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# Packing density/surface morphology relationship in thin sputtered chromium films

Alexander Höflich, Nathan Bradley, Colin Hall, Drew Evans, Peter Murphy, Eric Charrault *

*Future Industries Institute, University of South Australia, Mawson Lakes, SA 5095, Australia*

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ABSTRACT

Modifying and engineering the properties of materials can be achieved by coating them with thin films possessing specific characteristics. The final properties of the coating are determined by the deposition conditions and by the associated film's growth mode. To gain a better understanding and eventually control over the growth and properties of very thin films (thickness less than 50 nm), various chromium films were deposited by magnetron sputtering and their electrical and optical properties were measured. This paper presents the relationships between the stress, the material's surface morphology and the properties of such chromium thin films.

We observed an increase in electrical conductivity and photopic reflection of the films with the increase of the deposition power. Our analyses further revealed that the surface morphology is directly responsible for the enhancement of these properties, as surfaces presenting the least air fraction ratio (smooth surface with large grains and a Gaussian roughness distribution) were the most conductive and most reflective. We also demonstrated that calculating the residual film stress is an incomplete way of assessing the structure of the film, as films having similar residual stress exhibited different properties. In conclusion, the surface morphology and its roughness distribution represent a convenient way to estimate the packing density of sputtered thin films.

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## 1. Introduction

Thin film coating is an important industrial process used to enhance basic materials' properties and is widely applied throughout various applications and in various industries [1–3]. Sputter deposition is one of the most common physical vapour deposition (PVD) techniques to deposit thin films due to its speed of process and versatility in terms of candidate materials to be used. The final structure and properties of the film are directly influenced by the sputtering conditions through the seeding and subsequent growth of the deposited film.

An inherent characteristic of thin films deposited by PVD is the residual film stress, as the process is performed in non-equilibrium conditions. The residual film stress could lead to either positive or negative performances depending on the required properties of the final coating, but in general, high levels of stress (either compressive or tensile) can cause several undesirable interfacial issues, such as buckling or cracking. Controlling the level of residual stress in the film is one of the key factors in designing and developing high quality films.

Due to their lightweight, flexibility and formability, polymeric substrates have generated a growing interest for commercial applications and have started to replace more traditional materials, such as glass, for the development of next generation robust decorative coatings. Thus, linking the physical properties and performances of PVD coatings [4–9] to their structure, becomes critical to develop new products and gain more understanding of the growth mechanisms on such polymeric substrates. Other characteristics of polymers, such as their surface energy and chain lengths have already been reported to have an impact on the growth and morphology of thin films [10].

The general understanding of stress and of the phenomena driving it has been growing from empirical observations [11–14] to fundamental understanding of the atomic mechanisms of stress generation (grain boundary coalescence for tensile stress [15–18], atomic peening [19–21] and adatom diffusion for compressive stress [22–25]), over the past decades. The process–structure relationship has also been extensively investigated and, for instance, the early structural zone diagram by Thornton [26], which categorized the films' microstructure as a function of the “energy” present in the system (linked to the process variables), is still widely used. However, most of the work done have focused on thick films (>100 nm) and very thick films (>1 μm) [27] and not much has been done on very thin films (<50 nm). As the thickness of the thin films decreases, the volume to surface ratio of the material becomes extremely small. As a consequence, the characterization of the volume properties of the material becomes complicated, and the properties of the film are expected to become more influenced by the surface morphology, such as average grain size, roughness and roughness distribution. No clear correlation between stress and such quantitative surface aspects for very thin films has yet been reported.

* Corresponding author.
*E-mail address:* eric.charrault@unisa.edu.au (E. Charrault).

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To assess the relationship between residual stress, surface morphology and film properties for a defined microstructure, we deposited very thin Cr films with different residual stresses on various silica-like and polycarbonate substrates. By varying the deposition power, we observed correlations between the optical and electrical properties and both stress and surface morphologies of the films. This paper describes how the surface morphologies, and more particularly the roughness distributions, are related to the film's properties, and how they correlate with the residual film stress.

## 2. Experimental section

The PC and glass substrates were mounted on a rotating plate (20 rpm), within a custom-built magnetron sputtering chamber, and were coated with 33 ± 2 nm thick Cr films from a high purity Cr target (from plasmaterial) in an Ar environment at a pressure of $1.7 \times 10^{-3}$ mbar at 0.5, 1, 2, 3, 6 kW (estimated power densities were between 0.85 and 10.5 W/cm$^2$). To modify the substrate topography, intermediate 170 ± 5 nm $SiO_2$ layers were deposited in an Ar/$O_2$ environment at a pressure of $1.3 \times 10^{-3}$ mbar at various powers. To disregard the effect of temperature (up to 80 °C during the $SiO_2$ deposition) on the growth of the film and its residual stress, the samples were cooled down for 24 h prior to the 33 nm Cr deposition at 3 kW. To ensure similar plasma conditions, depositions of 3 kW Cr were done simultaneously on the various PC/glass/sputtered $SiO_2$ substrates.

The residual stress was calculated via the classical Stoney's equation [28]. The surface deflections were measured over a 3 cm long surface profile by mechanical profilometry (Dektak) on PC and glass substrates. Prior to the surface profile measurement, the samples were kept in a dry environment (11% RH) for at least 2 days, to minimize the artefact related to moisture uptake.

