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Effect of the variable profile of substrate conductivity on the dynamics of metal deposition on resistive tape

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ABSTRACT

The role of the variable conductivity profile $\kappa_t(x)$ of the resistive tape in the process of metal deposition on its surface is investigated by comparison two versions of the calculation of process dynamics taking into account non-uniform distribution of the metal and substituting it at each time step for the average thickness of the deposit. It is demonstrated that a narrow $\kappa_t(x)$ profile, sharply increasing to the current feeder, promotes substantial improvement of the uniformity of current distribution over the tape but its action is temporary. During subsequent deposition, as a result of the propagation of the deposit over the whole tape length and smoothing the steepness of the conductivity profile, gradual weakening of its leveling ability occurs. It has been established that the factors promoting an increase in the terminal effect (for example, a decrease in the conductivity of the seed layer and in average current density; an increase in tape length) at the same time enhance the leveling role of the $\kappa_t(x)$ profile. As a result, the sensitivity of the final deposit distribution over the tape to the initial non-uniformity of deposit distribution (including that caused by the non-uniform initial conductivity profile of the seed layer) decreases sharply.

1. Introduction

The process of metal deposition on a resistive substrate is widely used in manufacturing electronic devices, as well as micro- and nano-electromechanical devices [1,2]. Increased ohmic resistance of the substrate causes predominant localization of the current near the current feeder (so-called «terminal effect»). The regularities of this effect as applied to a uniform resistive tape were studied in [3–6], while the effect of various aspects of metal deposition process (in particular for copper) was investigated in [7–12]. It was shown that the metal is deposited on the tape extremely non-uniformly (mainly near the current feeder) but the uniformity of its distribution improves with time.

It was shown recently in [13] that the terminal effect depends not only on average conductivity of the tape, but also on the shape of the profile of its variable local conductivity. With the conservation of the average value, an increase in tape conductivity to the current feeder weakens the terminal effect while its decrease, quite contrary, sharply increases the non-uniformity of current distribution. Taking into account this effect, improvement of metal distribution over resistive tape during metal deposition can be caused by the joint action of two factors. The first one is an increase in the average thickness of metal layer on the tape with time, while the second one is automatic formation of the local tape conductivity profile $\kappa_t(x)$ increasing toward the current feeder. Evaluation of the contribution from each of these factors into the dynamics of metal deposition is the major goal of the present study.

2. Model formulation and calculation procedure

The dynamics of current redistribution on the resistive tape during metal electrodeposition was calculated as a set of steady current distributions with time-varying profile of local conductivity of the tape. The geometric arrangement of the electrochemical cell for the calculation of the dynamics of copper electrodeposition on the resistive tape is shown in Fig. 1. It was accepted for simplicity that the thickness of electrolyte layer inside the cell and, respectively, the working tape width $w = 1$ cm.

Then the distribution of potential in solution is determined by Laplace's equation

$$\Delta\varphi = \frac{\partial^2\varphi}{\partial x^2} + \frac{\partial^2\varphi}{\partial y^2} = 0, \tag{1}$$

with the boundary conditions at the equipotential anode (2) and insulating walls of the cell (3):

$$\varphi(x, h) = 0; \tag{2}$$

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Nomenclature

x, y	Cartesian coordinates; $0 \leqslant x \leqslant L$; $0 \leqslant y \leqslant h$
L	length of resistive tape cathode (cm)
h	distance between electrodes (cm)
w	working tape width (1 cm)
n, m	numbers of points of the equal partitioning along x and y axes
k	number of elementary strips of the equal partitioning along the tape length ($1 \leqslant k \leqslant (n-1)$)
x_k, x_{k+1}	coordinates of the boundaries of elementary strip number k (cm)
$x_{av,k}$	mean coordinate of the strip number k (cm)
$\varphi(x, y)$	potential in the electrolyte (V)
$P(x)$	potential on the surface of tape cathode (V)
$E(x)$	jump of potential at the boundary between the tape and the solution (V)
κ_L	specific conductivity of the solution (Ohm^{-1} cm^{-1})
$\kappa_t(x)$	local conductivity of resistive tape with account of seed layer (Ohm^{-1})
$\kappa_{t,ini}$	conductivity of the seed layer (Ohm^{-1})
$\kappa_{Cu,sp}$	specific conductivity of the coating (Cu) (Ohm^{-1} cm^{-1})
$\kappa_{t,av}$	conductivity of the coating corresponding to the average deposit thickness (Ohm^{-1})
$l(x)$	local thickness of copper layer (cm)
$i(x)$	local current density on the tape (A cm^{-2})
I_0	total current passing through the cell (A)
i_0	exchange current density ($8 \cdot 10^{-3}$ A cm^{-2})
i_{av}	average current density (A cm^{-2})
i_{max}, i_{min}	maximal and minimal current density on the tape (A cm^{-2})
i_{lim}	limiting diffusion current density (A cm^{-2})
$i_{av,k}$	local current density in the middle of the strip number k (A cm^{-2})
i_k, i_{k+1}	local current densities on the boundaries of the strip number k (A cm^{-2})
α_a, α_c	anodic and cathodic transfer coefficients ($\alpha_a = 0.75$ and $\alpha_c = 0.25$)
c_0	concentration of metal ions in the electrolyte volume ($5 \cdot 10^{-4}$ mol cm^{-3})
$c_s(x)$	concentration of discharging ions on the tape surface (mol cm^{-3})
F	Faraday constant (96487 C mol^{-1})
R	universal gas constant (8.314 J mol^{-1} K^{-1})
T	temperature (K)
z	charge of the discharging metal ions ($z = 2$)
D	Cu^{2+} diffusion coefficient ($7 \cdot 10^{-6}$ cm^2 s^{-1})
δ	effective thickness of diffusion layer (10^{-2} cm)
t, t_f	current and final deposition time (s)
Δt	time step (s)
$Q(x, t)$	modulus of the quantity of electricity at time moment t, related to the area of strip embedded between the neighboring points of uniform partitioning along the tape (C cm^{-2})
$m(x, t)$	mass of deposited metal, related to the area of strip embedded between the neighboring points of uniform partitioning along the tape (g cm^{-2})
M	molecular mass of the metal (g mol^{-1})
γ	specific weight of the metal (g cm^{-3})
σ	square mean deviation of relative current density

