formation of the nanobelts. The thin film can provide thermodynamically stable crystal structures acting as the seed for the nanobelt growth.^{12,13} It

has been reported that predeposited thin film was essential for the ensuing self-catalytic growth of nanowires.^{12,13} More details of the self-catalytic growth of $\text{TiO}_{2-\delta}$ nanobelts by MOCVD were reported elsewhere.¹²

In conclusion, Co-doped $\text{TiO}_{2-\delta}$ nanobelts were grown via a VS mechanism without the use of any metal catalysts using MOCVD. The nanobelts consisted of ~ 10 – 20 nm nanocrystallites, which were dominantly rutile structures and well-aligned to one another. An intrinsic effect seemed to significantly contribute to the anisotropic RTFM of the $\text{Ti}_{0.986}\text{Co}_{0.014}\text{O}_{2-\delta}$ nanobelt sample even though a few ~ 10 nm Co clusters per nanobelt were observed. By increasing the average Co doping concentration to 1.8 at. %, the nanobelt sample revealed isotropic magnetic characteristics due to enhanced Co clustering. Co clustering could not be suppressed even in such a lightly doped $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ ($x \sim 1.4$ at. %) nanobelts because of the very thin thickness (~ 20 nm) and high specific surface area of nanobelts.

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