ELSEVIER

Thin Solid Films 301 (1997) 149–153

thin solid films

Optical properties of nickel thin films deposited by electroless plating

E. Dumont [a,*], B. Dugnoille [a,1], J.P. Petitjean [b], M. Barigand [b]

[a] *Service Science des Matériaux, 56 rue de l'Epargne, Mons B-7000, Belgium*
[b] *Service de Chimie générale et Electrochimie, Faculté Polytechnique de Mons, 56 rue de l'Epargne, Mons B-7000, Belgium*

Received 17 October 1996; accepted 7 January 1997

Abstract

A nickel thin film is deposited onto a float glass substrate by means of an autocatalytic reducing reaction in a metallizing solution. The growth of this film is monitored in situ using an ellipsometer. By analysing the ellipsometric measurements, the changes in the complex optical index and the thickness of the film over time can be determined. A comparison of the complex optical index obtained from analysis of the experimental results and those predicted by various effective medium theories indicates that the Maxwell-Garnett theory is the best for modelling the optical properties of the nickel layer.

Keywords: Electrochemistry; Ellipsometry; Nickel; Optical properties

1. Introduction

The use of metallic layers on glass is an important area of the glass-making industry. The metal can give the glass substrate tailored optical properties (reflection, transmission) from the visible to the near-IR range. Metallic films have been used for many years in the manufacture of mirrors. More recent applications make use of very thin films (below 50 nm), for example for low emissivity window glass or for what are known as heat mirrors [1,2]. These applications are based on the optical behaviour of the films, which have optical constants different from those of bulk metal, depending on their thickness [3–5].

Although metallic films on glass can be produced by vacuum deposition, chemical deposition processes remain competitive because of their efficiency and low cost [6]. However, the increasing demand for very thin metallic films calls for a better understanding of the chemical deposition process in order to control the final properties of the film.

In most instances, chemical metallizing methods use autocatalytic reducing reactions which cannot be controlled or monitored by voltage or current supply as used in electrochemical reactions. Other monitoring methods such as Auger or ESCA cannot be used to monitor layer growth either, because the reaction takes place within a liquid. Optical methods such as ellipsometry, however, are well suited to monitor this kind of process, provided that the liquid medium is not too absorbent and the deposition rate of the layer not too high in comparison with the speed at which the ellipsometric data are recorded. Ellipsometry has been applied successfully to the monitoring of vacuum-deposited metallic films [7]. However, few studies have been published so far on the ellipsometric monitoring of metallic films produced by chemical reactions within a liquid [8].

Ellipsometry is an optical technique which measures the change in polarization of an incident light beam after reflection onto a sample. This yields information about the changes in the surface.

Nickel thin films chemically deposited onto float glass have been studied because they can be used in place of silver to make cheaper mirrors for domestic use. Determining the optical constants of the layer as a function of its thickness is essential for predicting the final properties of the mirror.

2. Nickel thin film preparation

The nickel is chemically deposited onto the float glass substrate by means of an autocatalytic reducing reaction (electroless plating).

* Corresponding author.
[1] E-mail: Dugnoil@fpms.fpms.ac.be

First the glass substrate is sensitized using an acid $SnCl_2$ solution. Then the glass substrate is activated using another solution containing a palladium compound [9–11]. These stages are necessary to create catalytic sites on the substrate.

The metallizing solution, which contains metal ions and reducing agents, is stable. The reaction takes place only when catalysed by metals such as Au, Pd or Ni. The catalytic sites created on the glass substrate allow the coating reaction to begin as the substrate comes into contact with the metallizing solution. The first ions of nickel which are reduced aggregate on the glass surface to form nuclei. The deposition process can continue after the catalytic sites are coated with nickel because it too is a catalyst for the reaction. The size of the nuclei then increases over time until they coalesce. The layer continues thickening and finally forms a continuous film. Sometimes such a film can have a rough surface. The deposited material contains mainly nickel with a small amount of phosphorus.

3. Experimental details

The ellipsometer used for our measurements is a Rudolph Research 2000 FT spectroscopic ellipsometer.

Since the metallizing solution is green, we chose a working wavelength equal to 511 nm, which corresponds to the highest transmission of light through the solution. As a substrate, we used 4 mm thick glass slabs. The substrate is placed in a cell containing the metallizing solution. This cell is trapezoidal in shape and has an input and an output window in the sides to allow the light beam to pass through the cell. The angle formed by the windows is equal to 70.36°. Reflection from the underside of the substrate has been eliminated by coating that side with a black absorbent substance.

