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COMPOSITION MODULATED, METAL-OXIDE THIN FILMS**

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Rate controlled synthesis of composition modulated, metal-oxide thin films

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ABSTRACT

The development of advanced deposition technologies is continuously evolving for the synthesis of oxide coatings used in optical applications. Recent progress is made in the use of magnetron sputtering to reactively deposit metal-oxide thin films. The sputter deposition parameters are chosen with respect to the reaction kinetics of the metal-oxide system to enable a variation of composition along the film growth direction. The key process parameter to control is the sputtering rate of the target. The shape of the composition profile directly corresponds to the preselected variation of deposition rate. By simply varying the sputtering rate using a working gas that consists of an inert-oxygen mixture, structures are synthesized with composition profiles which can be either abrupt or graded in the growth direction. The result is a compositionally modulated structure of the metal-oxide system. This procedure for composition modulated synthesis is demonstrated for metals which are highly reactive with oxygen as well as for those metals which are not. The development of this deposition methodology will facilitate the design of metal oxide films for optical applications, as in gradient-index filters for example. Results are presented for the reactive sputter deposition of metal oxide coatings in the yttrium-oxide, molybdenum-oxide, and copper-oxide systems.

Keywords: metal-oxide, reactive sputtering, composition modulated, thin films

1. INTRODUCTION

The conventional method of synthesizing metal-oxide thin films utilizes flow and pressure regulation of the reactive gas to control the composition of the growing film. As an example, consider the reactive sputter deposition of a yttrium target with a working gas of Ar-20%Oxygen.^[1] At a constant target power density ($9.5 \text{ Watts cm}^{-2}$) and constant working gas pressure (0.40 Pa), a hysteresis is formed between the change in gas flow and the resulting deposition rate (Fig. 1). In this scenario, at low flow rates the target sputters in metallic mode whereas when the flow is raised to a sufficiently high rate the deposition rate drops dramatically as the target surface is poisoned by the reactive gas and therefore sputters as an oxide. To remove the surface oxide from the sputtering target, the gas flow rate must then be reduced until there is insufficient reactive gas present to equilibrate the oxide layer at the target surface. A finite interval of time, however short, is required to change the sputtering mode of the target in a reactive gas using the method of cycling the working gas flow (and/or pressure). This time interval is equivalent to the time required for the pressure and flow controls to stabilize the change in gas flow and pressure plus the time required for the surface reaction between the target metal and reactive gas to reach an equilibrium state.

An alternative procedure has been recently developed to synthesize metal-oxide films. In this procedure, the time required to change sputter modes (metallic $\leftrightarrow$ oxide) is greatly reduced. The effect of sputter rate variation coupled to the reaction kinetics of the metal and oxygen enables the synthesis of both metastable and equilibrium oxide phases. First, the working gas composition, pressure and flow conditions are predetermined to enable the target sputtering mode as metallic. Then, rather than utilize a cycling of the working gas pressure and/or flow, the target power density can be cycled to produce an instantaneous change in the deposition rate. The change in deposition rate at the film surface produces an accompanying change in the metal-to-oxygen composition in the growing film. This method takes advantage of forming the desired metal-to-oxygen composition in the deposition flux or at the film surface rather than at the target surface. A broader range of metal-to-oxygen composition is attainable using this method. In fact, a continuous variation of oxide composition is possible for those metal-oxide systems which contains only a few equilibrium phases. For example, a continuous variation of metallic composition (from 40 to 75 at.% Y) is demonstrated for the yttrium-oxide system whereas the only equilibrium phase is Y_2O_3 .^[1] Another example is found in the synthesis of metal-rich oxide phases well beyond the 25-33 at.% Mo composition found in conventional bulk processing.^[2,3] For the Mo-O system (Fig. 2), the deposition rate can be continuously varied with applied target power where a constant Ar-20%Oxygen working gas pressure (of 0.67 Pa) and flow (of 21.5 cc min^{-1}) are used to sputter a 6.35cm diameter molybdenum target. As a consequence, this method produces a rate dependent behavior in the film composition (as measured using Auger electron spectroscopy coupled with depth profiling) parallel to the target power.^[2,3]

Fig.1 A hysteresis between deposition rate and gas flow is formed when yttrium is reactively sputtering with a constant flow of argon-20%oxygen gas.

Fig. 2 The target power and concentration variation with deposition rate for molybdenum when reactively sputtered with argon-20%oxygen gas.

