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Influence of the surface layer on the optical properties of island Al films on NaCl substrates *

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The Donnadieu model has been used for the investigation of the effect of the surface layer on the optical properties of island Al films on NaCl substrates. It has been assumed that ellipsoidal Al grains with a log-normal distribution of grain diameter are covered with surface layers having uniform thicknesses. Making use of the data reported by Barna et al., the thickness and electrical permittivity of the surface layer have been evaluated. Based on the modified Maxwell-Garnett theory, the wavelength-dependence of the imaginary part of permittivity for Al films has been determined by taking into account the surface layer effect.

1. Introduction

The earlier papers [1]–[3] give experimental data on the optical properties of discontinuous Al films on NaCl substrates. The results have been interpreted in terms of the modified Maxwell-Garnett theory, assuming that the islands consist of pure aluminium and that the surrounding permittivity is expressed both by substrate permittivity and air permittivity. The contribution of air permittivity is defined by the mixing parameter [4]. But, a great many of the experimental studies reported in the works [5]–[8] have shown that Al films (and islands as well) are covered with a surface layer, especially when exposed to atmospheric air. Measured permittivities [6] suggest that those surface layers fail to be homogeneous. This may be inferred from the presence of Al_2O_3 and also hydrated Al_2O_3.

In this paper consideration is given to the optical properties of discontinuous Al films on NaCl substrates. The investigation makes use of the modified Maxwell-Garnett model and takes into account the surface layer effect. The plots obtained in this study are compared with experimental data, as well as with relevant theoretical curves wherein the surface layer effect has not been included.

2. Theoretical

When investigating the surface layer effect on the optical properties of an island metal film, Donnadieu [9] and Bilboul [10] made use of the following assumptions:

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the island film is a system of rotational ellipsoids; each ellipsoid is of a permittivity ε_1, and is incorporated in a confocal ellipsoid of permittivity ε_2; the entire system is immersed in a medium of a dielectric constant ε_3, and the interisland spacing is y. The model is shown in Figs. 1 and 2.

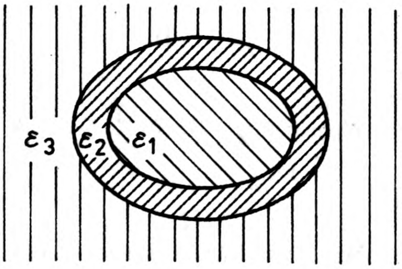


Fig. 1. Section of single island

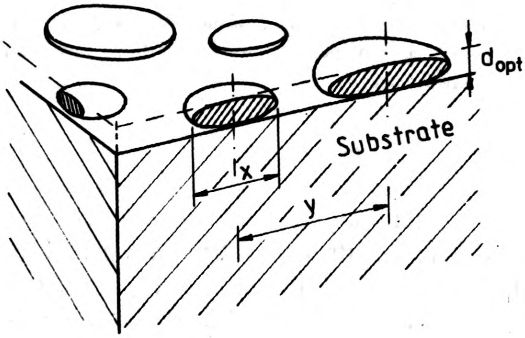


Fig. 2. Model of island film

The polarizability of a single ellipsoid may be written as follows:

$$\alpha_0 = \{k\varepsilon_2(\varepsilon_1-\varepsilon_3)+(\varepsilon_2-\varepsilon_3)[(\varepsilon_1-\varepsilon_2)(f_1-kf_2)+\varepsilon_2(1-k)]\}/$$
$$\{(\varepsilon_3-\varepsilon_2)(\varepsilon_2-\varepsilon_1)[f_1(f_2-m)+kf_2(1-f_2+m)]$$
$$-\varepsilon_2(\varepsilon_3-\varepsilon_2)(f_2-m)+(\varepsilon_1-\varepsilon_2)(\varepsilon_3 f_1-km\varepsilon_2)+\varepsilon_2\varepsilon_3\}$$

where k is ratio of volume of ellipsoids; f_1, f_2 denote depolarization coefficients of internal and external ellipsoid, respectively; $m = d_m/2y$ (d indicates mass thickness of the film). We have assumed that the electric field which polarizes the ellipsoid is perpendicular to the symmetry axis. Knowing the polarizability of the island (Eq. (1)), and using the Maxwell–Garnett theory [11] we can determine the effective permittivity ε' of the island film in terms of the following relation:

$$\varepsilon' = \varepsilon_3 \frac{1+2q\alpha/3}{1-q\alpha/3} \tag{2}$$

where

$$\alpha = \frac{\alpha_0}{\varepsilon_0 \varepsilon_2}, \tag{3}$$

and q is the volume fraction of the film. The term ε_3 represents the weighed average of air permittivity ε_0 and substrate permittivity ε_s [4]. Hence, we can write

$$\varepsilon_3 = p\varepsilon_0 + (1-p)\varepsilon_s, \quad 0 \leqslant p \leqslant 1. \tag{4}$$

