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Phase control of chromium oxide in selective microregions by laser annealing

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Laser annealing has been employed to decompose half-metallic CrO_2 into insulating Cr_2O_3 in air ambient. While both Cr_2O_3 and CrO_2 are present, the relative fraction of each phase was controlled by changing the duration and power of laser irradiation. Glancing angle x-ray diffraction and micro-Raman scattering were used to characterize samples before and after laser annealing. The laser-induced decomposition of CrO_2 into Cr_2O_3 that leads to a threefold enhancement of the low-field magnetoresistance and the realization of phase control of the CrO_2/Cr_2O_3 system in selective microregions by laser irradiation implies: (i) optical lithography can be used as a potential method to directly control the magnetotransport properties which are strongly depended on the interface tunneling barrier and (ii) The CrO_2 polycrytalline phase could be much more attractive as a high-density magnetic storage medium. © *2003 American Institute of Physics.*
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I. INTRODUCTION

Chromium oxide (CrO_2) has recently attracted significant interest because it exhibits complete spin polarization at the Fermi level and has been classified as being half-metallic.[1] Band-structure calculations predict almost 100% spin polarization for this material.[2] Spin polarizations of 95% and 90%, the highest among all materials, have been shown by spin-polarized photoemission[3] and point-contact Andreev reflection[4] measurements, respectively. With this half-metallic characteristic, ferromagnetic CrO_2 is expected to show a very large tunneling magnetoresistance (TMR).[5,6] Although previous studies of single-crystal CrO_2 showed little MR below T_C ($T_C \approx 397$ K), [7] several experiments on CrO_2 polycrystalline films and powder compacts have reported high values of MR.[6–9]

The insulating antiferromagnetic chromium oxide Cr_2O_3 has a Néel temperature of 307 K and is suitable for applications as a tunnel junction barrier both below and above the Néel temperature.[7] Hwang and Cheong reported a threefold enhancement of the low-field MR by introducing insulating Cr_2O_3 as an interface tunnel barrier.[8] Furnace thermal treatment is the only reported method used to introduce insulating Cr_2O_3; that is, decomposing CrO_2 into Cr_2O_3. Previous studies on CrO_2 polycrystalline films reported that oxygen ambient with a few hundred bars of oxygen pressure is necessary for decomposition of CrO_2 into Cr_2O_3 [8,10] This limitation was relaxed for the decomposition of CrO_2 powder, and the insulating Cr_2O_3 powder could be prepared by reducing the CrO_2 in vacuum at 500 °C.[7] More importantly for technological applications, the relative portion of Cr_2O_3 phase can be controlled by the oxygen partial pressure.[10] This indicates that the interface tunnel barrier characteristic that determines the magnetotransport properties can be directly controlled. In this work, an alternative method was demonstrated that could transform CrO_2 polycrystalline powder to Cr_2O_3 in macro- and selective microregions by laser annealing in air ambient. The relative fraction of each phase was controlled by adjusting the duration and power of laser irradiation.

II. EXPERIMENT

A Spectra-Physics Nd-YAG laser (LAB 170) operating at a wavelength of 532 nm with an approximately 4-ns pulse duration and 10-Hz repetition rate was used to decompose CrO_2 into Cr_2O_3 in macroregions. The laser beam first passed through an aperture and was then directed by a reflecting mirror. With the quartz plano-convex lens, the laser beam was focused onto the sample surface with a spot size of 5.5 mm in diameter and pulse energy 8.6 mJ, which corresponds to an energy density of $36\,mJ/cm^2$. The duration of laser irradiation was varied up to 90 s. The phase control of CrO_2 in selective microregions was realized by changing the power of an cw Ar-ion laser with an Olympus microscope attachment. The power of laser beam on sample surface was changed between 2 to 10 mW. Our CrO_2 samples were prepared from commercial powders used for magnetic recording (DuPont, 99.5% purity). CrO_2 disks with a diameter of 6 mm and a thickness of about 0.9 mm were cold pressed using a hardened steel die under a pressure of 0.5 GPa. The original CrO_2 powder was analyzed by scanning electronic microscopy (SEM). The phase analysis before and after laser annealing was carried out with a D8 ADVANCE x-ray diffractometer (Bruker Analytical X-ray systems) using glancing angle x-ray diffraction (GAXRD) configuration and a Raman spectrometer (ISA T64000 triple grating system) with an Olympus microscope attachment. In order to avoid laser annealing effect, laser power was limited at 2 mW during Raman measurements.

