Nanoscale colour control: W-O gradient coatings deposited by magnetron sputtering.

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Abstract. A new design of decorative tungsten oxide coatings is presented. The coatings were deposited with gradient refraction index by magnetron sputtering from a tungsten target and pulsing the reactive gas. The controlled injection of the reactive gas can produce a gradient concentration profile from pure tungsten to tungsten trioxide determining the final apparent colour of the coating. A dynamic sputtering model was built to simulate the coating growth during the reactive gas pulsing which was validated by the direct measurement of the oxygen content gradient in the deposited coatings. Finally these results were used for an optical model allowing describing the optical properties of the deposited tungsten oxide layer, again validated by experimental analysis. This procedure allows depositing coatings with a desired colour by using the models for finding the optimal oxygen pulse parameters. This proposed method can be easily applied to almost any metal/metal oxide system.

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1. Introduction

Many functionalities of decorative and optical thin films are often hindered by their insufficiently good mechanical properties and low resistance to wear damage [1]. Optical coatings with gradient refractive index layers are one of the most promising solutions for optical filters [2] and omnidirectional antireflective coatings [3,4]. Nevertheless, oxide [5,6] and oxynitride [7,8,9,10] materials with their hardness, chemical stability, resistance to oxidation and colour degradation, and tuneable optical properties could also be excellent candidates for protective optical films. The nitride or carbonitride coatings currently used in this field exhibit only a limited colour spectrum.

Gradient refractive index layers can be obtained by sol-gel methods [11], by co-evaporation of two materials [12], or by compositional changes during the layer growth [13]. Reactive magnetron sputtering is particularly suitable for the last of these methods, since it only requires a change in the reactive gas flow and allows large planar substrates to be covered with a high degree of homogeneity. The magnetron sputtering with reactive gas pulsing has been studied as an alternative process partially avoiding target poisoning and producing monolayer titanium oxide films [14]. However, reactive gas pulsing could lead to "multilayer" structure with gradient in chemical composition [15,16,17,18]. Multilayer tungsten oxide coating deposited with oxygen flow pulsing exhibited high hardness and adhesion on glass and steel substrates [17].

In this study, we present a new design for the deposition of decorative tungsten oxide coatings with gradient refractive index based on magnetron sputtering from a tungsten target with pulsing of the reactive gas. However, the controlled injection of the reactive gas can produce gradient films with increasing oxygen content (C_O) from pure tungsten to tungsten trioxide (W→W-O→WO_3). Thus, such coatings present a gradient concentration profile which, as we will show, can determine their final apparent colour. Compared to other transition metals, tungsten is much less reactive in relation to oxygen, which limits the formation of oxide species on the target and avoids the so-called hysteresis effect. Therefore, the discharge instabilities close to the critical

partial pressure of the reactive gas can be eliminated, thus allowing the deposition of films with any chosen composition in the W-WO_3 range.

2. Experimental details

Tungsten oxide coatings were deposited from a tungsten target (150 x 150 mm) by d.c. reactive magnetron sputtering. The argon pressure was kept constant at 0.2 Pa (12.5 sccm) and the reactive gas (oxygen) was cyclically injected using a rectangular signal defined by a period (T), an injection time (t_{on}) and a time without oxygen flow. The limits of the oxygen flow rate used for this study were 0 and 20 sccm; the latter value being the minimum flow necessary to reach deposition of stoichiometric WO_3. The deposition parameters were as follows: target current density J_W = 6 mA·cm^{-2}, inter-electrode distance 65 mm, substrate potential bias -70 V, no external heating (T < 350 ºC) and pumping speed of S = 100 l·s^{-1}. The coatings were deposited by repeating pulsing cycle in order to facilitate HR-TEM and XPS analysis on glass, Silicon wafers with (100) orientation, and M2 steel.

The microscopical investigation was carried out using an analytical high resolution transmission electron microscopy (HR-TEM) JEOL 2010-FEG, operated at 200 kV. The samples preparation for TEM analysis was performed according to a procedure described in detail in [19]; the coatings deposited on silicon wafers were used. The thickness of the samples used for cross-sectional HR-TEM characterization was typically between 20-35 nm. The oxygen distribution in depth was obtained using Gatan image filtering (GIF) system. GIF system was employed to acquire energy-filtered EF images with three- and two-window technique. The energy window width was 15 eV and the frame acquisition time was 30s. Background-subtracted intensity maps and jump-ratio images were acquired from O K electron energy loss edge over an area of 410 x 410 nm, with a pixel size of 0.8 x 0.8 nm.

Physical Electronics Quantum 2000 XPS equipment working with Al Kα (1486.6 eV) monochromatic wavelength with Ar ion beam (power of 2.5 keV and emission of 14 mA

corresponding to 1 Å/s of α-Fe; sputtering time was 6 s) was use to determine oxygen depth profile. The depth profile composition was calculated using Multipak program with the Target Factor Analysis.