The relation between polarizability and island diameter x is expressed in terms of the depolarization coefficients f_1, f_2 and the k-parameter (Eq. (1)). The dependence of α on the interisland spacing y is described by parameter m.

The distributions of island diameters and interisland spacings are assumed to be log-normal [2], [12]. Following the approach reported in reference [4], it has been anticipated that the islands are spherical in shape when $x \leqslant d_{\mathrm{opt}}$ (where $d_{\mathrm{opt}} = d_{\mathrm{m}}/q$). When $x > d_{\mathrm{opt}}$, the islands are ellipsoids.

The effective dielectric constant of a film was calculated as a two-dimensional statistical mean of the local dielectric constant by taking into account the distributions of island diameters and interisland spacings.

Making use of this model, the influence of the surface layer on the optical properties of island Al film on NaCl substrates was investigated. We have anticipated that ellipsoidal Al grains are covered with a surface layer of identical thickness. Taking into account the results reported in [6], the thickness d and the permittivity ε_2 of the surface layer (both assessed by interpolation) are adopted as being equal to 3.2 nm and 2.0 to 2.98, respectively. These values are smaller than those for Al_2O_3.

The modified Maxwell–Garnett theory was applied in order to determine the wavelength-dependence of the imaginary part of the effective permittivity im ε' for discontinuous Al films with and without consideration of the surface layer effect. The fitting parameters were the mixing parameter p and the oblateness coefficient s [4].

3. Discussion of results

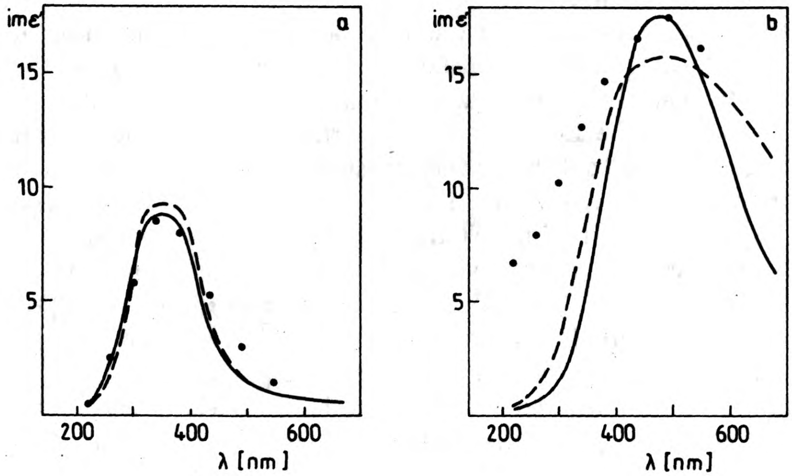
The Table gives a list of factors which characterize discontinuous Al films as well as the fitting parameters for the cases considered. The films under study differed from one another in the mean diameter $\bar{x}$ and in thickness d_{m}, d_{opt}.

Calculated and experimental data are plotted in Figs. 3**a**, **b**, **c**. Thus, solid lines and dashed lines represent the wavelength-dependence of im ε' with and without consideration of the surface layer effect, respectively. The points in this figure show the experimental results.

To illustrate the effect of the surface layer on the shape of the im ε' versus λ curve for a film of selected parameters p and s, the wavelength dependence of the imaginary part of film permittivity was calculated for various thicknesses d and various permittivities ε_2 of the surface layer. The results are plotted in Figs. 4 and 5. As

Experimental data and structural parameters

Sample	Mass thickness d_m [nm]	Optical thickness d_{opt} [nm]	Volume fraction q	Mean island diameter $\bar{x}$ [nm]
a	11.0±0.5	35.5	0.31	38
b	15.3±3.0	49.4	0.31	75
c	19.7±2.2	57.9	0.34	65