The coating reaction usually begins after 3 min. This induction period is necessary for chemicals to reach the catalytic sites through the laminar layer of water present on the glass substrate. The metal then begins to cover the glass and the sample becomes more and more absorbent. After full opacity is obtained, the light can no longer penetrate and the film behaves in the same way as a bulk substrate of nickel.

Ellipsometry gives two angles, delta (Δ) and psi (Ψ), which are a function of the modification of the polarization state of light after reflection on the sample [12]:

$$\rho = \frac{R_p}{R_s} = \tan\Psi \, e^{j\Delta}$$

Our ellipsometer can give one pair of (Δ, Ψ) per second, which is the average of 15 fast consecutive measurements. As the duration between the beginning of the coating and full opacity of the film is about 200 s, we can obtain approximately 200 ellipsometric (Δ, Ψ) values during the formation of the nickel film. We record values for (Δ, Ψ) and the time t. A typical result is shown in Fig. 1.

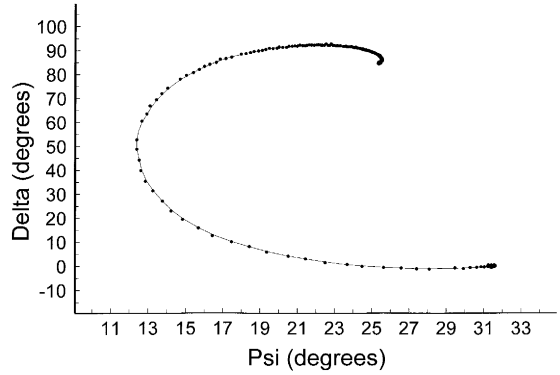

Fig. 1. Variation in the ellipsometric angles (Δ and ψ) vs. time during the growth of the nickel thin film: ● experimental values, ——— interpolation.

4. Results

4.1. Determining the complex effective optical index and of the thickness of the film

Drude theory and Fresnel equations allow Δ and Ψ to be determined on the basis of several physical properties of a smooth film deposited onto a substrate [12]. In our case, Δ and Ψ read as follows:

$$(\Delta(t), \Psi(t)) = f(N_A, N_S, N_{eff}(t), d_{eff}(t), \lambda, \phi_i) \qquad (1)$$

where $N_A = n_A - jk_A = 1.346 - j0.0$ is the complex optical index of the metallizing solution at 511 nm. This value has been obtained using an Abbe refractometer. $N_S = n_S - jk_S = 1.520 - j0.0$ is the complex optical index (at 511 nm) of the air side of the float glass substrate. $N_{eff}(t) = n_{eff}(t) - jk_{eff}(t)$ is the complex optical index of the nickel film, the value of which changes over time. $d_{eff}(t)$ is the thickness of the film. $\phi_i = 70.36°$ is the angle of incidence of the light beam.

For each time value t, this system of two equations with three unknowns ($n_{eff}(t)$, $k_{eff}(t)$ and $d_{eff}(t)$) is mathematically undetermined. To determine these unknowns, we must take two pairs of (Δ, Ψ). We then obtain a system of four equations with six unknowns.

If we take two successive time values t_1 and t_2, provided the deposition rate is not too high, we observe that the thickness has changed little (a few Å) and the optical indices are almost equal. We then assume that $n_{eff}(t_1) = n_{eff}(t_2)$ and that $k_{eff}(t_1) = k_{eff}(t_2)$ [7,13].

The system of equations reads:

$$\text{at } t_1 \quad (\Delta_1^{ex}, \Psi_1^{ex}) = f(n_{eff}, k_{eff}, d_{eff,1}) \tag{2}$$

$$\text{at } t_2 \quad (\Delta_2^{ex}, \Psi_2^{ex}) = f(n_{eff}, k_{eff}, d_{eff,2}) \tag{3}$$

which is a system of four equations with four unknowns.

To solve this system, we express it as follows:

$$(n_{eff}, k_{eff}) = f_1(\Delta_1^{ex}, \Psi_1^{ex}) \tag{4}$$

$$(n_{eff}, k_{eff}) = f_2(\Delta_2^{ex}, \Psi_2^{ex}) \tag{5}$$

$$d_{eff,1} = f_3(\Delta_1^{ex}, \Psi_1^{ex}, n_{eff}, k_{eff}) \tag{6}$$

$$d_{eff,2} = f_4(\Delta_2^{ex}, \Psi_2^{ex}, n_{eff}, k_{eff}) \tag{7}$$

Eq. (4) and Eq. (5) define a system of two equations with two unknowns (n_{eff}, k_{eff}). Using a method of bisection, we then calculate the value of n_{eff} and k_{eff}. Eq. (6) and Eq. (7) allow the calculation of $d_{eff,1}$ and $d_{eff,2}$ for values of n_{eff} and k_{eff} previously determined. This method provides, for each experimental time value t, the values of the complex optical index N_{eff} and the thickness d_{eff} of the nickel film. Figs. 2–4 show the evolution of the complex optical index of such a film and its thickness over time.

