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Ohm resistivity of electroless copper layers as a function of their thicknesses

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The electric Ohm resistivity of electroless Cu depositions on dielectric substrates as a function of their thicknesses is studied. Substantial deviations (up to 10–20 times) from the standard resistivity ($\rho_\infty = 1.7\ \mu\Omega\,\mathrm{cm}^{-1}$) below 0.5 μm thicknesses are observed. The experimental data show for the entire region of thicknesses ($d_\infty \sim 0.07$–$5\ \mu$m) a power function between the relative resistivity changes ($\Delta\rho/\rho_\infty$) and the inverse thickness of depositions (d_∞) – ($\Delta\rho/\rho_\infty$) $\sim (1/d_\infty)^{0.8}$. This empirical relation is discussed as an effect of the porous structure of the metallic layers deposited on the substrate. A scanning electron micrography was applied in order to visualize the morphology of the depositions. The micrographs clearly show the evolution of the deposition profile: starting from separate islands at the very beginning of the process, and gradually covering the entire area with continuous but porous metal layers.

1. Introduction

The properties of chemically deposited copper coatings, such as high conductivity, good soldering ability, deposition at room temperature, make them suitable as sublayers for metallization of dielectrics. Later, substantial successes were achieved in preparing more stable electroless plating baths with improved plating rates.

The process kinetics [1, 2], the mechanism of copper deposition [3–5], the role of the components and additives involved and the chemical nature of the reaction [6–8] are investigated in detail. The studies cited in the literature are mostly on the mechanical properties of chemically deposited copper films over 20 μm thick [9], while reports on the properties of thin films are very scarce.

The aim of the present study is to investigate the electrical properties of thin (less than 5 μm) chemically deposited copper films. In particular, the change in resistivity is traced as a function of the film thickness.

Prior to chemical deposition, the dielectric surface needs to be activated by treatment with solutions lowering the activation energy of individual points of the surface. These points become active centres for metal deposition. The island like structure thus obtained expands during the process of copper deposition to form a continuous but rough coating. The isolated metal centres have infinite resistance, so the coating exhibits conductivity not earlier than reaching a percolation point.

2. Experimental procedure

A chemical copper bath operating at a deposition rate of 2–3 $\mu\mathrm{m\,h}^{-1}$ at 50 °C was utilized. The two basic components ($CuSO_4$ and CH_2O) and the pH of the solution were monitored. The samples, with dimensions 10 × 100 mm, were made of epoxy fibreglass FR-4. The resistance of copper coated samples with deposition duration of 15 s to 120 min was measured. The ohmic properties of the thin films were analysed by the conventional approach, applied to the description of heterogeneous media. The substance was assumed to have a homogeneous structure, so the parameters of the other properties (electrical, optical, mechanical, etc.) were examined as effective. In this case, from the resistance, measured by the four probe method, using the known formula

$$\rho_\Omega = (s_\infty/L)R \text{ in } \mu\Omega\,\mathrm{cm}^{-1}$$

an effective specific resistance coefficient, ρ_Ω, was calculated. Here, s_∞ is the cross-section of a dense conductor with an area $s_\infty = ad_\infty$ (where a is the sample width, in this case 10 μm; L the sample length, equal to 100 μm; d_∞ the thickness of dense copper, proportional to the deposited amount, $M_{Cu} = (Ls_\infty)\rho_{Cu}$, where $\rho_{Cu} = 8.96\ \mathrm{g\,cm}^{-3}$ is the copper density. As becomes obvious, the cross-section, s_∞, and the thickness, d_∞, are proportional to the deposited quantity, M_{Cu}. They do not contribute additional information about the coating structure, but are very illustrative. That is why the experimental results are based on them, and, in particular, on the average coating thickness, d_∞. Beside measuring the resistance, R, the

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quantity of copper on the samples was determined. From the results of M_{Cu} and R, d_∞ and ρ_Ω were calculated, and afterwards the relation between them was sought.

3. Results and discussion

Fig. 1 shows the kinetics of the chemical deposition of copper on dielectric for the first 45 min. The constant deposition rate gives grounds to exclude the presence of structural changes during the process. Fig. 2 illustrates the relationship between ρ_Ω and d_∞ calculated from the experimental data about R and M_{Cu}. The same data are plotted in logarithmic scale in Fig. 3. The straight line with a slope 0.8 corresponds to the empirical relationship $(\rho_\Omega - \rho_\infty)/\rho_\infty = \text{const}/d_\infty^{0.8}$. The resistivity of dense copper, cited in the literature, is $\rho_\infty = 1.67\ \mu\Omega\,\text{cm}^{-1}$. The lowest values reached in the present experiments are $\rho_\infty \sim 2.0\ \mu\Omega\,\text{cm}^{-1}$ at thicknesses of about 5 μm.

