OPTICAL CONSTANTS AND MICROSTRUCTURE OF THIN SILVER FILMS

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Abstract:

Silver films of mass thickness t 25nm were prepared by conventional evaporation vacuum. Extensive studies were undertaken to determine and correlate their optical constants and resistivity with their microstructure. It was shown that the anomalous optical and electrical properties are due to the drastical change of the microstructure from continuous metal films to films with separated metal grains. The optical constants were used to test the theory of bounds due to Milton.

INTRODUCTION

It is known that thin films of some metals (Au, Ag, Al, Sb, Ni, ...) have anomalous optical and electrical properties. Beyond certain thickness, the change of the transport parameters is of such order that can not be explained without the knowledge of the film microstructure [1, 2]. In fact, the metal films become cermet ones of the type metal/air.

A number of possible applications (selective solar absorbers, sensors with enhansed activity, tunable and neutral filters, ... [3]) exist which motivate the extensive studies of the granular metal films. The problem of the theoretical description of the transport properties of two-phase inhomogeneous materials is of considerable importance and interest [4, 5]. Various theories have been proposed, and the testing with reliable experimental data is recomendable [6].

The results for the optical, electrical and microstructural properties of thin silver films which are presented in this work are one part of the broader study of the cermet properties, mainly those of Ag/MgF_2 [7].

EXPERIMENTAL

The studied samples were prepared by resistive evaporation of silver in vacuum of order 10^{-5} Pa. The mass thickness (t_i) of the films was measured in-situ with a quartz crystal oscillator (Inficon XMS1). Different substrates were used simultaneously: i) fused silica "Suprasil" — for optical measurements; ii) standard glass slides — for electrical measurements; and iii) NaCl-monocrystal, amorphous carbon films, and parlodion films — for transmittion electron microscopy. The dimensions of the samples were much smaller than the source-to-substrate distance. The substrates were thoroughly cleaned in a freon vapour/ultrasonic bath and treated with "Balzers" substrate cleaners.

The thickness of the deposited films was remeasured by a Talystep to yield the step thickness (t_t). This thickness was found to be higher than the mass thickness determined assuming bulk density of silver (10.5g/cm^3). From this difference it was possible to estimate the volume fraction of voids f_v in the thin silver films ($f_v = 1 - t_i/t_t \doteq 1 - f_{Ag}$).

The resistance of the films was measured by the four point method and a megaohm bridge.

The transmittance (T) and reflectance from the film side (R) and from the substrate side (R') were measured in the wave-length interval $0.2 \leqslant \lambda \leqslant 3.0 \mu m$ by a spectrophotometer (Cary 2000). Together with the optical properties of the substrate, these results were used in conjunction with the bivariate and the phase-variate methods [8] to compute the optical constants n and k of the films.

The study of the microstructure was performed on a JEOL 100CX transmittion electron microscope. The electron diffraction patterns, and the bright and dark field images were recorded for each sample. The substrate influence on the microstructure was also investigated.

RESULTS AND DISCUSSION

The thickness of the representative samples is given in Table 1, together with the calculated volume fractions of silver.

Table 1

Film	t_i(nm)	r_i(nm s^{-1})	t_t(nm)	f_{Ag}	f_M
Ag28	5.0	0.25	11.0 1.1	0.45±0.045	0.5±0.1
AG18	10.2	0.27	15.6 1.1	0.65±0.046	0.59±0.02
AG4	15.0	0.11	23.0 2.2	0.65	
AG9	15.5	0.62	21.5 0.4	0.72±0.02	0.83±0.03
AG26	25.0	0.38	30.1 0.7	0.83	

t_i — mass thickness; r_i — rate of deposition; t_t — step thickness; f_{Ag} — volume fraction of silver; f_M — Milton's bounds result

The electron micrograph in Fig. 1a) shows that the thinnest film (AG28) is in the post-nucleation stage of growth when silver grains of complex shapes (due to coalescing) are formed, but the structure is that of separated metal grains. At mass thickness of 10nm (Fig. 1b) the silver film possesses a labyrinthine structure. At t_i = 15.5nm the film is almost continuous with smaller voids which are not very obvious. The films are polycrystalline in all stages of growth without preffered orientation of the crystallites. The structure is FCC and the latice parameter a = 0.408nm (determined form the electron diffraction patterns) stays unchanged regardless of the grain sizes and the coallescence patterns.

