

# EQCM investigation of electroless Pt deposition using $\text{Ti}^{4+}/\text{Ti}^{3+}$ redox couple as reducing agent

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Electrochemical quartz crystal microgravimetry (EQCM) was used for the investigation of the kinetics of electroless deposition of Pt layer on the Cu surface using the  $\text{Ti}^{4+}/\text{Ti}^{3+}$  ion redox system as a reducing agent. It was found that the mass of the electrolessly deposited Pt increases in the course of time up to 360 s. Under optimum conditions the rate of the electroless Pt deposition was found to be ca.  $2.8 \mu\text{g cm}^{-2} \text{min}^{-1}$ . It has been determined that with further increase in time the rate of Pt deposition drops-off, as well as the open-circuit (mixed) potential shifts to the side of more positive values. The Pt film deposited on the surface of PVD Cu coated silicon wafer using the  $\text{Ti}^{4+}/\text{Ti}^{3+}$  redox couple as a reducing agent is continuous and compact.

**Keywords:** Pt,  $\text{Ti}^{4+}/\text{Ti}^{3+}$ , electroless deposition, EQCM

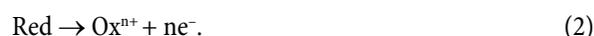
## INTRODUCTION

Electroless metal deposition is widely used for metallization of various dielectrics, fabrication of mirrors, galvanoplasty, formation of catalysts used in fuel cells, fabrication of micro-circuit, optoelectronics, etc. [1–4]. Nowadays the electroless metal plating solutions are applied in many areas of research and industry, e. g. in electronics for deposition of conductive metal layers on semiconductors or dielectrics (silicon wafers, resins, etc.) [5–14]. In general, electroless metal deposition

processes are now recognized to be electrochemical by nature and result from the coupling of two partial electrochemical reactions – the cathodic reduction of metal ions (Eq. 1) and the anodic oxidation of the reducing agent (Eq. 2):

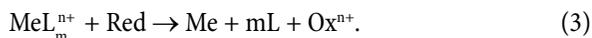


and



The overall reaction of electroless metal deposition is given in Eq. 3:

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According to the electrochemical mechanism, in the absence of an external current the electrode attains the mixed potential ( $E_m$ ) value due to simultaneously occurring of the both partial reactions (Eqs. 1 and 2) at equal rates.

From another point of view, an efficiently strong reducing agent is required for autocatalytic metal deposition. The use of traditional reducing agents (formaldehyde, borohydride, hypophosphite, etc.) is limited due to the parasitic reactions simultaneously occurred with the oxidation of a reducing agent. The use of hydrogen-containing reducing agents is also connected with environmental and technological problems: 1) the plating bath cannot be recycled, i. e. the reducing agent oxidizes irreversibly; 2) formaldehyde and most ligands are environmentally unacceptable; 3) the plating rate and solution stability are not high enough. Attempts are made to replace these solutions. The search of a new type of reducing agents – metal-ion redox couples with different oxidation state – is actual nowadays. In this case, multivalent metal ions of lower oxidation states are strong enough to reduce other metal ions to the metallic state:  $\text{Cr}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Ti}^{2+}$ ,  $\text{Ti}^{3+}$ ,  $\text{V}^{2+}$ ,  $\text{V}^{3+}$ ,  $\text{V}^{4+}$ ,  $\text{Cu}^+$ ,  $\text{Sn}^{2+}$ ,  $\text{Fe}^{2+}$ .

In the present study we investigated the possibility to use the new type reducing agent – titanium ion redox system ( $\text{Ti}^{4+}/\text{Ti}^{3+}$ ) for electroless deposition of Pt on the Cu surface. Kinetics of the electroless deposition of Pt on the Cu surface has been investigated mainly by means of electrochemical quartz crystal microbalance (EQCM). The morphology and structure of the surface of the deposited Pt film were examined by means of field emission scanning electron microscopy (FESEM).

