Control of Nano- and Micro-crystalline Copper Electrodeposits

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Abstract— In this paper, electrodeposition of nano- and micro-crystalline copper films and thin-layers with direct and pulse periodic currents is effectively controled. Electrical and physico-chemical characterizations of the copper films are realized, and the optimized electrodeposition parameters are so determined. Next, they are applied to micromolding. The attention is focused on microstructure, surface roughness, hardness, and on process parameters leading to major differences in final products. The obtained results show that the addition of a spike and a decrease in forward current can improve the throwing power in plating quality. Decrease in the grains dimension of the copper layers results in an increase of both the corrosion rate and the double layer capacitance but then charge transfer resistance decreases.

I. INTRODUCTION

THE electrodeposition is a versatile technique for producing nano- and micro-crystalline materials. The low electrical resistivity of copper and the ability of electrodeposition to superconformally fill high aspect ratio features has made electrodeposited copper as the interconnect material of choice in silicon technology.

Similar to more classical evaporation or sputtering techniques, electroplating allows one to deposit a broad range of materials on various substrates (wafer, polymer, etc. either with a seed layer or directly on semiconductor [1]–[6]). The demand for manufacturing semiconductor IC devices such as computer chips with high circuit speed and high packing density requires the downward scaling of feature sizes in ultra-large-scale integration (ULSI) and very-large-scale integration (VLSI) structures. The trend to smaller device sizes and increased circuit density requires decreasing the dimensions of interconnect features such as a via or trench formed in a dielectric substrate which is then filled with metal to yield an electrically conductive inter-connect.

For microelectronics related applications, electrochemical deposition has the following advantages over vacuum techniques: *(i)* room-temperature process, thus reducing problems with thermal stress; *(ii)* low cost of equipment, no vacuum required; *(iii)* high rate of deposition; *(iv)* artificial material structuring such as multilayers; *(v)* conformal deposition or deposition through resist masks; v*(i)* great reliability for high aspect ratio structures and excellent shape fidelity.

Recently, significant progress has been made in various aspects of synthesis of nano-scale materials. Properties of nano-structured electrodeposits such as hardness, wear and corrosion resistances as well as thermal and electrical conductivities are strongly grain size dependent. Microcrystalline copper deposits and nanocrystalline copper deposits and composite surface layers with grain sizes smaller than $100nm$ attract high technological and scientific interests due to their improved electrochemical, mechanical and physical properties being useful for extensive applications. Corrosion properties are also affected by nanocrystallization [7]-[9].

The aim of the present work is to study the optimized electrodeposition parameters determining properties of nano- and micro-crystalline copper surface electrodeposits under direct current (DC), periodic pulse current (PPC) and periodic pulse reverse current (PPRC) using the mathematical modeling and scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction (XRD), and transmission electron microscopy (TEM).

II. CHARACTERIZATION OF COPPER ELECTRODEPOSITS

Recently, copper electrodeposition has become one of the most important processes for integrated circuit interconnects and packaging applications. One of the methods of improving the copper properties is to electrochemically produce materials with nanocrystalline structure. The experimental appliances, which allow the simultaneous variation of all experimental studied factors are shown in Fig.1. In an acid solution, the cation Cu^{2+} associates with the anion SO_4^{2-} to form copper sulfate. At the cathode, the Cu^{2+} is reduced to metallic Cu by gaining two electrons. The result is the effective transfer of Cu from the anode source to a plate covering the cathode. With the introduction of pulse plating reversal equipment the distribution of the electroplated metal can be improved [10].

Current metallization technology employs three layers, a barrier metal, typically tantalum, a PVD copper seed and electrodeposited copper (Fig.2). Although electrodeposition has been one of the method for nanocrystalline materials manufacturing, properties of nanocrystalline copper electro-deposits are less evaluated, especially for tribological

