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Correlation between structural and optical properties of WO_3 thin films sputter deposited by glancing angle deposition

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ABSTRACT

Tungsten oxide WO_3 thin films are prepared by DC reactive sputtering. The GLancing Angle Deposition method (GLAD) is implemented to produce inclined columnar structures. The incident angle α between the particle flux and the normal to the substrate is systematically changed from 0 to 80°. For incident angles higher than 50°, a typical inclined columnar architecture is clearly produced with column angles β well correlated with the incident angle α according to conventional relationships determined from geometrical models. For each film, the refractive index and extinction coefficient are calculated from optical transmittance spectra of the films measured in the visible region. The refractive index at 589 nm drops from $n_{589} = 2.18$ down to 1.90 as α rises from 0 to 80°, whereas the extinction coefficient reaches $k_{589} = 4.27 \times 10^{-3}$ for an incident angle $\alpha = 80°$, which indicates that the films produced at a grazing incident angle become more absorbent. Such changes of the optical behaviors are correlated with changes of the microstructure, especially a porous architecture, which is favored for incident angles higher than 50°. Optical band gap E_g, Urbach energy E_u and birefringence Δn_{617}, determined from optical transmittance measurements, are also influenced by the orientation of the columns and their trend is discussed taking into account the disorder produced by the inclined particle flux.

1. Introduction

Transition metal oxides represent a very attracting class of materials because of the wide range of physical and chemical properties that they exhibit. Among these oxide compounds, tungsten oxide thin films have been extensively investigated due to their important applications as active layers for electrochromic window devices [1–5], sensors for toxic gases [6–10], optical coatings with high refractive index [11–13] or transparent and low resistive oxide materials [14–16]. It is well known that many chemical and physical characteristics of metal oxide thin films are strongly connected to their chemical composition, especially the oxygen-to-metallic concentrations ratio, which can be tuned in order to get a metallic, semi-conducting or insulating behavior according to the metalloid content in the film [17–20]. However, playing with the chemical composition is not the only approach to tune the properties of metal oxide thin films. The structure at the sub-micrometric scale can also influence the film performances for many applications [21]. So, the design and the growth control of nanostructures in thin layers appear as important issues, e.g. in order to control the optical properties by playing on structural features. To this aim, various strategies have been proposed for the structuration of thin films [22].

In the last decade, the interest of nanostructuration by evaporation and/or sputtering techniques was particularly boosted by the GLancing Angle Deposition (GLAD) method [23]. This method is based on the preparation of thin films on fixed or mobile substrate, with an oblique incidence of the incoming particle flux. Indeed, when the atomic vapor flow comes up at a non normal incident angle α, the nucleation sites intercept the flow of particles. This creates a shadowing effect and there is a tilted grain growth of columnar shape leading to inclined columnar structures with an angle β with respect to the normal of the substrate surface. Nature, crystallography, temperature and surface conditions of the substrate, energy and interactions of the condensed particles with the substrate, among other parameters, have a decisive role in the growth mode of the coating. As a result, the GLAD technique can control the structure of thin films at the micro- and nanoscales. The experimental setup has two degrees of freedom: a rotation axis at an angle α, which allows to vary the incident angle of the particle flux, and a rotary axis at an angle ϕ (also called azimuth angle), which modifies in an indirect way, the position of the particle source. The produced architectures can be of type i) columnar and inclined; ii) chevron or zigzag by alternating periodically the incident angle of particles from $+\alpha$ to $-\alpha$ maintaining constant ϕ angle (azimuthal angle around the substrate) or with a 180° rotation of ϕ keeping constant α angle; and

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iii) spiral or helical thanks to a continuous rotation of ϕ at a constant incident angle α. This latter type adds to the potential of the GLAD technique. Moreover, changing wisely α and ϕ angles as well as speeds of rotation, more original structures can be obtained such as porous columnar structures with variable diameters [24] or helical columns with squared sections [25]. In the end, the GLAD technique exploits the effects of shadowing created by a tilted substrate relative to normal incidence and a change of the direction of the particle flux through a rotation of the same substrate during the deposition. The two combined can generate different forms of columns and varied architectures. For example, Robbie et al. [26,27] or Van Popta et al. [28] have deposited by evaporation some structured films with columnar architectures showing sinusoidal, helical and more complex forms. This variety allows envisaging applications in many fields such as biomedical system [29], photonic devices [30], microsensors [31], etc. Moreover thin films deposited by GLAD have high porosity and anisotropic behaviors, which can be used as rugate filters [32], wavelength-selective polarizer [33], or antireflection coating [34].

The purpose of this article is to study the structural and optical properties of the sputter deposited tungsten oxide WO_3 nanostructured thin films grown using various incident angles α of the particle flux from 0 to 80°. We systematically investigate how the structure and optical properties (refractive index, extinction and absorption coefficients, optical band gap and birefringence) of such oriented thin films can be tuned by changing the incident angle of the sputtered particles. The evolution of the porous structure connected to the columnar orientation is especially analyzed in order to discuss and understand some relationships between the architecture of the films and their resulting optical behaviors.