$$\frac{\partial \varphi}{\partial x}(0, y) = \frac{\partial \varphi}{\partial x}(L, y) = 0. \tag{3}$$

On the resistive tape cathode, the following equation is fulfilled:

$$\frac{d}{dx}\left(\kappa_t(x) \cdot \frac{dP}{dx}\right) = i(x) = \kappa_L \frac{\partial \varphi}{\partial y}(x, 0), \tag{4}$$

with the corresponding boundary conditions:

$$\frac{dP}{dx}(0) = 0; \tag{5}$$

$$\frac{dP}{dx}(L) = \frac{I_o}{\kappa_t(L) \cdot w}. \tag{6}$$

To describe the rate of copper deposition at the boundary of the resistive tape with the electrolyte, we use the Butler–Volmer equation:

$$i(x) = i_0\left(\exp\left(\frac{\alpha_a zF}{RT}E(x)\right) - \frac{c_s(x)}{c_0}\exp\left(-\frac{\alpha_c zF}{RT}E(x)\right)\right), \tag{7}$$

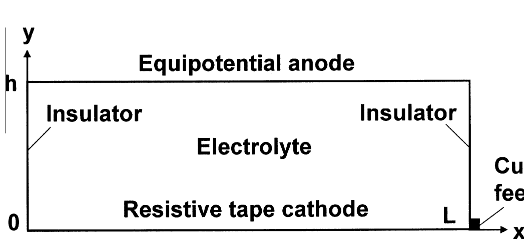

Fig. 1. Schematic of the electrochemical cell for copper deposition on the resistive tape cathode.

$E(x) = P(x) - \varphi(x, 0)$ is the jump of potential at the boundary between the tape and the solution; for the equilibrium potential $E(x) = 0$ V. Taking into account

$$\frac{c_s(x)}{c_0} = 1 - \frac{i(x)}{i_{\lim}}, \tag{8}$$

where the limiting diffusion current is

$$i_{\lim} = zFc_0\frac{D}{\delta}, \tag{9}$$

we obtain after simple transformations:

$$i(x) = \frac{i_0\left(\exp\left(\frac{\alpha_a zF}{RT}E(x)\right) - \exp\left(-\frac{\alpha_c zF}{RT}E(x)\right)\right)}{1 + \frac{i_0}{i_{\lim}} \cdot \exp\left(-\frac{\alpha_c zF}{RT}E(x)\right)}. \tag{10}$$

In all subsequent calculations we used the following values of the parameters: $c_0 = 5 \cdot 10^{-4}$ mol cm^{-3}, $i_0 = 8 \cdot 10^{-3}$ A cm^{-2}, $z = 2$, $\alpha_a = 0.75$, $\alpha_c = 0.25$ [14], $D = 7 \cdot 10^{-6}$ cm^2 s^{-1} [15], effective thickness of diffusion layer for the conditions of natural convection $\delta = 10^{-2}$ cm [16].

Function $i(E)$ is nonlinear, so, in combination with the boundary problem for Laplace's equation (1)–(6), a nonlinear boundary problem for the search for potential and current distribution in electrolyte solution and on tape surface arises. At the given average current density $i_{av} = I_o/(L \cdot w)$ due to the difference approximation of derivatives, the nonlinear boundary problem was reduced to the system of nonlinear algebraic equations and solved using Newton–Raphson iteration method. At each iteration, the system of linear equations with non-subdiagonal matrix of the $n \times m$ dimensionality (where n and m are the number of uniform partition points along the x and y axis, respectively) was solved using Gauss' method.