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applications or potential applications in very large scale of integration devices such as micro- and nano-electro-mechanical systems.The focus is now shifting from synthesis to manufacture of useful structures and coatings having not only superior electric and thermal conductivities but also greater hardness, wear and corrosion resistances. Now, interconnect structures built up on ULSI microchips consist of 10 thin-film layers, and will soon reach 12 layers [4].
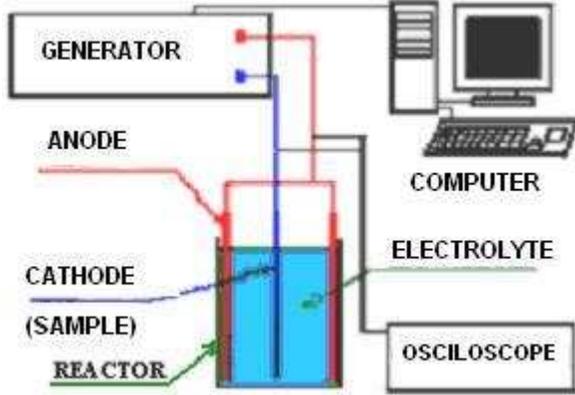
Fig.1. Scheme of experimental apparatus for copper electrodeposition study

In nearly every application of electrodeposition, the pursuit of deposit *uniformity,* especially thickness uniformity, has been a technical imperative. A major contributing factor to the versatility of electrolytic copper and alloy deposition is the capability of modifying the deposit properties by the use of periodic electrodeposition or *pulse plating.*
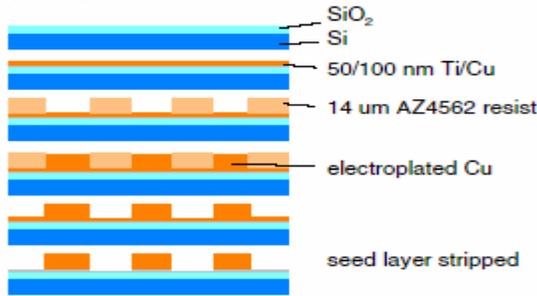
Fig 2. Scheme for fabrication of single-metal, test structures with features having lateral dimensions in the 20-to-100 nm range.

It should be emphasized that the pulse electrodeposition has several advantages over conventional electrodeposition. By varying the duty cycle, that is, (on time)/(on time + off time), changes in deposit structure, mainly grain size can be achieved, because of forced nucleation during each new cathodic pulse. It is clear that adsorption/desorption as well as recrystallization takes place. The main purpose of carrying out pulse reversal plating is to obtain better film thickness with good adherence yielding higher conversion efficiencies for photoelectrochemical cells fabricated using these films. In the present work, Cu films were direct and pulse current plated from an acidic solution. Films were also deposited by applying pulse reversal for short durations.

III. MATHEMATICAL MODEL OF COPPER ELECTROPLATING

The process of copper layers electrodeposition is described by a mathematical model derived from Maxwell equations and mass balance equations [11] as follows

$$\nabla^2 E(M,t) = -\rho_c(M,t) + \nabla \cdot \vec{P}(m,t), \qquad (1)$$

$$\frac{\partial c_i(M,t)}{\partial t} = -\nabla \cdot \vec{J}_i(M,t) + \xi_i(M,t), \quad \text{with } 1 \le i \le m$$

where the state variables $E(M,t)$ and $c_i(M,t)$ denote the potential and concentration, respectively, of species i at point M and time t.

The first of these $(m+1)$ coupled equations generalizes the Poisson equation, where ρ_c is the electric charge density per unit volume and $\vec{P}(M,t)$ denotes the dielectric polarization. The second set of equations generalizes the hydrodynamic equations and applies to the m types of chemical entities involved in the system; c_i is either a surface or a bulk concentration, $\vec{J}(M,t)$ is the total flux of ions, and $\xi_i(M,t)$ is a term representing the sources (production and consumption) of the entities i, generally arising from chemical and electrochemical reactions. The above models are valuable not only for their ability to describe deposit uniformity but also for the insight how they can provide into the interrelation of the potential field and various measurement techniques. In the reaction model considered in this paper the term $\xi_i(M,t)$ is equal to zero.

