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Metal–insulator transitions in $(V_{1-x}Cr_x)_2O_3$ thin films deposited by reactive direct current magnetron co-sputtering

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ABSTRACT

Vanadium oxides are promising candidates for application in memory devices based on the control of their various metal–insulator transitions. We report here on the thin films deposition of the strongly correlated system $(V_{1-x}Cr_x)_2O_3$ over a wide range of composition $0 \le x \le 0.60$ by reactive DC magnetron co-sputtering of pure V and Cr targets. Thin films were characterized by Scanning Electron Microscopy, Energy Dispersive X-ray spectroscopy, X-ray diffraction and transport measurements. These studies demonstrates the existence of compressive stress reaching 0.8 GPa in 200 nm thick films, whereas thicker 1 μm films exhibit lower internal stress. This compressive stress modifies significantly the phase diagram of the 200 nm films, shifting the critical chromium content triggering the bandwidth-controlled metal–insulator transition from $x = 0.011$ in unstressed films to more than 0.04. This work highlights the need for an accurate control of the Cr content and of the compressive stress to stabilize the Mott insulator phase in $(V_{1-x}Cr_x)_2O_3$ thin films.

1. Introduction

Metal–insulator transitions (MIT) in correlated systems is a topic of long-standing interest in materials sciences [1,2]. Beyond the continuous researches aiming at clarifying the mechanisms driving these MITs, a lot of efforts were recently dedicated to exploit this striking property in emerging electronics devices [3,4]. Among the systems displaying MITs, vanadium oxides phases are especially appealing, since most of the known V-O phases (VO, V_2O_3 [1], Magnéli phases V_nO_{2n-1} [5], VO_2 [6] and Wadsley phases V_nO_{2n+1} [7]) display temperature-driven MITs. So far, vanadium dioxide VO_2 has attracted the largest interest for applications. Its MIT temperature ($T_{MIT} = 340$ K) located above room temperature and the huge change of resistivity at T_{MIT} by five orders of magnitude indeed allow to envision promising applications. For example, VO_2 could be used as a selector in a cross-point array type Resistance Random Access Memory (ReRAM) [8,9], using Joule heating to switch from the insulating to the metallic phase. A lot of attention was also dedicated to the vanadium sesquioxide system, either pure (V_2O_3) or substituted with chromium $(V_{1-x}Cr_x)_2O_3$. This system is known as a canonical correlated system. Its phase diagram, first established by McWhan et al. [10,11], indeed corresponds nicely to theoretical predictions for a one band Hubbard Hamiltonian solved by the Dynamical Mean Field Theory [12]. At room temperature (RT) V_2O_3 is a paramagnetic metal and undergoes a first order MIT to an antiferromagnetic insulating (AFI) phase at $T_{AFI} \sim 155$ K, with a resistivity increase of seven orders of magnitude at T_{AFI}. In the $(V_{1-x}Cr_x)_2O_3$ system, another MIT of completely different origin can occur at RT: increasing the chromium level above $x = 0.011$ indeed leads to an MIT between the metallic and a paramagnetic Mott insulator (PMI) phases. This MIT, controlled by the ratio between the on-site repulsion U and the bandwidth W, is usually referred to as a bandwidth-controlled MIT [2] and appears as an almost vertical line in the temperature–chromium content x phase diagram. McWhan et al. have shown that application of a moderate (1 to 3 GPa) hydrostatic pressure, which slightly enhanced the bandwidth W, causes the reversed transition from PMI to metal in $(V_{1-x}Cr_x)_2O_3$ with $x_{Cr} > 0.011$ [10]. This extreme sensitivity of $(V_{1-x}Cr_x)_2O_3$ to external perturbation is a direct consequence of its extremely narrow Mott-Hubbard gap E_G, which is below 0.1 eV for x slightly above the critical value $x_{Cr} = 0.011$ [13].

