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Effect of deposition inhomogeneity on the Ohm resistance of thin electroless copper layers

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The electric Ohm resistivity ρ of electroless Cu layers on glass substrates as a function of deposition thickness is studied. Deviations up to 200 times from the standard resistivity (ρ_∞ (Cu) = 1.7 $\mu\Omega$ cm) below 100 nm deposition thickness reported in other papers are confirmed. A comparative analysis shows different reasons for the higher resistivity of thin electroless layers and evaporated ones. A diagram with variables taken from the so-called *Fuchs* theory correct for thin evaporated metallic layers quantitatively illustrates conductance differences of electroless and evaporated layers. It is supposed that at electroless layers the isolated areas of deposition as well as the strong branching of the conducting circuits play major role. Calculation of the relative resistivity ρ/ρ_∞ of a real sample show good agreement with the proposed model.

1. Introduction

The development of the microelectronics continuously increases the demand for a higher quality of the interconnecting elements. Number of properties such as solder ability, ductility, adhesion and especially a high electrical conductivity had made copper layers indispensible conducting material in hitech. In addition to the above-mentioned attributes, the tendency toward scaling-down of device sizes had also contributed to the demand for thinner metallic layers. And here, it appears one of the biggest problems in the making of the most appropriate copper layers. It is known that thin metallic layers, both electroless and evaporated, show tendency to increase their Ohm resistivity compared to thick wires-like conductors. In evaporated layers, the thickness at which a similar increase of Ohm resistivity is observed, is at about 40 nm [1], while the electroless layers are in the region of 1 μm, i.e. about 25 times thicker [2]. It should be noted that the commentaries in the present communication concern primarily electroless copper layers.

The reason for the increased Ohm resistivity of thin metallic layers could be divided into two groups: (i) ultra small but relative homogeneous thickness and (ii) macroscopic roughness of relative thick layers. The increased resistance of ultra thin layers is due to electron scattering by film surfaces. The relative role of this effect increases when film thickness approaches the so-called electron mean free path in metals. In publications about mean free path of Cu the accepted value is about 40 nm [3], which corresponds quite well to the above mentioned experimental observed thickness of increased resistance of evaporated copper layers. The electron scattering effect is successfully modeled in the theory of Fuchs [4], as well as of its development in the Mayadas-Shatzkes model [5]. Notably absent in this group is any reference to the model of Namba [6], since it is closer to the effects stemmed from thickness heterogeneity.

In an earlier article [2] we published data about observed increased resistance of electroless Cu-layers in thickness diapason of 0.07–5 μm up to 20 times. In interpreting the results in the current study it is important to note that the cited in [2] thickness was not measured directly, instead it was estimated based on the quantity of deposited Cu per unit substrate area. Thus, the estimated thickness is close to the actual only when the thickness is evenly distributed throughout the entire substrate surface. Our research with SEM established that relatively even distribution is observed only

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in thickness over 1 μm. As it will be seen, direct TEM pictures show that below 70 nm electroless depositions are very rough (Fig. 2). Even more, in thickness about 20 nm, an island structure begins to form on the surface.

The purpose of the present paper is to analyze the factors determining the Ohm resistivity of extreme thin electroless copper layers.

2. Experimental procedures

A chemical bath operating at a deposition rate of 2–3 μm/h at 50°C was utilized. The two basic components ($CuSO_4$ and HCHO) and the pH-values of the solution were monitored. The depositions in the present study are carried out on glass substrates.

One of the most important electrical characteristics of thin metallic layers is their specific coefficient of resistance ρ. It was calculated (in $\mu\Omega$ cm) by using the known relation

$$\rho = \frac{s}{L}R \tag{1}$$

where R is the Ohm resistance; $s = ad$ is the area of wire cross-section, with a as a sample width, d as a deposition thickness; L is the sample length.

As it can be seen for calculation of the resistivity ρ via Equation 1 experimental values of two parameters, that of the resistance R and that of the deposition thickness d are needed. The resistance R was measured by the conventional four-probe method and here there are no problems for discussion. More complicated, however, is the situation with the deposition thickness values d. Here the problems are connected with the rough matter distribution of thin metallic layers onto substrate surfaces. In addition, in the thinnest layers TEM pictures show that depositions have island structure; a significant percentage (exceeding 30%) of substrate area remains uncovered; the conductive paths are strongly branched out (see Figs 2 and 3). Please note that the data about the percent of uncovered area addresses only samples with already established conducting layers, i.e. at deposition degrees beyond the so-called percolation threshold. It is well established that the percolation threshold starts at about 50% coating [7].

