

Superconformal Electrochemical Deposition of Gold for Metallization in Microelectronic Devices

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A novel process for superconformal electrochemical deposition of gold has been proposed and demonstrated using 3-mercapto-1-propanesulfonic acid sodium salt (MPS) as additive in a sulfite-based gold electrolyte. At the optimized process conditions true bottom-up gold deposition was achieved, with which aggressive features such as those that are straight-walled and even re-entrant were completely filled without voids. In the process, the additive MPS functions as a suppressor that hinders electrochemical deposition of gold, as opposed to its function as an accelerator in electrochemical deposition of copper. The results obtained appear to suggest that the driving force leading to superconformal deposition of gold with the sulfite-based gold electrolyte in the presence of the grain refiner thallium and the additive MPS may primarily stem from the depletion of MPS inside features of interest as a result of its consumption and limited supply.

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While copper is widely used for metallization in silicon-based microelectronic devices,¹⁻⁵ gold is the metal of choice for metallization in compound semiconductor devices because of its unique chemical, physical, and electrical properties.⁶ Traditionally, gold metallization (e.g., interconnection) is performed using through-mask electrochemical deposition (electroplating). However, gold metallization using damascene electrochemical deposition is needed in many circumstances, especially when fine (submicrometer scale) structures are to be formed.

One of the challenges associated with damascene electrochemical deposition is how to achieve void-free filling of features (i.e., cavities) that include trenches and vias. Since the introduction of copper for interconnect metallization,^{1,2} superconformal electrochemical deposition (or superfilling) of copper has been intensively studied.^{3,7-19} As a result of the efforts of both industrial and academic communities, several proprietary copper electrolytes, where organic additives are used to achieve superconformal filling, have been made commercially available. Several models describing superconformal deposition of copper have also been developed.^{3,10-16} In addition, superconformal filling of copper using chemical vapor deposition in the presence of iodine^{20,21} and superconformal electrochemical deposition of silver²²⁻²⁴ have been demonstrated. Prompted by the industry's interest in damascene electrochemical deposition of gold and by the observation that features of interest could not be satisfactorily filled using commercially available gold electrolytes, we investigated superconformal gold deposition using sulfite-based gold electrolytes.²⁵ Superfilling of gold in submicrometer trenches using a cyanide-based gold electrolyte has also been reported.²⁶

In the present paper, we report the development of superconformal electrochemical deposition of gold for gold metallization in microelectronic devices through damascene processing. We first describe the issues we encountered when using a commercially available sulfite-based gold electrolyte for gap filling and discuss the possibilities of using additives such as thiol and disulfide compounds that are capable of interacting with gold and altering interfacial properties to achieve superconformal deposition. We then discuss the results obtained with the use of representative thiols that were selected on the basis of their potential interaction with gold and the consequent influence on heterogeneous electron transfer. Specifically, we found that with the use of 3-mercapto-1propanesulfonic acid sodium salt (MPS), gap-filling capability of the gold electrolyte could be dramatically improved. At the optimized process conditions true bottom-up gold deposition was achieved, with which complete filling of aggressive features was accomplished. Finally, we made an attempt to rationalize the effect of the

additive on gold electrochemical deposition behavior, based on the superconformal deposition results and electrochemical behavior of gold deposition in the presence of the additive.

Experimental

The additives MPS (90%) and 2-mercaptoethylamine (MEA, 95%) were purchased from Aldrich and used as received. The sulfite-based gold electrolyte (Sel-Rex Neutronex 309i) was purchased from Enthone-OMI. The electrolyte is referred to as base gold electrolyte in the present paper. The electrolyte contains gold sulfite, sodium sulfite, a pH buffer, and thallium as grain refiner. Gold electrochemical deposition was performed at 50°C with the sulfite-based gold electrolyte at pH 9.4 in the absence and presence of additives under investigation. Deionized water with a specific resistance of ~18 M Ω cm was used whenever needed.