From time values 0 to about 200 s, the values of (Δ, Ψ) do not change and remain equal to those of the glass substrate. After this induction period, the coating process begins and the ellipsometric parameters (Δ, Ψ) begin to vary with time.

During thickening, the variation in Δ and Ψ as a function of the thickness of the film diminishes. Therefore, solving the system of Eq. (4) and Eq. (5) no longer gives physical solutions because of the increasing measurement errors due to the small variation in Δ and Ψ. For very thick films, the complex optical index has been assumed to be equal to that of bulk deposited material N_F. This value has been measured on a thick film by ellipsometry: $N_F = 2.262 - j2.375$. From this fixed value and the experimental (Δ, Ψ) values, the thickness of the film has also been computed using Eq. (6) and Eq. (7).

For thicknesses below 50 Å, the measurement errors are too high to obtain precise results and the (Δ, Ψ) values have not been analysed.

Figs. 2–4 point to several conclusions:

The optical indices of the film show a high degree of variation during the first 40 s of the coating, which corresponds to a thickness below around 150 Å. This variation over time is due to the variation in the film structure during this time (nucleation and coalescence of the nuclei).

For thicknesses above 150 Å, the indices tend asymptotically to constant values equal to the indices for bulk material.

The variation in the film thickness over time can give directly the deposition rate of the layer during the coating process. Fig. 4 shows that this rate is constant for the analysed part as well as the asymptotic part of the curve. This speed is about 2.65 Å s^{-1}.

Large fluctuations in n_{eff}, k_{eff} and d_{eff} are due to measurement errors of the ellipsometric angles (Δ, Ψ).

The model described above to compute the values of n_{eff}, k_{eff} and d_{eff} from the experimental (Δ, Ψ) values

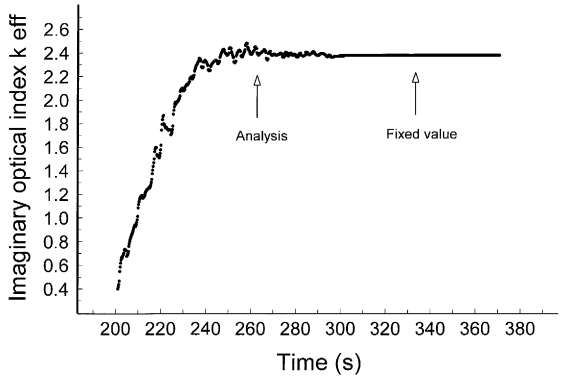

Fig. 3. Evolution of the imaginary optical index k_{eff} of the nickel thin film during growth.

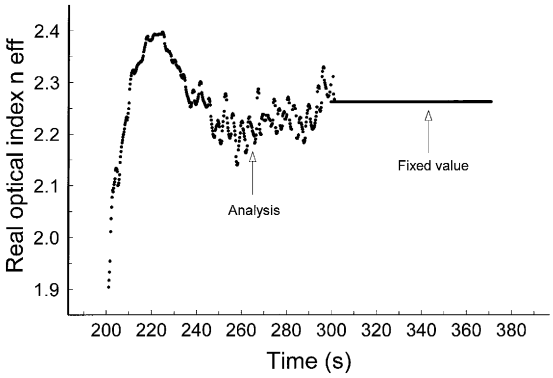

Fig. 2. Evolution of the real optical index n_{eff} of the nickel thin film during growth.

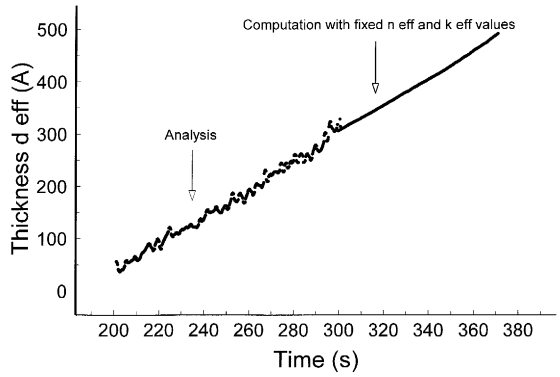

Fig. 4. Evolution of the thickness d_{eff} of the nickel thin film with time.

assumes that the nickel thin film is smooth and homogeneous, which is not actually the case because the film contains nickel nuclei during most of its growth period. The nuclei surrounded by the metallizing solution form a heterogeneous medium. The dielectric behaviour of this medium can be simulated using an effective medium theory.

