KINETICS OF COOPER PHOTOELECTROCHEMICAL DEPOSITION ON SILICON

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ABSTRACT

This work investigates the kinetics mechanism of photoelectrochemical deposition of copper on p-silicon. The cooper thin film was obtained by a copper sulfate solution under HeNe laser illumination. Using the law of potential sweep rate dependence with the current density peak, for the reaction reduction $Cu^{2+} + 2 e^- = Cu$, by several light power densities, the controlling mechanism of this reaction was determined. The kinetics mechanism depends on the flux of photocarriers with the potential sweep rate. It was observed that the mechanism could be controlled by electron hole generation; in this case, the film obtained is dense and uniform. The kinetic equation for the photodeposition process was determined. The photodeposition reaction rate decreases linearly with the deposition time. The following equation describes the growth rate dependence with reaction time for a specific laser power: $r = (0.051 \pm 0.002) - (4.4 \pm 0.2) \times 10^{-4} t$.

1. INTRODUCTION

Copper metal is one of the most important substances in the electric or electronic field. It has been used either as electric cables for electrical transfer or as part of the devices. Presently, copper thin film has been proposed to be used in new-generation display devices based on organic electroluminescent elements. These are constituted by an organic light-emitting layer, a transparent electrode membrane semiconductor and metal thin film. The thin film can be prepared with each one of the following metals or their alloys: silver, palladium, gold, copper or platinum [1]. For the new-generation solar cells the use of an electrode equipped with a photo-absorption layer made of P-typed semiconductor copper, indium and calcium compound and selenium compound [2] has been proposed. However, it is in the microelectronic industry, especially those related to the new-generation of integrated circuits that the presence of copper thin film is more important.

The pace of introducing new materials and processes has been increasingly accelerated in the semiconductor industry [3]. The microelectronic industry depends on the continuous improvement of device speed and functionality. At the moment, the interconnect resistance-capacitance delay time is a crucial limiting factor, because the device dimensions shrink and device densities increase. To overcome these difficulties, the technology depends on introducing low dielectric constant (low-k) materials as interlayer dielectrics, and their integration with copper, the low resistivity interconnect metal of choice, replacing the conventional Al(Cu)/SiO2 interconnect scheme [4].

Advanced packaging has been explored to continue the drive for increased functionality in less space [5]. Three dimensional packaging using stacked chips for high density has received considerable attention [6]. Packages have an important role in the overall cost and performance of the device and integrated circuit (IC) interconnects are becoming the limiting factor in IC performance. Among the several processes of advanced packing, Through Wafer Interconnects (TWIs) has distinct advantages to the others [7]. With this technology the power consumption can be reduced, since the length of wires is also reduced [8]. The key of this technology is creating an electrical via through the silicon wafer and coating this via with conducting material [9]. Electroplated copper has been suggested as the conducting material in this technology, where copper coats the front and the back of the wafer and fills the vias [10].

In order to keep or improve the electrical characteristics of the devices, thin films used in those devices have to be compact and uniform [11-13]. If the electrical interconnection lines are constituted by porous and dendrite type materials, the electric resistance line increases and the device performance decreases [11-13].

Electrochemically formed films under mass transport controlled processes should be rough, due to the non-uniform thickness of the Nernstian diffusion layer [14-15]. However, electrochemically formed films controlled by electron-hole generation are more uniform than those grown at mass transport control conditions [14-15]. Due to the photodeposition process, it occurs only under illuminated areas, such deposition processes are interesting means to directly obtain the desired pattern by metal deposition or corrosion on silicon. The photoelectrochemical deposition processes are based on the illumination of an electrochemical electrode. A potential is applied to the semiconductor to create a depletion layer which separates holes and electrons produced by illumination [16]. Electrons migrating towards the surface cause reduction of cations present in the solution and are deposited on the solid surface [16]. Like an ordinary electrochemical process, photoelectrochemical deposition can be

