Catalytic Activity of Sputtered Palladium Films For Electroless Nickel Plating Studied Using a Quartz Crystal Microbalance

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The catalytic activity of palladium films sputtered on a quartz resonator was studied using a nickel bath in which a quartz crystal microbalance was used to determine electroless plating processes. An adhesive interface between the Pd layer and the quartz surface influenced activity. A chromium underlayer suppressed the catalytic activity of Pd film, but a gold underlayer did not. A palladium layer formed on Au a layer operated as a catalyst. The catalytic activity of Pd film on the Cr underlayer was greatly enhanced by cathodic treatment in dilute hydrochloric acid.

Quartz crystal microbalances (QCM) and electrochemical QCMs(EQCMS) are useful mass sensors for detection of very small mass changes, such as adsorption, ^{1,2} intercalation,³ and continuous mass accumulation up to mg/cm2 (µm thickness), as well as vacuum deposition,⁴ electroless deposition⁵ and electrodeposition⁶ in situ.

Electroless metal deposition was monitored in situ optically^{7,8} or by photoacoustic spectrometry⁹ to determine product quality and to collect information on plating bath control. Optical measurements are sensitive to initial deposition, but are not applied to monitoring of steady-state deposition because they are based on light absorption by the deposited metal layer. Light absorption becomes too great to be detected during early steady-state deposition. Photoacoustic spectrometry is expensive. The QCM monitors electroless deposition from initial to steady-state sensitively and inexpensively.

The QCM used as an electroless plating monitor requires a palladium catalyst on the electrode surface of a quartz resonator. A submonolayer of colloidal Pd was generally formed as a catalyst using palladium(II) chloride and tin(II) chloride solutions, or a mixture of them. In our experiment, such catalyst formation produced Pd nuclei and metal deposition, not on a quartz resonator, but on the resonator housing. The sensor and housing caused successive lowering of metal deposition rate in the small volume of the bath because bath species consumption and the accumulation of reaction products, such as protons and phosphite, occurred several tens of times faster because of the larger surface area for metal deposition. Additional procedures were also required to dissolve metal deposited on the housing. It became necessary to form a Pd catalyst layer on the resonator using another housing. A Pd catalyst layer was electrodeposited on the QCM electrode from a dilute palladium sulfate solution,¹⁰ but this also left palladium nuclei on the sensor housing.

We used a sputtered Pd layer as a catalyst because it is easily prepared on the resonator and used as received. Cata-

Table 1
Electroless Nickel Plating Bath Composition

Compound	Concentration
Nickel sulfate hexahydrate	20 g/dm^3
Lactic acid	$3 \text{ cm}^3/\text{dm}^3$
Sodium acetate trihydrate	5 g/dm ³
Trisodium citrate dihydrate	5 g/dm^3
Sodium phosphinate monohydrate	10 g/dm ³
(pH adjusted to 5.0 with NaOH)	

lytic activity of this sputtered Pd layer was tested for electroless Ni plating.

Experimental Procedure

Quartz crystal resonators were 6 MHz At-cut, 25.4 mm in diameter and 0.3 mm thick. As a resonator, chromium was sputtered on the active side of a quartz crystal to serve as an adhesive interface 50 nm thick, and palladium was successively sputtered on a Cr adhesive layer at about 200 nm thick. The surface area of the Pd electrode shaped as a keyhole with a diameter of 13 mm was 1.45 cm². Gold was sputtered as a contrast resonator for frequency change instead of a Pd electrode. The resonator was installed on a housing of Teflon resin for connection to an oscillation circuit. The composition of the electroless nickel plating bath is shown in Table 1. Sodium phosphinate was used as an electron donor.

Electroless nickel plating was done at 70 °C in a 300-mL beaker, containing 200 cm³ of plating solution in a circulating water bath. Frequency change was measured using a frequency counter with a calculator and a Y-t recorder.

