Communication—Underpotential Deposition of Lead for Investigating the Early Stages of Electroless Copper Deposition on Ruthenium

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Continued interconnect scaling because of device miniaturization presents numerous challenges to current state-of-the-art dual damascene process flow. As interconnect dimensions shrink, void-free filling using conventional Cu electrodeposition becomes increasingly difficult due to the poor step coverage of the non-conformally sputtered Cu seed layer. To overcome this challenge, alternative metallization approaches are under development, such as direct electroless Cu deposition on Ru liners. Electroless Cu deposition on Ru provides uniform deposit distribution (lack of terminal effects) on large-area wafers. However, insights into electro-nucleation phenomena during thin-film fabrication via electroless Cu deposition on Ru are still lacking. In a recent report by Inoue et al., smooth electroless Cu films in the ~100 nm thickness range were deposited on Ru. Kim et al. investigated the electroless Cu growth process on Ru using atomic force microscopy and linear sweep voltammetry. These investigators suggested that, in the early stages of electroless Cu nucleation, two-dimensional (2D) growth of Cu monolayers is favored on Ru.

In this paper, we applied an ex situ electrochemical technique based on Pb_{upd} to further understand the early stages of electroless copper deposition on Ru. Recognizing that the onset potential for Pb_{upd} is surface-sensitive, we achieved selective Pb_{upd} on Ru-covered Cu-covered portions of a substrate’s surface. Coulometry measurements during selective Pb_{upd} formation provided fractional surface coverage of Cu on Ru as a function of the electroless deposition time. Our investigation provides a convenient surface analytical method while providing further evidence for the 2D electrochemical growth mode during electroless Cu deposition on Ru.

**ECS**

Experimental

**Electroless Cu deposition.**—Electroless Cu deposition was performed onto Si wafers pre-coated with a barrier layer (2 nm PVD-Ta) and a Ru liner layer (2 nm PVD-Ru). Before electroless Cu deposition, the Ru-coated substrates were rinsed with ethanol and deionized (DI) water. The substrates were then immersed in a solution containing 1.5 M dimethylamine borane (DMAB, 98%, Acros Organics) at 60 °C for 1 min to remove Ru surface oxides. After pretreatment, the substrates were rinsed with de-oxygenated DI water for 10 s before immersion into the electroless Cu bath. The electroless bath contained 0.1 mM copper sulfate pentahydrate (Fisher Scientific), 50 mM ethylenediaminetetraacetic acid (Fisher Scientific), 0.1 M sodium hydroxide (Fisher Scientific), and 40 ppm 2,2’-dipyridyl (Acros Organics) as stabilizer. Electrolyte pH was adjusted to 12.5. Deposition temperature was maintained at 60 °C. After deposition, substrates were rinsed again with de-oxygenated DI water and dried with argon.

Pb underpotential deposition.—An electrolyte containing 0.2 mM Pb(ClO_4)_2 (99% purity, Acros Organics) and 10 mM HClO_4 (Fisher Scientific) was used for cyclic voltammetry (CV) studies of Pb_{upd}. The electrolyte was de-oxygenated by bubbling Ar for 1 hour prior to use. CV was performed on PVD-Cu, PVD-Ru and electroless Cu deposited Ru substrates. Electroless Cu deposition on PVD-Ru was performed for various time periods: 10, 30, 60 and 90 s using the bath described above. The electroless-plated coupon was transferred to the Pb_{upd} electrolyte minimizing air exposure to <1 min. During voltammetry of Pb_{upd}, a Pt wire served as counter electrode. Ag/AgCl with single junction served as reference electrode. A VersaSTAT 4 potentiostat (Princeton Applied Research) was used for electrochemical measurements.

**Results and Discussion**

**Characterization of Pb_{upd} on Cu and Ru substrates.**—Pb exhibits UPD on Cu and on Ru. Figure 1 shows CVs (scan rate = 20 mV/s) of a PVD-Cu (Fig. 1a) and a PVD-Ru (Fig. 1b) electrode in a 0.2 mM PbCl_2- containing electrolyte. For reference, background voltammograms in the absence of Pb^{2+} are also shown. According to the Nernst equation, the onset potential for Pb electrodeposition is ~0.45 V vs. Ag/AgCl, and therefore the potential range scanned in Fig. 1 does not correspond to Pb overpotential deposition. Following observations are made:

(i) Pb_{upd} on Cu (Fig. 1a): The cathodic peak observed at ~0.32 V vs. Ag/AgCl corresponds to Pb_{upd} on Cu. The anodic peak observed at ~0.22 V corresponds to stripping of the Pb_{upd} layer. The charge density associated with Pb_{upd} stripping was around 370 μC/cm² (assuming an electrode area of 1 cm²).