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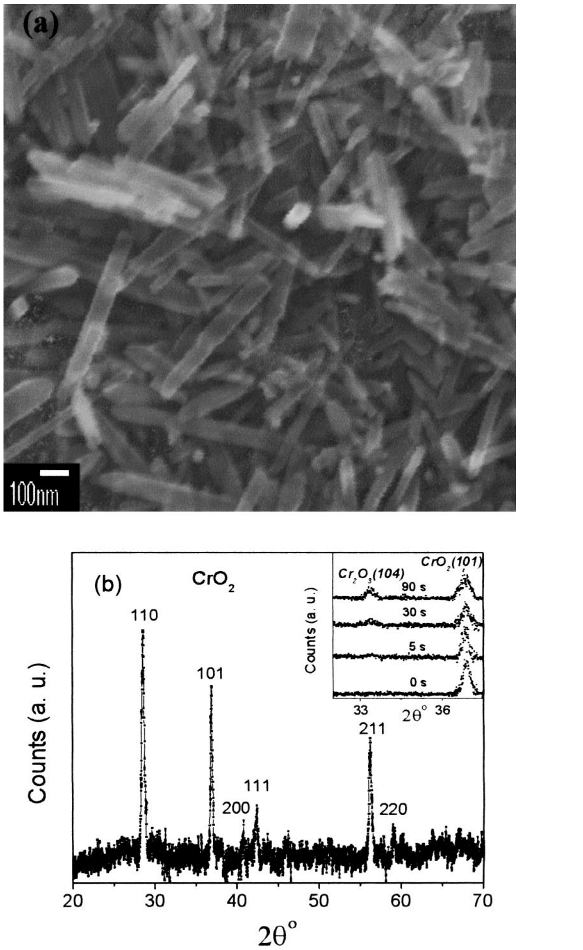

FIG. 1. (a) SEM image and (b) XRD pattern of the original CrO_2 powder. Inset shows the detailed XRD patterns of pulsed-laser annealed CrO_2 powder for various durations.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the SEM image of the original cold-pressed CrO_2 sample. The CrO_2 powder is composed of rod-shaped particles. The aspect ratio of these particles is about 8:1, and the average length is about 300 nm. It is also clearly shown that the elongated CrO_2 particles oriented randomly.

Due to its sensitivity to the sample surface,[11] GAXRD was used to characterize the CrO_2 powders before and after pulsed-laser annealing. Figure 1(b) shows the XRD pattern of the original CrO_2 powder. Six peaks at 2θ angles of 28.5°, 36.9°, 40.8°, 42.4°, 56.1°, and 58.9° were observed, corresponding to the (110), (101), (200), (111), (211), and (220) planes of the polycrystalline CrO_2, respectively.[12,13] It demonstrates that the original CrO_2 powder is of high purity and contains no measurable Cr_2O_3. Figure 1(b) also shows the detailed XRD patterns of laser-annealed samples for various laser irradiation times from 0 to 90 s. A weak and broad peak centered at 2θ angle of about 33.4° was observed in the XRD trace of the 5-s laser-annealed sample. This peak grew stronger with increase in anneal duration, and was assigned to the (104) plane of Cr_2O_3.[14] Our micro-Raman scattering study discussed subsequently strongly supported this assignment and also identified the second phase as Cr_2O_3. When the original CrO_2 sample was subjected to a laser annealing for 30 s, the broad diffraction peak was greatly strengthened and became obvious. The appearance of the Cr_2O_3 diffraction peak demonstrates that the decomposition of half-metallic CrO_2 into insulating Cr_2O_3 can be triggered by laser annealing. Upon laser annealing for 90 s, the Cr_2O_3 diffraction peak was well established. Estimation of the normalized intensity of the XRD peaks[14] shown in Fig. 1(b) inset indicates that increasing the laser irradiation time under a fixed laser power density can dramatically increase the relative fraction of the Cr_2O_3 phase.

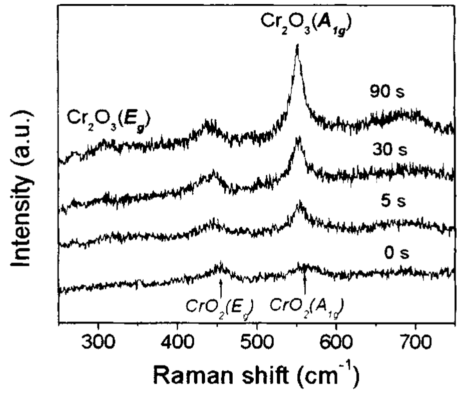

FIG. 2. Raman spectra of the samples before and after pulsed-laser annealing.

Raman spectroscopy was also employed to characterize the laser-annealed samples. CrO_2 has a rutile structure with $P4_2/mnm$ space group. There are eight normal modes given by