## EXPERIMENTAL

### Chemicals

Trisodium citrate, glycine,  $\text{NH}_3$ ,  $\text{H}_2\text{PtCl}_6$ ,  $\text{HCl}$ ,  $\text{TiCl}_3$  (20% of  $\text{TiCl}_3$  in 3%  $\text{HCl}$ ) were used. Analytical grade chemicals and triply distilled water were used to prepare the solutions.

### Electroless Pt deposition using $\text{Ti}^{4+}/\text{Ti}^{3+}$ redox couple as reducing agent

Electroless Pt films were deposited onto the surface of PVD Cu coated silicon wafer without any additional treatment or activation. 0.5 cm × 2 cm sheet of one side of the Cu coated silicon wafer was immersed into an electroless platinum plating bath. The electroless platinum plating bath was prepared as follows: at first, a solution containing 0.15 M sodium citrate, 0.025 M glycine, 0.32 M  $\text{NH}_3$  and 0.004 M  $\text{H}_2\text{PtCl}_6$  was prepared. The solution pH was 12 adjusted by adding of  $\text{HCl}$ . The solution was purged with Ar. Then, the required amount of  $\text{TiCl}_3$  (the final concentration was 0.05 M) was added to the electroless plating solution

and the solution pH reached 9.5. The electroless deposition of Pt was carried out at a temperature of 20 °C.

### Characterization of Pt films

The surface morphology of the electrolessly deposited Pt films was characterized using a scanning electron microscope EVO-50 EP (Carl Zeiss SMT AG, Germany) with energy dispersive and wave dispersion X-ray spectrometers (Oxford, UK).

### EQCM measurements

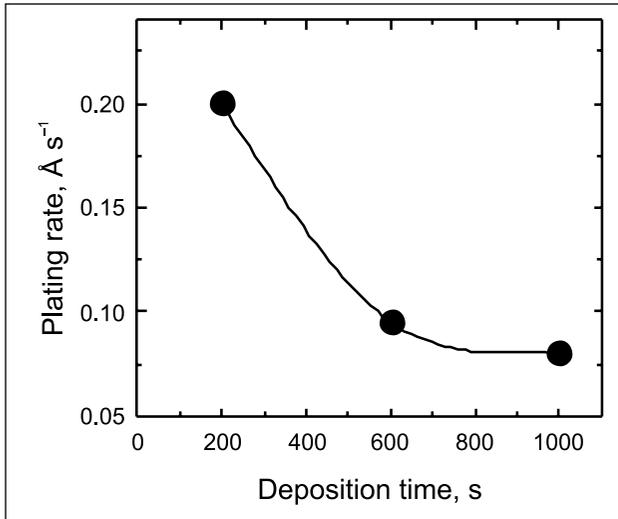
Simultaneous cyclic voltammetry and microgravimetric studies were performed with a Quartz Crystal Microbalance QCM922 (Princeton Applied Research, USA), two digital voltmeters B7-46/1 connected to a PC through the GPIB-USB-B controller cable (National Instruments, USA). A programming potentiostat PI-50-1 and a sweep generator PR-8 (Russia) were used. AT-cut quartz crystals of 6 MHz fundamental frequency (from Intellectrics Ltd., UK) sputtered by gold from both sides were used. The geometric area of the working electrode was 0.636 cm<sup>2</sup>. The sensitivity constant with respect to the piezoelectric-active area of the electrode was 7.8 ng Hz<sup>-1</sup>. A standard three-electrode configuration was employed with one side of the quartz crystal as a working electrode, an  $\text{Ag}/\text{AgCl}/\text{KCl}_{\text{sat}}$  electrode as a reference and a Pt-wire as a counter electrode. The measured electrode potential, the current and the frequency were transferred to the PC every 1.0 s.

