Optical characterization of thin and ultrathin chromium films

J.M. Siqueiros[1], R. Machorro[1], Shu Wang[1], L.E. Talavera[1], and J. Portelles[1,2]
[1] *Centro de Ciencias de la Materia Condensada, Universidad Nacional Autónoma de México*
Apartado postal 2681, 22800 Ensenada, Baja California, Mexico
[2] *Facultad de Física, Universidad de La Habana*
Vedado, La Habana, Cuba 10400

F. Villa
Centro de Investigaciones en Óptica, A.C.
Apartado postal 1-948, 37000 León, Gto., Mexico

Recibido el 6 de mayo de 1999; aceptado el 1 de septiembre de 1999

Thin and ultrathin chromium films were grown on glass by thermal evaporation in vacuum of the order of 10^{-4} Pa with the purpose of studying the characteristics of these layers used as adhesion promoters in a number of applications. Ellipsometry is used to obtain the optical properties of chromium and chromium oxide as well as the equivalent ultrathin layer for films with thickness from a fraction to a few nanometers. Experimental measurements and theoretical modeling showed that the ultrathin films essentially consist of chromium/chromium oxide clusters with heights of the order of the measured thickness as determined by a quartz microbalance indicating a Vollmer-Weber growth mechanism. Percolation was found for thickness above 30 nm.

Keywords: Chromium; chromium oxide; thin films; optical properties; ellipsometry

Se depositaron películas delgadas y ultradelgadas de cromo sobre vidrio por evaporación trmica en vacíos del orden de 10^{-4} Pa con el propósito de estudiar las características de estas capas utilizadas como promotoras de adhesión en diferentes aplicaciones. Se utiliza elipsometría para obtener las propiedades ópticas del cromo y del óxido de cromo, así como de las capas ultradelgadas equivalentes en el caso de espesores desde una fracción hasta varios nanometros. Las medidas experimentales y el modelaje teórico mostraron que las películas ultradelgadas consistían esencialmente de cúmulos de cromo/óxido de cromo con alturas del orden de los espesores medidos experimentalmente mediante una microbalanza de cuarzo, sugiriendo un mecanismo de crecimiento del tipo Vollmer-Weber. Se observó percolación para espesores mayores de 30 nm.

Descriptores: Cromo; óxido de cromo; películas delgadas; propiedades ópticas; elipsometría

PACS: 78.66.-w; 78.66.Bz; 81.15.Ef

1. Introduction

There are many applications where the use of intermediate thin films to promote adherence between substrate and coating is necessary [1–11]. One important example is the case of Pt films on SiO_2/Si substrates that require a Ti or TiO_2 underlayer for good adherence [12–17]. Ta films are often used in the RuO_2/SiO_2/Si systems [18]. chromium thin films, however, have been probably the most commonly used for the purpose of adhesion especially for gold and for dielectric films of importance in the ophthalmic industry [2–4]. The optical properties of metallic chromium are available in the literature [19] but those of the ever present chromium oxide, at least to our knowledge, are not. On the other hand, to obtain the optical properties of a layer of a few angstroms of chromium, several different approaches were tested. A mixture of metallic chromium with chromium oxide on its surface in a dielectric matrix (air) using an effective medium approximation was tried with no success. The best results were obtained by substituting the experimental deposit by an optically equivalent layer and fitting the ellipsometric experimental data with a classical oscillator model with a correction of a Drude term. The optical constants of metallic chromium and chromium oxide were also obtained from the ellipsometric measurements. The actual topography of the layers was probed with an atomic force microscope (AFM) and the chemical composition by Auger electron microscopy (AES) and energy dispersive spectroscopy (EDS).

2. The experiment

The studied samples were prepared by depositing chromium films a few angstroms thick as well as a relatively thick film (160 nm) by thermal and electron gun evaporation at base pressures of the order of 10^{-4} Pa. The films were deposited from 99.99% purity pellets and the film thickness was monitored and controlled with a quartz microbalance. The deposition rates were 0.2 Å/s for thermal evaporation and 0.1 Å/s for the electron gun technique. At these deposit rates and base pressure, at least partial oxidation of the chromium is expected.

Spectroscopic ellipsometry in the 1.5 to 5.0 eV photon energy range was used to obtain the optical properties of the films. Electronic spectroscopies such as Auger electron spec-

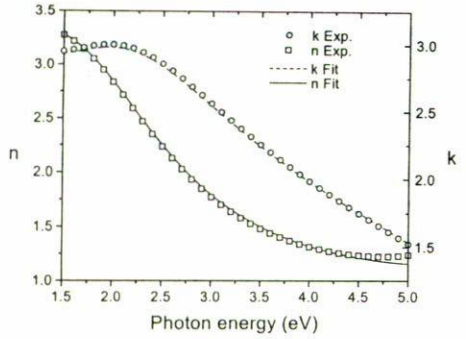

FIGURE 1. Measured real and imaginary parts of the refractive index for an opaque chromium film and its natural oxide deposited on glass and the fit by classical oscillators.