The total flux of an ion is given by

$$J_i = -D_i \nabla c_i + c_i u - z_i F u_i c_i \nabla V \qquad (2)$$

where $-D_i \nabla c_i$ is the contribution of the diffusion, $c_i u$ denotes the contribution of the convection and $-z_i F u_i c_i \nabla V$ is the contribution of the migration. The unknowns in the mass conservation equations are the ion concentrations and the potential in each point of the solution. Hence, the electroneutrality condition,

$$\sum_{i=1}^{N} z_i c_i = 0 \qquad (3)$$

is added. This condition is most often assumed to be valid everywhere in the solution, except in the diffuse double layer. The electrode kinetic processes over the compact double layer are encompassed in the boundary conditions

$$v(\xi) = V_m - V - E_0 \qquad (4)$$

representing the electrode overpotential, i.e. the difference between the imposed potential on the electrode (V_m) and the solution potential at the other side of the double layer (V), this with respect to the equilibrium potential E_0. In general, the values of V_m and V can vary along the electrode surface. The overpotential v depends on the local current density in

$$i = i_0 \left[\frac{(c_{red})_i}{(c_{red})_0} exp\left(\frac{\alpha_a nFv}{RT}\right) - \frac{(c_{ox})_i}{(c_{ox})_0} exp\left(\frac{-\alpha_c nFv}{RT}\right)\right] \qquad (5)$$

$$= i_a + i_c$$

accord to Butler–Volmer equation

in which i_0 is the value of either of the (equal) electron-emitting and electron-accepting partial current densities at the reversible electrode. Concentration constants are: c_{red} and c_{ox}, respectively. Sensitivities of the transition state of the anode and cathode to the applied voltage are reflected by α_a and α_c, respectively. Anodic and cathodic currents are: i_a and i_c, and $v = V - E_0$ is the overpotential, n - the number of valency electrons, α_a and α_c - anodic and cathodic, respectively, transfer coefficients, R - molar gas constant and T - absolute temperature. For identical surface and bulk concentrations

$$i = i_0 \left[exp(\frac{\alpha n F v}{RT}) - exp(\frac{-(1-\alpha)nFv}{RT}) \right] \qquad (6)$$

In this situation the quantity $v = V - E_0$ reflects the activation energy required to force current i to flow. However, as a voltage different to that of E_0 is applied then different responses are observed depending upon the value of i_o. When i_o is 'large' then a small change in $V - E_0$ results in a large current change. At the other extreme when i_o is very 'small' then a large value of $V - E_0$ is needed to alter the current (Fig.3). Low overpotential $v < 10$ mV near E_0 gives a possibility to linearize the above relation and get

$$i = (i_0 nF / RT)v \qquad (7)$$

For high overpotential , i.e. v >52mV the rate of oxidation becomes negligible and we can neglect i_a term and obtain

$$i = i_0 exp(-\alpha \cdot nFv / RT) \qquad (8)$$

So current density varies exponentially with v but taking ln of both side of (8) gives

$$lni = lni_0 + (-\alpha \cdot nF / RT)v \qquad (9)$$

which has the form of equation of a line.

The thickness d of the deposited copper layer is determined as follows

$$d = \beta \frac{Mit}{zF\rho A} \qquad (10)$$

where M is the mol mass of the deposited metal, z denotes the number of electrons taking part in electrode processes of
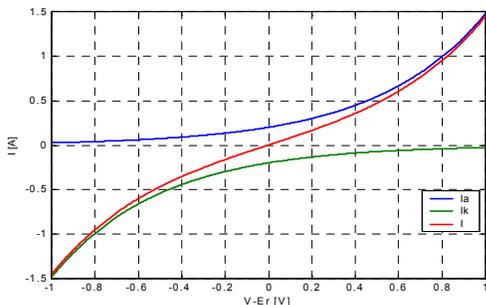
Fig.3. Characteristic of current- overpotential of copper electrodeposition *oxidation or reduction, $F = 96485\ C \cdot mol^{-1}$–Faraday constant, i – current in the solution, t – time of layer deposition, ρ -*

mass density of the deposited material, A - surface of active part of the cathode. Dimensionless coefficient β is depending on the choice of parameters of realized process. The developed dynamic model consists of aspects which are most critical for optimal operation of surface thin-layer copper electrodeposits. The details related to each of particular aspects are presented in the following subsections.

IV. CONTOL OF NANO- AND MICRO-CRYSTALLINE COPPER

The process, which includes chemistry, bath configuration and power, needed to be developed prior to implementation into the existing metal finishing product. However, it should be emphasized that PPR technology should not be considered a competing technology to DC. Several investigations carried out in the scope of this study have proved such a point of view.