Voltammetric, chronoamperometric, and chronopotentiometric investigations were carried out using an EG&G 263A potentiostat/ galvanostat, coupled with an EG&G model 616 rotating electrode assembly and a conventional three-electrode electrochemical cell which consists of a gold-deposited platinum rotating disk electrode, a saturated calomel electrode (SCE), and a platinized titanium piece as the counter electrode. The geometric surface area of the platinum disk is 0.126 cm². Prior to each distinct use, the platinum disk electrode was electrochemically cleaned and then deposited with ca. 0.5 μ m gold in the base gold electrolyte. Visually, the deposited gold was essentially mirror-smooth. All current densities reported in the present paper were calculated using geometric surface area, and potential values are presented with respect to the SCE.

Electrochemical deposition of gold on wafer segments was performed with the rotating electrode assembly, coupled with a homemade adaptor that affixes a wafer segment onto the assembly and defines exposed surface area using a sealed ring contact.²⁷ On full wafers, deposition of gold was performed using Semitool's electrochemical deposition (ECD) tool, which allows the operator to process wafers at predetermined process conditions such as temperature, electrolyte flow rate, wafer rotation, and applied current. Prior to electrochemical deposition, all wafers (either 100 or 150 mm diam) were deposited with a gold seed layer using physical vapor deposition. The effect of process conditions, including the chemical nature and concentration of the additives, on gap filling was evaluated based on cross-sectional scanning electron micrographs (SEM) taken with a focused ion beam/scanning electron microscope (FEI Dual Beam 820).

Results and Discussion

Unlike a through-mask electrochemical deposition process where the electrically conductive seed layer lies only at the bottom of the features into which a metal is deposited and thus the deposition is a naturally bottom-up process, a damascene electrochemical deposition process usually requires superconformal deposition capability

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Figure 1. Cross-sectional SEMs of trenches deposited with gold using the base gold electrolyte at current densities of (A) 4 mA/cm² and (B) 0.08 mA/cm² that correspond to nominal deposition rates of 0.25 and 0.05 μ m/min, respectively.

for achieving complete fill of features, especially those that are aggressive in shape (e.g., straight-walled or re-entrant) and in aspect ratio. Shown in Fig. 1 are representative cross-sectional SEMs obtained with the base gold electrolyte. The SEM in Fig. 1A is the result of gold deposition at the process condition optimized for normal through-mask deposition. Obviously, because of the premature pinch-off at the entrance, the features were left with large voids. After the process parameters such as current density, agitation, and the duty cycle of pulsed power supply were optimized for the present damascene electrochemical deposition, marked improvement in gap filling was observed (Fig. 1B). While the optimization of process conditions resulted in a significant improvement in gap filling, from subconformal to near-conformal, at the expense of deposition rate, the features of interest were still left with seam voids. The nominal deposition rate used for achieving this nearconformal deposition is 0.05 μ m/min, which is only one-fifth of the deposition rate typical of the through-mask gold deposition process.

At the optimized process conditions, the base gold electrolyte may be used to fill nonaggressive features such as V-shaped ones. For aggressive features such as those that are straight-walled or re-entrant, seam voids would be unavoidable with the base gold electrolyte that deposits conformally at best. As a result of the above observation we explored superconformal deposition of gold with candidate additives.

Additive selection.— It is generally believed that superfilling with a metal (e.g., copper) in electrochemical deposition is determined by the interaction of additives with the surface of the metal substrate and, in some cases, with the to-be-deposited metal ions in the electrolyte. In other words, superconformal deposition is primarily governed by the chemical nature of the additives used. Thiols and disulfides are known to adsorb strongly on gold as the corresponding thiolate through the cleaving of S–H and S–S bonds,²⁸ spontaneously forming monolayers on gold surfaces.²⁸⁻³³ The chemisorption of unfunctionalized or functional group-terminated thiols and disulfides on gold yields surfaces that are vastly different in water wettability, electrostatic interaction ability, and complexation capability and may accordingly influence the heterogeneous electron-transfer reactions involved. It is therefore rational to explore the use of these types of compounds as additives for the present application.



Figure 2. Effect of additive MPS on cathodic polarization at a gold-deposited platinum electrode. (A) Linear-scan voltammograms obtained in the absence and presence of MPS: (a) no MPS, and (b) 0.3, (c) 1.2, (d) 2.4, and (e) 4.8 mL/L MPS. (B) Plot of electrode potential at 4 mA/cm² against MPS concentration. Initial scan potential 0 mV. Scan rate 5 mV/s. Electrode rotating speed 100 rpm.

