Half-metallic chromium dioxide (CrO$_2$) nanostructures and field-dependent magnetic domain evolution

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Both polycrystalline and epitaxial chromium dioxide structures in nanoscale have been fabricated using selective-area growth technique. Multiple grains were formed in the polycrystalline CrO$_2$ dots larger than 100 nm, however, below which only a single grain was allowed to exist. The lateral growth rate of epitaxial CrO$_2$ nanocrystals was found to be highly anisotropic, which is affected by both the orientation and the deposited thickness. Field-dependent magnetic force microscopy was used to study the domain structures of single crystal CrO$_2$ nanowires. The magnetization states were found to be closely related to the wire width. A striplike domain structure with alternating magnetization parallel to the magnetic easy axis was observed within the CrO$_2$ nanowires aligned along the [010] directions, indicating the existence of a strong uniaxial magnetocrystalline anisotropy. © 2008 American Institute of Physics. [DOI: 10.1063/1.2832315]

Half-metallic chromium dioxide (CrO$_2$) nanowires have high spin polarization at the Fermi level. The existence of such ferromagnets was predicted theoretically long time ago. However, experimentally, chromium dioxide is the only material that has been unambiguously determined to be half metallic.

Studies on different properties of CrO$_2$ have been carried out in the past several years. However, most of the researches were done on bulk films or micron-sized structures. On the other hand, magnetic behaviors are closely related to the element size and dimensionality. As the length scales approach the size of domain wall widths (nanometer scale), lateral confinement and interparticles exchange effects may dominate, rendering different properties from bulk materials. Thus, both for applications and for understanding the fundamental spin-related physics, the study of half-metallic CrO$_2$ nanostructures is of significance.

In this work, we report on the fabrication process of both polycrystalline and epitaxial CrO$_2$ nanostructures. The difference between them is discussed with emphasis on the anisotropic lateral growth rate of epitaxial nanodots. We have investigated the field-dependent domain structures of single crystal CrO$_2$ nanowires using magnetic force microscopy (MFM).

High quality chromium dioxide films can be grown using chemical vapor deposition (CVD) technique with chromium trioxide as a precursor. The crystal properties of CrO$_2$ films made this way are greatly affected by the substrate used. Epitaxial (100)-CrO$_2$ structures were deposited pseudo morphically on single crystal (100)-TiO$_2$ substrates. We also grew polycrystalline CrO$_2$ structures, based on a seed layer of polycrystalline TiO$_2$ film, which was made by oxidizing at 800 °C the Ti film (∼100 nm) sputtered on SiO$_2$-covered silicon wafer.

Since chromium dioxide is not a thermodynamically stable phase at atmospheric pressure and room temperature, it inevitably decomposes and forms a native oxide Cr$_2$O$_3$ layer on the surface. Prior to this work, various methods have been attempted to pattern CrO$_2$ small structures such as reactive ion etching (RIE), wet etching, ion beam milling, and focused ion beam milling. All these methods applied etching to deposited chromium dioxide thin films, which increased the transformation from CrO$_2$ to Cr$_2$O$_3$, resulting in degradation of the quality of CrO$_2$. An alternative approach to make chromium dioxide structures is the selective-area growth technique. It utilizes the fact that during the CVD process, CrO$_2$ grows readily on the surface of TiO$_2$ but not on amorphous SiO$_2$. This way avoids the postdeposition etching and subsequent reduction of CrO$_2$. In this work, we have extended the selective-area growth technique and obtained CrO$_2$ nanostructures down to sub-100-nm scale.