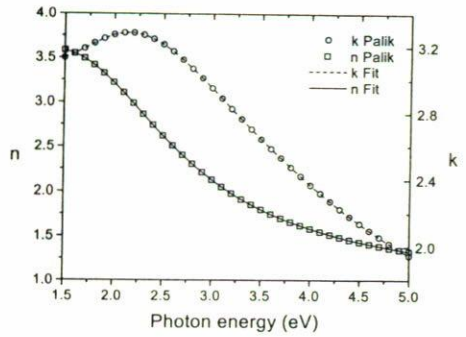

FIGURE 2. Classical oscillator fit to the experimental data for chromium from Ref. 19.

troscopy (AES) and energy dispersive spectroscopy (EDS) were used to determine the chemical composition of the samples. The surface structure of the films was probed with an atomic force microscope (AFM).

3. Results

The optical properties of the chromium oxide/chromium/glass system measured by ellipsometry are shown in Fig. 1 as function of the photon energy. The modeled system consisted of a chromium oxide film a few angstroms thick on an optically opaque chromium substrate (thickness $\tau = 160$ nm). The optical properties of chromium were determined following previously reported work [20, 21] by extracting from the experimental data the values of the dielectric constant modeled by a classical damped oscillator represented by the following expression:

$$\varepsilon = \varepsilon_\infty + \sum_{j=1}^{2} \frac{f_j \omega_{oj}^2}{\omega_{oj}^2 - \omega^2 + i\gamma_j \omega}. \qquad (1)$$

Here, ε_∞ is the high frequency dielectric constant, f_j is the oscillator strength, ω_{oj} is the characteristic frequency of the j^{th} oscillator and Γ_j the corresponding damping factor. The relation $N(\lambda) = [\varepsilon(\lambda)]^{1/2}$ was also used.

For the chromium oxide a Cauchy model for the refractive index, $N(\lambda) = n(\lambda) + ik(\lambda)$ where

$$n(\lambda) = A + \frac{B \times 10^4}{\lambda^2} + \frac{C \times 10^9}{\lambda^4},$$

$$k(\lambda) = D \times 10^{-5} + \frac{E \times 10^4}{\lambda^2} + \frac{F \times 10^9}{\lambda^4} \qquad (2)$$

was used. Here A, B, C, D, E and F are the fitting coefficients.

The results of the ellipsometric measurements of a 160 nm chrome film on glass and the theoretical fit using a classical oscillator model are shown in Fig. 1, where a fitting process based on the Levenberg-Marquardt method [22] was used. The fitting process was performed on the ellipsometric parameters Ψ and Δ. The goodness of the fit was given by the value of χ^2 and, in this case, $\chi^2 = 0.324$ for $\tau = 1.96$ nm.

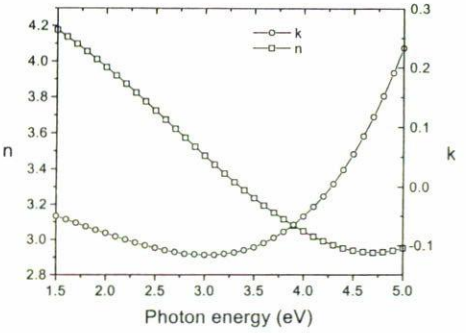

FIGURE 3. Complex refractive index of the natural oxide of chromium obtained by a Cauchy model fit to experimental data.

Consideration of surface roughness was unnecessary since a better fit was obtained for a smooth film. The optical properties of chromium obtained from the experiment were compared with the data published by Palik [19] and the coincidence was excellent, as shown in Fig. 2. The optical properties (n, k) of the natural chromium oxide obtained with a Cauchy model for absorbent materials are plotted in Fig. 3 as functions of the photon energy.

The numerical values for the fitting parameters for chromium and chromium oxide are presented in Table I.

The optical properties of chromium and chromium oxide thus obtained were used to model the refractive index of the ultrathin films (0.7, 2.5 and 3.5 nm thick) deposited by thermal evaporation starting from the ellipsometric measurements and leaving the thickness (τ) as the only fitting parameter. Atomic force microscopy (AFM) indicated that the deposit consisted of non-coalescent clusters of chromium oxide/chromium on glass instead of a continuous film. Auger electron spectroscopy (AES) indicated percolation only above 30 nm thickness where no charging of the samples due to the electron beam was observed. A model with such characteristics was also intended with different chromium-oxide/chromium ratios with very limited success. Here the film consisted of the chromium oxide/chromium clusters embedded in a dielectric matrix (air) put together through an effective medium approximation. Finally, an equi-

TABLE I. Fitting parameters for chromium (classical oscillators) and chromium oxide (Cauchy model).