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also controlled by mass transport or electron-hole generation. As a consequence of mass transport control, the punctual current densities are also not uniform; they are higher in those regions where the thickness of the Nernstian diffusion layer is smaller and are lower where this layer thickness is bigger [14-15]. Thus, it seems interesting determining the experimental conditions on which the photoelectrochemical kinetics is controlled by the electron-hole generation. The main scope of this work is to demonstrate a methodology to obtain dense and uniform copper films, by photoelectrochemical reactions controlled by electron-hole generation, and to determine the kinetic equation, which describes the reaction rate dependence with time. This study can be used comprehensively; this procedure can be applied to determine the experimental conditions to deposit, by an electrohole generation controlled process, other metals over another kind of semiconductor than silicon.

2. EXPERIMENTAL

A homemade Teflon™ electrochemical cell was prepared where: the working electrode was a slice of p-Silicon (Wacker Co. 4.9 to 9.1 ohm cm <100>), the reference electrode was the calomel-saturated (SCE) electrode and the counter electrode was a wire of palladium. The electrolyte solution was prepared with the dissolution of 0.05 mol of $CuSO_4$ and 0.1 mol of Na_2SO_4 in 1.00 liter of deionized water. The silicon electrode was irradiated with a HeNe laser (λ=632.8 nm) at normal incidence. The experiments were carried out using a Princeton Applied Research (362 model) to control the potentials. A linear potential ramp from 0.0 to 1.6 (V/SCE) was performed at different potential speed rates (v): 2, 5, 10, 20, 50, 100, 200 and 500 mV/s. The silicon electrodes were irradiated with 0.95 mW (A) and 1.73 mW (B) HeNe laser. The copper films were obtained using a current density of 0.018 Acm^{-2} under the irradiation of a 0.95 mW laser using the following time intervals: 3, 5, 10, 20, 40, 60, 80, 100, and 120 minutes. The profile of those films were measured by a profiler equipment (Sloan, mod. DEKTAK^3 ST). The silicon electrodes were analyzed by scanning electron microscope (SEM).

3. RESULTS AND DISCUSSION

Figure 1 shows the relationship between the peak of the cathodic current density, for the $Cu^{2+} + 2e^- \rightarrow Cu$ reaction, with the square root of the potential sweep rate $(v)^{1/2}$ for the experiments A and B. The peak of the cathodic current density was independent of the sweep rates for the experiments A. However, for the experiments B, there is a linear dependence from 2 to 100 mV/s and after 100mV/s the current is also independent of the sweep rates. There is an indication that the cathodic reaction is controlled by the mass transport at 2-100 mV/s range for experiments B [14-15]. However, for values higher than 100 mV/s, the process starts to be controlled by the electron-hole generation, which is indicated by the independence between the peak of the current density and the

sweep rate. Therefore, to deposit copper films on a silicon surface by electron-hole control an adequate relation between current density and laser beam output power should be experimentally determined.

The films grown under mass controlled condition must have porous and dendritic grains. However, if their growth is controlled by electron-hole generation they must be constituted by dense and compact cooper grains. A thin copper film was deposited on a silicon electrode irradiated with a 0.95 mW HeNe laser beam, at 0.018 Acm^{-2} for the current density for 10 minutes.
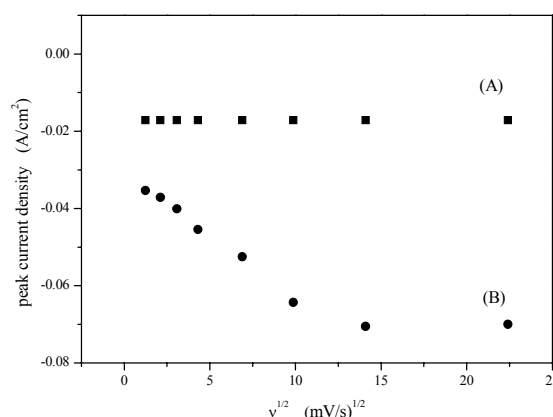

Figure 1 - Dependence of the current density peak on $(v)^{1/2}$. The closed square is related to experiments A and the closed circle to B.