(ii) Pb_{upd} on Ru (Fig. 1b): The background CV (in the absence of Pb^{2+}) on Ru shows a broad peak at ~0 V vs. Ag/AgCl. Charge integration for the voltage sweep from +0.28 V to ~0.25 V corresponding to the broad peak yields a charge density of ~240 μC/cm², which is in agreement with reported charge densities of Ru surface oxide reduction. The significant cathodic current observed at potentials negative to ~0.30 V is hydrogen evolution catalyzed by Ru. In the presence of Pb^{2+} in the electrolyte, the broad peak around ~0.14 V is attributed to Pb_{upd} on Ru.

We note that the Pb_{upd} peak position on Ru (~0.14 V, Fig. 1b) and that on Cu (~0.32 V, Fig. 1a) differ by about 180 mV. This sensitivity of the Pb_{upd} deposition potential to the nature of the underlying substrate (Cu vs. Ru) will be used in the following discussion to characterize the
Figure 1. Cyclic voltammograms of PVD-Cu (a) and PVD-Ru (b) in two electrolytes: 0.2 mM Pb(ClO_4)_2 + 10 mM HClO_4 (solid) and 10 mM HClO_4 only (dotted). Scan rate was 20 mV/s.

Surface coverage of Cu during early stages of electroless Cu deposition on Ru.

Characterization of electroless Cu surface coverage on Ru—Electroless Cu was deposited on Ru for various time periods (10–90 s). After deposition, the Cu was potentiostatically (at 0.30 V vs. Ag/AgCl) stripped in de-oxygenated H_2SO_4 and the Cu deposit mass was estimated from the stripping charge. Fig. 2 shows the integrated Cu stripping charge (left Y-axis) as a function of the electroless Cu deposition time. As expected, the stripping charge density increases linearly with deposition time indicating a steady deposition rate. Using charge density of 0.6 μC/cm² for one Cu monolayer, the measured charge density in Fig. 2 was converted into the equivalent number of Cu monolayers. This is plotted on the right-side Y-axis of Fig. 2. The equivalent number of Cu monolayers approached unity after 60 s of electroless deposition.

To characterize the partial surface coverage of electroless Cu on Ru, we utilized the properties of Pbupd deposition discussed above. The methodology employed for this characterization is schematically depicted in Fig. 3. First, electroless Cu was deposited on Ru for various deposition times (10–90 s). The substrates were then rinsed with de-oxygenated DI water, dried and immersed into an electrolyte containing 0.2 mM Pb(ClO_4)_2 and 10 mM HClO_4. The substrate potential was scanned from OCP to −0.45 V vs. Ag/AgCl at 20 mV/s. During the scan from OCP to −0.25 V, Pbupd proceeds on exposed Ru sites but not on deposited Cu. The potential scan from −0.25 V to −0.45 V facilitates Pbupd on Cu-covered portions of the electrode surface. Fig. 4a shows voltammetry scans collected (using above protocol) on Ru substrates covered with different thicknesses of electroless Cu. For reference, the background voltammogram collected on blank Ru (0 s, black curve) is also shown. After 10 s of electroless Cu deposition (red curve), the voltammogram shows a broad peak centered around −0.14 V corresponding to Pbupd on Ru though the peak current (∼30 μA/cm²) decreases slightly compared to that on blank Ru (∼45 μA/cm²). Also, at potentials negative to −0.30 V, an increase in the cathodic current compared to that on blank Ru substrate was observed. This is due to the charge associated with Pbupd on electrolessly deposited Cu. The absence of well-defined Pbupd peak on Cu at short electroless deposition times (10, 30 s) could be due to hydrogen evolution at potentials negative to −0.30 V. Increasing the deposition time further (30–60 s) lowers the current associated with the Pbupd peak on Ru. Eventually, after 90 s of electroless Cu deposition, the Pbupd peak decreased to a level where it could not be distinguished from the background current. This suggests that after 90 s of deposition, the Cu surface is almost completely covered with Pbupd.
Figure 4. (a) Pb upd voltammetry scans collected on blank Ru (0 s, black curve) and electroless-deposited Cu on Ru for 10 s (red), 30 s (blue), 60 s (magenta) and 90 s (orange). (b) Partial electroless Cu surface coverage on Ru as a function of the equivalent number of Cu monolayers deposited.