The fabrication process is described as follows. First, a layer of SiO$_2$ (∼100 nm) was deposited onto the TiO$_2$ substrate by radio frequency magnetron sputtering of a Si target in a mixture of argon and oxygen. Then, a layer of positive polymethylmethacrylate (PMMA) with molecular weight of 950 kD was spin coated onto the sample. After a bake at 185 °C for 30 min, the sample was covered with a very thin layer of Cr (∼5 nm) by electron beam evaporation, which served as a charge dissipation layer during the subsequent electron beam lithography. The Cr layer was first removed in chemical etchant solution, and then the sample was developed for 60–65 s in a 1:3 solution of methyl isobutyl ketone: isopropyl alcohol (IPA) followed by rinsing in IPA. The developed PMMA was used as the etching mask for the RIE of the underlying SiO$_2$ layer in the CHF$_3$ atmosphere. Finally, the sample was carefully cleaned in acetone, IPA, and de-

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ionized water before loading into furnace to deposit CrO$_2$ using CVD.

The scanning electron microscopy (SEM) images of polycrystalline CrO$_2$ nanodot arrays are shown in Figs. 1(a) and 1(b). We can see that multiple grains are formed in the dots with diameter $d=250$ nm. However, when $d$ is reduced to about 100 nm, each dot contains only one single grain. This can be understood by considering that, when the size of the holes on the SiO$_2$ template is smaller than the mean grain diameter of the TiO$_2$ substrate ($\sim$100 nm), there is only one TiO$_2$ grain below each hole to support the growth of CrO$_2$. Upon increasing the thickness, the deposited CrO$_2$ reaches the top of the mask and then overgrows both vertically and laterally. Figure 1(c) displays the overgrown CrO$_2$ from 150 nm sized holes. As can be seen, the borders of the holes are completely covered by the CrO$_2$ above the SiO$_2$ mask. The SEM image of a 150 nm wide zigzag wire is shown in Fig. 1(d). The clear grain facets and borders reflect that every grain was grown naturally without any postdeposition damage.

Figure 2(a) displays the SEM image of 100 nm sized epitaxial CrO$_2$ nanodots. As can be observed, all the dots are distinct and aligned in the same crystal direction. Figures 2(b)–2(d) show the morphology of the CrO$_2$ nanodots with different deposited thicknesses $t$. All the dots grew naturally into a rectangular shape, which implies that the lateral (in-plane) growth rate was anisotropic during the CVD process. Otherwise, the dots would form a round shape instead of a rectangular one, since the antidot patterns defined on the SiO$_2$ template were circular. Furthermore, we can see that the aspect ratio of the rectangle is not a constant, and changes with the CrO$_2$ thickness. Hence, the mean lateral growth rate $V$ is affected by both the direction, represented by angle $\theta$ in Fig. 2(f), and the thickness $t$ of the deposited CrO$_2$.

The CrO$_2$ nanocrystal growth process can be physically described as follows. At the beginning of the deposition, CrO$_2$ first covered the TiO$_2$ at the bottom of the holes, but not the adjoining SiO$_2$ due to the selective-area growth. Then beyond a certain thickness, the deposited CrO$_2$ deformed with a preferential lateral growth direction along the $c$ axis, as evidenced in Fig. 2(b). This means that when $t$ was small, $V(\theta,t)$ was maximum for $\theta_m=0^\circ$. It can be attributed to the fact that there is a large lattice mismatch between TiO$_2$ and CrO$_2$ of $\sim$3.79$\%$ along the $b$ axis ([010] direction) and only 1.48$\%$ along the $c$ axis ([001] direction). The chemical vapor deposition favors the growth along the [001] direction for higher lattice match in order to reduce the internal strain energy. When $t$ increased, CrO$_2$ starts to overgrow laterally over the amorphous SiO$_2$ mask. We can see in Fig. 2(c) that in the meanwhile a rectangular shape with long side parallel to the $c$ axis was formed for every dot, indicating the maximum $V(\theta,t)$ was achieved at an angle $\theta_m$ between $0^\circ$ and $45^\circ$, more specifically, the diagonal direction of the rect-

![FIG. 1. SEM images of polycrystalline CrO$_2$ nanostructures: (a) 100 nm sized dots array, (b) 250 nm sized dots array, (c) overgrown CrO$_2$ from 150 nm sized holes, and (d) a zigzag-shaped nanowire with 150 nm in width. The small patterns other than the CrO$_2$ structures are the polycrystalline TiO$_2$ grains below the amorphous SiO$_2$.]