Two theoretical models are coupled in order to simulate the optical properties of gradient tungsten oxide coatings deposited by magnetron sputtering with rectangular reactive gas pulsing (the cycle, T, consists of sputtering with constant oxygen flow, t_{on}, and without reactive gas t_{off}). The first model allows calculation of the gradient in the chemical composition of the film as a function of the sputtering conditions and the second one the simulation of the optical properties of a graded coating.

Since reactive magnetron sputtering is a well-established technique for thin film deposition, modelling of the process at steady-state has been extensively studied [20,21]. However, only a limited amount of work has been carried out concerning the description of dynamic processes, where one or more parameters are changing with time. Therefore, recently, a new model has been developed for the deposition process with reactive gas pulsing [22]. The model is based on the concept introduced by Berg et al. [23]. In the original model, the formation of compound is attributed only to the chemisorption of reactive gas at the target and substrate surface. A balance between the formation of a compound by chemisorption with implantation of the reactive gas and its removal by ion bombardment is assumed at the target surface. At the substrate, there is no substantial bombardment effect and therefore only the flux of the sputtered material and the chemisorption of the reactive gas have to be considered. Several extensions have been done in order to describe the dynamics of sputtering process. Unlike the classical steady-state approach, the presence of a relatively thick surface layer of oxide (~tens of nm) on the sputtering target is an important factor in determining the response time and must be taken into account [22]. Also, direct implantation of reactive gas and recoil implantation has to be accounted for [24]. The subsurface region is divided into several layers to describe the compositional depth profile caused by implantation effects. The model is one dimensional, i.e. a uniform distribution of the ion

current density over the target erosion area and deposition flux over the substrate surface is assumed. The complete set of time-dependent differential equations has been described elsewhere [22]. The output of this model includes the composition of the synthesized films versus time for given processing parameters, such as the reactive gas pressure or the discharge voltage. Parameters used for simulations were taken from [22].

The optical properties of tungsten oxide gradient coatings were modelled using the transfer matrix formalism, taking into account all the multiple reflections at the interfaces inside the sample. Considering a normal incidence, a set of reflectance spectra for coatings with different oxygen profiles was produced. Each coating presented an increasing oxygen concentration (C_O), from the bottom (C_O = 0 at. %) to the top (C_O = 75 at. %) of the film, and it is deposited onto a buffer layer of pure tungsten.

3. Results and discussion

Figure 1 shows a comparison of the experimental results with the sputtering model for one set of pulsing parameters (T = 50 s and t_{on} = 25 s). The target voltage is a better indicator of the status of the sputtering target than the pressure due to the much shorter response time of the power supply meter in relation to that of the pressure gauge.

The composition profile of the coatings grown during one experiment was analyzed by X-ray photoelectron spectroscopy (XPS) after successive etching during chosen times by ion bombardment. Scale transformation of the ion-bombardment time into the eroded thickness was done approximately from the sputtering yields of tungsten and sub-stoichiometric tungsten oxides. The sample deposited with T = 50 s, t_{on} = 25 s was scanned by Gatan image filtering (GIF) allowing the measurement of the oxygen distribution through the gradient coating in true length scale. The scale transformation referred to above was compared with the GIF result (figure 2 a); both profiles were identical taking into account experimental error and hence no further scale modification was required for XPS. As shown in figure 2 b), very good agreement

was found between the simulations of the coating growth and the experimental results. Therefore, the dynamic reactive magnetron sputtering model can be used for the selection of the optimum processing conditions to obtain coatings with the desired in-depth graded chemical composition. Furthermore, an optimal waveform (i.e. pulsing parameters T, t_{on}) of the gas flow or the sputtering power may be designed to produce a specific chemical composition gradient, required to obtain certain optical properties.

For modelling purposes, the gradient coatings were considered as multilayer structures where each layer has a fixed oxygen concentration, see figure 3. Furthermore, to determine the layer thicknesses (d_i) for each coating, the independently measured composition profile was approximated to as shown in table 1. For each layer of the coating, the real refractive index (η) and the extinction coefficient (κ) were calculated as a function of the wavelength using an empirical polynomial relationship, known as the Cauchy dispersion law. Although the electrical and optical properties of tungsten trioxide have been studied for more than half a century [25,26,27,28], there is still a lack of information about sub-stoichiometric WO_{3-x} coatings (particularly for $x < 2.5$). Therefore, a set of coatings was deposited by a conventional sputtering process with constant oxygen flow, keeping the other deposition parameters identical to those of the reactive gas pulsing [17]. Following this, the adjustable coefficients of the Cauchy dispersion polynomials were obtained using the experimental data from these homogeneous thick films obtained by ellipsometric measurements. It should be borne in mind that the optical properties of the homogeneous thick films, which are employed for the calculation, can only be used if they have a structure identical to the corresponding part of the gradient coating. HR-TEM representation of the gradient W-O layer shown in figure 4 exhibits an amorphous-like structure with no visible grains or voids, which corresponds to the results of the structural analysis of bulk W-O coatings [29]. The thickness of the tungsten layer was high enough to consider it as a bulk material. This was demonstrated by comparing the reflectance curves of a multi-cycle coating to those of a film produced with only one cycle. To simulate identical deposition conditions,

following procedure was used to deposit one-cycle coating: 2 minutes sputtering with the maximum oxygen flow followed by one rectangular cycle. For modelling, the buffer layer thickness was fixed at 10 μm and the respective dielectric function was calculated according to the Drude model.