Interestingly an alternative way to induce insulator to metal transition in narrow gap Mott insulators was recently unveiled. It was indeed shown that the application of short electric field pulses led to a strong non-volatile decrease of the resistivity in the narrow gap Mott insulators AM_4Q_8 (A = Ga, Ge; M = V, Nb, Ta, Mo; Q = S, Se). Experimental and theoretical studies have revealed that this transition is associated to an electronic avalanche effect [14–16]. Moreover this property is not specific to AM_4Q_8 but corresponds to a universal feature of all

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narrow gap Mott insulators, including $(V_{1-x}Cr_x)_2O_3$ [17]. The main difference with the switching effects observed in VO_2 is that the resistive switching discovered in narrow gap Mott insulators can be non-volatile, which paves the way for their use as active materials in non-volatile ReRAM memories. However, using this functionality in memory devices requires the deposition of thin films. So far, memory devices based only on thin films of the chalcogenide compound GaV_4S_8 have been achieved [18–20]. The oxide system $(V_{1-x}Cr_x)_2O_3$ appears as a promising candidate for ReRAM applications, since the chromium substitution level provides an interesting degree of freedom to control the proximity of the bandwidth-controlled MIT. So far, many studies have been dedicated to the growth of V_2O_3 thin films (see e.g. Ref. [21] and references therein). By contrast, there are only a few reports on Cr-doped V_2O_3 thin films [21,22] and none of them used the sputtering technique, which is one of the most appropriate methods for large-scale applications.

Here we show that reactive DC magnetron co-sputtering is an efficient and versatile method to deposit $(V_{1-x}Cr_x)_2O_3$ thin films over a wide range of composition $0 \leq x \leq 0.60$. Our study indicates that compressive stress in films with small thicknesses (200 nm or lower), well appropriate for applications in electronic devices, induces a strong shift of the critical chromium content x necessary to induce the bandwidth controlled metal–insulator transition.

2. Methods

2.1. Thin film deposition

Thin films were deposited in a commercial AC 450 sputtering chamber (Alliance Concept, France) by reactive magnetron co-sputtering of two metallic targets of V and Cr (99.99% purity, 2" diameter) in confocal configuration, supplied by two independent direct current (DC) power sources, as displayed in Fig. 1. In such a confocal configuration, polycrystalline $(V_{1-x}Cr_x)_2O_3$ thin layers were synthesized with a wide range of Cr content by varying the DC power supply on the Cr target. Thin films were deposited in reactive mode on SiO_2/Si (300 nm/525 μm) substrates without intentional heating in argon/oxygen atmosphere, with an Ar/O_2 flow rate ratio of 99/1 and a working pressure regulated at 2.5 Pa. As shown in Table 1, the V target power supply was set at 300 W and various Cr contents were obtained by varying the Cr target DC power in the 0 to 200 W range. The deposition time was adjusted in order to obtain thin films of two different thicknesses, 1 μm and 200 nm.

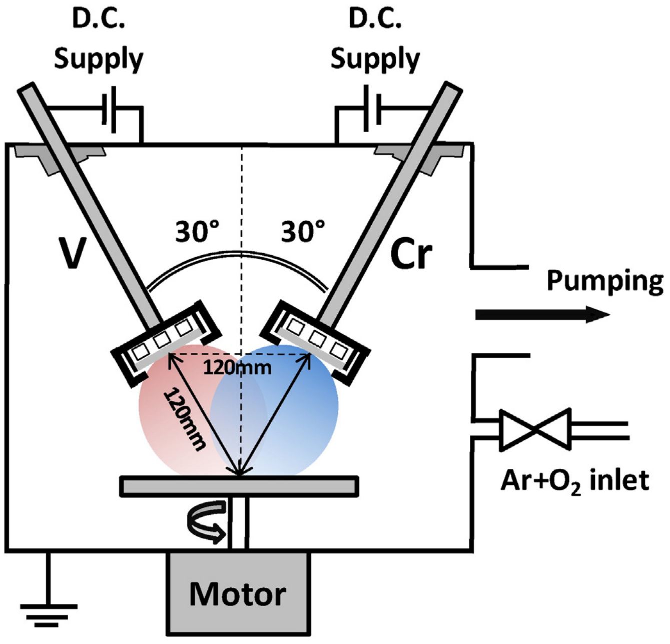

Fig. 1. Schematic representation of the magnetron co-sputtering experimental device with the two metallic V and Cr targets (2 inches diameter, 99.99% purity) in confocal configuration.