The synthesis of a compositionally modulated structure of a metal-oxide system using the variation of sputter rate as the controlling deposition parameter was first shown for the Mo-O system.^[4] In this case (with reference to Fig. 2), the target power was cycled between 95 and 125 Watts producing deposition rates of 0.3 and 0.7 nm s⁻¹, respectively.^[2,3] This deposition cycle created alternating layers that were 13.6 and 14.0 nm thick with molybdenum concentrations of 25 and 40 at.%, respectively.^[2,3] A high resolution electron micrograph (Fig. 3) of the Mo-O multilayer (deposited on a silicon wafer) prepared and viewed in cross-section reveals the discrete layering which results using an abrupt change (less than 1.0 sec) of target power.^[4] A second composition modulation example has also been demonstrated for the highly reactive yttrium-oxide system.^[5] For this case, using a working gas of Ar-20%Oxygen (at constant 0.4 Pa pressure and 8 cc min⁻¹ flow) the target power was cycled between 140 and 390 Watts producing deposition rates of 0.6 and 1.4 nm s⁻¹, respectively.^[5] This deposition cycle created alternating layers that were each 0.35 μ m thick with yttrium concentrations of 40 and 60 at.%, respectively.^[1] A scanning electron micrograph (Fig. 4) of the Y-O multilayer (deposited on a Ta₁₀W substrate) prepared and viewed in cross-section reveals the layering which results using a gradual change of target power.^[5] The composition change is more characteristic of a sinusoidal variation for the Y-O multilayer as opposed to a square wave for the Mo-O multilayer. The results for the Cu-O system are introduced in this paper, wherein the variation from a "pure" metal layer to an oxide layer is shown for the first time.

Fig. 3. A high resolution electron micrograph of a Mo-O multilayer as viewed in cross-section.

Fig. 4 A scanning electron micrograph of a Y-O multilayer as viewed in cross-section.

2. EXPERIMENTAL METHOD

The metal-oxide films are prepared by reactive sputter deposition using planar magnetrons operated in the dc mode. The vacuum chamber is cryogenically pumped to a base pressure of 5.3 μ Pa. For the synthesis of Cu-O multilayer films, the working gas is mixed by combining flows from pure Ar and Ar-20%Oxygen supplies at a constant pressure of 0.67 Pa. The room temperature silicon substrates are situated 10 cm across from the 6.35cm diameter target of 0.99995 purity. The ratio of pure Ar to Ar-20%Oxygen is first determined by establishing the conditions for the deposition rate - gas flow hysteresis. The contribution of the Ar-20%Oxygen gas source to a total flow of gas at 24.5 cc min⁻¹ is gradually reduced while the target power is maintained at 140 Watts power (Fig. 5). A sudden increase in rate is observed when the Ar-20%Oxygen flow declines below 6.4 cc min⁻¹. This mixture of gas flow should enable both metallic and oxide modes of target sputtering. A gas mixture of 15.2 cc min⁻¹ pure Ar and 6.8 cc min⁻¹ Ar-20%Oxygen is then used to synthesize the Cu-O multilayer. Under these constant flow conditions, the dependency is determined of deposition rate upon applied target power (Fig. 5). As expected, a sudden increase of deposition rate is found above a target power of 140 Watts. A significant change in oxide content should then result if the target power is cycled between levels which are above and below 140 Watts. A target power of 105 Watts yields a deposition rate of 0.38 nm s⁻¹, whereas a 205 Watts yields 1.13 nm s⁻¹. The multilayer to be examined consists of 16 layer pairs - the 32nm thick Cu-rich layers are formed at 205 Watts target power for 30 sec and the 68nm thick copper-oxide layers are formed at 105 Watts for 180 sec.

The Cu-O films are structurally characterized using x-ray diffraction (XRD) and transmission electron microscopy (TEM). The films are examined in a powder diffractometer, operated in the $\theta/2\theta$ mode, using a graphite monochromator and Cu $K\alpha$ radiation. Interplanar spacings are measured via Bragg reflections which also indicate the texture and crystalline phases present in the thin film. Bright field imaging of the multilayer specimens prepared in cross-section reveal the film growth morphology and layer structure. Selected area diffraction (SAD) patterns are used to compliment phase identification from the XRD patterns. The TEM sample preparation procedure is described in typical detail elsewhere.^[6] High resolution images of the cross-sectioned specimens are acquired at the Scherzer defocus condition.

The Cu-O films are compositionally characterized using Auger electron spectroscopy (AES) coupled with depth profiling. The vacuum chamber is pumped to a base pressure of 0.67 nPa. A 3 KeV, 10 μ A electron beam generates characteristic Auger electrons. The measured intensities of the CKLL (272 eV), O KLL (503 eV) and Cu LMM (920 eV) Auger peaks, from data accumulated in the derivative mode, are used to compute the atomic concentrations. A 5.0 KV, 2.0 μ A argon ion beam is used to sputter etch a 25 mm² area of the multilayer at a gas pressure of 2.7 mPa.