A. Control of copper deposits by current waveforms

Copper deposition on high-end thin-layers and on other product in cutting-edge technologies was at the very limit of what DC processes could achieve, and it turned out PPR technology could go beyond that (Fig.4). All major process studies concentrate currently around the PPR copper technology and the general metal finishing products.

In such situation the copper use in electrodeposition applications in MEMS and nanotechnology, such as DC plating, pulse plating, and periodic reverse pulse plating is cost-effective for a wide range of research and development applications, and laboratory requirements such as: a)reducing porosity and intrinsic stress, b) improving uniformity, c)increasing hardness and decreasing grain size of electroplated thin-films for physical, chemical, biological transducers and microsensors.
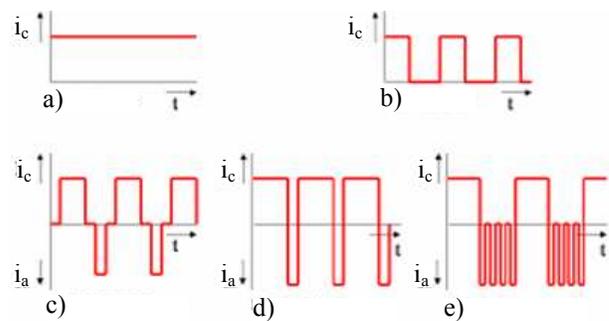
Fig. 4. Current waveform examples: a) Direct (DC), b) Periodic Pulse (PP), c) Periodic Pulse Reverse with Deadline (PPRD), d) Periodic Pulse Reverse (PPR), e) Periodic Pulse with Segmented Reverse (PPSR)

Reversal pulse plating wave is defined by J_c (A/dm^2): cathodic pulse current density, T_c (s): on time or cathodic pulse length, J_a (A/dm^2): anodic pulse current density and T_a (ms): reverse on time or anodic pulse length.

The evaluation of the factor range for reversal pulse plating (RPP) is difficult due to the numerous factors involved (Fig.4). Solutions to a successful PPR application include the optimization of the following: (*i*) electrolyte

composition, *(ii)* additive package, *(iii)* bath agitation, *(iv)* cell (bath) design, *(v)* supplying source design, *(vi)* pulse pattern. Current densities, cathodic (on time) and anodic (reverse on) times as well as temperature can be varied independently, forming a five-fold parameter space.

While most plating cells use a continuous direct current, some employ a cycle of 8–15 seconds on followed by 1–3 seconds off. In order to deal with the uneven plating rates that result from high current densities, the current is even sometimes reversed, causing the *valleys* to be filled without over-plating the *peaks*. This is common on rough parts or when a bright finish is required (Fig.5). The pulse current density, i_p is divided into the capacitive current density, i_c, and the faradaic current density, i_F as

$$i_p(t) = i_C(t) + i_F(t) \qquad (11)$$

The capacitive current density is related to the double layer potential by

$$i_C(t) = C_{dl} \frac{dv_1(t)}{dt} \qquad (12)$$

where $v_1(t)$ is the potential drop within the double layer and C_{dl} is the capacitance of double layer .

Since the applied current density is low, the relationship between faradaic current and overpotential can be assumed

$$i_F(t) = \frac{v_1(t)}{R_{ct}} \qquad (13)$$

Combining (i), (ii) and (iii) gives

$$C_{dl} \frac{dv_1(t)}{dt} + \frac{v_1(t)}{R_{ct}} = i_p(t) \qquad (14)$$

The copper ions are firstly adsorbed on the electrode and reduced to copper adatoms in two steps. The first is the reaction of copper ions disproportion, and the other is the dissolution of metal. Similar to $v_1(t)$, the response of the potential drop $v_2(t)$, corresponding to metal dissolution, is

$$C_{psd} \frac{dv_2(t)}{dt} + \frac{v_2(t)}{R_{sd}} = i_p(t) \qquad (15)$$

where C_{psd} and R_{sd} denote the dissolution capacitance and resistance, respectively.

In this way the total surface overpotential $v(t)$ is

$$v(t) = v_1(t) + v_2(t) \qquad (16)$$

zEarly treatments correctly predicted that since peak current densities in pulse plating were higher than the time-average-equivalent DC current densities, the nonuniformity would be larger, according to

$$W_t = \frac{2.303RTk}{jZfL} = \frac{R_t}{R_e} \qquad (17)$$

i.e. this is charge transfer resistance divided by the ohmic resistance with k as solution conductivity and L - length .