Prior to the measurements of the electroless deposition of Pt, a Cu layer was electrodeposited on a gold sublayer onto quartz crystals installed at the bottom of the cell from the solution containing 1.0 mol l<sup>-1</sup>  $\text{CuSO}_4$  and 0.5 mol l<sup>-1</sup>  $\text{H}_2\text{SO}_4$  at a current of 10 mA for 1 min.

## RESULTS AND DISCUSSION

At first, the kinetics of Pt deposition on Cu was investigated in this study. Thin Pt films were deposited on the PVD Cu coated silicon wafer surface using the  $\text{Ti}^{4+}/\text{Ti}^{3+}$  redox system as a reducing agent. Figure 1 presents the kinetics of Pt deposition. The highest Pt deposition rate (ca. 0.2 Å s<sup>-1</sup>) was obtained after 200 s of plating. In the course of time the rate of Pt deposition decreases up two times (Fig. 1) – the possible reasons of such behaviour are discussed together with the data of EQCM measurements (see below). The SEM view of the Pt film deposited on the surface of PVD Cu coated silicon wafer using the  $\text{Ti}^{4+}/\text{Ti}^{3+}$  redox pair as a reducing agent is shown in Fig. 2. It is evident that the Pt film obtained is continuous and compact (Fig. 2).

The electroless deposition of Pt on the Cu electrode was investigated in more detail by means of electrochemical quartz crystal microbalance. This method is basically a mass sensing device with the ability to measure very small mass changes as a fraction of the monolayer or single layer of atoms on a quartz crystal resonator in real-time [15]. QCM

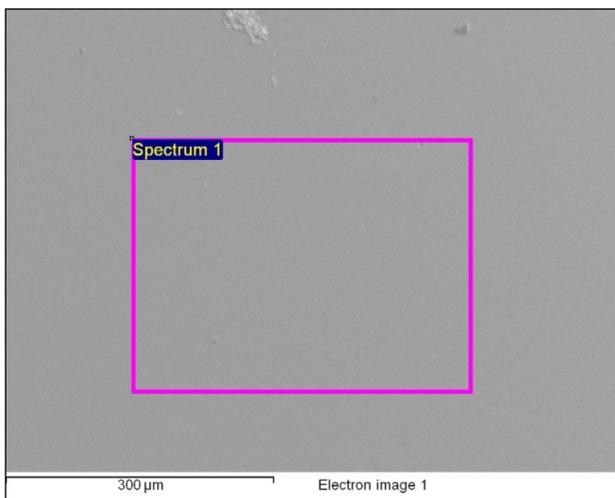


**Fig. 1.** Kinetics of electroless Pt deposition on the surface of PVD Cu coated silicon wafer. Solution composition: 0.004 M  $\text{H}_2\text{PtCl}_6$ , 0.05  $\text{TiCl}_3$ , 0.15 M trisodium citrate, 0.025 M glycine, 0.32 M  $\text{NH}_3$ , HCl up to pH 9.5; 20 °C

measurements are based on the Sauerbrey's equation [16] where the measured frequency changes of the quartz crystal are correlated with the mass changes (Eq. 4):

$$\Delta f = -2 \frac{f_0^2 \Delta m}{S \sqrt{\mu_q \rho_q}} = -K \Delta m. \quad (4)$$

