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Epitaxial growth of ruthenium dioxide films by chemical vapor deposition and its comparison with similarly grown chromium dioxide films

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Abstract

Epitaxial ruthenium oxide (RuO_2) thin films have been grown on (100) TiO_2 substrates by chemical vapor deposition at temperatures as low as 300 °C using tris(2,2,6,6-tetramethyl-3,5-heptanedionato)ruthenium [$Ru(TMHD)_3$] as a precursor with oxygen carrier gas. These films exhibit low resistivity, with room-temperature values as low as ~40 μΩ cm. The surface morphology, epitaxial strain and resistivity as a function of film thickness have been compared with those of similarly deposited epitaxial CrO_2 films on TiO_2. The temperature dependence of the resistivity for both set of films can be fit well using a combination of the Bloch-Gruneisen formula for electron–phonon scattering and additional scattering terms, including magnon scattering in the case of CrO_2.
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1. Introduction

Ruthenium dioxide (RuO_2) exhibits a rare combination of material properties; including a relatively low resistivity (~35 μΩ cm at room temperature), good thermal stability and high resistance to chemical corrosion [1]. These desirable characteristics have attracted attention for its application in diverse fields both in the electronics and chemical industry. In the area of microelectronics, RuO_2 has been proposed for use as an interdiffusion barrier and also as a precision resistor element [2–4]. Recent studies have also demonstrated its utility as a contact electrode material in ferroelectric random access memory devices that offers superior polarization fatigue properties with very low leakage current [5–7].

Bulk RuO_2 has a tetragonal structure (a=b=0.4499 nm, c=0.3107 nm), and is closely lattice matched with isostructural rutile oxides, such as TiO_2 (a=b=0.4594 nm, c=0.2958 nm) and CrO_2 (a=b=0.4421 nm, c=0.2916 nm). While TiO_2 is an insulating oxide, CrO_2 is a ferromagnetic half-metal in which the carriers are completely spin polarized [8]. In the past, our group and others have reported on the epitaxial growth of CrO_2 thin films on TiO_2 substrates using chemical vapor deposition (CVD) under atmospheric conditions and have studied its electrical and magnetic properties [9–12]. In this paper, we report on the low-temperature epitaxial growth of RuO_2 films on (100)-oriented TiO_2 substrate using atmospheric pressure CVD and compare its structural and electrical properties with similarly grown CrO_2 films. In recent years, there have been a number of reports on the CVD growth of RuO_2 films using various metal-organic precursors [13]. However, most of the effort has been

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directed towards deposition of polycrystalline thin films on substrates relevant for present-day electronic applications, such as Si and SiO_2. There has been limited work on the epitaxial deposition of RuO_2 films on lattice-matched substrates, such as TiO_2, MgO and Al_2O_3, and for the most part the growth in these cases have required relatively high temperatures (≥500 °C) [14–16].

Motivated by the giant magnetoresistance (GMR) effect in traditional ferromagnet/metal/ferromagnet multilayers, we have been interested in the possibility of fabricating heteroepitaxial oxide structures, such as $CrO_2/RuO_2/CrO_2$, and investigating their magnetoresistive (MR) properties. Band structure calculations suggest that such heterostructures can possibly exhibit significantly enhanced MR resulting from transport of completely spin-polarized carriers from the ferromagnetic CrO_2 layers across the conducting, but non-magnetic, RuO_2 spacer layer and interfaces [17]. The fabrication of such multilayer structures has, however, proven to be a challenging task, primarily because of the process limitations. Because of the metastabilty of CrO_2, it is difficult to synthesize at normal atmosphere, and there is only a narrow temperature window around 400 °C that single-phase epitaxial films of this material can be grown using CVD. In addition, CrO_2 is unstable at much higher temperatures, as it decomposes to form Cr_2O_3. It is thus necessary to identify an adequate precursor(s) that will enable growth of RuO_2 under process conditions compatible with the growth and stability of CrO_2. By using tris(2,2,6,6-tetramethyl-3,5-heptanedionato)ruthenium [$Ru(TMHD)_3$] as a CVD precursor [18], we have achieved growth of high-quality epitaxial RuO_2 films at temperatures as low as 300 °C. The ability to deposit RuO_2 films under conditions that are well-suited with the growth of CrO_2 now offers the possibility of fabricating RuO_2/CrO_2 heterostructures and investigating their MR properties and magnetic anisotropy.