In the theory of electrical conductivity of thin films, the models of Fuchs–Sondheimer and Mayadas–Shatzkes [10], related to the resistance of dense metal thin films, are most prominent. In both cases, the final results are reduced to one and the same dependence of the resistance on the thickness $\Delta\rho/\rho_\infty \sim d_\infty^{-1}$. For evaporated (dense) copper films, the range of thicknesses at which noticeable changes in the resistivity are observed, is determined by the free paths of the electrons in the metal (20–40 nm for copper [10, 11]). The conventional technique for deposition of dense thin metal films is by evaporation. In [11, 12] there are data about $\rho_\Omega(d_\infty)$ of evaporated copper on a quartz (glass) surface. They correspond qualitatively to the theoretically predicted relation in the thickness range $d = 0.03$–0.3 μm and show values $\rho_\Omega(d_\infty) = 5$–$3\ \mu\Omega\,\text{cm}^{-1}$, that are several times lower than those measured at the same effective thickness. In this case, the changes in ρ_Ω are observed as early as $d_\infty \sim 3$ μm and they vary in the range 30–2 $\mu\Omega\,\text{cm}^{-1}$ at thicknesses, d_∞, of 0.1–3 μm (Fig. 2). This indicates that the nature of the effects governing the conductivity of chemical coatings, is different from that in dense conductors.

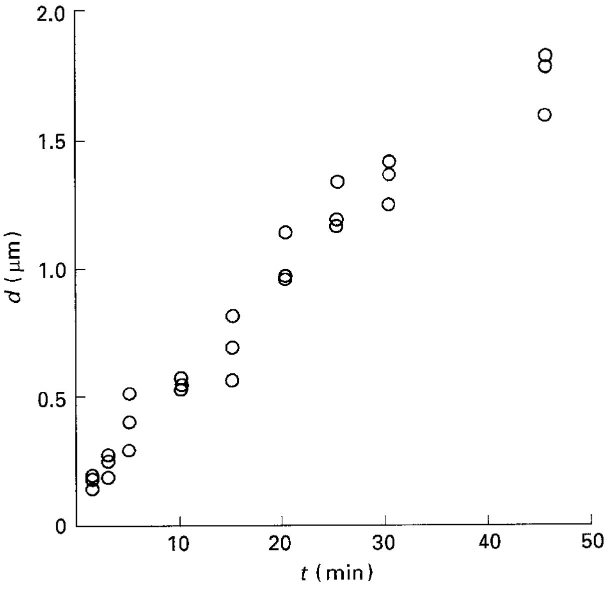

Figure 1 Kinetics of deposition of electroless copper on epoxy fibreglass substrate.

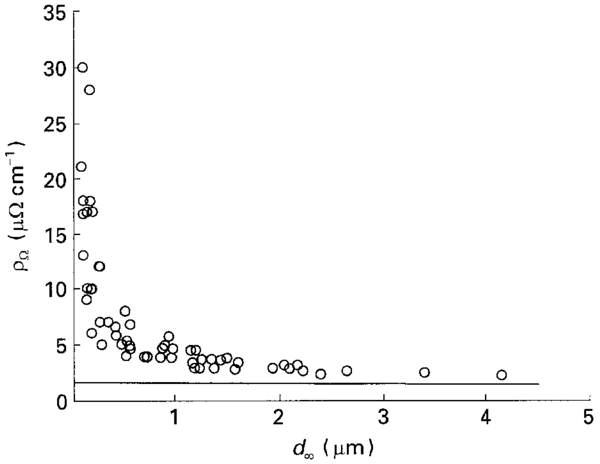

Figure 2 Resistivity of electroless thin copper films as a function of their average thickness. The asymptote $\rho_\infty = 1.7\ \mu\Omega\,\text{cm}^{-1}$ corresponds to the resistivity of thick films.