$$\Gamma = A_{1g} + B_{1g} + B_{2g} + E_g + A_{2u} + 3E_u,$$

in which four optic modes are Raman active ($A_{1g} + B_{1g} + B_{2g} + E_g$) and four are infrared active ($A_{2u} + 3E_u$).[15] Figure 2 shows the Raman spectra of the samples before and after laser annealing. Similar to results reported in the literature, only two weak peaks at 455 and 573 cm^{-1}, corresponding to the E_g and A_{1g} modes of CrO_2, respectively,[16] were observed in the Raman spectrum of the original CrO_2 sample. In comparison with the XRD results, the Raman spectrum of the 5-s laser-annealed sample shows a sharp peak centered at 549 cm^{-1}, which corresponds to the A_{1g} mode of Cr_2O_3.[17] Since the A_{1g} Raman peak of Cr_2O_3 is strong, Raman spectroscopy provides higher sensitivity compared with XRD.[18] With a spatial resolution of about 0.5 μm, Raman spectroscopy is also advantageous in characterizing patterned samples with small features. Another Raman mode, the E_g mode[17] of Cr_2O_3 at 303 cm^{-1} appeared after 30-s laser annealing. Upon 90-s laser annealing, both the E_g and A_{1g} modes belonging to the Cr_2O_3 were further strengthened and well established, implying the increased amount of Cr_2O_3. Our Raman results are in good agreement with the XRD phase analysis showing that the decomposition of the half-metallic CrO_2 into the insulating Cr_2O_3 can be triggered by laser annealing in air ambient and the relative fraction of each phase depends on the laser irradiation time.

The decomposition of CrO_2 into Cr_2O_3 in selective microregions was studied by SEM and micro-Raman scattering in this work. As shown in Fig. 3(a), upon scanning a cw laser

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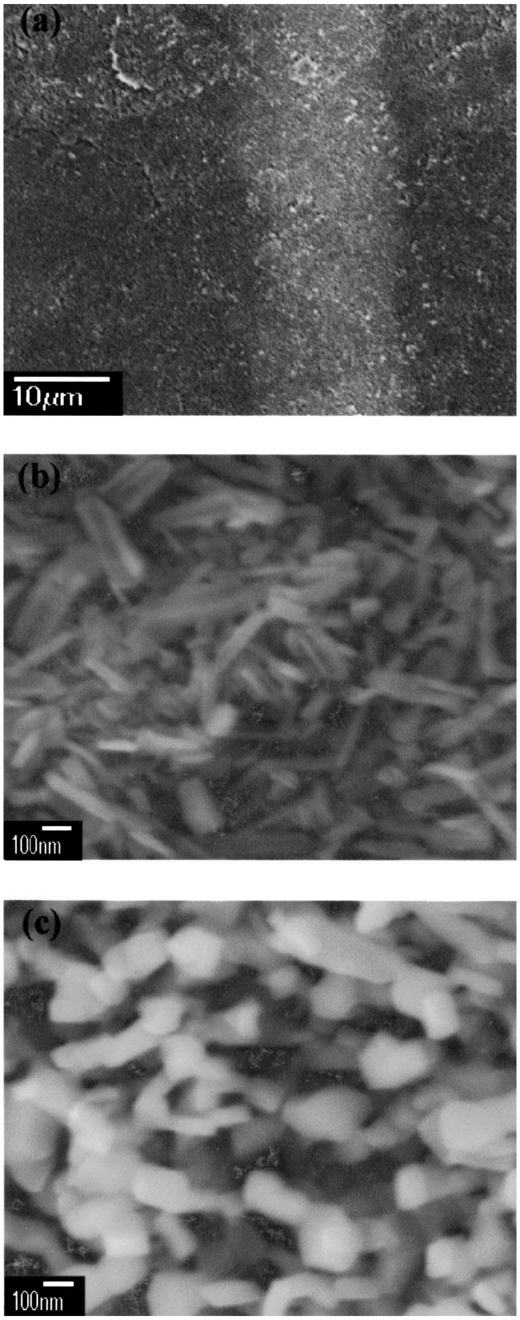

FIG. 3. SEM images of the selectively laser-annealed microregions of CrO_2 powder with laser power of (a), (b) 6 mW and (c) 10 mW.

of 6-mW power, a line about 12 μm in width was clearly observed. The obvious difference in the round grain boundary and the appearance of spherical particles shown in Fig. 3(b) compared with the rod-shaped morphology of the original CrO_2 powder [Fig. 1(a)], implies that a second phase may be formed under this condition. After laser annealing at a higher power (10 mW), as shown in Fig. 3(c), the rod-shaped CrO_2 particles were almost completely transformed into spherical particles expected for Cr_2O_3.[14]

The Raman spectra of the corresponding selective microregions shown in Fig. 3 are similar to the Raman scattering results derived from pulsed-laser annealing in macroregions, whereas no CrO_2 phase was observed upon laser annealing with 10-mW laser power [SEM image shown in Fig. 3(c)]. The appearance, subsequent development, and finally the establishment of pure Cr_2O_3 spectrum demonstrate the ability of laser annealing in controlling the fraction of CrO_2/Cr_2O_3 phase.

IV. CONCLUSION

Phase control of half-metallic CrO_2 powder in macro- and microregions has been realized by laser annealing in air ambient. The ability to control the relative fraction of CrO_2 and Cr_2O_3 phases with the laser irradiation time and power indicates that optical lithography is a potential method to directly control the magnetotransport properties determined by the interface tunnel barrier, Cr_2O_3 in this work. The study on laser-induced phase control of CrO_2 polycrystalline film, in selective areas micro/nano in size, is in process. This opens an interesting approach for designing useful MR properties for MR materials, especially for materials with TMR properties.

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