2. Experimental details

WO_3 films were sputter deposited by DC reactive magnetron sputtering using a homemade system [35,36]. A tungsten target (5 cm diameter with purity 99.9 at. %) was powered at a constant current density $J = 25.5\ A \cdot m^{-2}$, with an argon partial pressure $P_{Ar} = 0.1$ Pa and an oxygen partial pressure $P_{O^2} = 0.08$ Pa. Substrates (grounded and kept at room temperature) were glass plates and (100) silicon wafers. The distance between the target and the substrate was fixed at 60 mm. For these operating conditions, the resulting target potential was $U_W = (515 \pm 10)$ V. The growth of the films was stopped at a thickness close to 1 μm thanks to the calibration of the deposition rate (deposition rate depends on the incidence angle and changes from 690 to 90 $nm \cdot h^{-1}$ as α rises from 0 to 80°). A systematic change of the incident angle from $\alpha = 0$ to 80° with a 10° increment was performed to tune the inclined columnar structure. Due to the design of the method, inclined columnar structures produced by GLAD are intrinsically inhomogeneous in terms of thickness. In order to cope with this drawback, the samples dimension was $1 \times 1\ cm^2$. In addition, the surface area involved for the characterization was those located in front of the target centre. Thus, the size of the probing light spot was limited to 1 mm^2 for the optical properties. Films deposited on glass substrates were characterized thanks to optical transmittance spectra measured with a Lambda 900 Perkin Elmer spectrophotometer in the visible range from 1.55 to 3.10 eV (i.e. wavelength in-between 800 to 400 nm). Refractive index, extinction coefficient and absorption coefficient were determined from interference fringes obtained with experimental optical transmittance spectra using Swanepoel's method [37]. Films prepared on (100) silicon wafers were cross-sectioned and observed by field effect scanning electron microscopy (SEM) with 5 kV operating voltage using a JEOL 6400 F. WO_3 structures were also characterized by X-ray diffraction (XRD). Measurements were carried out using a Bruker D8 focus diffractometer with a cobalt X-ray tube (Co $\lambda_{K\alpha} = 1.78897$ Å) in a $\theta/2\theta$ configuration.

3. Results and discussion

3.1. Structural characterization

Tungsten oxide thin films prepared with an incident angle α lower than 50° do not exhibit a clear inclined columnar structure. A densely packed feature is rather observed with a smooth surface topography. However, a further increase of the incident angle (α higher than 50°) leads to a rougher film/air interface and a more defined columnar growth. Observations by SEM of surfaces and cross-sections of WO_3 thin films sputter deposited with an incident angle α of 70 and 80° are shown in Fig. 1. It is worth noting that the top of the columns has a rather sharp appearance (Fig. 1a), which is even more emphasized for $\alpha = 80°$ (surface state becomes irregular and more voided as illustrated in Fig. 1c). Such increase of the surface roughness versus incident angle of the sputtered particles is in agreement with previous investigations focused on metal oxide coatings produced by GLAD [38,39]. It is mainly attributed to the shadowing effect at the atomic scale, which prevails over the surface diffusion of adatoms as the incident angle rises. The structural anisotropy (formation of growth islands connected to each other by chains perpendicular to the plane of incidence) previously claimed by Tait et al. [40], is slightly marked for sputtered tungsten oxide films. The top of the columns appears more or less connected to each other according to the x direction and perpendicular to the particle flux (Fig. 1a and c).

Inspection of the cross-sectional view ensures that the GLAD WO_3 films are composed of slanted columns and inter-columnar voids (Fig. 1b and d). The columns are inclined towards the direction of the incoming vapor flux. The column angle β, defined as the angle between the substrate surface normal and the long axis of the slanted columns, is measured from the cross-section SEM images. For incident angle α lower than 50°, the column angle β cannot be accurately determined since no clear columnar growth has been produced but a densely packed structure. For higher angles of incidence ($\alpha > 50°$), SEM images exhibit morphologies composed by columns and inter-columnar gaps. The columns become increasingly separated and can easily be distinguished at an incident angle α of 70° and even more at 80°. The resulting column angles β are 50 and 54° for incident angles α of 70 and 80°, respectively. Such column angles deviate from the empirical tangent rule [41], which predicts 53 and 70°, respectively. This rule provides a first order approximation of the expected β angles. Since the growth can be disturbed by many parameters (temperature, particle energy, pressure), the tangent rule fails to well describe experimental column angles, especially for grazing incident angles. This is indeed relevant for thin films deposited by the sputtering process, where column angles are often lower than those calculated with various ballistic rules [42,43]. However, our produced WO_3 column angles are in good agreement with relationships proposed by Tait et al. [44]. The sputtering pressure required to maintain the glow discharge restricts the mean free path of the sputtered particles and thus, reduces the shadowing effect. As a result, the theoretical column inclinations predicted by the simple tangent rule is systematically overestimated.

Since tungsten oxide thin films have been deposited at room temperature (substrate temperature is lower than 0.3 times the melting point of WO_3 compound), one could expect a poorly crystallized material. However, XRD analyses exhibit diffracted signals (Fig. 2). Peaks corresponding to the WO_3 monoclinic structure are clearly identified for incident angles included between $\alpha = 0$ and 80°. For normal incidence ($\alpha = 0°$), as-deposited films are weakly crystallized since the major diffracted peaks exhibit low intensity and the average crystallite size calculated from the Scherrer equation is smaller than 37 nm. An increase of the incident angle α up to 40° leads to more intense peaks for all crystallographic planes, without any preferential orientation. In addition, the crystallite size reaches 42 nm for $\alpha = 40°$ and the diffracted patterns (peak position, intensity or full-width-at-half-maximum) do not evolve