Under this experimental condition the photoelectrochemical reaction is controlled by the electron-hole generation and dense and compact films must be grown from this reaction. This conclusion can be confirmed in Figure 2, where a thin copper film deposited under this set of conditions is analyzed by SEM microscopy. This figure shows that the thin film is made up of pyramidal and dense copper grains.

Figure 3 shows a microphotograph of a thin film of copper deposited under the following experimental conditions: 0.95 mW HeNe laser, 0.018 Acm^{-2} for the current density for 5 minutes. It is expected that the thickness of the film has the same profile as the laser beam intensity. It is well known that the beam light of the HeNe laser has a Gaussian pattern, which is more intense at the centre, and its intensity decreases along the light beam radius. Figure 3 shows an image provided from an optical microscopy of the same deposit shown in Figure 2. One can observe that the thin film has the same profile of the laser intensity along the radius. The copper grains are more concentrated at the center of the film and more distributed at the edge. The presence of several small nucleuses can be observed at the edge of the film. The deposition rate is not uniform along the film radius; it is more elevated at the central spot than at the extremity.

Figure 4 shows the profiles of the film deposit with the deposition time. This film was obtained under the following experimental condition: laser with 0.95 mW power density and current density equal to 0.018 Acm^{-2}. At this condition

it is also expected that the kinetic of the cooper photoelectrochemically deposited be controlled by the electron-hole generation. The profiles of each deposited copper film do not show dendrites type grains at this measurement resolution. It is possible to observe a correlation between the pattern of the light intensity radial distribution and the thickness film at the direction of the spot deposit diameter.
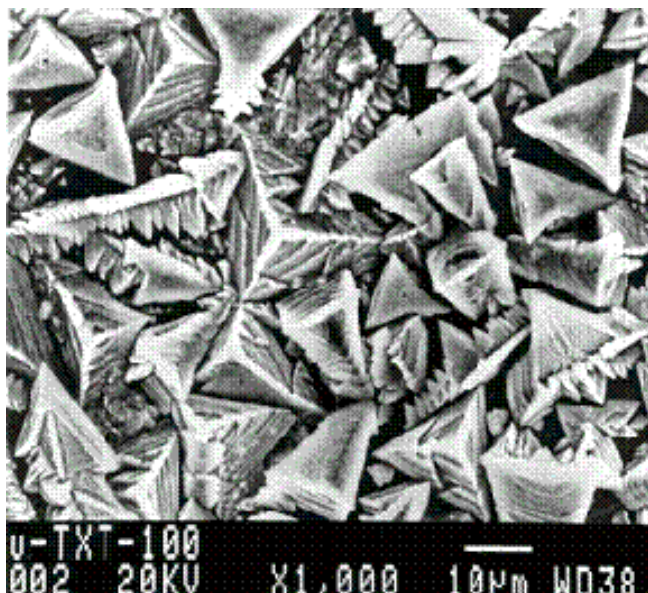

Figure 2 - Microphotograph of copper deposited under electron-hole controlled process conditions.
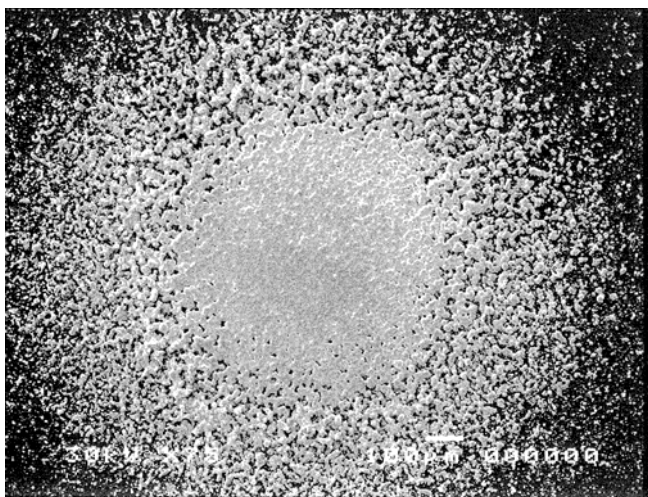

Figure 3 - Copper photoelectrochemical deposited under the same conditions as Figure 2, using low magnification.