4.2. Effective medium theories

An effective medium theory describes the dielectric behaviour of a heterogeneous material as a function of its composition. In our case, the heterogeneous material is a mixture composed of nickel nuclei and a metallizing solution. These nuclei are several nanometres in size and are small compared with the wavelength of the light beam (511 nm). However, they are large enough to have their own dielectric behaviour. The metallizing solution has a dielectric behaviour close to that of water: its complex optical index N_A $(1.346 - j0.0)$ is close to that of water $(1.333 - j0.0)$.

The heterogeneous medium can be replaced by an effective homogeneous medium characterized by an effective complex optical index N_{eff} or by an effective dielectric function ϵ_{eff} $(\epsilon_{eff} = N_{eff}^2)$. ϵ_{eff} depends on the dielectric functions of the nickel solution ϵ_A and the nuclei ϵ_F, the volume fraction of the nuclei in the film f_F (with $f_F + f_A = 1$) and the screening parameter g. This parameter characterizes the way the components of the film screen the electrical field of the light beam.

Assuming that the heterogeneous medium has all its boundaries parallel to the electrical field, the effective dielectric function is [14–17]

$$\epsilon_{eff} = f_A \epsilon_A + f_F \epsilon_F \tag{8}$$

where ϵ_A is the dielectric function of the metallizing solution, ϵ_F is the dielectric function of the metal nuclei, ϵ_{eff} is the dielectric function of the effective medium, f_A is the volume fraction of the metallizing solution in the effective layer, and f_F is the volume fraction of the metal nuclei in the effective layer.

This relationship corresponds to the minimal theoretical screening $(g = 0)$. It defines a straight line passing through points ϵ_A and ϵ_F in the complex plane of the effective dielectric function (Fig. 5).

If the heterogeneous medium has all its boundaries perpendicular to the electrical field, the effective dielectric function is

$$\frac{1}{\epsilon_{eff}} = \frac{f_A}{\epsilon_A} + \frac{f_F}{\epsilon_F} \tag{9}$$

This relationship is the equation of a circle passing through points ϵ_A and ϵ_F in the complex plane of the dielectric function. This corresponds to the maximal screening $(g = 1)$.

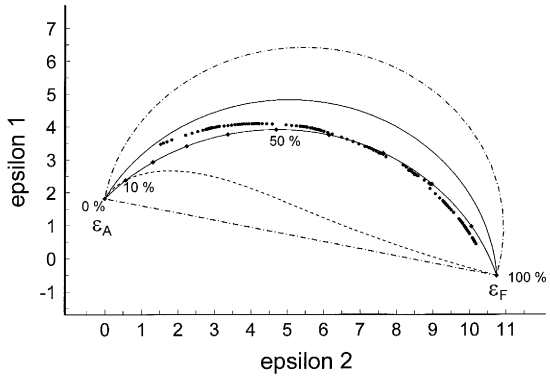

Fig. 5. Gaussian-plane plots of the effective dielectric function of a mixture of nickel and metallizing solution using various theories: – · – Wiener bounds, – – – Bruggeman isotropic theory, ———— Maxwell-Garnett theory with $g = 1/3$ (isotropic screening) and -◆- $g = 0.241$ (fit of the experimental values), ● experimental (computed) values. The numbers are the volume fractions of nickel in the mixture.

These two extreme screening values are called the Wiener bounds. Between these bounds, the screening parameter can have any value between zero and unity. The effective dielectric function for every value of g is

$$\epsilon_{eff} = \frac{g\epsilon_A\epsilon_F + (1-g)\epsilon_H(f_A\epsilon_A + f_F\epsilon_F)}{(1-g)\epsilon_H + g(f_A\epsilon_F + f_F\epsilon_A)} \tag{10}$$

where ϵ_H is the dielectric function of the host medium.

g is equal to $1/3$ for an isotropic microstructure of the medium. For a different value, the medium is anisotropic and different optical indices must be used for the three space coordinates.

If $\epsilon_H = \epsilon_A$ and $g = 1/3$, Eq. (10) reduces to the isotropic Maxwell-Garnett theory [18], with the metallizing solution as matrix and spherical nuclei as inclusion elements. This theory describes the optical behaviour of nuclei separated from each other and dispersed in a matrix.