2. Experimental details

Epitaxial RuO_2 films are grown on (100)-oriented TiO_2 substrates by the thermal decomposition of $Ru(TMHD)_3$ precursor (99%, STREM Chemicals) under atmospheric conditions in a 1-in. diameter quartz CVD reactor tube placed inside a two-zone furnace. The precursor material is loaded inside a small quartz boat in the source zone, while the substrates are placed in the higher temperature reaction zone on a specially designed susceptor with independent heating capability. Prior to placement in the susceptor, the TiO_2 substrates are ultrasonically cleaned with acetone and isopropyl alcohol and then dipped in a dilute HF bath for a few minutes. They are subsequently rinsed in de-ionized water and blown dry. Oxygen is used as a carrier gas for the precursor with typical flow rates of about 50 cm^3/min. The use of a susceptor that has independent temperature control provides added flexibility for optimizing the process conditions for film growth and uniformity by controlling the decomposition zone of the organometallic precursor in the proximity of the substrate. We have achieved epitaxial growth of RuO_2 films, with good uniformity, at substrate temperatures of 300–400 °C, while the source temperature maintained at 130 °C. The film roughness has been observed to increase with growth temperature, and all the reported results in this paper are for RuO_2 films grown at 300 °C, unless mentioned otherwise. The same setup has been utilized for the epitaxial growth of CrO_2 films on (100) TiO_2 substrates using CrO_3 as a precursor [9]. For optimal growth, the precursor and substrate temperatures in this case are maintained at 260 and 400 °C, respectively. The film surface morphology is characterized on a Digital Instruments AFM with Veeco Nanoscope III SPM controller and standard TappingMode with Si cantilever tips oscillating at about 200 kHz are used for all the measurements. The structural characterization is performed in a Philips X'Pert XRD system operating with Cu Kα1 and Kα2 radiation. Film resistivity is measured with four-probe method on Hall bars (8:1 aspect ratio) patterned along *b* or *c* directions by ion-milling.

3. Results and discussion

Although RuO_2 and CrO_2 possess the same rutile structure, there are significant differences in the lattice-strain properties of the respective films deposited on (100) TiO_2 substrate that influence their growth characteristics. As compared to the TiO_2 lattice, bulk RuO_2 has a lattice mismatch of about −2.1% and +5.0% in the [010] and [001] directions, respectively. The equivalent mismatch numbers for CrO_2 are −3.8% and −1.4%. Thus, RuO_2 thin films experience a combination of tensile and compressive strain in the two in-plane directions, with more influence of the latter directed along [001]. In contrast, the CrO_2 films grow with tensile strain in both directions, with [001] being the direction of lower strain. Interestingly, the differences in the strain characteristics of the two films are reflected in their growth morphology, as seen in the atomic force microscopy (AFM) images in Fig. 1. For the growth of both materials, one observes the formation of rectangular platelets, with the orientation of the long axis of the platelets being along the direction of lower strain. Thus, in the case of RuO_2, the grains nucleate and grow preferentially along the [001] direction leading to formation of platelets oriented in this direction, whereas for CrO_2 the platelets are aligned along the [001] direction. The aspect ratio of the platelets appears to be controlled by the strain anisotropy, with the CrO_2 films exhibiting platelets with smaller aspect ratio because of the lower anisotropy. In addition, the average grain size and the root mean square (RMS) roughness scale linearly with thickness in both cases (see Fig. 1), with the ratio of the RMS roughness to the thickness being ~5.6% and 3.2% for the RuO_2 and CrO_2 films, respectively. We have previously reported on the growth of strain-free CrO_2 on TiO_2 substrates

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