Selective-area growth, which consists of depositing a material over a substrate in such a fashion that material is deposited on specific regions of a substrate that have been appropriately modified, is an established technique in the field of compound semiconductor and metal deposition.\(^1\)–\(^4\)

For example, selective-area growth followed by lateral epitaxial overgrowth has been used for the production of improved quality thin films of a variety of III/V compounds for optoelectronic devices.\(^1\)–\(^3\) Similarly, in the case of metals, selective growth has been used for applications such as plugs for hole filling in integrated circuits.\(^4\) Other materials of technological interest, such as ferromagnetic and ferroelectric oxides, can also benefit from selective growth if suitable processes can be developed for these materials.

Chromium dioxide (CrO\(_2\)) is a ferromagnetic oxide that is widely used as a particulate recording medium in storage applications.\(^5\) Theoretical calculations\(^6\) and experimental results\(^7\) suggest that CrO\(_2\) also has a half-metallic band structure, where the electrons are completely spin polarized, with one spin channel being metallic while the other semiconducting. This makes it attractive for use in ferromagnetic/insulator/ferromagnet tunnel junctions with enhanced low-field magnetoresistance.\(^8\) Since CrO\(_2\) is not readily etched in reactive plasma or with wet chemicals, the conventional method of patterning blanket thin films using photolithography and etching is difficult. Selective growth would then be a preferred approach for fabricating tunnel junctions since it requires no subsequent etching steps. Moreover, by utilizing the property of lateral overgrowth that arises from selective growth, high quality, defect-free CrO\(_2\) layers can be produced for other applications.

In this letter we report on the selective-area growth of CrO\(_2\) on top of a TiO\(_2\) template using chemical vapor deposition (CVD). Selective-area epitaxy and lateral overgrowth has been achieved on single crystal TiO\(_2\) substrates patterned with a TiO\(_2\) thin film mask. Localized deposition of polycrystalline CrO\(_2\) has also been obtained on patterned single crystal TiO\(_2\) substrates deposited on oxidized silicon wafers. The titanium layer in this case is oxidized prior to deposition. Suzuki and Tedrow have recently reported a similar approach for selective growth of CrO\(_2\) on glass substrates.\(^9\)

We have previously reported on the growth of high-quality thin films of CrO\(_2\) on TiO\(_2\) and Al\(_2\)O\(_3\) substrates using a simple atmospheric pressure CVD system.\(^10\)\(^11\) Briefly, oxygen is used as a carrier gas in a two-zone furnace to transport sublimed CrO\(_3\) precursor from the source region to the reaction zone where it decomposes on the substrate to form CrO\(_2\) with evolution of O\(_2\). The phase purity and morphology of the films is dependent on the substrate and source temperatures, and the oxygen flow rate. Single-phase films have been obtained at substrate temperatures of 390–450 °C, with a source temperature of around 280 °C, and oxygen flow rate of ~100 sccm. We have found that the deposition of CrO\(_2\) is highly sensitive to the surface of the substrate. While CrO\(_2\) grows readily on a clean TiO\(_2\) surface, it does not deposit on amorphous SiO\(_2\). Thus, the spatial growth of CrO\(_2\) can be controlled selectively by appropriately prepatternning the substrate surface.

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Epitaxial growth of CrO$_2$ has been achieved on single crystal TiO$_2$ substrates with (100), (110), and (001) orientation. Figures 1(a)–1(c) shows the normal $\theta$–$2\theta$ x-ray scans around the (200), (220), and (002) peaks of the film and the substrate for films grown on TiO$_2$ substrates with the three orientations. The higher order peaks could not be accessed using our setup. There is a large lattice mismatch between CrO$_2$ and TiO$_2$, being $-3.79\%$ along (100) and (010), and $-1.48\%$ along (001). This results in an in-plane tensile strain in the film, and a corresponding compression in the perpendicular direction. Accordingly, there is a shift in the normal Bragg peak positions for the CrO$_2$ films to higher angles than in the bulk. The rocking curve full width at half maximum (FWHM) of the CrO$_2$ peaks on the three substrates are quite narrow, being $\sim0.1^\circ$, $0.4^\circ$, and $0.3^\circ$ for films grown on (100), (110), and (001) oriented substrates, respectively. These results can be reproducibly obtained provided the substrates are adequately cleaned prior to deposition.\(^{11}\)

