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Temperature dependence of electrical resistivity in oxidized vanadium films grown by the GLAD technique

Verónica Collado [a], Nicolas Martin [a,*], Paulo Pedrosa [a], Jean-Yves Rauch [a], Marta Horakova [b], Mohammad Arab Pour Yazdi [a], Alain Billard [a]

[a] Institut FEMTO-ST, UMR 6174 CNRS, Université Bourgogne Franche-Comté, 15B, Avenue des montboucons 25030 BESANCON Cedex, France
[b] Department of Material Engineering, Czech Technical University in Prague, Karlovo namesti 13, CZ-121 35 Prague 2, Czech Republic

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ABSTRACT

Vanadium and vanadium oxide thin films are deposited by DC magnetron sputtering. A first series of pure vanadium films are prepared by glancing angle deposition (GLAD). The incident angle α of the particle flux is systematically changed from 0 to 85°. For the second series, the angle α is kept at 85° and oxygen gas is injected during the growth by means of the reactive gas pulsing process (RGPP). A constant pulsing period $P = 16$ s is used whereas the oxygen injection time t_{ON} is varied from 0 to 6 s. After depositing, films are annealed in air following 11 incremental cycles from room temperature up to 550 °C. For both series, the DC electrical resistivity is systematically measured during the annealing treatment. Vanadium films sputter deposited by GLAD become sensitive to the temperature for incident angles α higher than 60°. The most significant annealing effect is observed for films prepared with $\alpha = 85°$ with a strong increase of resistivity from 2.6×10^{-5} to 4.9×10^{-3} Ωm. It is mainly assigned to the oxidation of GLAD vanadium films, which is favoured by the high porous morphology produced for the highest incident angles. The resistivity *vs.* temperature evolution is also measured and related to the occurrence of the VO_2 phase. By combining GLAD and RGPP processes, the reversible variation of resistivity associated to the VO_2 phase is even more pronounced. Oxygen pulsing during deposition and the voided structure produced for the highest incident angles enhance the oxidation of vanadium through the films thickness. The porous architecture by GLAD and the oxygen injection by RGPP have to be carefully controlled and optimized for the growth of vanadium oxide compounds, especially to favour the formation of the VO_2 phase.

1. Introduction

In the past decade, vanadium oxide based thin films have been one of the most actively studied materials among transition metal oxides. The growing interest is due to the VO_2 single crystal, which exhibits a reversible semiconductor-to-metal phase transition at the temperature near 68 °C [1–3]. This phenomenon is related to the monoclinic-to-tetragonal phase transition that undergoes by heating or cooling the material [4,5]. This kind of binary compound is interesting because it shows a large variation of many physical properties, such as 4 to 5 orders of magnitude of electrical resistivity changes as the temperature varies from 30 to 100 °C and reciprocally [6]. However, due to the complexity of the vanadium-oxygen system (multivalent vanadium ions from +II to +V), the synthesis of the pure VO_2 phase can become a challenging task. Other VO_x compounds also exist, namely *Magnéli* phases (V_nO_{2n-1} with n = 3 to 9) or *Wadsley* phases (V_nO_{2n+1} with n = 2 to 6), and the fabrication of vanadium oxide often leads to the growth of multi-phased materials [7–10]. It becomes a much more complex challenge when the VO_2 phase has to be prepared in thin films [11–13]. Oxygen-to-vanadium ratio is not the only criterion, which governs the VO_2 synthesis but other parameters like the substrate materials, the operating growth or the deposition methods strongly influence the type of vanadium oxide which can be obtained [14–16]. Thus, many different approaches have been developed to prepare VO_x films in order to reach the single VO_2 phase [17–20]. Among the deposition methods, reactive sputtering is a particularly attractive technique. Starting from a pure vanadium metallic target, the oxygen reactive gas can be injected into the sputtering process and leads to the synthesis of vanadium oxide thin films with tuneable oxygen and vanadium concentrations. Nevertheless, the reactive sputtering mode typically exhibits non-linear phenomena of the process parameters (*e.g.* hysteresis loop of the deposition rate, discharge characteristics, reactive gas partial pressure *vs.* mass flow rate) due to poisoning of the metallic target surface by the oxygen species [21,22]. As a result, some chemical compositions cannot be reached by conventional reactive sputtering and some improvements of the process have been developed such as high pumping speeds, feedback control systems, pulsing of the sputtering power or a gas pulsing technique [23–26]. On the other hand, and especially for the formation of the VO_2 phase, deposition procedures at temperatures