TABLE I
COMPOSITIONS OF COPPER ELECTROPLATING BATH

Symbol	Additive substance	Content [g/dm³]
Cu1	-	-
Cu2	HCl	0.01
Cu3	$H_2N\text{-}CS\text{-}NH_2$	0.20
Cu4	HCl	0.01
	$H_2N\text{-}CS\text{-}NH_2$	0.20
Cu5	$C_7H_5NO_3S$	0.20
	$C_{12}H_25NaO_4S$	0.44
	HCl	0.01
Cu6	$C_{12}H_{25}NaO_4S$	0.44
	$C_7H_5NO_3S$	0.20
Cu7	HCl	0.01
	Cu-189	6 ml
Cu8	HCl	0.01
	$C_{12}H_{25}NaO_4S$	0.44
	$H_2N\text{-}CS\text{-}NH_2$	0.20

B. Control of copper deposits by bath compositions

The components of the Cu electrolytic plating bath may vary widely depending on the substrate to be plated and the type of Cu deposit desired. Pure and other baths prepared at contents of appropriate additives are represented by Cu1, Cu2,..,Cu8, respectively. They are correspond to specifications given in Table I. Organic additives are chemicals such as wetting agents, carriers, leveling agents, brighteners, and grain refiners.
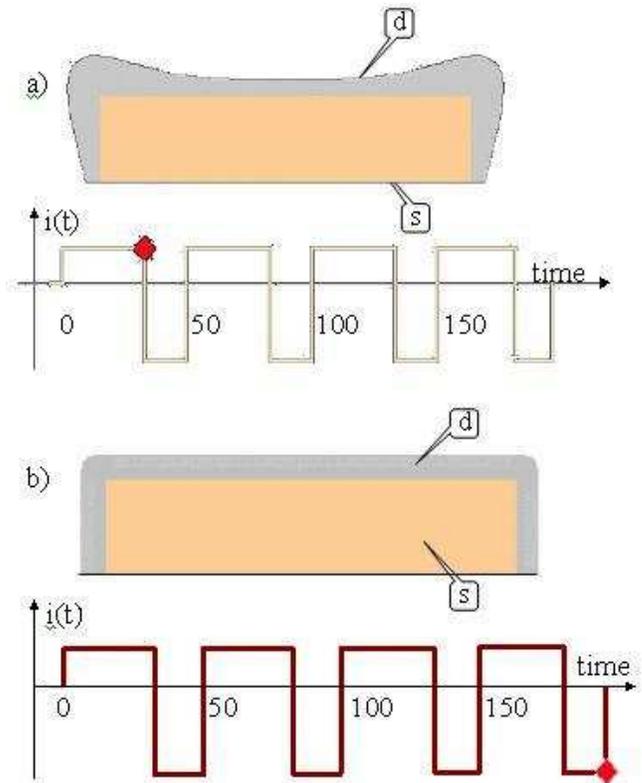
Fig. 5. Illustration of PPR plating effects: a) direct pulse , b) reverse pulse

They are adsorbed on the surface of the substrates and slow down the diffusion of the chemicals in the bath to the surface of the substrate. as well as some additives used to provide desired surface finishes for the Cu plated metal and to initiate bottom-up filling of interconnect features.are electrochemically active and the type of supplying current waveform is important.

Moreover, the other additives, such as brighteners, grain refiners or levelers, are electrochemically active and the type of supplying current waveform is important.
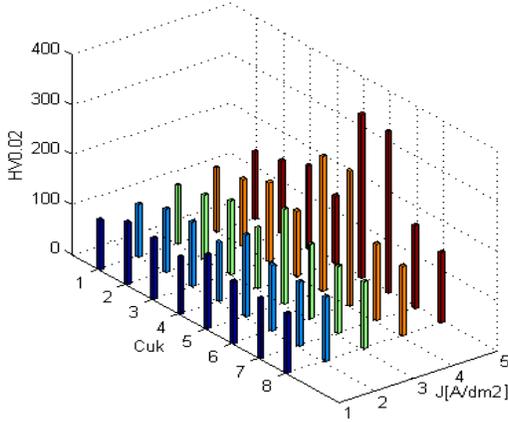
Fig.6. Hardness of the copper deposits versus current density and bath composition

Thus, the additive system must be designed to work at high current densities. Influences of solution bath composition on the hardness of copper thin layer produced by DC process are presented on Fig. 6. The diagram shows that the highest hardness of copper electrodeposits can be obtained at bathes Cu4 and Cu5 at current density 5 A/dm^2.