Various methods for measuring the thickness of coating have been published. For example, in [1] via Auger Electron Microscopy measurements of the local thickness of evaporated Cu-layers were obtained. Similar 'local' methods are appropriate for relative homogeneous deposited layers, such as the evaporated ones. For electroless thin layers, where deposition profiles are rather inhomogeneous (including existence of uncoated substrate areas) the so-called integral methods are more appropriate. In [2] we proposed such an integral method for determining of electroless copper layer thickness. And after a few improvements, this method became suitable for determining both: the completely coated samples and the partly coated ones. This method consists of: (i) determination of the deposited amount (mass) of a metal m on the substrate (in particularly in our case this metal is copper); (ii) determination of the coated fraction of the substrate surface

TABLE I Three coating parameters of electroless copper deposites: global mean thickness d_m (see Section 1 (Experimental Procedures)); coating fraction f_{coat} and actual thickness d (see Equation 2)

Deposition time	Global mean thickness d_m	Coating fraction f_{coat}	Actual thickness d Equation (2)
15″	50 nm	0.60	83 nm
30″	80 nm	0.75	106 nm
45″	90 nm	0.80	113 nm

f_{coat} (=coated area/total substrate area). The deposited mass m is titrimetrically determined. Via the relation $m = \rho_m\ Lad_m$, where ρ_m(=8.96) is the copper specific gravity, one evaluates the global mean deposition thickness d_m. Here *global mean deposition thickness* refers to mean thickness supposing complete evenly coated substrate. At incomplete coated substrate the actual deposition thickness d is larger than the mean thickness $d_m(d_m < d)$. By use of mass conservation, here coinciding with conservation of deposition volume $A_{\text{coat}}d = Ad_m$ one obtains:

$$d = \frac{d_m}{f_{\text{coat}}}, \tag{2}$$

Here $A(=La)$ is the total substrate area, and A_{coat} is the coated one respectively. Data of the above defined coating fraction $f_{\text{coat}}(=A_{\text{coat}}/A) \leq 1$ are given in Table I. Further discussions of deposition sizes (A_{coat}, d) are given in Section 3.

Transmission Electron Microscopy (TEM) is a suitable method for determining deposition morphology, in our study degree of coating, degree of merging and branching of deposition. Fig. 2 shows typical TEM-pictures of samples at 15″, 45″ deposition times. The TEM pictures underwent image analysis ("ImageC" Version 2.50a, using measuring-module "MICRO" for particle analysis) and its results are presented in Table I.

It is known, that image analysis is rather sensitive about the level of gray threshold that differentiate coated from uncoated surface. Presently, we do not have an objective basis for the threshold level definition, therefore the cited findings about the coated/uncoated surface (see Table I) are rather subjective. Here, the problem with the arbitrary selection of the level of gray threshold is partially eliminated due to the conducted comperative analysis. In particular, in the present study the comparative analysis consists in determining the coating fraction f_{coat} (15″), f_{coat} (30″), f_{coat} (45″), etc. at constant gray threshold.

3. Results and discussion

The core results (in log-log scale) are presented in Fig. 1. The graphic's coordinates $\Delta\rho/\rho_\infty$ (relative resistivity increase, see below) and $1/d$ (inverse deposition thickness) are selected to coincide with variables in Sondheimer approximation of Fuchs theory (see for instance [8]).

According to this theory at deposition thickness d greater than mean free path $\lambda\,(d > \lambda)$ the relative increase of resistivity is proportional to inverse layer

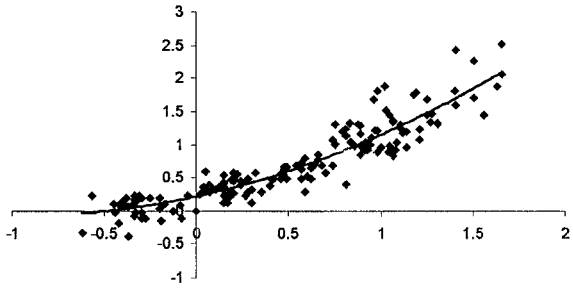


Figure 1 Experimental data of $\lg(\Delta\rho/\rho_\infty)(\equiv y)$ vs $\lg(1/d)(\equiv x)$ with a parabolic fit: $y = 0.3194x^2 + 0.6029x + 0.2203$. Note that the argument $\Delta\rho/\rho_\infty$ is dimensionless while $1/d$ has dimension μm^{-1} (see in the text).

thickness [9]:

$$\frac{\Delta\rho}{\rho_\infty} = \frac{3}{8}(1-p)\frac{\lambda}{d} \tag{3}$$

where $\Delta\rho = \rho - \rho_\infty$, with ρ_∞ as a specific coefficient of resistance of thick wire. For copper, $\rho_\infty(\text{Cu}) = 1.68\ \mu\Omega$ cm. Relation (3) is known as Sondheimer approximation of Fuchs theory.