Among the thiols and disulfides available, the amine-terminated, carboxylic acid-terminated, and sulfonic acid-terminated species are especially intriguing. In addition to their reasonably high solubility, these thiol and disulfide species bear terminal groups that may interact electrostatically and/or chemically with gold species in solution. Sulfonic acids exist fully deprotonated in most circumstances, even in strongly acidic conditions; surface-tethered sulfonate species are capable of interacting electrostatically with the positively charged free (uncomplexed) gold ions in solution. At the operational pH of ca. 9.4, amines are partially protonated. Surface-tethered amine species are expected to be able to interact electrostatically with negatively charged gold-sulfite complex ions and perhaps chemically with free gold ions. In the sulfite-based gold electrolyte that is slightly alkaline, carboxylic acids are essentially completely deprotonated. Surface-tethered carboxylate species would be capable of interacting electrostatically with free gold ions as well. In this regard, carboxylic acid-terminated thiols and disulfides are expected to be similar to sulfonate-terminated thiol and disulfide species.

In the present work that is limited in scope, we have focused our investigation on sulfonic acid- and amine-terminated thiol additives, or MPS and MEA. Our experimental results obtained with these two additives indicate that the introduction of MEA into the base gold electrolyte resulted in no appreciable improvement in gap filling (SEM images not shown). The use of MPS, on the other hand, brought about marked improvement in gap filling (vide infra). As a consequence, we further investigated the effect of MPS on gold electrochemical deposition behavior and optimized gap-filling process conditions.

Process condition optimization.— Superconformal electrochemical deposition of metal is not only governed by the chemical nature of the additives used but is also affected by the concentration of the additives in the electrolyte and by other process conditions. Presented in Fig. 2A are cathodic polarization curves obtained (a) in the base gold electrolyte and (b–e) in the presence of the additive MPS at various concentrations as indicated in the caption. A plot of the electrode potential at a current density of 4 mA/cm² vs the concentration of the additive MPS is shown in Fig. 2B. Obviously, the concentration of the additive MPS has a significant effect on deposition potential; the deposition potential becomes more cathodic with increasing MPS concentration and then gradually levels off with the further increase in MPS concentration.

From the viewpoint of process control, an additive concentration in the leveled-off region is preferred over the preceding region where a slight change in additive concentration would cause a marked change in deposition potential (Fig. 2) and most likely a significant change in gap-filling capability. Accordingly, our investigation of the effect of additive concentration on gap filling has focused in this region. The results obtained at the concentration of 3 mL/L additive are presented in Fig. 3, which shows the realization of superconformal deposition of gold by detailing the profile evolution of gold deposit inside the features of interest. The thickness of gold deposit indicated in the caption is nominal, calculated from surface area and coulombs passed. The results were observed on full wafers. In addition, as can be clearly seen, the features shown in Fig. 3 are significantly more aggressive than those shown in Fig. 1.

Besides the chemical nature and concentration of the additive under investigation, other process conditions are also important in affecting gap filling. In general, process conditions that favor mass transport of metal species of interest would benefit gap filling. For instance, raising gold concentration and/or temperature benefits mass transport of gold and thus promotes gap filling at a given deposition rate. For electrochemical deposition of gold, however, the degree of freedom in changing these process conditions may be limited to a large extent, especially when a sulfite-based gold electrolyte is used. For instance, raising gold concentration and/or temperature is limited by bath stability. As compared with nonpulse plating, pulse plating at a lower duty cycle generally produces better fill results, which may be explained by the fact that pulse plating at a lower duty cycle and a moderate pulse frequency allows the transient concentration of gold inside the features of interest to be maximized. Additionally, current density, which determines deposition rate, has a pronounced effect on gap filling. In general, deposition at a lower current density benefits gap filling. Increasing current density may make a superconformal deposition process become a conformal or even subconformal deposition process. Presented in Fig. 4 are SEMs obtained at two different current densities, with other process conditions being the same. As is evident, at the lower current density the features under investigation were completely filled (Fig. 4A), whereas at the higher current density the features were left with voids (Fig. 4B). In essence, the effect of both duty cycle and current density on gap filling is the reflection of the impact of mass transport of gold species on gap-filling capability.