C. Control of copper electrodeposits by throwing energy

One challenge is that there are many different ways to accomplish 3-D copper electrodeposit integration, each with different cost implications. Currently it is generally agreed upon that PPR technology is not just a component-wise plug-and-play replacement for DC technology. An illustration of influences of pulse supplying current frequency in relation to DC regime is shown in Fig.7.

D. Control of microstructures of copper deposits

The current density (amperage of the electroplating current divided by the surface area of the part) in the copper plating process strongly influences the deposition rate, plating adherence, and plating quality. This density can vary over the surface of a part, as outside surfaces will tend to have a higher current density than inside surfaces (e.g., holes, bores, etc.).The higher the current density, the faster the deposition rate will be, although there is a practical limit enforced by poor adhesion and plating quality when the deposition rate is too high. Influences of the current density and kind of the bath solution are illustrated in Fig.8.

Under influence of electric current, the following changes of ion concentrations take place:
-during the current on interval we have

$$c(t) = c_0 + c_j \left[1 - 8\pi^2 \sum_{m=1}^{\infty} A_m\right] \quad (18a)$$

$$A_m = \frac{1}{(2m-1)^2} exp\left[\frac{\pi^2}{4}(2m-1)^2 a(t-PT)]K\right], \quad (18b)$$

$$K = \frac{1-exp[-\frac{\pi^2 a}{4}(2m-1)^2 \tau]}{1-exp[-\frac{\pi^2 a}{4}(2m-1)^2 T]} \quad (18c)$$

where c_0 – concentration of the electrolyte solution , c_j – parameter dependent on current amplitude I_p, diffusion layer thickness d, Faraday constant F, rate n of ion oxidation, diffusion coefficient D, number of current cycles P.
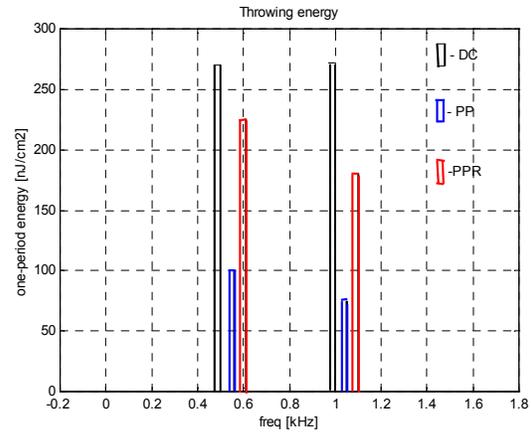
Fig. 7. The values of energy of copper coatings obtained in three different processes: DC, pulse periodic, pulse periodic reverse plating

- during the current off interval we obtain

$$c_p(t) = c_0 + c_j \left[8\pi^2 \sum_{m=1}^{\infty} A_{mp}\right], \quad (19a)$$

with

$$A_{mp} = \frac{1}{(2m-1)^2} exp\left[\frac{\pi^2}{4}(2m-1)^2 a(t-PT)]K_p\right], \quad (19b)$$

$$K_p = \frac{1-exp[-\frac{\pi^2 a}{4}(2m-1)^2 (T-\tau)]}{1-exp[-\frac{\pi^2 a}{4}(2m-1)^2 T]} \quad (19c)$$

The above result indicates that the current amplitude I_p and coefficient α of the current rate as well as frequency $f = 1/T$ have significant influence on the quality of deposited copper layer. Applications of PPR current give relatively easy control of the microstructure, thickness and useful properties of the deposited copper layers. Differences in their microstructure are shown in Fig.10. We have observed significant growth of selected grains in a polycrystalline interconnect, which subsequently become more susceptible to surface offset formation with further cycling (Fig.11).