Before proceeding further, we must explain the calculation procedure and the meaning of the coefficient ρ in (3). The ρ is calculated via Equations 1 and 2, supposing substrates are evenly coated. As it will be shown, the intrinsic resistivity coefficient in our model actually remaines unchanged, instead changed is the conductive area of the due to non-homogeneous, unevenly distribution of the deposited metal on substrate. However, for convenience we retained the form of Equation 3, by introducing effective coefficient ρ according to formula:

$$\rho\frac{L}{s} = \rho_\infty\left(\frac{L}{s}\right)_{\text{actual}} \tag{4}$$

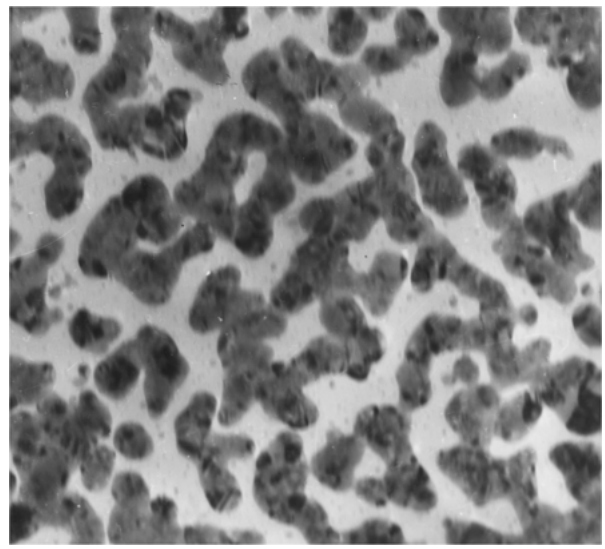
In (4) L and $s(=ad_m)$ are 'idealized' deposition sizes, where L and a coincide with the sample length and sample width (see Fig. 3); d_m is the global mean deposition thickness (see Equation 2). L_{actual} and s_{actual} are actual sizes of the conducting circuit. For example, thickness d in $s_{\text{actual}}(=ad)_{\text{actual}}$ accounts for the actual coating degree of samples via Equation 2. L_{actual} and a_{actual} are different in each case and evaluated separately (see the calculation procedure of Fig. 3). The coefficient p in Equation 3 accounts for the fraction of specular reflected electrons from the wire surfaces and lies in the interval $0 < p < 1$ [8]. The remaining $(1-p)$ electrons are diffusively scattered, and it is them (the remaining scattered electrons) that cause the increased resistance. The coefficient p is defined empirically and the problem with its definition is detailed in the critical article of [8]. As we'll see below, the exact value of p is not important to the findings of this analysis. The mean free path of electrons λ is also empirically defined. The values for λ (of copper) are in the interval at about 30 nm [1] up to about 39 nm [3].

In a standard log-log scale variables should be in dimensionless form. The natural dimensionless variables of diagram in Fig. 1 are $(\Delta\rho/\rho_\infty)$ and (λ/d) (see Equation 3). In fact, the ordinate is dimensionless while the abscissa variable $(1/d)$ is with dimension μm^{-1}. The reason being that the mean free path λ of electroless thin layers is unknown and must be determined by the experiment. In this case, the mean free path is equal to the segment at the ordinate axis. The segment value in Fig. 1 is 0.22 and via Equation 3 for λ one obtains:

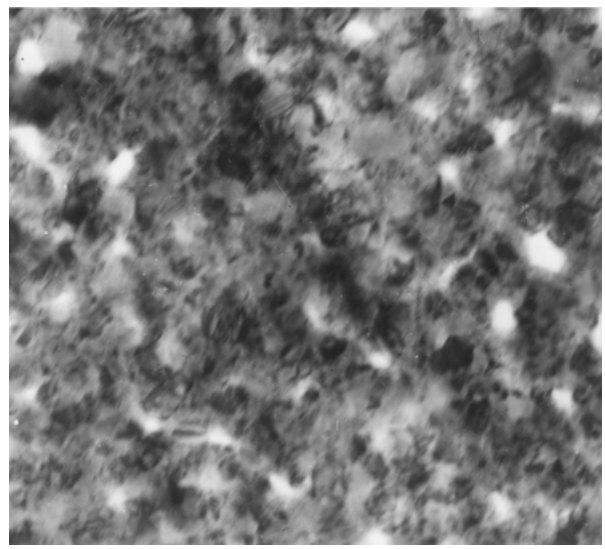
$$\lambda = \frac{8}{3}\frac{10^{0.22}}{1-p} \geq 4.4\ \mu\text{m} \tag{5}$$

The λ value 4.4 μm is the low limit derived (at $p = 0$). Obviously, this value exceeds any reasonable limits of electrons mean free path in metals, which proves that Fuchs-Sondheimer model is inadequate in explaining the reason behind the increased resistance of electroless layers.

The same conclusion is reached through the experimentally proven dependence of $\lg(\Delta\rho/\rho_\infty)$ on $\lg(1/d)$. The points of Fig. 1 are fitted with a parabola. It is



(a)



(b)

Figure 2 Transmission electron micrographs of electroless copper layers of different deposition times: (a) at 15 sec. and (b) at 45 sec.

possible to use another fit, but in any case the experimental points cluster would not correspond to a linear dependence as agreed in Fuchs-Sondheimer model (see, Equation 3).

We'll conclude our discussion with a brief overview of the actual thickness values. As described in Section 2 thickness evaluation d consists of two steps: (i) determination of global mean thickness (d_m), and (ii) coating fraction (f) determination. Only the second step is of interest: coating fraction determination.

Table I shows the resulting parameter values from these procedures. As expected, coating fractions f_{coat} increase with deposition time and in accordance with percolation limit theorem [7], f_{coat} is to be found between 50% and 100%.

Corrected through Equation 2 thickness d (see Table I) once again reveals the shortfall of thin electroless copper layers conductivity with Fuchs–Sondheimer model: the thickness of electroless copper layers are far above the mean free path λ (more than two times) and the expected relative increase of resistivity $\Delta\rho/\rho_\infty$ within the framework of Fuchs–Sondheimer-model could not exceed 20% (see Equation 3). The question then arises as to the reason for the high Ohm resistivity in these relatively thick layers. We believe that the isolated areas of deposition as well as the strong branching of the conducting circuits play major role.

Typical samples of TEM pictures for 15″ and 45″ deposition time are given on Fig. 2. It is obvious that both isolated spots and branches do not take part in current conduction and must be excluded from the calculation for the specific conductivity. Fig. 3 shows the scheme of the conductive area of the sample shown in Fig. 2a.

For clarity, the different substrate parts in Fig. 3 are shaded as follows: the uncoated parts are white, the coated but non-conducting parts (isolated or branched ones) are gray, and conducting elements are black. The ρ/ρ_∞-values is arrived at according to Equation 4. As previously noted, Equation 4 means that the entire increase in resistance is attributed to the effective resistivity ρ, while in fact the increased resistivity is the result of the limited conducting parts of deposition. In particular, the conducting net of Fig. 3 is a circuit series but with a variable cross section area s. According to the rules of electrotechnics, the integral resistance of a circuit with variable cross section is a sum

$$(L/s)_{\text{actual}} = \sum_i (L/s)_i,$$

where $(L/s)_i$ are sizes of circuit parts with constant (or quasi-constant) cross-section areas s_i. The global mean thickness (d_m) and the actual one (d) are related via Equation 2 which allows Equation 4 to be rewritten in a form containing only directly measurable from the picture geometrical variables a_i and L_i:

$$\frac{\rho}{\rho_\infty} = \frac{\sum_i (L/s)_i}{(L/s)} = f_{\text{coat}} \frac{\sum_i (L/a)_i}{L/a} \qquad (6)$$

For ease of measuring a_i and L_i a 50×50 grid overlay was applied to the sample in Fig. 3. One can directly verify that in these grid units $\sum_i (L/a)_i \approx 30$. In the same units of measure the value of the denominator in Equation 6 is unity ($L/a = 1$) as long as all sample sizes are equal ($L = a = 50$). Accounting for that $f_{\text{coat}}(15'') = 0.6$ (see Table I), for the Ohm-resistivity relation in this particular case one obtains $\rho/\rho_\infty \approx 18$. On the other hand the ρ/ρ_∞ value could also be determined when in the parabolic fitting equation of

