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Enhanced magnetoresistance in pulsed laser deposited stable chromium oxide thin films

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ABSTRACT

Granular thin films of primarily rutile type tetragonal chromium dioxide (*t*-CrO_2), along with a minor phase of hexagonal Cr_2O_3 were deposited on rutile type TiO_2 layers by KrF excimer laser based pulsed laser deposition (PLD) technique using Cr_2O_3 targets. The TiO_2 under-layer was also deposited by PLD process on oxidized Si substrates followed by annealing at 1100 °C for 10–15 min under O_2 ambient. The lattice-matched interfacial TiO_2 layer stabilizes the metastable Cr (IV) phase of CrO_2, otherwise it readily converts into its stable phase of Cr (III) oxide, Cr_2O_3, under ambient conditions. Studies with X-ray diffraction (XRD) and Raman spectroscopy confirmed the stable *t*-CrO_2 phase in the films. The microstructure in the films was studied with field emission scanning electron microscope (FESEM) and magnetic force microscope (MFM). As revealed by electrical analysis, the ferromagnetic (FM) *t*-CrO_2 grains in conjunction with the antiferromagnetic (AFM) Cr_2O_3 phase in the tailored thin films effectively support an electrical transport process based on inter-granular spin-dependent tunneling (SDT) mechanism, giving rise to significantly high magnetoresistance (MR). A typical sample exhibits a markedly improved MR-value, *viz.*, −30% at an applied field (*H*) of 438 kA/m at 278 K, than reported values in CrO_2 thin films. Such a large MR value in the Coulomb blockade regime arises primarily not only because of the considerably suppressed spin flipping but also as a result of the highly effective SDT mechanism through an interlinked FM-AFM structure of chromium oxides in this specially engineered microstructure of the thin films. Such type of stable half-metallic thin films with low-*H* switching behavior is attractive for pertinent use in spintronics and magnetic sensing based applications.

1. Introduction

Half-metallic CrO_2 is an attractive functional material having almost 100% spin-polarization (typically at low temperatures) along with a high Curie temperature (T_C) of 395 K [1–9]. It displays low-*H* magnetic switching behavior, which makes it suitable for advanced applications in broad areas in spintronics and magnetic sensing [8,9]. CrO_2 is a half-metal because of its typical spin population distribution at the Fermi level E_F, where one spin species shows metallic character and the other semiconducting nature [1,5–7]. The observed peculiarity in the spin structure of CrO_2 makes it a highly effective spin-injector for spin field effect transistors (*spin*-FETs) and other SDT-based devices [2–4,8]. An efficient spin-facilitating channel in between the source and drain electrodes of CrO_2 with high spin-injection and spin-detection efficiencies coupled with the low-*H* switching behaviour can form an highly-efficient *spin*-FET structure for logic and memory operations [10–12]. Furthermore, magneto-optical properties of CrO_2 can add appealing features to the unusual spin-dependent transport properties, and applications based on the coupling of the two phenomena can be realized [13–16].

In spite of the above advantages, the main difficulty associated with CrO_2 is its natural conversion to Cr_2O_3, the most stable oxide phase of Cr, under ambient conditions [4–7]. In air, it reacts with moisture, forming a topotactic CrO(OH) surface layer [4,8,14]. If not controlled, the layer grows into β-CrO(OH) polymorph in a hexagonal or distorted orthorhombic crystal structure [4,14,17]. As a result, CrO_2 surface degrades into Cr_2O_3 at a temperature of 200 °C. A complete $CrO_2 \rightarrow Cr_2O_3$ conversion occurs at temperatures above 400 °C according to microstructure [17–19]. Liang et al. [20] observed such conversions even at room temperature in CrO_2 thin films grown with chemical vapour deposition (CVD) technique. Consequently, the structural defects that deteriorate the saturation magnetization (M_S) and other magnetic and electrical properties vary sensitively, and are not easy to cure permanently by annealing such CrO_2 particles or thin films in O_2 gas [14,21]. The appearance of Cr_2O_3 as a surface layer in such CrO_2 particles is confirmed conclusively with X-ray photoelectron spectroscopy (XPS)

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studies [15]. Such Cr_2O_3 surface layers, if not controlled, expands at the cost of the useful CrO_2 phase. However, a uniform surface layer of Cr_2O_3 modifies the CrO_2 grain boundaries and acts as an ideal tunnel barrier (improves MR and other properties) for the intergranular SDT in small CrO_2 particles or granular thin films [2–4,8,18,22–24].