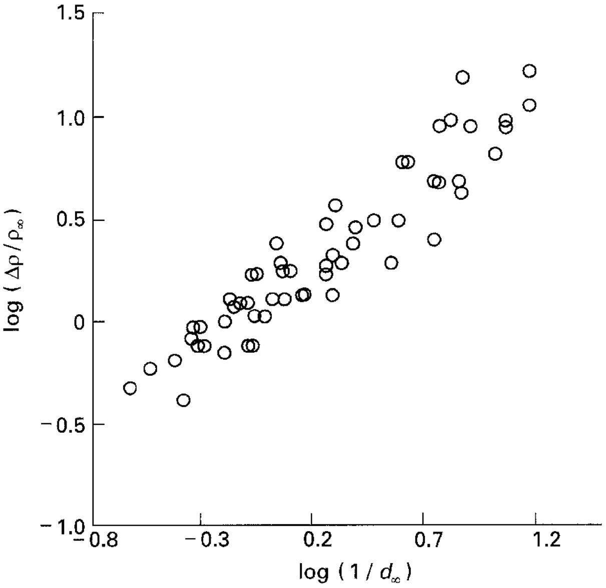

Figure 3 The results from Fig. 2 plotted in logarithmic scale. The linear regression analysis yields a straight line with a slope 0.8.

One possible explanation of this effect is that chemical coatings have definitely a rough structure, rather than a dense structure. The micrographs from a scanning electron microscope for different deposition times help trace the formation of the copper coating. As seen from Fig. 4f, the dielectric is studded with craters. The formation of the copper film begins on the edges of the craters and subsequently the craters become full (Fig. 4a–e). Fig. 4a displays filled craters, but the rough structure of the coating is clearly visible. Similar is the outlook of chemical copper coatings at $d_\infty \sim 5$ μm on other types of substrate (acrylnitryl sublayer, copper foil, glass, unpublished data). This shows that over a certain thickness the structure of the chemical coating probably is not influenced by the substrate, but depends only on the physico–chemistry of the process [13].