Chromium		Chromium oxide	
ε_∞	0.629	A	4.475
f_1	11.251	B	−21.492
f_2	336.486	C	7.460
ω_{01}	2.207	D	1.200
ω_{02}	3.222	E	−3.905
γ_1	2.364	F	3.284
γ_2	−18.564		

TABLE II. Fitting parameters for the equivalent layers of the chromium ultrathin films.

τ =0.7 nm		τ =2.5 nm		τ =3.5 nm	
ε_∞	8.966	ε_∞	20.252	ε_∞	12.954
ε_S	1.000	ε_S	1.000	ε_S	1.000
f_1	602.844	f_1	73.241	f_1	67.351
f_2	−535.358	f_2	−92.401	f_2	−68.174
ω_{01}	1.820	ω_{01}	2.419	ω_{01}	1.862
ω_{02}	2.231	ω_{02}	2.013	ω_{02}	1.916
γ_1	3.896	γ_1	4.138	γ_1	3.516
γ_2	−5.753	γ_2	−4.242	γ_2	−3.976
ω_P	−36.794	ω_P	−22.385	ω_P	−16.390
Γ_D	20.352	Γ_D	3.490	Γ_D	5.327

valent layer approach (ELA) was used with satisfactory results. The technique consists, essentially, in proposing a hypothetical layer with thickness equal to the experimental value and optical properties given by a suitable model. Classical oscillators with a Drude correction represented by:

$$\varepsilon_D = \frac{\varepsilon_S \omega_P^2}{\omega^2 + i\Gamma_D \omega} \tag{3}$$

was a good choice for the chromium system. Here, ε_D is the Drude dielectric function, ε_s represents the static dielectric constant, ω_P stands for the plasma frequency and Γ_D for the damping factor. The optical properties of the substrate (glass) were previously measured by ellipsometry. By fitting the experimental data as was done for the thicker films described above a completely characterized equivalent layer is obtained and its optical properties may be used for multilayer design.

Figures 4, 5, and 6 show the results of fitting an equivalent layer to the 0.7, 2.5 and 3.5 nm thick ultrathin chromium films, respectively. It can be noticed that the fit is better for the 2.5 and 3 nm films. The fitting parameters are presented in Table II.

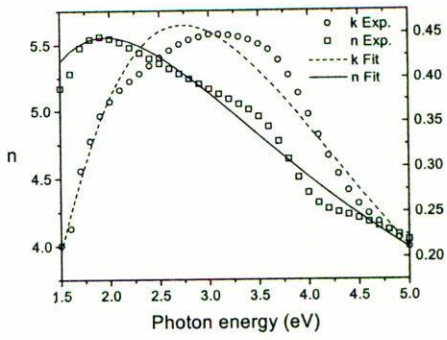

FIGURE 4. Classical oscillator fit to the experimental data of the refractive index for a 0.7 nm chromium film on glass.

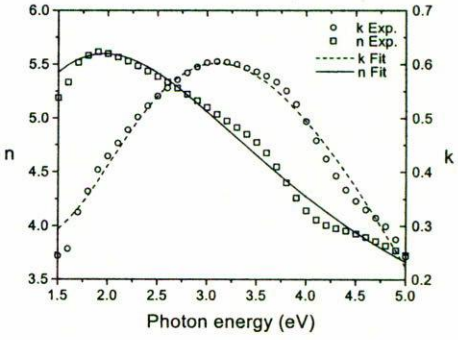

FIGURE 5. Classical oscillator fit to the experimental data of the refractive index for a 2.5 nm chromium film on glass.

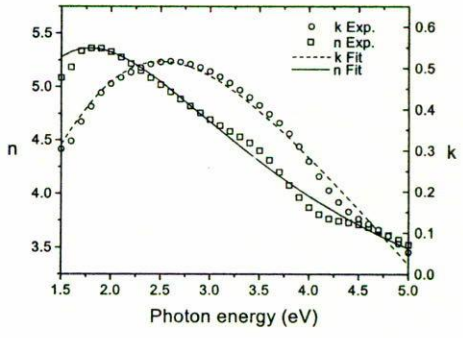

FIGURE 6. Classical oscillator fit to the experimental data of the refractive index for a 3.5 nm chromium film on glass.

It is evident from the numerical results that the optical properties are more sensitive to some of the parameters than to others. In the case of the Cauchy model, the variation of D had little effect in the results. For the classical oscillators and drude models, ε_∞, ε_S ,f_1 ,f_2 and ω_P, had to be varied in large relative intervals to have an effect in the final result. However, to obtain acceptable values of χ^2 (< 1), they must be considered. EDS and AES measurements were performed in the thicker samples and nothing but chromium and oxygen were detected.