The benefits of reverse pulse current plating are evident because it allows a precise control of the deposited material, including its composition, its crystallographic structure, and texture and grain size. The higher the current density, the grain are finer (Fig.12).
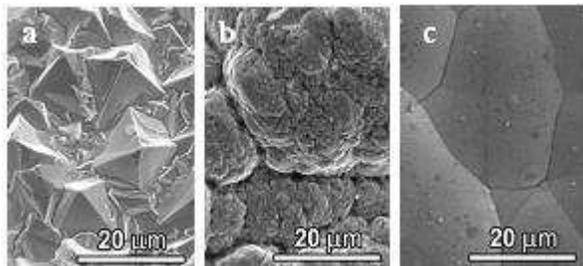
Fig.8. Surface morphologies of copper layers produced with different current densities and various additives in bath solutions: a) 3A/dm^2 and HCl, b) 5A/dm^2, c) 3A/dm^2 and organic substance
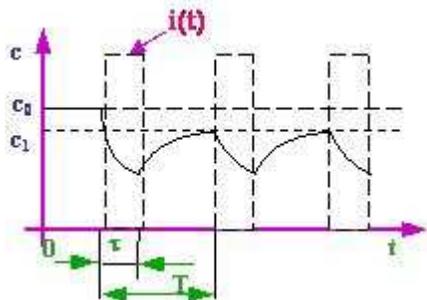
Fig.9. Variations of the current and ion concentration in the diffusion layer
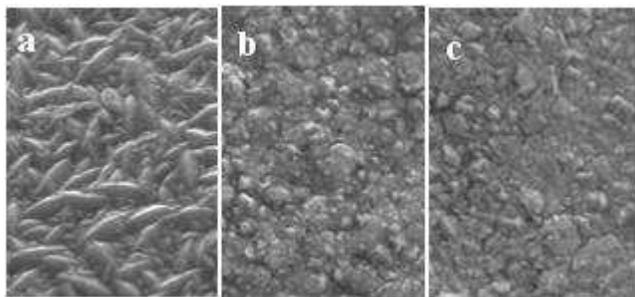
Fig.10. Surface morphology of copper electrodeposits with: a) DC , b) PC at f = 0.5 kHz , c) PC at f =10 kHz
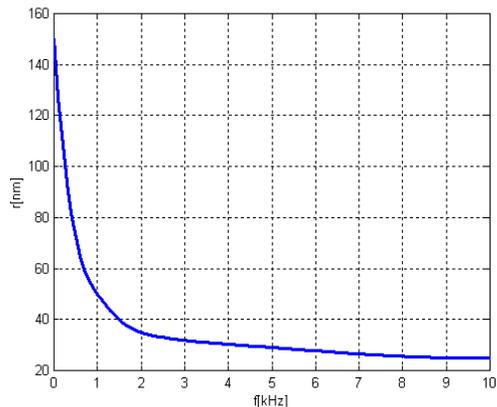
Fig.11. Influence of the PPC frequency on crystallite dimensions

V. SUMMARY AND CONCLUSIONS

Morphologies of copper deposits obtained at the higher limiting diffusion current density and overpotentials related to the plateau of current-potential curve were examined by the scanning electron microscopy (SEM) technique.
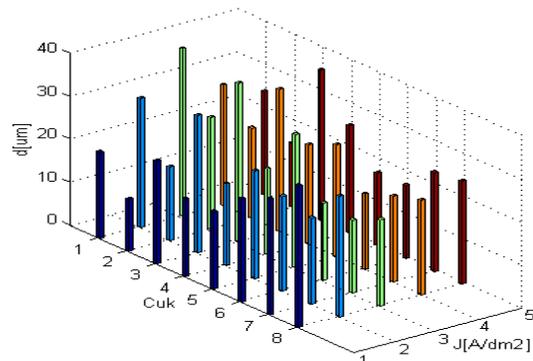
Fig.12. Thickness of the copper deposits versus current density and bath composition

The obtained copper structures consisted of agglomerates ofcopper grains being a function of the current density of electrodeposition. Pulse periodic reverse current can be used to give improved distribution of copper on high aspect when compared to direct current plating. An acid copper electrolyte has been developed for use in combination with pulse period reversal which is capable of delivering the benefits in copper plating. The paper covers also an investigation of the effects of periodic reverse current and pulsed direct current on properties of copper electrodeposits.

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