Results & Discussion

Catalytic Activity of Pd FilmSputtered on Cr Underlayer When the quartz resonator having gold film sputtered on a Cr layer with the housing was immersed from room atmosphere in an electroless Ni bath at 70 °C, resonator frequency instantaneously decreased about one kHz, then gradually decreased over time (curve a, Fig. 1). This frequency change resulted from changes in density, viscosity and electrical conductivity of the medium,^{11,12} and a thermal transition of the sensor with the housing and the oscillation circuit because gold is inactive as a catalyst for electroless plating. Curve b (Fig.1) was obtained when the same resonator immersed in distilled water at 70 °C for 15 min was transferred to the plating bath to reduce the frequency change by thermal change of the resonator. The resonator's frequency also decreased about 0.5 kHz instantaneously, then decreased



Fig. 1—Frequency traces of quartz resonators with sputtered Au electrode on Cr underlayer: Curve a - resonator transferred from room atmosphere to electroless Ni-plating bath at 70 °C; Curve b - resonator transferred from water at 70 °C to plating bath at 70 °C.



Fig. 2—Frequency traces of quartz resonators transferred from water at 70 °C to electroless Ni plating bath (instantaneous frequency decrease excluded): Curve a—resonator with Pd electrode sputtered on Cr underlayer; Curve b—resonator with Pd electrode sputtered on Au underlayer; Curve c - resonator with Pd layer formed chemically.

with the rapid electroless plating. This problem was reduced when the sensor was first immersed in distilled water at $70 \,^{\circ}$ C, then transferred to the electroless plating bath.

Curves in Fig. 2 show the frequency trace after the instantaneous decrease caused by the change of medium. When a quartz resonator with a Pd layer sputtered on a Cr layer two days before was immersed (curve a), the frequency decreased gradually and, after about 10.5 min, the frequency showed large constant decrease, indicating electroless Ni plating. The time from the immersion to the start of the large decrease is referred to as the induction time. The frequency decrease during induction is a result of the thermal transition because the frequency trace is similar to curve b in Fig. 1. Honma *et al.* reported that no metal deposition occurred during induction.⁸

The catalytic activity of the Pd film was not affected by 15 min of immersion in 70 °C water, because identical induction was obtained when the quartz resonator was immersed in the



Current Density & Polarization										
<u>1 mA/cm²</u>			<u>5 mA/cm²</u>			<u>10 mA/cm²</u>				
Solution	1 min	5 min	10min	1 min	5 min	10 min	1 min	5 min		
M HCl	—	—	Х	Х	470 sec	165 sec	Х	60 sec		
M HCl	Х	265 sec	195 sec	115 sec	265 sec		—	—		
X : no electroless Ni plating within 30 min —: no experiment M : mol/dm ³										

gradually. А comparison of curves a and b showed that the instantaneous frequency decrease is mainly a result of the change of medium, following a large, gradual frequency decrease because of a thermal transition. It was difficult to distinguish the frequency change as a result of the electroless plating from the large frequency change resulting from the thermal transition when the resonator was transferred from room atmosphere to the plating bath and plating bath without preheating. A long induction period of 10 min was a result of the lower catalytic activity of Pd film rather than the nature of the electroless Ni plating bath, because electroless Ni plating occurred almost immediately when a Pd layer was chemically formed by two-step immersion (curve c in Fig. 2). The electrode catalyst with long induction was unsuitable for monitoring the early stage of electroless plating.

Catalytic Activity of Pd Film Sputtered on Gold Layer

The low activity of the Pd layer on the Cr underlayer was thought to be a result of the nature of the sputtered Pd itself or the effect of the Cr layer. Sputtered gold film with strong adhesion is formed on quartz crystal in place of a Cr layer, so Pd was sputtered on the Au layer and its catalytic activity was evaluated. This is depicted as curve b in Fig. 2, where the Pdfilm electrode was sputtered two days earlier. Compared to the activity of Pd film sputtered on the Cr layer, the induction time of Pd film on the Au layer was very short, about one min. It was concluded that a Pd layer sputtered on the gold underlayer could be used as a QCM electrode to monitor electroless plating.