For selective-area growth, patterned SiO$_2$ was obtained on the TiO$_2$ substrates using conventional photolithography and liftoff using a radio-frequency (rf) magnetron sputtering. Figure 2(a) shows a scanning electron microscopy (SEM) image of selective-area epitaxial growth of CrO$_2$ on a (100) TiO$_2$ substrate prepatterned with SiO$_2$. As seen in Fig. 2, CrO$_2$ grows selectively within the stripe window opening on TiO$_2$, but not on the adjoining SiO$_2$ surface. The growth on the TiO$_2$ surface is of high quality as evidenced from the smooth growth microstructure. Similar results have also been obtained for growth on (110) and (001)-oriented TiO$_2$ substrates prepatterned with SiO$_2$ mask. Since CrO$_2$ is a metastable phase, the presence of a crystalline template is important to provide epitaxial stabilization of the phase. It is believed that because of the favorable interfacial energy, nucleation of CrO$_2$ is facilitated on the TiO$_2$ surface, but not on the amorphous SiO$_2$ surface—thereby resulting in the selectivity.

With increasing thickness, the deposited CrO$_2$ grows vertically to the top of the mask and then grows both laterally over the mask and vertically. This is evidenced in the cross-sectional SEM photograph shown in Fig. 2(b). Lateral overgrowth from the sides onto the SiO$_2$-covered surface occurs due to the growth of the side facets of the deposited CrO$_2$. In the vertically grown regions, the CrO$_2$ will have a high dislocation density because of the large mismatch with the TiO$_2$ substrate. The lateral overgrowth is, however, expected to be substantially defect-free, since the surface is amorphous SiO$_2$, and offers no lattice mismatch.\(^{2,3}\) Thus, the defects propagate upwards on the CrO$_2$ growth in the defective region and no lateral migration of the defects occurs on the overgrowth region. It should be noted that this is a general technique, and has been successfully employed in the past for the growth of compound semiconductors such as GaAs and GaN.\(^{1-3}\)

We have found that the lateral overgrowth rate and facet formation behavior is dependent on the orientation of the stripe openings relative to the crystallographic axes of the substrate. Figure 3 shows a SEM photograph of selective-area growth and lateral overgrowth of a 1.4 $\mu$m film from a series of 2 $\mu$m parallel stripe openings in SiO$_2$ separated by 2 $\mu$m for four different orientations on a (100) TiO$_2$ substrate.

FIG. 1. Normal $\theta$–$2\theta$ x-ray diffraction patterns for CrO$_2$ films grown on (100), (110), and (001)-oriented TiO$_2$ substrates. The plots show only the scan range around the (200), (220), and (002) peaks for the respective films in (a), (b), and (c).

FIG. 2. Scanning electron microscopy (SEM) photograph of: (a) selective-area growth of an epitaxial stripe of CrO$_2$ on (100) TiO$_2$ substrate prepatterned with SiO$_2$; (b) cross-section image showing lateral overgrowth of CrO$_2$ on the SiO$_2$ masked region. The SiO$_2$ thickness is $\sim1000$ $\AA$ and the CrO$_2$ film is 1.2 $\mu$m thick.

FIG. 3. SEM photograph showing selective-area and lateral overgrowth of CrO$_2$ film on (100) TiO$_2$ substrate for four different stripe orientations marked in the figure. The substrate is prepatterned with a series of 2 $\mu$m parallel stripe openings in SiO$_2$ separated by 2 $\mu$m for the four orientations. Inset at the bottom left shows a magnified view of the overgrowth for the 90° orientation showing the isosceles trapezoidal cross section. The 0° and 90° orientations correspond to the (010) and (001) crystallographic orientations, respectively.
In summary, selective-area and lateral overgrowth of CrO$_2$ using CVD has been demonstrated on single crystal TiO$_2$ substrates with SiO$_2$ mask. The lateral growth rate and facet formation behavior is dependent on the orientation of the stripe openings. Polycrystalline CrO$_2$ films can also be deposited selectively by using a prepatterned Ti film that is oxidized prior to growth. The selective growth process should prove useful for patterned deposition of CrO$_2$ films in a number of applications, including magnetic tunnel junctions and storage media.

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