4. Conclusions

Two systems of chromium/chromium oxide have been studied by ellipsometry: the first one is a continuous, optically opaque metal film with its natural oxide where the refractive index of chromium oxide is obtained for the visible part of the spectrum. The second, a system of ultrathin chromium/chromium oxide films consisting, according to AFM measurements, of non-coalescent clusters. The opaque film was readily analyzed using a classical oscillator model obtaining thus the optical properties of metallic chromium. A Cauchy model proved to be an excellent choice to model its natural oxide. It is well known that the optical properties of thin film will vary from one film to the other since they strongly depend on the deposition technique and conditions. However, based on a good number of experiments, it can be said with confidence that the Cauchy model is appropriate for chromium oxide films. The thickness obtained for the chromium oxide ($\sim$ 2 nm), can be considered as a representative value for the natural oxide of any chromium surface. The numerical values for the refractive index thus obtained were used to model the optical properties of the ultrathin films, following the cluster geometry obtained from the AFM measurements with no success. The equivalent layer approach where an optically equivalent layer is proposed worked very well. For the studied system a combination of classical oscillators and a Drude term was an adequate choice. It is clear that in this approach any polynomial that fits the experimental results would do and it would be very difficult to attribute any physical significance to the fitting parameters. Nevertheless, the numerical results are valid. The useful result would then be that if the experimental measurements are repeatable as in the set of samples used in this study, the optical properties thus obtained might be used for multilayer design. No quantitative measurements of adhesion were performed. Moreover, it is interesting to see that adhesion of subsequent layers is enhanced by chromium even though the film is not continuous. Actually, thicker continuous films would be too absorbent for most optical applications.

Acknowledgments

This work was partially supported by CoNaCyT, project No. 26314-E and DGAPA-UNAM, project No. IN108995. The technical support by J. Nieto, I. Gradilla, and G. Soto is acknowledged. We thank C. Falcony and C. Vázquez from CINVESTAV for the AFM measurements.

1. E. Daniels, *Zeiss Informationen* **48** (1963) 50.
2. D. Matox, *Sandia Corp.* **R-65** (1965) 852.
3. J. Chapman, *J. Vac. Sci. Technol.* **11** (1974) 106.
4. Berry, P.M. Hall, and M.T. Harris, *Thin Film Technology*, (Van Nostrand, Princeton, NJ, 1968) p. 584.
5. H.K. Pulker, *Thin Films Science and Technology*, **6** (1984) 64.
6. D. Mattox, *Thin Solid Films* **18** (1973) 173.
7. K.L. Mittal, *Electrocomp. Sci. Technol.* **3** (1976) 21.
8. R. Beeching, *Phil. Mag.* **22** (1936) 938.
9. Navy Dept. Bureau of Ordinance, U.S. Optics Filming, Report No. OP1512 (1945) 103.
10. H. Levinstein, *J. Appl. Phys.* **20** (1949) 306.
11. O.S. Heavens, *J. Phys. Radium* **11** (1950) 355.
12. D.J. Taylor, J. Geerse, and P.K. Larsen, *Thin Solid Films* **263** (1995) 221.
13. S.T. Kim, H.H. Kim, M.Y. Lee, and W.J. Lee, *Jpn. J. Appl. Phys.* **36** (1997) 294.
14. K. Sreenivas, I. Reaney, T. Meader, and N. Setter, *J. Appl. Phys.* **75** (1994) 232.
15. I. Kondo, T. Yoneyama, and O Takenaka, *J. Vac. Sci. Technol. A* **10** (1992) 3456.
16. J.O. Olowalafe *et al.*, *J. Appl. Phys.* **73** (1993) 1764.
17. K. Abe *et al.*, *Jpn. J. Appl. Phys.* **30** (1991) 2152.
18. T. Takagi, I. Oizuki, I. Kobayashi, and M. Okada, *Jnn. J. Appl. Phys.* **34** (1995) 4104.
19. D.W. Lynch and W.R. Hunter, *Handbook of Optical Constants of Solids*, edited by E. Palik, (Academic Press, New York, 1985) p. 341.
20. J.M. Siqueiros, R. Machorro, and S. Wang, *Rev. Mex. Fís.* **43** (1997) 1021.
21. R. Machorro, J.M. Siqueiros, and S. Wang, *Thin Solid Films* **269** (1995) 1.
22. W.H. Press, S.A. Teukolsky, W.T. Vetterling, and B.P. Flannery, *Numerical Recipes in C*, Second Edition, (Cambridge University Press, New York, 1992); D.W. Marquardt, *Journal of the Society for Industrial and Applied Mathematics* **11** (1963) 431.