Additive role.— In superconformal deposition of copper, thiol and disulfide species such as MPS and bis(3-sulfopropyl)disulfide (SPS) function as accelerators that make copper deposition faster at a given deposition potential. This behavior of thiol and disulfide species is particularly conspicuous in the presence of suppressors such as polyalkylene glycols and/or levelers such as polyamines that inhibit the deposition of copper. The role of thiol and disulfide species in the deposition of copper. The role of thiol and disulfide species in the deposition of copper. The difference might be due to the differentiation of their interaction with gold and copper. It has been suggested that compared with a S–Cu bond that is quite ionic, a S–Au bond is strongly covalent in character.³⁴

It is well known that the presence of thiolate monolayers on gold strongly hinders heterogeneous electron transfer.²⁹ In the process of electrochemical deposition where the substrate surface is continuously refreshed, thiols and disulfides may only sparsely adsorb on the substrate surface instead of forming a fully covered monolayer. However, even the sparsely adsorbed organic species on the substrate surface would exert an appreciable effect on heterogeneous electron transfer. As shown in Fig. 2, in the deposition of gold the



Figure 3. Cross-sectional SEMs showing the profile evolution of gold deposit inside trench features: (A) before electrochemical deposition of gold, and (B) 0.23, (C) 0.47, (D) 0.55, and (E) 2.0 μ m gold deposited in the presence of 3 mL/L MPS.

presence of MPS actually causes an increase in cathodic polarization, characteristic of a suppressor that makes the deposition slower at a given deposition potential.

One of the prevailing models proposed to describe superconformal deposition of copper is based on the assumption that thiol and disulfide species such as MPS and SPS accumulate inside features of interest as deposition progresses and the surface area inside the fea-



Figure 4. Cross-sectional SEMs of wafers deposited with gold at current densities of (A) 1.6 mA/cm² that corresponds to a nominal deposition rate of 0.10 μ m/min, and (B) 2.4 mA/cm², corresponding to a nominal deposition rate of 0.15 μ m/min.

tures decreases. This model has been successfully used to explain the observed superconformal deposition of copper in features and the following momentum deposition that leads to the formation of bumps on top of the filled features in the presence of both accelerator (thiol or disulfide species) and suppressor (polyalkylene glycols such as polyethylene glycols).^{11-15,35} In the case of gold deposition, because of the strong interaction of thiol and disulfide species with gold, the surface-tethered thiol and disulfide species (as thiolate) might be readily buried in the deposit during deposition. As a consequence of the incorporation, coupled with the limited supply of the species into features, the local concentration of the species inside features would be lower than that on the surface of the substrate onto which gold is deposited. The reduction in the concentration of the inhibiting species inside features would allow faster deposition of gold in the features, particularly at the bottom of the features where the concentration of the inhibiting species is the lowest.

In an attempt to understand the role of thiol and disulfide species such as MPS in the deposition of gold, we performed gold deposition under potentiostatic and galvanostatic conditions on gold substrates underivatized and derivatized with MPS. The deposition was carried out in the base gold electrolyte without the addition of MPS on a gold-deposited platinum rotating-disk electrode. For deposition on an underivatized gold substrate, the gold-deposited rotating-disk electrode was used without further modification. For deposition on a derivatized gold substrate, the electrode was modified with MPS at room temperature in the gold electrolyte containing MPS. The modified electrode was rinsed with deionized water before being transferred to the base gold electrolyte for gold deposition.

Figure 5 shows the chronoamperometric transients observed on the underivatized and derivatized gold substrates. At the experimental condition indicated in the caption, gold deposition on the underivatized substrate a occurred upon the application of the deposition potential and reached a steady-state deposition rate (or current density), which is representative of the current density used to achieve superconformal deposition of gold, in about 1 min. On the substrate b that was derivatized in 3 mL/L MPS gold electrolyte for 2 min, gold deposition to reach the steady-state current density observed with the underivatized substrate. On the substrate c that



Figure 5. Chronoamperometric transients of gold deposition in the base gold electrolyte at gold substrates: (a) underivatized; (b) derivatized in the gold electrolyte containing 3 mL/L MPS for 2 min; and (c) derivatized in the gold electrolyte containing 20 mL/L MPS for 10 min. Deposition potential -350 mV. Electrode rotating speed 100 rpm.

was derivatized in the gold electrolyte containing 20 mL/L MPS for 10 min, gold deposition was hindered to the extent that the onset of the deposition did not occur until about 20 min after the application of the deposition potential. It also took much longer for the deposition, after its onset, to reach the characteristic steady-state current density observed on the underivatized substrate.