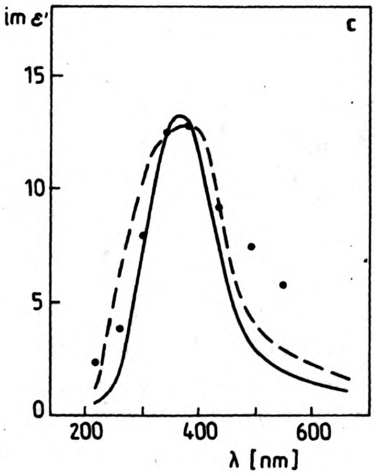
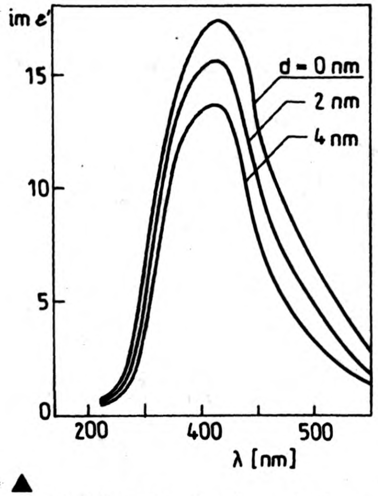
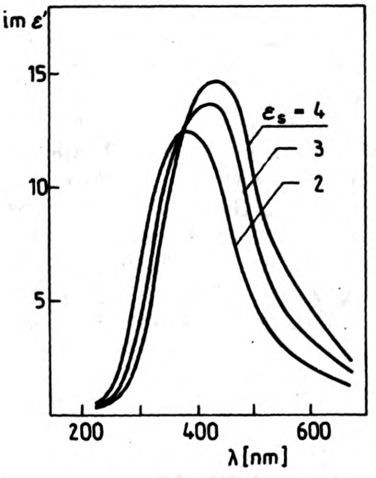


Fig. 3. Wavelength-dependence of im ε' for three films with different thicknesses. Experimental results (points), theoretical curve with consideration of the surface layer (solid line), theoretical curve without consideration of the surface (dashed line).
a – $d_m = 11$, **b** – $d_m = 15.3$, **c** – $d_m = 19.7$

Fitting parameters				
Excluding surface layer		Including surface layer		
mixing parameter p	oblateness parameter s	mixing parameter p	oblateness parameter s	surface layer permittivity ε_2
1	0.53	1	0.50	2.0
1	0.35	0.3	0.47	2.98
1	0.53	0.7	0.60	2.98





▲ Fig. 4. Effect of surface layer thickness on the wavelength-dependence of im ε' (structural parameters as for sample c)

Fig. 5. Effect of electrical permittivity of surface layer on the wavelength-dependence of im ε' (structural parameters as for sample c)

shown by these curves, the maximum of im ε' decreases with the increasing surface layer thickness and corresponds to the same wavelength (Fig. 4). The increase of permittivity ε_2 raises the position of the maximum and brings about a shift towards longer waves (Fig. 5).

4. Conclusion

For the films under study, the mixing parameter p and the oblateness coefficient s, which show good agreement between theoretical and experimental im ε' versus λ curves, begin to differ from each other when the surface layer effect in neglected or included (Table).

When the surface layer effect is included, the oblateness coefficient increases with the increasing volume fraction from about 0.5 for $q = 0.31$ to 0.6 for $q = 0.34$. When the mean island diameter $\bar{x}$ increases, the mixing parameter decreases. This is an indication (Eq. (4)) that the effect of substrate on the surrounding permittivity increases.

As shown by the plots of Fig. 3 (**a**, **b**, **c**), the agreement between theoretical and experimental data for the fitting parameters (p and s) is better when the surface layer effect is taken into consideration.

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Влияние поверхностной пленки на оптические свойства островковых пленок аллюминия на подложках хлористого натрия

Исследовано влияние поверхностной пленки на опитические свойства островковых пленок аллюминия на подложке хлористого натрия. Предположено, что эллипсоидальные зерна аллюминия с логарифмически-нормальным распределением диаметров покрыты пленкой одинаковой толщины. При использовании экспериментальных результатов Барна и др. вычислено толщину и диэлектрическую постоянную поверхностной пленки. С помощью модели Доннаде, опирающейся на модифицированной теории Максвелля–Гарнета, вычислено зависимость мнимой эффективной части диэлектрической постоянной островковых пленок аллюминия, учитывая влияние поверхностной пленки.