Fig. 5 The dependence of deposition rate on gas flow and target power for copper reactively sputtered with a mixture of argon and argon-20%oxygen.

3. EXPERIMENTAL RESULTS

The XRD scans reveal the presence of both pure Cu and the Cu₂O crystalline phases in the Cu-O multilayer film. Although the film layers are polycrystalline, a preferred (111) texture is apparent for both phases. Examination of the individual films produced at 105 and 205 W of target power yield different intensity ratios between the Cu₂O and Cu (111) Bragg reflections. The 105 Watt film is almost completely Cu₂O whereas the 205 Watt film is almost completely pure Cu.

The TEM cross-section image (Fig. 6) reveals the composition modulation of the Cu-O multilayer. The copper-rich deposition appear as the darker thin layers. The copper-rich layers are one-half the thickness of the more oxygen-rich layers, as per the deposition parameters. The polycrystalline nature of the individual grains leads to some diffraction contrast within each layer. Layering is continuous across the densely packed columnar boundaries which are typical for sputtered thin films. The multilayer SAD pattern (Fig. 7) is indexed to the Cu and Cu₂O crystalline structures, in agreement with the XRD results.

Fig. 6 A transmission electron micrograph (shown to the left) of the Cu-O multilayer as viewed in cross-section.

Fig. 7 The selected-area diffraction (shown to the right) of the Cu-O multilayer as imaged in plan-view.

The AES profile shows a composition modulation through the film thickness consistent with a multilayer deposition (Fig. 8). Quantitatively, the 205 Watt layer is nearly pure Cu whereas the 105 Watt layer is 60 at.% Cu. These concentration values agree with the XRD phase identification of the individual 105 and 205 Watt films. Concentration levels of carbon and oxygen are at the baseline detection limit for the first layer. The ratio of oxygen concentration between the 105 and 205 Watt layers decreases from a maximum of 7:1 for the first layer pair to 5:1 by the third layer pair. This reduction is caused by non-uniform etching of the exposed surface in addition to layer intermixing during the depth profile process. The sputter time between Cu-rich peaks remains constant during the depth profile.

Fig. 8 The atomic concentration profile of the Cu-O multilayer as determined from the Auger electron spectroscopy analysis.

4. CONCLUDING REMARKS

The optical constants measured for the Mo-O thin films range sufficiently for potential use in optical applications, as gradient-index or rugate filters.^[4] Such metal-oxide multilayer filters require precise control to form the desired oxide layer thicknesses and interface composition profiles. At a nominal thickness of 1.5 μm , the transmission of the Mo-O films (with reference to Figs. 2 and 3) range from transparent (25 at.% Mo) to translucent (40 at.% Mo) to opaque and specular (>50 at.% Mo). A null ellipsometer is used to measure the optical constants with the red hydrogen line at a wavelength of 656.3nm. The reflection ellipsometry measurement procedure and calculation method are detailed elsewhere.^[7] The refractive index n_c and extinction coefficient k are observed to vary with the deposition rate, that corresponds with changes in the oxide composition (Fig. 9). The refractive index can be varied by a factor of three whereas the extinction coefficient ranges over three-orders of magnitude. For comparison, many dielectric materials have $n_c \approx 2$ to 3 and $k \approx 0$ to 0.2.

The reactive deposition of metals is shown to be feasible for a wide range of material systems. A measure of the reactivity of the metal-oxide system is the oxide heat of formation. An order of magnitude in difference of the heat of formation ΔH_O is found (in Table I) from metal systems which are highly reactive (as Y-O) to those which are not as reactive (as Cu-O).^[8]

Even though there is a great difference in heat of formation for metal-oxide systems, a method of reactive sputter deposition has been developed based on rate control to synthesize a continuous oxide composition range. Oxide phases can be prepared which are both equilibrium as well as metastable.^[5] The rate-control method enables the deposition of multilayered oxide films with designed control over the composition profiles, which can be abrupt and/or continuous as desired.

Fig. 9 The variation of refractive index and extinction coefficient with deposition rate of Mo-O.

Table 1. Metal-Oxide Heat of Formation^[8]

Oxide Compound	Y ₂ O ₃	MoO ₃	MoO ₂	NiO	Cu ₂ O	CuO
ΔH_O (gm-kcal mole ⁻¹)	-419.6	-182.7	-132.9	-57.64	-40.55	-37.74

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