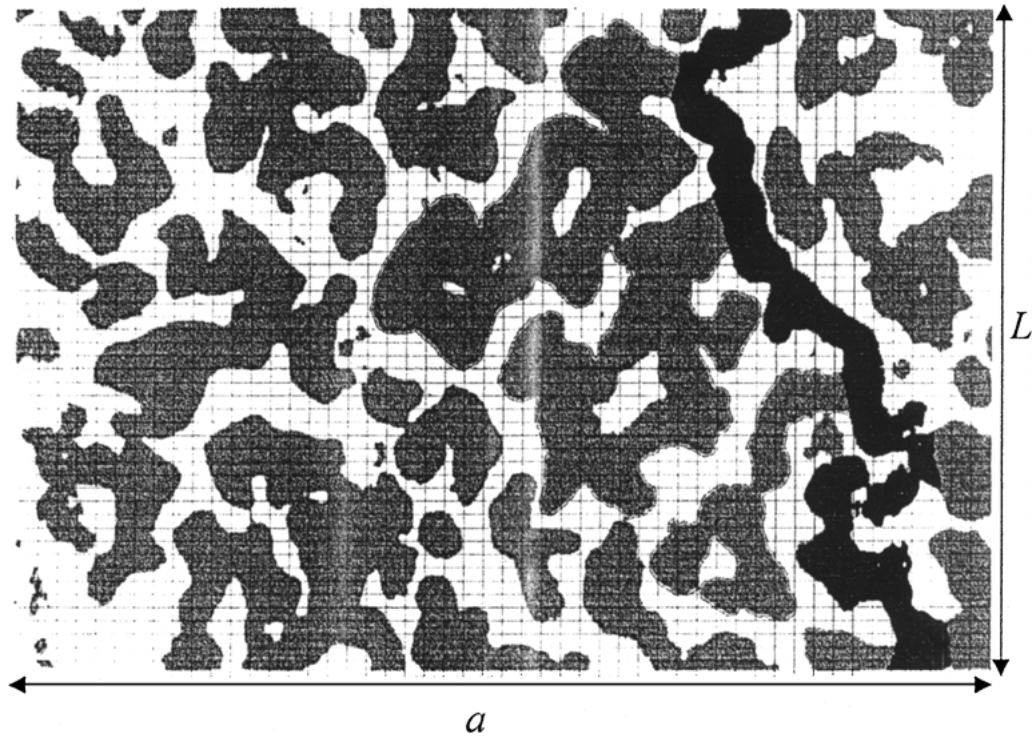


Figure 3 A scheme of the conductive area of the sample, shown in Fig. 2a. White are the uncoated substrate parts, gray are the coated but non-conducting ones, and black are the conducting elements (see in the text).

Fig. 1 one inserts the thickness value from Table I $d_{\text{actual}}(15'') = 0.083\ \mu$m, i.e. $x = \lg(1/0.083) = 1.08$. The result $y(x = 1.08) = 17.4$ corresponds to $\rho/\rho_\infty = 18.4$. Of course, this coincidence by no means should be overestimated for it is only the result of a single sample. However, it well illustrates the developed hypothesis of the effect of deposition inhomogeneities, i.e. the effect of isolated areas and strong branching of conducting circuits in thin electroless Cu-layers.

4. Conclusions

The analysis in these study shows that there are different reasons leading to reduced electric conductivity of thin electroless, respectively evaporated copper layers. In other words, it is the result of the differences (about 25 times) in the thickness of the layers where the conductivity resistance begins (in copper). In electroless layers this thickness is at about 1 μm and for evaporated ones, it is at about 40 nm. The reason of the increased Ohm resistivity for evaporated thin layers is due to the increased intrinsic coefficient of resistivity ρ (Fuchs model). At electroless layers the reason resides in inhomogeneous distribution of metallic layers on the substrate. From this point of view, our interpretation is closer to the model of Namba [6] and Elsom *et al*. [10].

The unevenness in the layers is characterized by the presence of uncoated substrate areas in addition to coated but isolated spots. Other contributing factors for the reduced conductivity of the covered area (i.e. reduced conductive area) are also the strong branching of the conductive path that is eliminated from conducting the current.

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