Based on the findings reported in the literature that thiols and disulfides spontaneously adsorb on gold and form monolayers that are resistive to heterogeneous electron transfer,^{28,29,32,33} it is rational to attribute the hindrance of the derivatized substrates to gold deposition to the presence of MPS on the substrates and ascribe the difference in hindrance degree to MPS coverage on the substrates. The coverage of MPS on substrate c is expected to be significantly higher than that on substrate b, as the former was derivatized longer in a higher concentration of MPS solution. Consequently, gold deposition on substrate c was more strongly hindered than on substrate b. It is also reasonable to attribute the gradual increase in current density on the derivatized gold substrates after the onset of gold deposition to the reduction in MPS coverage on the substrates. The reduction in the surface coverage of MPS might be due to the incorporation of MPS into the gold deposit and/or its dissolution into the gold electrolyte. However, considering the strong interaction of MPS with gold, it might be more reasonable to suspect that the reduction in MPS surface coverage was primarily due to its incorporation into the gold deposit as deposition progressed.

After the elimination of the adsorbed MPS, gold deposition on a derivatized gold substrate would eventually come close to that on an underivatized one. The trend can be seen from Fig. 5. Figure 5 also shows that the current density on the derivatized substrates actually surpassed the characteristic current density on the underivatized substrate. The higher current density on the derivatized substrates was most likely due to the larger electrochemical surface area as a result of the increase in deposit surface roughness. On the derivatized gold substrates, gold deposition might have first occurred at localized small areas such as the pinholes of the MPS adlayers, resulting in a rougher surface and a correspondingly larger electrochemical surface area. The effect appeared to be particularly noticeable with substrate c, where the highest current density reached about 1.1 times the characteristic current density of the underivatized substrate. After the elimination of MPS from the gold substrate, the surface roughness on the derivatized substrate might improve as the deposition further progressed, accounting for the observation that the current density on substrate c afterward decreased and leveled off (Fig. 5).

Consistent with the chronoamperometric results, the chronopotentiometric results also suggest that the presence of MPS on a gold surface suppresses the deposition of gold, and the degree of suppres-



Figure 6. Chronopotentiometric transients of gold deposition in the base gold electrolyte at gold substrates: (1) underivatized; (2) derivatized in the gold electrolyte containing 3 mL/L MPS for 2 min; (3) derivatized in the gold electrolyte containing 20 mL/L MPS for 10 min; and (4) derivatized in the gold electrolyte containing 20 mL/L MPS overnight. Deposition current density 2 mA/cm². Electrode rotating speed 100 rpm.

sion depends on the coverage of MPS on the surface (Fig. 6). At the galvanostatic condition the elimination of the surface-adsorbed MPS appeared to be significantly faster than at the previous potentiostatic condition, although both of them are representative of the deposition current and the corresponding deposition potential under which superconformal deposition of gold was achieved. As shown in Fig. 6, steady-state deposition on the derivatized substrates was reached in less than 2 min on all the derivatized substrates, including the one derivatized in 20 mL/L MPS overnight. In the galvanostatic deposition, which more closely resembles the actual gold deposition on a wafer than the potentiostatic deposition, the surface-adsorbed MPS might be more readily buried in the deposit because of the faster initial deposition rate resulting from the higher deposition potential (Fig. 6).

The mechanism that is responsible for superconformal deposition of gold in the presence of such species as MPS is certainly a subject that needs to be further explored. For instance, the grain-refiner thallium that functions as a depolarizer in the electrolyte may play an important role in affecting the gap-filling capability of the electrolyte. It was observed that the introduction of thallium into the gold electrolyte that contains MPS but no thallium significantly improves deposit surface roughness. However, the results obtained so far appear to suggest that the driving force leading to superconformal deposition of gold was primarily due to the depletion of thiol or disulfide species inside the features of interest. This is analogous to the copper superfilling model proposed based on the assumption of differential inhibition by diffusion-controlled additives.³ The momentum deposition, which is common in superconformal deposition of copper, was not observed in the present superconformal deposition of gold.