Voltammogram shows virtually no Pb upd peak on Ru with the appearance of a well-defined Pb upd peak on Cu. From Fig. 4a, we computed the total charge ($Q_{Ru}$) of Pb upd on Ru and Ru oxide reduction by integrating the current between OCP and $-0.25 \, \text{V}$. We did not use the Pb upd charge on Cu because of the presence of parasitic H$_2$ evolution in that potential window. The partial surface coverage of Cu ($\theta_{Cu}$) was estimated using the following equation:

$$\theta_{Cu} = 1 - \theta_{Ru} = 1 - \frac{Q_{Ru}}{Q_{upd}}$$  \[1\]

where $Q_{upd}$ corresponds to the charge associated with deposition of Pb upd monolayer on blank Ru and Ru surface oxide reduction ($= 560 \, \mu\text{C/cm}^2$). Fig. 4b shows partial surface coverage of Cu ($\theta_{Cu}$) on Ru at different electroless Cu deposition times, expressed as the equivalent number of Cu monolayers. After deposition of 1 monolayer equivalent of electroless Cu, we find that $\theta_{Cu}$ exceeds 0.8. This indicates that during initial stages of electroless Cu deposition on Ru, the deposit growth is largely two-dimensional and leads to near complete coverage of Ru with a monolayer of Cu.

Summary

The early stage of electroless Cu nucleation on Ru from a glyoxylic-acid based electrolyte was investigated. The partial surface coverage of electroless Cu on Ru was measured using an ex situ electrochemical technique involving Pb upd. Owing to the difference in the onset potential for Pb upd on Cu vs. Ru, surface coverage data could be obtained. Results show that, in the early stage of Cu nucleation, 2D growth of electroless Cu on Ru is favored.

Acknowledgments

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References

1. International Technology Roadmap for Semiconductors (ITRS) 2013 edition: http://www.itrs.net.
2. S. M. Rossnagel, Thin solid films, 263, 1 (1995).
3. K. H. Kim, T. Lim, K. J. Park, H. C. Koo, M. J. Kim, and J. J. Kim, Electrochim. Acta, 151, 249 (2015).
4. F. Inoue, H. Philipsen, M. H. van der Veen, S. Van Huylenbroeck, S. Armini, H. Struyf, and T. Tanaka, J. Electrochem. Soc., 161, D768 (2014).
5. F. Inoue, H. Philipsen, A. Radisic, S. Armini, Y. Civale, P. Leunissen, M. Kondo, E. Webb, and S. Shingubara, Electrochim. Acta, 100, 203 (2013).
6. Q. Chen, X. Lin, V. Raneccasio Jr, R. Hurtubise, and J. A. Abys, US Pat. no. 7998859 B2, 2011.
7. T. P. Moffat, J. Phys. Chem. B, 102, 10020 (1998).
8. R. Vasilic, N. Vasiljevic, and N. Dimitrov, J. Electroanal. Chem., 580, 203 (2005).
9. C. Thambidurai, Y. G. Kim, and J. L. Stickney, Electrochim. Acta, 53, 6157 (2008).
10. H. Siegenthaler and K. Jutner, J. Electroanal. Chem. Interfacial Electrochem., 163, 327 (1984).
11. G. M. Bristar, E. Zenati, H. A. Gasteiger, N.M. Markovic, and P. N. Ross, Langmuir, 13, 2390 (1997).
12. C. N. Van Houten and M. J. Gonzalez-Tejera, J. Electroanal. Chem. Interfacial Electrochem., 244, 249 (1988).
13. J. X. Wang, N. S. Markovic, H. Zajonz, B. M. Ocko, and R. R. Adzic, J. Phys. Chem. B, 105, 2809 (2001).