* Corresponding author.
E-mail address: nicolas.martin@femto-st.fr (N. Martin).

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higher than 400 °C or post-annealing treatments are required to favour the growth of such phase [27,28]. Another approach consists in starting from a pure metallic vanadium thin film, followed by an annealing in air. Nevertheless, the typical dense and packed structure of sputtered films strongly prevents a continuous and controlled oxidation through the film thickness. Understanding the kinetics of vanadium oxide phases formation as well as oxidation mechanisms of vanadium-based sputtered thin films still remain an open discussion due to the complexity of the vanadium-oxygen system. It is also important to note that *in situ* diagnosis tools during thermal oxidation of vanadium films have been investigated a little in order to measure the phases transformation of vanadium oxide compounds [29,30].

In this paper, we report on the evolution of electrical resistivity *vs.* temperature of sputter-deposited vanadium and vanadium oxide films. Oriented columnar vanadium films are obtained by GLancing Angle Deposition (GLAD) and vanadium oxide films are produced combining GLAD and the Reactive Gas Pulsing Process (RGPP). Several incremental annealing cycles in air are applied and the electrical resistivity of the films is systematically measured as a function of the temperature changes. We show that the oxidation process can be favoured and better controlled through the GLAD films and not only on the surface as commonly encountered in conventional sputtered films. The GLAD + RGPP association appears as an original way to enhance the sensitivity of the vanadium oxidation. Variations of electrical resistivity with the temperature are discussed and correlated with the phase evolution, especially the gradual and reversible metal-to-insulator transition, which can be optimized as a function of the depositing and annealing conditions.

2. Experimental details

Films were deposited by DC magnetron sputtering from a vanadium metallic target (51 mm diameter and 99.9 atomic % purity) in a home-made deposition chamber. The latter was pumped down to 10^{-5} Pa before each run by means of a turbomolecular pump backed by a primary pump. The target was sputtered with a constant current density $J = 100\ Am^{-2}$. The glass and (100) silicon substrates were placed at 65 mm from the target surface. They were grounded and no external heating was used. The thickness of the film was measured by profilometry and the deposition time was adjusted in order to get a constant thickness of 400 nm. Two series of samples were produced. The first one was prepared by GLAD (GLancing Angle Deposition). A home-made GLAD substrate holder allowed an orientation change of the incident angle of the particle flux from 0 to 90°. To this aim, this incident angle, namely α, was taken from the normal to the substrate and the normal of the target (*i.e.* the main direction of the sputtered atoms flux). For the first series, the angle α was systematically changed from 0 to 85°. A pure argon atmosphere was implemented setting an argon mass flow rate of 2.40 sccm and the pumping speed was maintained at $S = 13.5\ Ls^{-1}$ (the corresponding argon sputtering pressure was 0.30 Pa).

A constant incident angle $\alpha = 85°$ was fixed for the second series and the Reactive Gas Pulsing Process (RGPP) was implemented. Argon was injected following the same operating conditions as the first series, whereas the oxygen gas was periodically supplied into the sputtering chamber. A rectangular pulsed signal was employed for the oxygen flow rate *vs.* time evolution. The pulsing period was set at $P = 16$ s. The maximum oxygen flow rate was $q_{O2Max} = 0.40$ sccm. It corresponds to the critical flow required to avalanche the process in the compound sputtering mode. The minimum oxygen flow rate was $q_{O2min} = 0$ sccm. Thus, the injection time of the oxygen gas was changed from $t_{ON} = 0$ to 12 s.