The spectral range selected for the calculated results corresponds only to the visible wavelengths (400 nm < λ < 700 nm), for which ellipsometry data were available, allowing the correct application of the Cauchy dispersion law to the tungsten oxide gradient films. As already mentioned, the reflectance and transmittance spectra of the gradient coatings were modelled by applying the transfer matrix formalism [30]. Qualitatively good agreement was achieved between the experimental and the theoretical reflectance spectra for several samples with different oxygen concentration profiles (figure 5).

The spectra obtained enable us to predict the apparent colour of each coating as a function of layer thickness and composition profile. It is known that the apparent colour of a sample is mainly determined by the position of the maximum in the reflectance spectrum. We have investigated how changes in the oxygen concentration profiles could influence the experimental reflectance spectra. From the analysis of figure 5, it can be concluded that only the profiles similar to the 'a' type can be used for obtaining a desired colour, since it is only for profiles with such a shape that a reflectance spectrum with a well-defined maximum can be produced. For the 'a' type concentration profiles, our simulation also shows that the colour variation is strongly influenced by the changes in the thicknesses of the internal layers of the gradient films, i.e., by the layers with the lowest oxygen concentration.

4. Conclusions

The procedure described above can be used to produce coatings with a desired apparent colour. With our optical simulation, we could adjust a few model parameters (one or two) of the most influencing coating's sub-layer, in order to obtain a determined position and magnitude for the

reflectance maximum. This would allow optimization of the composition profile of the gradient coating, to obtain a desired colour on demand. On the other hand, the dynamic sputtering model can be used to find out whether realistic settings of sputtering parameters (i.e. parameters of the gas flow and sputtering power) could be found to achieve such a colour. Obviously, the process presented is very versatile and can be used for virtually all sputtered metals in oxygen atmosphere, provided that the optical properties of their oxides are known. Moreover, it can be extended to pulsing processes with two reactive gases using oxygen, nitrogen or carbon-based gases. Recent results concerning the optical properties of the Nb-O-N [15] and Ta-O-N [16] systems deposited with constant nitrogen flow and pulsed oxygen clearly demonstrate the potential of our proposed control of the gradient layer. Finally, magnetron sputtering with reactive gas pulsing can also be used to deposit multi-cycled coatings without a metal layer and the optical properties would be driven by the synergetic effect of the refractive index gradient and the optically-active multilayered structure.

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List of tables

Table 1. The table gives the layer's thicknesses (d_i) and the oxygen concentration (C_O) for two distinct tungsten oxide gradient coatings, considered as multilayer structures with seven layers (layers 1 and 7 correspond to the top and bottom of the structure, respectively).

Layer	C_O (at. %)	d_i (nm)	
		T=50s t_{on}=45s	T=100s t_{on}=90s
1	75	96.0	151.6
2	73	4.6	8.2
3	70	17.2	6.9
4	63	15.1	26.4
5	46	1.3	15.8
6	30	0.6	1.3
7	0	0.5	2.6

Figures captions

Figure 1. Experimental (solid) and simulated (dashed) process parameters during pulsing of reactive gas. Process curves for the discharge voltage (a) and total pressure (b) are shown for T = 50 s and t_{on} = 25 s.

Figure 2. Comparison of the depth profile obtained by XPS (W and WO_3 curves) and GIF (G curve, where oxygen concentration was recalculated corresponding to WO_3) (a) and simulation of the coating growth (b). The oxygen pulsing parameters were T = 50s, t_{on} = 25s; the direction of coating growth is from right to left. The TEM image shows the multilayer structure deposited by continuous oxygen pulsing.

Figure 3. Qualitative representation of the concentration profile for a typical gradient coating and its discretization (d_b corresponds to the thickness of the pure tungsten buffer layer in which the gradient coating is deposited). For the modeling, the real concentration profile of each sample is approximated by a set of step functions.

Figure 4. Gradient coating (T = 50s, t_{on} = 25s) observed by TEM. The image on the right shows the detail of the transition from tungsten to tungsten trioxide caused by the injection of the oxygen flow.

Figure 5. Typical effect of the three selected oxygen concentration profiles (presented in the inset and labelled a, b, and c, see text) on the calculated reflectance spectra (upper) and comparison between simulation and experiment (lower) for coatings deposited with T = 50 s, t_{on} = 45 s and T = 100 s, t_{on} = 90 s.