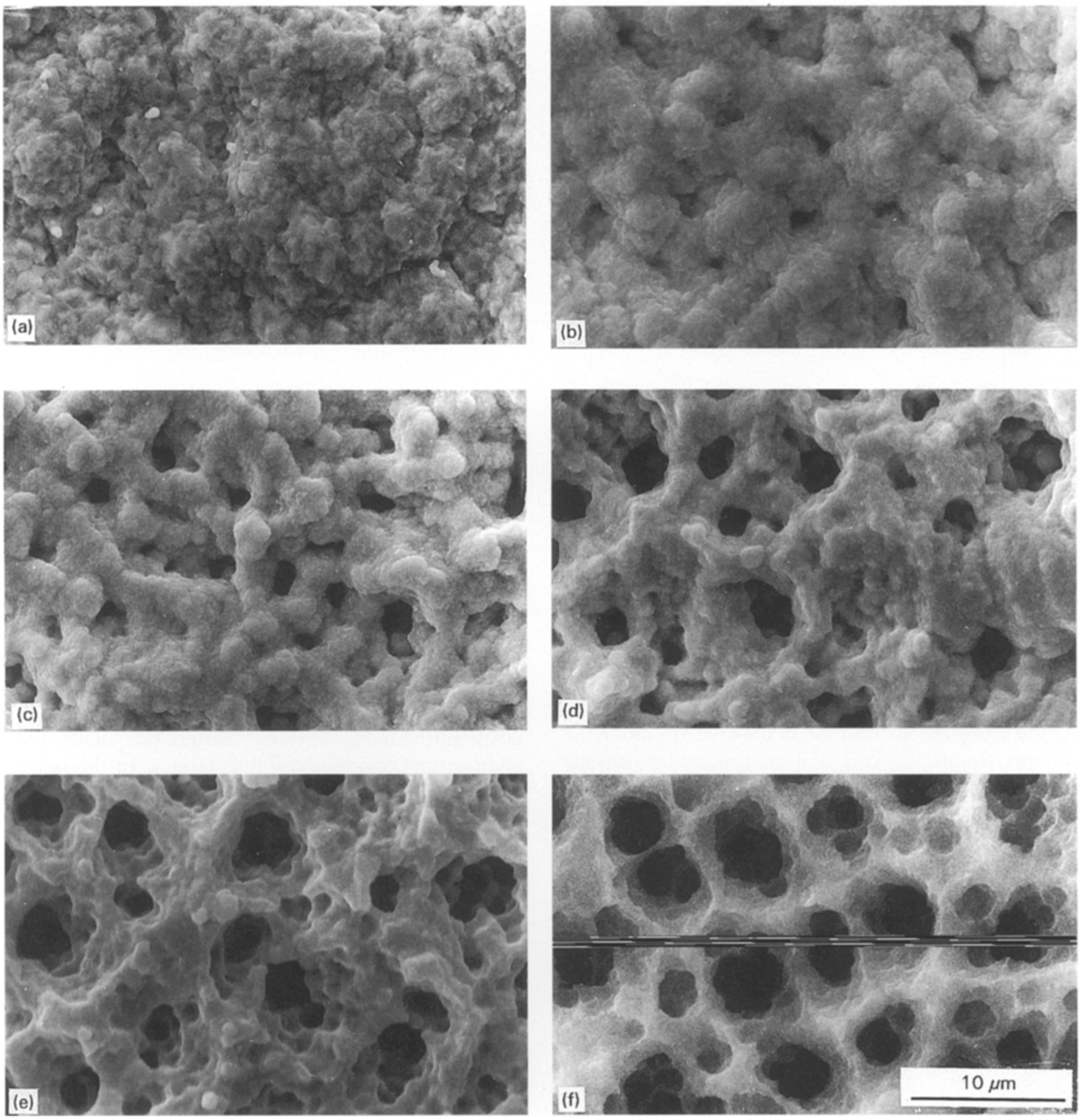

Figure 4 Scanning electron micrographs of electroless copper deposits of different thicknesses from a chemical bath at 50 °C: (a) 4.2 μm, (b) 2.3 μm, (c) 1.6 μm, (d) 1.28 μm, (e) 0.67 μm and (f) the surface morphology of the epoxy fibreglass FR-4 used as a substrate.

The rough structure imposed a more detailed monitoring of the distribution of the resistance along the sample. Fig. 5 illustrates the results from the measurements of the resistance of electroless copper depositions ($d_\infty \sim 4$–0.4 μm) at 100 mA d.c. current along the sample. The ten measurement points are equally spaced from one another. The linearity of the plots shows macrohomogeneity of the coating, and the lack of an intercept indicates that the contact resistance is negligibly small. These data prove the correctness of the experiment.

Ohm law, in the form $R = \rho_\infty L/s$, is valid for dense conducting media. Porous media can be modelled as a net of parallel and in series connected conductors with resistance, R, in accordance with the well known formula

$$R = \rho_\infty \int_0^L dl / \sum_i s_i(l) \qquad (1)$$

Here L is the length of the sample, and $s_i(l)$ is the area of the ith separate conductor at a given cross-section of the sample.

From the rule of the parallel conductors it follows that, for the resistance to be of importance the total conducting area must be $S(l) = \Sigma s_i$, rather than the conductor distribution. Thus, the resistance of a network with complex bounded elements becomes equivalent to the resistance of a single conductor with an area $S(l)$ equal to the sum of the areas of the separate conductors

$$R = \rho_\infty \int_0^L dl/S(l) \qquad (2)$$

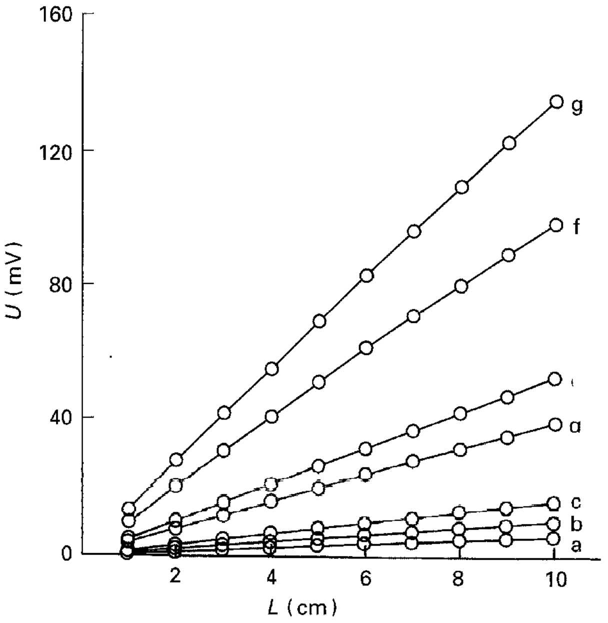

Figure 5 Verification of the macrohomogeneity of the coatings at different thicknesses, along the samples. The voltage (d.c. current, $I = 100$ mA) is a linear function of the length of the conductor with zero intercept: (a) 4.14 μm, (b) 2.9 μm, (c) 1.5 μm, (d) 1.15 μm, (e) 0.88 μm, (f) 0.53 μm and (g) 0.43 μm.