Despite the thin film thickness increase with deposition time, the defects on the film thickness are at the same position for all profiles. It implies that the defects are generated by the low homogeneity distribution of light power in the laser beam spot. As the process is able to reproduce the local differences of the homogeneity of the light power, one can conclude that the process indicates an elevated degree selectivity at the photoelectrochemical deposition. The film growth at a perpendicular direction increases the film di-

ameter. However, those growths at axial direction increase the film thickness.

Table 1 shows the average thickness values of each profile with deposition time. These data were used to prepare Figure 5. This Figure shows the actual film thickness evolution with deposition time. At the beginning of the deposition process the rate deposition is more elevated than at the end of the process. In this Figure the squares are the experimental data and the line is the second order polynomial equation fitted to the experimental data. This Figure suggests that the film would stop growing after a long period of time. These mathematical fittings can be described by Equation 1:

$$H = A + B_1 t + B_2 t^2 \qquad (1)$$

where, H is the average thickness of the profile, A is a time independent constant, B_1 is the first order and B_2 is the second order time dependent constant. The values of constants and the correspondent errors are: $A = (0.42 \pm 0.04)$ μm, $B_1 = (0.051 \pm 0.002)$ μm/min, and $B_2 = (-2.2 \pm 0.1) \times 10^{-4}$ μm/min. These values were obtained by fitting the experimental data to a second order polynomial equation with 95 % of reliability.
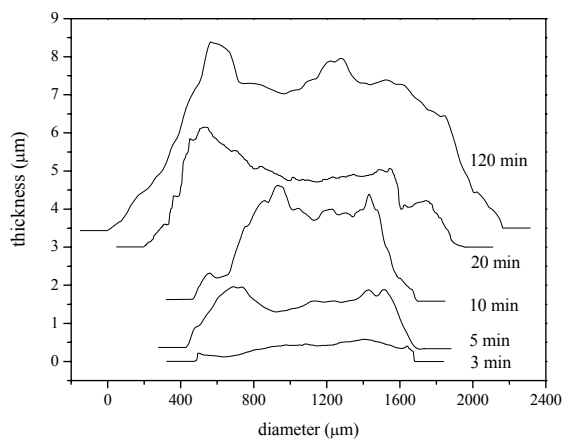

Figure 4 - Profiles of cooper film deposition on the spot.

Table 1 - Time deposition and the average thickness of the copper film photoelectrochemically deposited.

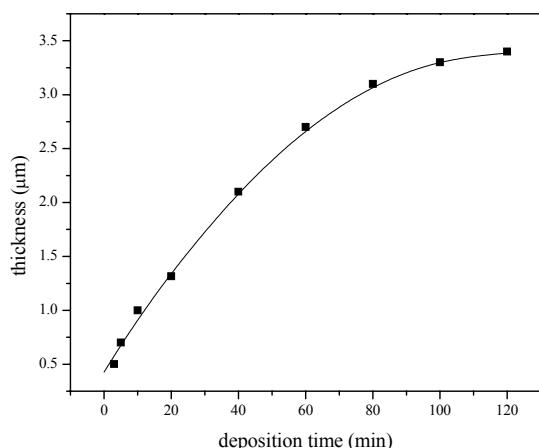| Deposition time (min)	Average thickness (μm)
0	0
3	0.500
5	0.700
10	1.00
20	1.31
40	2.10
60	2.71
80	3.14
100	3.36
120	3.42

Figure 5 - Fitting the experimental data to a second order polynomial equation.