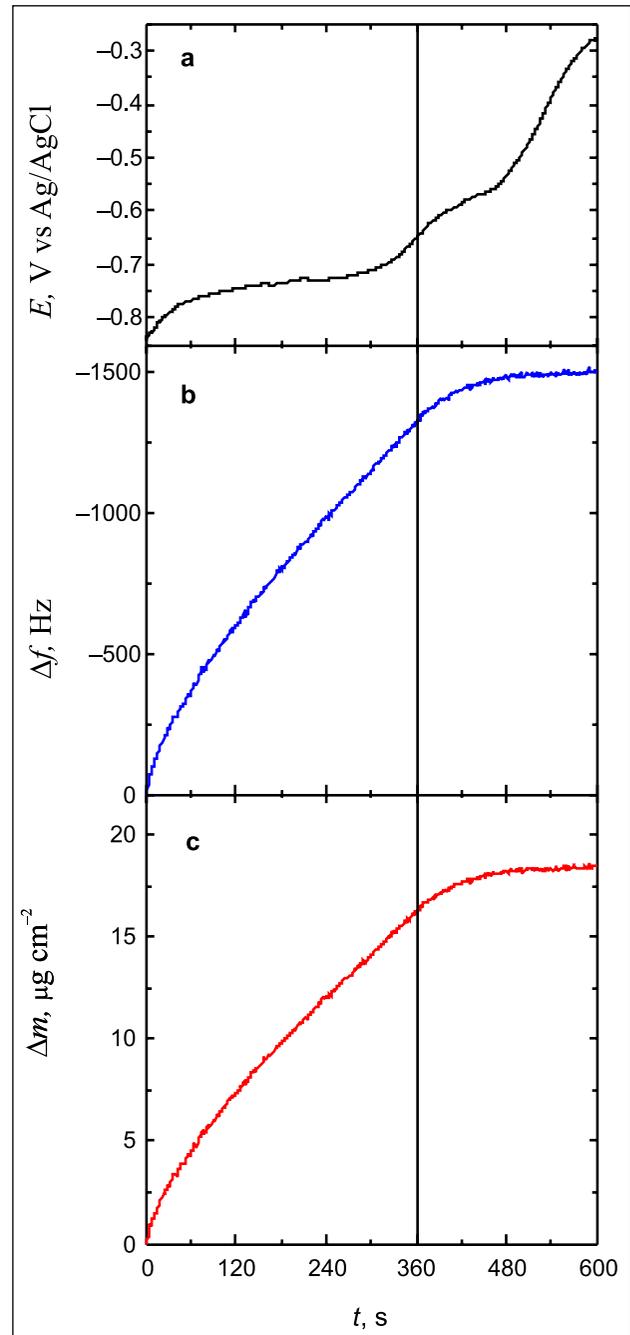
Here  $f_0$  is the resonant frequency of the quartz crystal,  $S$  is the piezoelectrically active area ( $\text{cm}^2$ ),  $\mu_q$  is the shear modulus of the quartz ( $2.947 \cdot 10^{11} \text{ g cm}^{-1} \text{ s}^{-2}$ ), and  $\rho_q$  is its density ( $2.648 \text{ g cm}^{-3}$ ) [15].  $K$  includes all the constants of Eq. (4) and for a fundamental resonance frequency of 6 MHz is equal to  $128.152 \cdot 10^6 \text{ Hz g}^{-1}$  corresponding to a sensitivity



**Fig. 2.** SEM view of the Pt film deposited on the surface of Cu coated silicon wafer. Solution composition: 0.004 M  $\text{H}_2\text{PtCl}_6$ , 0.015  $\text{TiCl}_3$ , 0.5 M trisodium citrate, 0.025 M glycine, 0.32 M  $\text{NH}_3$ , HCl up to pH 9.5; 20 °C

of  $12.26 \text{ ng Hz}^{-1} \text{ cm}^{-2}$ . Due to its sensitivity this method allows determining *in situ* small changes in the electrode mass which are proportional to the changes in the quartz crystal resonant frequency.