An AFM Multimode 8 (Bruker) was used for the surface morphology investigation. Tapping mode tips from NT-MDT were used, whose specifications per the manufacturer are k = 70 N/m, R = 10 nm, $f_0$ = 200 kHz. Only films deposited on glass substrates were imaged and were kept in a dry environment prior to imaging to minimize water condensation on their surfaces. An amplitude ratio A/As (with the amplitude setpoint, As = 300 mV) was kept high at around 0.7. The surface parameters, root mean square roughness ($R_q$), skewness ($S_{sk}$) and kurtosis ($S_{ku}$) were calculated using the nanoscope analysis software (Bruker).

Micro X-ray diffractometer measurements (micro-XRD Max Rapid II, Rigaku) were performed to determine the texture of the Cr films. A Cu anode was use to generate the radiation at an angle of 10° and X-rays diffraction patterns were recorded over a 2θ range 20–60°.

Using the four point probe technique, and a current of at least 1 mA, sheet resistance measurements were taken for each of the samples, which were then converted to conductivity (σ) using the relationship: $\sigma = 1 / (\rho \cdot t)$, where ρ is sheet resistance and t is the film's thickness. Samples were also kept in a dry controlled environment prior to measurement (no effect of ambient moisture or ageing were noticed).

The photopic specular included reflectance ($R_{rsi}$), corresponding to the lightness value Y, was measured with a HunterLab Ultrascan Pro instrument using an integrating sphere and an illuminant A/2.

## 3. Results and discussion

### 3.1. Stress/properties relationship

To characterize the properties of the metallic films, surface conductivity and photopic light reflection were chosen due to their ease of measurement and their convenience as far as metals are concerned.

The thin film's residual stress was calculated as an indirect structural measure of the deposited thin films, via the measurement of the surface deflection and the classical Stoney's equation [28]. By depositing an intermediate $SiO_2$ layer prior to the Cr film, the surface and the mechanical properties of the PC and glass substrates were altered. The stress values due to the Cr layer was calculated using a superposition equation [29]:

$$\sigma_{Cr} = \frac{1}{h_{Cr}}\left[\sigma_{SiO2/Cr} * h_{SiO2/Cr} - \sigma_{SiO2} * h_{SiO2}\right], \quad (1)$$

where $h_n$ and $\sigma_n$ are the thickness and residual stress of the "n" layer. Several post-deposition phenomena, such as ambient moisture uptake, compressive stress relaxation mechanism [23,30], potentially Cr film passivation upon atmosphere exposure [31], tensile stress relaxation mechanism by crazing [32,33] of the Cr films on PC, induced significant variations in the residual stress measurements but did not seem to have any significant effect on the film's properties. To minimize those effects, all samples were stored in a dry environment (11% RH) prior to and after deposition and measurement were performed after 2–3 days after deposition (the reported stress values correspond to an average calculated over 3 days after stabilization of the stress value).

Fig. 1 shows the evolution of electrical conductivity as a function of the mean residual stress values. Conductivity measured for all samples (Cr on glass, sputtered $SiO_2$ and PC) are depicted in the graph and mainly differentiated by the power used (0.5, 1 kW low powers, and 2, 3, 6 kW high powers). Regardless of the deposition power, a high average level of tensile stress (≈1 GPa) was measured on both glass and PC substrates, and is similar to values reported for thin Cr films [34]. It is the typical result due to the coalescence of grain boundaries for films growing via the Volmer–Weber growth [35]. Two major trends stand out from this plot as the conductivity at low power seems to be only slightly dependent of the mean stress, with a constant value of around 3500 S/cm for all samples, while the conductivity increases linearly with stress at higher powers. The high levels of tensile stress were partially relaxed by the formation of crazing [32,33] in the films deposited on PC (see micrographs in Fig. 1). The resulting conductivities on PC were much lower than that on glass. The dense interconnected crazed network at 3 kW (c) exhibits the lowest residual stress value, and the high density of air gaps between the metallic domains offer a lot of "air" resistance, resulting in the lowest electrical conductivity. Similarly at 6 kW, a less dense network of non-interconnected crazing reduces the conductivity significantly, however the stress value remains highly tensile (crazing not fully connected) as the larger metallic domains are still connected. On the contrary, the surface do not present any crazing at low power, indicative of no stress relaxation (lighter features seen on the micrograph (a) are moulded defects present at the surface of the polycarbonate substrate). The metallic surface maintains its continuity, allowing the electrons to move "freely" on the surface. Hence why the conductivity is comparable to that of a film deposited on glass.

Fig. 2 illustrates the evolution of the reflection as a function of the mean residual stress of the Cr film. Surfaces are more reflective when prepared at high power (up to 64% R) and both reflection levels increase similarly with the mean stress. When deposited at high power, films having a large residual stress seem to reach a reflection plateau value.

The crazing observed on PC has not affected the reflection of the film as all three measurements on PC are similar to their glass counterparts, with around 62% reflection at high power and around 52% at low power. Considering the maximum stress before stress relief, which was measured at around 1 GPa, the reflection of the 3 kW cracked film on PC would align well with the general trend (b).

Contrary to the electrical conductivity, which is a measure through and mainly across the film via the sheet resistance, the reflection depends greatly on the thickness and the volume of the film. Indeed, from the percolation thickness, for which the deposited film forms a continuous layer on the substrate, the film becomes less and less transparent, as more material is present to absorb and reflect the incoming light off the surface. As such for films having similar thicknesses, a change in reflection could indicate different packing density or material volume fraction. A theoretical reflectivity of around 65% is calculated for

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