The deposition rate is defined as $r = dH/dt$, and it can be obtained by the first differentiate of equation 1:

$$r = B_1 + B_2 t \tag{2}$$

Using the values of the constants obtained in the fitting step, the thickness rate deposition can be described in units of μm/min by the following equation:

$$r = (0.051 \pm 0.002) - (4.4 \pm 0.2) x 10^{-4} t \tag{3}$$

Equation 3 describes that the copper deposition rate decreases linearly with the deposition time. This is produced by a filtering effect caused by the deposited films. It decreases the light intensity that reaches the silicon surface. The growth film filters the incident light the same way that a colored solution filters an incident beam light, by Beer-Lambert law. In this law the transmitted light decreases linearly with the medium thickness. These considerations are in accordance with equation 3, where the deposition rate decreases linearly with time.

4. CONCLUSION

Thin copper film was obtained by a photoelectrochemical process in an experimental condition where the chemical reaction is controlled by the electron-hole generation. SEM micrographs showed that the thin film is constituted by dense, compact and pyramidal copper grains. It was observed that film grows in a Gaussian pattern and the deposition rate is more elevated at the central spot than at the extremity. The deposition process occurs perpendicularly and axially to the laser beam and the growth rate law on the axial direction is:

$$r = (0.051 \pm 0.002) - (4.4 \pm 0.2) x 10^{-4} t$$

ACKNOWLEDGMENTS

REFERENCES

1. HOSOKAWA, C.; KUSUMOTO, T., Patent Number: JP2008218430-A; Derwent Primary Accession Number: 2008-K82151 [64].
2. ZOU, Y., Patent Number: CN201069776; Derwent Primary Accession Number: 2008-L22026 [66].
3. LEE, T.H., *Scientific American* 286 (2002) 52.
4. FISHER, I.; EIZEMBER, M., *Thin Solids Films* 516 (12) (2008) 4111.
5. BALIGA, J., *Semiconductor International* 23 (2000) 91.
6. BALIGA, J., *Semiconductor International* 28 6 (2005) 7.
7. SOH, H.T.; YUE, C.P.; MCCARTHY, A.; RYU, C.; LEE, T. H.; WONG, S.S.; QUATE, C.F., *Japanese Journal of Applied Physics* 38 (1999) 2393.
8. JOYNER, J.W.; MEINDL, J.D., *Proceedings of 2002 IEEE Interconnect Technology,* Burlingame, USA, 2002, p. 148.
9. SUN, J.J.; KOND, K.; OKAMURA, T.; OH, S.J.; TOMISAKA, M.; YONEMURA, H.; HOSHIN, M.; TAKAHASHI, K., *Journal of Electrochemistry Society* 150 (2003) G355.
10. JOZWIAK, J.; SOUTHWICK, R.G.; JOHNSON, V.N.; KNOWLTO, W.B.; MOLL, A.J., *IEEE Transactions on Advanced Packaging* 31 1 (2008) 4.
11. TORRES, J., *Applied Surface Science,* 91 (1995) 112.
12. AWAYA, N.; ARITA, Y., *Journal of Electronic Materials* 21 (1992) 959.
13. MIYAZAKI, H.; HINODE, K.; HOMMA, Y.; MUKAI, K., *Japanese Journal of Applied Physics* 48 (1987) 329.
14. GREEF, R.; PEAT, R.; PETER, L.M.; PLETCHER, D.; ROBINSON, J., *Instrumental Methods in. Eletrochemistry,* John Wiley & Sons Ltd., Ellis Horwood Limited, New York, 1985.
15. [BOCKRIS, J.O.M.; REDDY, A.K.N., In: *Modern Electrochemistry* Volume 2, A Plenum Roseta Edition – Pub. By Plenum Publishing Corporation, New York, 1977.
16. VAN DORP, D.H.; KELLY, J.J., *Journal of Electroanalytical Chemistry* 599 (2007) 260.