Figure 3 presents the data of QCM measurements of the kinetics of electroless Pt deposition on the Cu electrode under stationary conditions and when deaerating with Ar: open-circuit potential (a), change in frequency (b), and Pt mass gain (c). It is evident that in the absence of an exter-



**Fig. 3.** Kinetics of electroless Pt deposition on the Cu electrode under stationary conditions: (a) open-circuit potential, (b) change in frequency, and (c) Pt mass gain. Solution composition: 0.004 M  $\text{H}_2\text{PtCl}_6$ , 0.05  $\text{TiCl}_3$ , 0.15 M trisodium citrate, 0.025 M glycine, 0.32 M  $\text{NH}_3$ , HCl up to pH 9.5; 20 °C

nal current the electrode attains the mixed potential ( $E_m$ ) value (Fig. 3a). The open-circuit potential of the Cu electrode coated by depositing platinum in the course of electroless deposition is quite stable (slightly shifting to the side of more positive potentials) during the electroless Pt deposition process up to 360 s, whereas later its potential shifts sharply to the side of more positive values in the course of time (Fig. 3a). The abrupt changes of the mixed potential values in the course of time indicate a complicated character of the investigated process.

After the beginning of the electroless Pt deposition, the frequency of the quartz crystal begins to decrease, i. e. the mass of coating formed starts to increase constantly in the course of time up to 360 s (Fig. 3b, c). It was found that the rate of the electroless Pt deposition is ca.  $2.8 \mu\text{g cm}^{-2} \text{min}^{-1}$ . With further increase in time, the changes in frequency (i. e. mass changes) are negligible, indicating that the electroless deposition of Pt slows down and stops. The simultaneously observed decrease in the mass change of the electrode and the continuous sharp shift of the open-circuit (mixed) potential to more positive values indicate diminishing of the reducing activity of  $\text{Ti}^{3+}$  species (Fig. 3), obviously due to the decrease in  $\text{Ti}^{3+}$  concentration or/and the retarding effects of  $\text{Ti}^{4+}$  formed in the course of  $\text{Ti}^{3+}$  oxidation reaction. The retardation of the process could seemingly be related to the adsorption of  $\text{Ti}^{4+}$  formed on the surface to be plated.

Such phenomenon of the suppression of the electroless deposition process after a comparatively short time (ca. 6 min) is observed for the first time and needs additional investigations in the future.

## CONCLUSIONS

When investigating the kinetics of the electroless deposition of Pt using the new reducing agent – titanium redox couple ( $\text{Ti}^{4+}/\text{Ti}^{3+}$ ) by means of electrochemical quartz crystal microbalance, it was found that:

1. The mass of the electrolessly deposited Pt increases in the course of time up to 360 s. Under optimum conditions the rate of the electroless Pt deposition was determined to be ca.  $2.8 \mu\text{g cm}^{-2} \text{min}^{-1}$ .

2. With further increase in time the rate of Pt deposition slows down and stops, as well as the open-circuit (mixed) potential shifts to the side of more positive values. With high possibility, the retardation of the process can be related to the adsorption of  $\text{Ti}^{4+}$  formed on the surface to be plated.

3. The Pt film deposited on the surface of PVD Cu coated silicon wafer using the  $\text{Ti}^{4+}/\text{Ti}^{3+}$  redox couple as a reducing agent is continuous and compact.

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**Pt CHEMINIO NUSODINIMO, REDUKTORIUMI  
NAUDOJANT  $Ti^{4+}/Ti^{3+}$  REDOKSO PORĄ, TYRIMAS  
EKKM BŪDU**

*S a n t r a u k a*

Pt cheminis nusodinimas, reduktoriumi naudojant  $Ti^{4+}/Ti^{3+}$  redokso sistemą, buvo tirtas taikant elektrocheminę kvarco kristalo mikrogravimetriją (EKKM). Nustatyta, kad optimaliomis sąlygomis Pt cheminio nusodinimo greitis –  $2,8 \mu\text{g cm}^{-2} \text{min}^{-1}$ . Parodyta, kad ant vario paviršiaus nusodinta Pt danga yra tolygi ir kompaktiška. Pastebėta, kad laikui bėgant (maždaug po 6 min.) platinos cheminio nusodinimo greitis staigiai sumažėja, kol procesas visai sustoja. Įvardytas reiškinys, matyt, susijęs su proceso metu susidariusio  $Ti^{4+}$  adsorbicija ant dengiamo paviršiaus.