If $\epsilon_H = \epsilon_{eff}$ and $g = 1/3$, Eq. (10) reduces to the isotropic Bruggeman theory [19]. This theory describes the optical behaviour of a material with two components randomly distributed in a film. These components may have contact. In that case, both components are optically equal.

4.3. Analysis of results

Fig. 5 shows the Wiener bounds of a mixture of nickel and metallizing solution. On this figure, we also represent the dielectric function of such a mixture calculated using various theories. The experimental values of the dielectric function have also been drawn on the same figure. From this figure, we can conclude the following.

Our experimental results lie between Wiener bounds.

The number of experimental points is high and they

cover a large range of film thicknesses. The effective dielectric function measured during the growth of the film cannot be described either by the isotropic Maxwell-Garnett theory or by the isotropic Bruggeman theory. However, the experimental curve has a shape similar to that of the Maxwell-Garnett curve.

If the screening parameter of the anisotropic Maxwell-Garnett theory is fitted to the experimental points, we obtain a value of g equal to 0.214. The fitted curve is also drawn on Fig. 5. We must say that the found g-value is only considered as a fitting parameter.

5. Conclusion

From ellipsometric measurements recorded in situ during the coating of a nickel thin film on float glass, we have been able to compute the evolution of the effective complex optical index of the film and its thickness over time. From these results, information has been obtained about the growth of the film and its dielectric behaviour.

After an induction time, the chemical reaction begins and nickel nuclei develop on the catalytic sites present on the glass. The growth of these nuclei is characterized by the rapid variation in the effective complex optical index of the film. At a constant rate of deposition, the nuclei grow and coalesce and the film becomes continuous. This is observed from the fact that the effective complex optical index of the film tends towards that of the bulk material composed of nickel and phosphorus.

During its growth, the film has dielectric behaviour similar to that predicted by the Maxwell-Garnett theory with a screening parameter equal to 0.214.

Acknowledgements

This work was conducted with a FIRST grant from the Ministère de la Région wallonne.

References

[1] W.G. Driscoll and W. Vaughan (eds.), *Handbook of Optics*, McGraw-Hill, New York, 1978, Chapter 8, p. 71.
[2] C.M. Lampert, *Sol. Wind Technol., 4* (3) (1987) 347.
[3] E. Dobierzewska-Mozrzymas and P. Bieganski, *Appl. Opt., 32* (13) (1993) 2345.
[4] R.R. Singer, A. Leitner and F.R. Aussenegg, *J. Opt. Soc. Am. B, 12* (2) (1995) 220.
[5] U. Kreibig and M. Vollmer, *Optical Properties of Metal Clusters*, Springer Series in Materials Science, Vol, 25, Springer, 1995.
[6] K.-L. Lin and C.-S. Jong, *Mater. Chem. Phys., 35* (1993) 53.
[7] M. Yamamoto and T. Namioka, *Appl. Opt., 31* (1992) 1612.
[8] J.N. Hilfiker, D.W. Thompson, J.S. Hale and J.A. Woollam, *Thin Solid Films, 270* (1995) 73.
[9] T.M. Tam, *J. Electrochem. Soc.*, (May 1985) 1152.
[10] T. Osaka, H. Nagasaka and F. Gato, *J. Electrochem. Soc.*, (November 1980) 2343.
[11] C.H. de Minjer and P.F.J. Boom, *J. Electrochem. Soc.*, (December 1973) 1644.
[12] R.M.A. Azzam and N.M. Bashara, *Ellipsometry and Polarized Light*, North-Holland, Amsterdam, 1977, Chapter 4, p. 270.
[13] T.F. Thonn and R.M.A. Azzam, *Thin Solid Films, 127* (1985) 215.
[14] D.E. Aspnes, *Optical Properties of Microstructurally Nonuniform Materials, Technical Symposium East'82, Arlington, VA, May 1982*.
[15] S. Berthier, *Optique des Milieux Composites*, Polytechnica, 1993, p. 133.
[16] G.A. Niklasson, C.G. Grandqvist and O. Hunderi, *Appl. Opt., 20* (1981) 26.
[17] D.E. Aspnes, *Am. J. Phys., 50* (1982) 704.
[18] J.C. Maxwell-Garnett, *Philos. Trans. R. Soc. London, 203* (1904) 385.
[19] D.A.G. Bruggeman, *Ann. Phys. (Leipzig), 24* (1935) 636.