Table 1
Experimental parameters used for the deposition of $(V_{1-x}Cr_x)_2O_3$ thin films by DC magnetron co-sputtering.

Target	Vanadium (V)	Chromium (Cr)
DC power (Watt)	300	0–200
Argon flow rate (sccm)	99	
Oxygen flow rate (sccm)	1	
Working Pressure (Pa)	2.5	
Substrate rotation rate (rpm)	5	

2.2. Characterization methods

Chemical compositions of deposited films and V/Cr ratio were determined by Energy-Dispersive X-ray Spectroscopy (EDXS) measurements carried out in a Scanning Electron Microscope (SEM) Jeol-5800, equipped with an Energy Dispersive Spectroscopy detector — Princeton Gamma Tech. Prism 2000. SEM observations of surface morphology and cross sections were achieved in a JEOL JSM 7600F Field Emission Gun Scanning Electron Microscope (FEG-SEM), with acceleration voltages in the 5 to 10 kV range. The deposition rate was calculated from the layer thickness measured with a profilometer (DEKTAK8). X-ray diffraction measurements were carried out using a Siemens D-8 diffractometer using a Cu $K_{\alpha1}$ radiation ($\lambda = 1.540598$ Å) operating in Bragg-Brentano configuration. We refined the cell parameters with the Le Bail method using the JANA2006 software [23], using pseudo-Voigt functions to fit the peaks profiles. Electrical transport measurements were performed using a source-measure unit Keithley 237 and a standard four probe technique with gold wires of diameter 40 μm contacted on top of the layers by carbon paste (Electrodag PR 406).

3. Results and discussion

3.1. Reactive DC magnetron sputtering

3.1.1. Sputtering with single vanadium or chromium targets

Before performing V and Cr co-sputtering in reactive Ar/O_2 atmosphere, we investigated the behaviour of each target operating independently while varying the target DC power from 0 to 300 W. Fig. 2 displays the evolution of the deposition rate versus DC power for V target (Fig. 2a) and Cr target (Fig. 2b) both in pure Ar and in reactive Ar/O_2 atmosphere. In both cases, the deposition rates vary almost linearly with DC power in pure Ar and reach, at 300 W, 24 and 45 nm/min for the V and Cr target respectively. Such linear variation in Ar discharge is expected but strongly contrasts with the behaviour observed in reactive Ar/O_2 plasma. For both V and Cr targets, two different linear regimes are observed. At low DC power, a first regime appears, with extremely low deposition rates. A rate lower than 3 nm/min is indeed obtained up to 175 W and 100 W for the V and Cr targets respectively. Subsequently, for both targets, a sudden increase of deposition rate is observed and then, above a threshold power of 200 W (V target) and 150 W (Cr target), a second linear regime is reached. At 300 W, high deposition rates of 38 and 65 nm/min are obtained for the V and Cr target respectively. The existence of those two regimes is related to a competition between surface oxidation and sputtering of the V or Cr targets. At low discharge power, the oxidation process is favoured, leading to a decrease of the sputtering rate compared to non reactive Ar plasma. In the high discharge power regime, plasma species have gained enough kinetic energy to avoid the formation of an oxidized layer at the target surface. As expected, a sputtering rate higher than in neutral Ar atmosphere is yielded in this regime, due to incorporation of oxygen atoms in the deposited layer.

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