Stabilization of the tetragonal crystal structure of CrO_2 in the form of thin films or granular particles has been a matter of intense research interest in the recent past. Extensive research efforts were devoted to obtain high quality stable CrO_2 thin films utilizing lattice-matched interfacial layer or substrates of RuO_2, Al_2O_3, or TiO_2 [2,3,25–37]. However, the TiO_2 received the maximum attention, primarily because of its easy deposition process, high resistivity (ρ), cost effectiveness and being the most apposite for integration with Si microelectronics. Detail description of the deposition of CrO_2 thin films on TiO_2 substrates by CVD or physical vapour deposition (PVD) type techniques are available in many of these reports. For example, Suzuki and Tedrow reported the deposition of CrO_2 thin films by CVD on TiO_2 layer prepared by oxidation of Ti metal on Si(111) substrates [25]. Bullen and Garrett reported the deposition of epitaxial CrO_2 (110) films on TiO_2 (110) substrates by CVD [28]. Liu et al. reported the MR studies of CrO_2 films deposited on lattice-matched TiO_2 prepared by DC sputtering of Ti metal target and subsequent oxidation on $LaAlO_3$ substrates [29]. Son et al. deposited epitaxial CrO_2 films on $Pt/TiO_2/SiO_2/Si$ substrates with *c*-axis oriented along in-plane direction [31]. Gupta et al. reported on selective area deposition method of CrO_2 thin films in specific regions of a pre-patterned surface on SiO_2 grown on single crystal TiO_2 substrates and on oxidized Ti films [38]. In literature, there are also few reports on the deposition of CrO_2 thin films using relatively unconventional laser based methods [39–45]. Such techniques are considered to be suitable for depositing thin films of metastable phases, non-stoichiometric compositions or multi-component phases at relatively low temperatures [46]. Shima et al. used KrF excimer laser based PLD process to grow CrO_2 (200) films on Si (111) substrates using Cr_2O_3 targets [39]. Popovici et al. reported the deposition of thin films of a mixture of chromium oxides from Cr_8O_{21} targets by PLD process [40]. Guinneton et al. also followed PLD process to deposit CrO_2 films using CrO_3 and Cr_8O_{21} targets [41]. Heinig et al. fabricated needle and plate-like nanostructures of CrO_2 on MgO (100) substrates by pulsed laser ablation technique of metallic Cr in O_2 ambient [42]. Jalili et al. extensively used PLD technique for the deposition of chromium oxide films on MgO(100), Al_2O_3(0001), $SrTiO_3$(100), $LaAlO_3$(100) and Si (100) substrates [43]. Madi et al. followed plasma assisted PLD method to deposit thin films of chromium oxides on Si(100) using Cr_2O_3 target [44]. Caricato et al. deposited thin films of a mixture of chromium oxides on Si substrates by KrF laser ablation of Cr target in O_2 atmosphere by reactive pulsed laser ablation technique [45]. The humongous efforts being made in the development of stable CrO_2 thin films by different processes highlights the importance and need of this material in fabricating advanced devices. Although PLD technique has been used for the deposition of stable CrO_2 thin films, still there are several complicacies, which are to be resolved for successful use of this rather simple technique in fabricating high quality reproducible CrO_2 thin films for state of the art applications.

Here, we report on the deposition of stable granular thin films of *t*-CrO_2 on lattice matched TiO_2 layers, as a part of our task on the development of CrO_2-based *spin*-FET devices. The wide band gap TiO_2 is selected not only as a buffer layer to stabilize the top CrO_2 layer but also as an active component (tunnel barrier layer) of the proposed *spin*-FET devices. The PLD process parameters were optimized to deposit stable CrO_2 thin films using Cr_2O_3 targets. The TiO_2 layer was also deposited by PLD process on oxidized Si substrates. Structural, magnetic and MR properties of the films were reported in correlation with the film microstructure.