In order to calculate the integral in Equation 2 one has to know the distribution of the area $S(l)$ along the sample length, L. This is a complicated stochastic problem, but in any case the real profile can be presented by its mean value and variance, i.e.

$$S = \langle S\rangle \pm [\langle(\Delta S)^2\rangle]^{1/2}$$

where the mean value is defined as

$$\langle S\rangle = L^{-1}\int_0^L S(l)\,dl$$

and the variance as

$$\langle(\Delta S)^2\rangle = L^{-1}\int_0^L (S - \langle S\rangle)^2\,dl$$

respectively. With the same degree of accuracy the integral in Equation 2 could be replaced by the sum

$$\int_0^L \frac{dl}{S(l)} = \frac{L}{2}\left[\frac{1}{\langle S\rangle + [\langle(\Delta S)^2\rangle]^{1/2}} + \frac{1}{\langle S\rangle - [\langle(\Delta S)^2\rangle]^{1/2}}\right]$$

and for the resistance, R, one gets

$$R = \rho_\infty \frac{\langle S\rangle L}{\langle S\rangle^2 - \langle(\Delta S)^2\rangle} \geqslant \rho_\infty \frac{L}{\langle S\rangle} \quad (3)$$

The last inequality emphasizes the fact that the resistance of a conductor with homogeneous cross-sectional area is smaller than that with variable area at constant amount of conducting matter ($M_{\mathrm{Cu}} = \text{const}$). From Equation 3, and the definition introduced above, $\rho = (S/L)R$, one obtains easily

$$\frac{\rho_\Omega - \rho_\infty}{\rho_\infty} = \frac{\langle(\Delta S)^2\rangle/\langle S\rangle^2}{1 - \langle(\Delta S)^2\rangle/\langle S\rangle^2} \quad (4)$$

This is the final result of the model here proposed, giving the effective resistance, ρ_Ω, of a conductor with a constant intrinsic resistance, ρ_∞, but with variable cross-section (approximately characterized by the relative fluctuation, $\langle(\Delta S)^2\rangle/\langle S\rangle^2$). The present experimental results for the same quantity, ρ_Ω, have shown an empirical relation (see Fig. 3)

$$(\rho_\Omega - \rho_\infty)/\rho_\infty \sim 1/d_\infty^{0.8} \quad (5)$$

As a matter of fact, the presented viewpoint turns the problem of the conductivity of thin electroless copper films into a problem of their structure. Further, it would be useful if Equation 5, with the help of Equation 4, and the definition $S = ad_\infty$ (at $a = \text{const}$) was to be rewritten as a relation for the thickness fluctuations, Δd, and thickness mean value, d_∞

$$\frac{\langle(\Delta d)^2\rangle/d_\infty^2}{1 - \langle(\Delta d)^2\rangle/d_\infty^2} \sim \frac{1}{d_\infty^{0.8}} \quad (6)$$

The empirically established dependence, Equation 6, represents a reasonable tendency: the thicker the deposition (the more deposited matter), the smaller the relative thickness (density) fluctuations. In the range of thicker layers, where $\langle(\Delta d)^2\rangle/d_\infty^2 \langle 1 (d_\infty \rangle 2$ μm, see Fig. 2), Equation 6 tends to

$$\langle(\Delta d)^2\rangle/d_\infty^2 \sim 1/d_\infty^{0.8} \quad (7)$$

The result, Equation 7, resembles the well known law of thermodynamic fluctuations $\langle(\Delta\lambda)^2\rangle/\langle\lambda\rangle^2 \sim 1/\langle\lambda\rangle$. The smaller power 0.8 in the case discussed here, could be interpreted as a sign of correlation during the electroless deposition. Note, that the power one in the case of thermodynamic fluctuations reflects a total non-correlated process.

4. Conclusions

It is shown that the ohm resistivity of electroless copper films is a power function of their inverse thicknesses. The observed higher resistivity is treated as an effect of the porous structure of the deposition. This model is visualized by scanning electron micrography showing clearly separate copper islands at the beginning of the process, gradually covering the substrate area with continuous but porous metal layers.

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