The films deposited on NaCl—monocrystal show coarser features as can be seen from Fig. 1 c) and d).

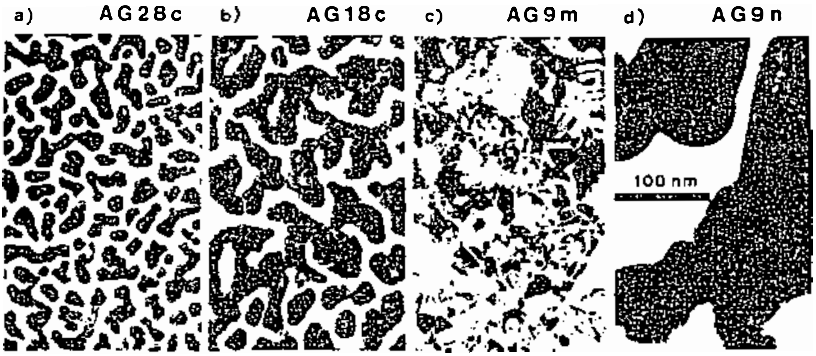

Fig. 1.

Having information about the microstructure, it becomes easier to interpret qualitatively the results from the electrical and optical measurements. The quantitative explenation requires extenstive theoretical analysis.

The resistvitiy of the thin silver films is presented in Fig. 2 as a function of the volume fraction of silver. From the typical bulk values, the resistivity increases abruptly at $f_{Ag} \approx 0.65$ by ten orders of magnitude to obtain insulator-like values. The labyrinthine silver film is conductive, but $\rho > \rho_{Ag}$ because the dimensions of the metal clusters are smaller than the mean free path of the electrons in silver. When the metal grains are isolated by the air matrix, $\rho < \rho_{air}$ because of the tunelling.

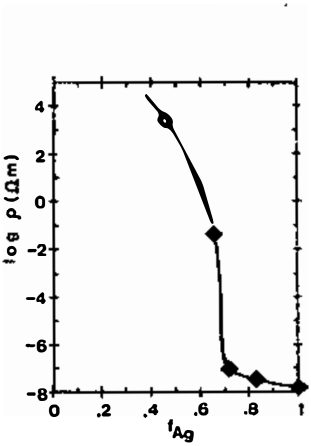

Fig. 2.

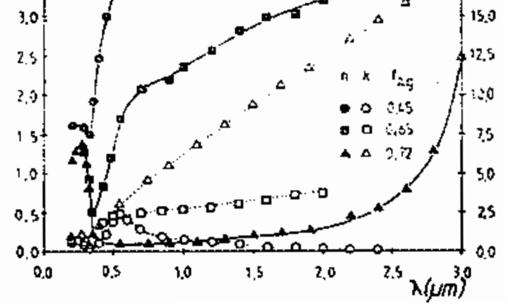

Fig. 3.

The optical constants (n, k) for the three typical films are given in Fig. 3. The wide variety of dispersion characteristics is a function of the volume fraction and can not be explained by simple addition of the properties of silver and air. The absorption peak which is formed in the visible region by increasing f_V is responsible for the good selective absorption of the very thin metal films.

The experimentaly determined optical constants were analysed by the method of Milton's bounds [9] to yield the volume fraction of silver. The results (RHS column of Table 1) are in good agreement with the experimentaly determined values which confirmes the applicability of this theory to two-phase composite materials.

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