2. Experimental details

As described elsewhere [24], *p*-type Si (100) wafers (ρ = 0.04–0.07 Ω-m) were used in this work. Dry thermal oxidation (1100 °C, 2 h) was performed to grow an 80 nm thick layer of SiO_2 on the wafers. A PLD system of *COHERENT COMPexPro 201* with a KrF excimer laser (248 nm) was employed to deposit the TiO_2 and CrO_2 films. The duration and repetition rate of the laser pulses were 30 ns and 10 Hz, respectively. The target-to-substrate distance was 0.058 m during both depositions. The substrate temperature was 700 °C during the TiO_2 deposition and 350 °C for the CrO_2 films. The initial pressure in the PLD chamber was 10^{-3} Pa. However, O_2 was introduced in the chamber at a controlled rate during both depositions. The O_2 pressure was 1 Pa and 100 Pa during the deposition of TiO_2 and CrO_2 (on the TiO_2 layer), respectively. Before depositing CrO_2, the TiO_2 films were annealed under continuous flow of O_2 gas at a flow rate of 0.8 l per minute at 1100 °C for 10–15 min to obtain completely rutile type TiO_2 films. The laser fluencies were 2×10^4 J/m^2 and 3.5×10^4 J/m^2 during the depositions of TiO_2 and CrO_2 layers, respectively. A total of 14,000 and 9000 laser shots were allowed on the TiO_2 and Cr_2O_3 targets, respectively. The high laser fluence ablates the surface of the Cr_2O_3 target to form a plume of the ablated materials, which subsequently oxidizes and get deposited as CrO_2 at the optimized O_2 pressure of 100 Pa. The high kinetic energy of the plume (ensures high mobility) along with the tailored thermodynamic conditions effectively support the deposition and subsequent stabilization of the metastable CrO_2 phase on the hot $TiO_2/SiO_2/Si$ substrate.

The crystalline structure of the deposited TiO_2 and CrO_2 thin films was studied with a PANalytical *X'Pert Pro* X-ray diffractometer using CuK_α radiation (0.1540 nm). Grazing-incidence analysis (1° angle) was performed to study the thin layers exclusively. The microstructural features of the films were imaged using a RAITH150 FESEM at an accelerating voltage of 10 kV. MFM analysis was performed with a Veeco Nanoscope IV microscope using Co-Cr coated tips from Bruker (Model MESP). Raman analysis of the thin films was performed with a Horiba JobinYvon LabRAM *HR800* instrument employing a continuous wave air-cooled Ar-ion laser source of wavelength 514.5 nm. For the electrical analysis, circular contact pads (area 0.28×10^{-6} m^2 with centre-to-centre distance of 0.0022 m) of Cr(40 nm)/Au(200 nm) were deposited on the CrO_2 films using a thermal evaporator (HHV Ltd., model 12A4D). The measurement of ρ of the films in the 50–300 K range was performed with Keysight B1500A Semiconductor Device Analyzer and a Lake Shore 336 temperature controller. Magnetic properties of the films were analyzed using Quantum Design MPMS SQUID VSM system, with a maximum *H* of 1 T. The MR measurements were performed ($H \perp$ film plane) with a probe station setup of Lake Shore Cryotronics, Inc.

3. Results and discussion

Fig. 1(a) shows the typical X-ray diffractogram of the TiO_2 thin films deposited by PLD process and subsequently annealed at 1100 °C for 10–15 min in O_2 ambient. The (110) plane of rutile type tetragonal crystal structure appeared as the dominant crystalline orientation in the films along with some weak minor peaks from (200), (111) and (210) planes. The post-deposition annealing ensures the single phase of rutile type in the grown TiO_2 films [47–51]. As outlined before, the lattice-matched seed layer of TiO_2 provides the perfect arena for the stabilization of the *t*-CrO_2 phase. The average crystallite size (δ) in the TiO_2 films is 21 nm, as estimated from Debye-Scherrer analysis [52]. Rietveld analysis disclosed the lattice constants, $a = 0.4597$ nm and $c = 0.2963$ nm ($c/a = 0.6446$), unit cell volume $V_0 = 0.0626$ nm^3, and density $\rho = 4.235 \times 10^3$ kg/m^3 in the annealed TiO_2 thin films. Tanemura et al. [53] reported values of $a = 0.4460$ nm and $c = 0.3120$ nm in rutile type TiO_2 thin films deposited by sputtering technique. Nair et al. [54] reported values of $a = 0.4589$ nm and $c = 0.2956$ nm in similar type of sputtered thin films. In bulk TiO_2, the values are