The sputtering of Pd metal was the same whether the underlayer was Cr or Au. The formation of Cr oxide by air oxidation of Cr atoms diffused through the Pd layer caused the suppression effect of the Cr underlayer. The Cr species on the Pd surface was studied by XPS, but was not detected. Another possibility is an interaction between Pd and Cr layers that affected the catalytic nature of the surface Pd atoms. We do not yet know the interaction mechanism, however.

The activity of Pd film sputtered on Au film was maintained at least three months by storing in a desiccator without desiccant.

Activation of Pd Film on Cr Underlayer

Cathodic treatment of a Pd electrode on a Cr layer brought about enhancement of catalytic activity, although it was done under a mistaken concept: removal of surface chromium oxide species by cathodic reduction. The experiment was done using resonators having Pd electrodes that did not show induction within 30 min. Constant cathodic current was applied to sputtered Pd films in several solutions. Results are summarized in Table 2. No improvement in activity was obtained by polarization at 10 mA/cm² for 10 min in 1 mol/ dm³ sodium hydroxide or sodium sulfate solution. Dramatic catalytic enhancement was observed by cathodic polarization in dilute hydrochloric acid solution. The longer the polarization, the shorter the induction (Table 2). The activity of Pd film treated at 5 mA/cm² for 5 min in 1 mol/dm³ HCl was the same as that of Pd film sputtered on a Au underlayer.

The cathodic treatment of Pd film electrode in diluted sulfuric acid (0.5 mol/dm³) did not improve activity because of adsorption of sulfate ions on the Pd surface because, when cathodic-treated Pd film under optimum conditions (Table 2) in hydrochloric acid was immersed in sulfuric acid solution, its activity was lost.

Findings

Catalytic activity, determined by induction, of sputtered Pd film for electroless plating was influenced by the metal underlayer serving as an adhesive layer for the Pd layer. The poor influence of a Cr underlayer was remarkable and that of an Au layer less so or none. The Pd layer sputtered on a Au underlayer is usable as an active electrode for monitoring electroless plating. If a very thin Pd layer is sputtered on the Au layer, it may show the same activity as that of one chemically formed. The catalytic activity of the Pd layer sputtered on a Cr underlayer was largely enhanced by cathodic treatment in dilute HCl solution.

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References

- 1. W H. King, Jr., Analyt. Chem., 36, 1735 (1964).
- 2. J. Hlavay & G.G. Guilbault, Analyt. Chem., 49, 1890 (1977).
- 3. J.K. Kaufman, K. Kanazawa & G.B. Street, Phys. Rev. Lett., 53, 2461 (1984).
- 4. C.-S. Lu & O. Lewis, J. Appl. Phys., 43, 4385 (1972).
- 5. K.K. Kanazawa & S.K. Doss, Plat. and Surf. Fin., 74, 52 (July 1987).
- 6. K. Kobayakawa, K. Morishita, Y Sato & E. Fujimoto, Hyomen Gijutsu, 46, 37 (1995).
- 7. J. Dumesic, J.A. Koutsky & T.W. Chapman, J. Electrochem. Soc., 121, 1405 (1974).
- 8. H. Honma & M. Noguchl, Hyomen Gijutsu, 41, 164 (1990).
- 9. K. Irle, M. Kobayashi, I. Miura, S. Yoshihara & E. Sato, Hyomen Gijutsu, 43, 158 (1992).
- 10. N. Arlizumi, Y Shimizu, M. Shibata & N. Furuya, Hyomen Gijutsu, 49, 794 (1998).
- 11. K.K. Kanazawa & J.G. Gordon II, Analyt. Chem., 5, 1770 (1985).
- 12. S. Bruckenstein & M. Shay, Electrochim. Acta, 3, 1295 (1985).

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