![FIG. 2. SEM images of single crystal CrO$_2$ nanostructures grown on (100)-TiO$_2$ substrate: (a) 100 nm sized dot array, 250 nm sized dot array with different thicknesses (b) $t=100$ nm, (c) $t=160$ nm, and (d) $t=250$ nm; (e) a 100 nm wide zigzag wire with overgrown CrO$_2$ along the [011] direction, and (f) schematic diagram for the mean lateral growth rate $V$ dependent on the orientation, represented by angle $\theta$.]
angle. Upon further increasing the amount of overgrown CrO$_2$, the aspect ratio of the rectangular dots gradually became smaller and stabilized to 1. Our result reveals that when $t$ is large ($\geq 250$ nm), $V(\theta, t)$ is maximum for $\theta_m = 45^\circ$ ([011] direction) giving every dot a square shape. The preferred lateral growth along the [011] direction can also be observed in epitaxial CrO$_2$ zigzag nanowire shown in Fig. 2(e). At this point, the detailed kinetic process for the transformation from a high-aspect-ratio rectangle to a square is unknown. However, we believe that the anisotropic surface binding energy drives this CrO$_2$ nanocrystal growth. Other factors, such as the internal strain due to the lattice mismatch, may also play an important role.

We also investigated the magnetic switching behavior of the epitaxial chromium dioxide nanowires using field-dependent MFM. The sample was first saturated along the magnetic easy axis ([001] direction) and then imaged with a field $H$ applied in the same direction. Figure 3 displays the MFM images of CrO$_2$ wires of various linewidths $w$ aligned along the [010] axis under three different external fields. A single domain structure with magnetization along the applied field direction was observed in Fig. 3(a) for the epitaxial wire with $w=1$ $\mu$m. Upon decreasing the linewidth, multidomain structures were formed with a small number of domains having opposite polarities. This result can be explained by considering the demagnetizing field $H_{d}$, which was found to be roughly proportional to the inverse of linewidth $1/w$.

When $w$ decreased from 1 $\mu$m to 200 nm, the internal field, $H_{\text{int}} = H_{250 \text{ Oe}} - H_{d}$, dropped significantly and thus was energetically unfavorable to maintain a single domain structure. In Fig. 3(b) where the external field $H$ was reduced to 100 Oe, the nucleation of antiparallel domains can be clearly observed as the number of domains with the magnetization reverse to the field direction increased. When the magnetic field was further reduced to zero, the MFM image reflects the remnant magnetization state, which is displayed in Fig. 3(c). A tip-like domain structure, with magnetization parallel or antiparallel to the magnetic easy axis, was observed. It should be noted that the remnant state of the epitaxial CrO$_2$ nanowires are determined mainly by both the shape and magnetocrystalline anisotropy. The former favors an alignment of the magnetic moment parallel to the wire axis, while the latter prefers the magnetic easy axis direction. In our case, the wire axis is perpendicular to the magnetic easy axis, which means that these two effects are in competition with each other. The existence of stripelike domain configuration even for the wire with $w=200$ nm indicates that the magnetocrystalline anisotropy in epitaxial CrO$_2$ is very strong, which makes the shape induced effect almost negligible. Upon further increasing the field in the reverse direction, domains start to annihilate and a similar reversal process has been observed (not shown here).

In summary, we present a new method to fabricate both polycrystalline and single crystal chromium dioxide nanostructures. The use of the selective-area growth technique prevents the damage caused by postdeposition etching and allows us to study the nanocrystal growth process. The epitaxial lateral overgrowth rate was found to be maximum at the [011] directions of (100)-TiO$_2$ substrate. We have also investigated the magnetic reversal process of epitaxial CrO$_2$ nanowires. Due to the strong magnetocrystalline anisotropy, stripe-domain structures were observed for wires with axes perpendicular to the magnetic easy axis direction.

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