After deposition, the subsequent thermal annealing procedure of the films was performed. It consisted in heating the films in air using 11 cycles starting from 30 °C and up to a given temperature. The first cycle was from 30 to 50 °C at 5 °C min^{-1} then back to 30 °C with the same negative ramp. The second one was 30–100–30 °C; the third one was 30–150–30 °C, and so on until the 11th cycle for which 550 °C was reached (50 °C incremental temperature). For all cycles, a ramp of ± 5 °C min^{-1} was applied. During this annealing procedure, the DC electrical resistivity of the films deposited on glass substrates was measured by means of the four-probe method in the van der Pauw geometry. In order to warrant the Ohmic behaviour of the four contacts, I-V curves were systematically plotted and the linear evolution was checked for all van der Pauw combinations. All resistivity measurements were performed in a dark environment. These operating conditions allow an accurate determination of the resistivity *vs.* temperature (better than 1%) and precise calculations of the temperature coefficient of resistance.

The crystallographic structure was investigated by X-ray diffraction (XRD) with a Bruker D8 focus diffractometer using monochromatized Co $K_{\alpha 1}$ radiation ($\lambda = 1.78896$ Å) with a Bragg-Brentano $\theta/2\theta$ configuration. Morphology, microstructure and columnar orientation of the films deposited on (100) Si substrates were observed with a Jeol JSM-7800F field emission gun scanning electron microscope (FEG-SEM) on the fractured cross-section. The chemical state of vanadium and oxygen atoms was determined by X-ray photoelectron spectroscopy (XPS). X-ray photoelectron analyses were performed with a Thermo VG Alpha 110 apparatus to investigate the compositions and the chemical environments of vanadium and oxygen elements in the films deposited on silicon substrate. These measurements were obtained using the magnesium $K\alpha_1$ monochromatic ray (1253 eV with a power of 200 W and a pressure of 2.3×10^{-7} Pa). XPS profiles were obtained after bombarding the sample surface with Ar^+ ions sputtering of 3 keV for 15 min at 5×10^{-6} Pa argon pressure in order to remove the contamination layer on all films. This cleaning procedure was optimized until a steady state of the signals was reached. Photoemission peak areas were calculated after smoothing and background subtraction using a Shirley routine.

3. Results and discussion

3.1. Pure vanadium films with $\alpha = 0$, 60 to 85°

SEM images of as-deposited pure vanadium thin films produced with different incident angles α are shown in Fig. 1. A dense and poorly defined microstructure is observed for vanadium films prepared by conventional sputtering (Fig. 1a). As expected and taking into account the structural zone models [31,32], a fine fibre texture develops in pure elemental films sputtered with a low deposition temperature (Zone I corresponding to a negligible adatom diffusion). Since the melting point T_m of vanadium is 3287 K and no external heating was used during deposition (the substrate temperature T_s reached a few tens of degrees above the room temperature at the end of the deposition time), the T_m/T_s temperature ratio is lower than 0.15, which corresponds to the first zone of the structural zone models. Thus, unclear columns can be viewed with an orientation perpendicular to the substrate surface. This poorly defined microstructure is produced for vanadium films prepared by GLAD up to an incident angle α close to 60°. This dense and packed microstructure has ever been reported for other sputtered materials by GLAD [33–35] in spite of an important orientation of the particle flux (>40°). As a result, this range of incident angles close 60° often is referred as a threshold value where the shadowing effect begins to be significant. So, growth dynamics, morphology and many resulting properties of the films are determined by the competition between atomic surface diffusion and self-shadowing, the latter prevailing for large incident angles.

Well defined and inclined columns are clearly observed for an incident angle $\alpha = 60°$ (Fig. 1b). The films exhibit a clear porous structure and a higher surface roughness compared to conventional sputtering ($\alpha = 0°$ in Fig. 1a). From the cross-sectional view, the column angle $\beta = 44°$. This angle is lower than the corresponding incident angle