Conclusions

Superconformal electrochemical deposition of gold has been demonstrated by utilizing a thiol species, MPS, as an additive in a sulfite-based gold electrolyte. The developed process was proven to be a true bottom-up process with which aggressive features such as straight-walled and re-entrant ones can be successfully filled without seam voids. The achievement of superconformal deposition of gold allows us to completely fill fine features of interest and thus makes the implementation of gold metallization through damascene processing feasible.

Voltammetric, chronoamperometric, and chronopotentiometric studies reveal that the thiol species MPS in the present superconformal deposition system functions as a suppressor that hinders electrochemical deposition of gold, in contrast to its function as an accelerator in a superconformal copper deposition system. The experimental results, coupled with the expected strong interaction of the thiol species MPS with gold substrates, lead us to believe that

superconformal deposition of gold in the presence of thallium, which functions as a depolarizer, and MPS was most likely driven by the depletion of MPS inside the features of interest as a result of its consumption through incorporation into the deposit in conjunction with its diffusion-limited supply. On this basis, it can be expected that other water-soluble thiol and disulfide species such as carboxylic acid-terminated thiols and disulfides as well as sulfonic acid-terminated disulfides that strongly adsorb on gold and hinder heterogeneous electron transfer would have similar effects on the deposition of gold and promote superconformal deposition.

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References

- 1. D. Edelstein, J. Heidenreich, R. Goldblatt, W. Cote, C. Uzoh, N. Lustig, P. Roper, T. McDevitt, W. Motsiff, A. Simon, J. Dukovic, R. Wachnik, H. Rathore, R. Schulz, L. Su, S. Luce, and J. Slattery, Tech. Dig. - Int. Electron Devices Meet., 1997. 773.
- 2. S. Venkatesan, A. V. Gelatos, V. Misra, R. Islam, B. Smith, J. Cope, B. Wilson, D. Tuttle, R. Cardwell, I. Yang, P. V. Gilbert, R. Woodruff, R. Bajaj, S. Das, J. Farkas, D. Watts, C. King, P. Crabtree, T. Sparks, T. Lii, C. Simpson, A. Jain, M. Herrick, Capasso, S. Anderson, R. Venkatraman, S. Filipiak, B. Flordalice, K. Reid, J. Klein, E. J. Weitzman, and H. Kawasaki, Tech. Dig. - Int. Electron Devices Meet., 1997. 769.
- 3. P. C. Andricacos, C. Uzoh, J. O. Dukovic, J. Horkans, and H. Deligianni, IBM J. Res. Dev., 42, 567 (1998).
- 4. P. Singer, Semicond. Int., 21, 90 (1998).
- 5. M. E. Gross, C. Lingk, W. L. Brown, and R. Drese, Solid State Technol., 42, 47 (1999)
- 6. R. Williams, Modern GaAs Processing Methods, Artech House, Boston, MA (1990)
- 7. K. Kondo, T. Matsumoto, and K. Watanabe, J. Electrochem. Soc., 151, C250 (2004).
- T. P. Moffat, D. Wheeler, and D. Josell, J. Electrochem. Soc., 151, C262 (2004). 9. M. Hayase, M. Taketani, K. Aizawa, T. Hatsuzawa, and K. Hayabusa, Electrochem.
- Solid-State Lett., 5, C98 (2002). Y. Cao, P. Taephaisitphongse, R. Chalupa, and A. C. West, J. Electrochem. Soc., 10.
- 148, C466 (2001). 11. D. Josell, D. Wheeler, W. H. Huber, J. E. Bonevich, and T. P. Moffat, J. Electrochem. Soc., 148, C767 (2001).
- A. C. West, S. Mayer, and J. Reid, Electrochem. Solid-State Lett., 4, C50 (2001). 12.
- T. P. Moffat, D. Wheeler, W. H. Hubber, and D. Josell, Electrochem. Solid-State 13. Lett., 4, C26 (2001).
- 14. Y. H. Im, M. O. Bloomfield, S. Sen, and T. S. Cale, Electrochem, Solid-State Lett., 6, C42 (2003).
- 15. A. C. West, J. Electrochem. Soc., 147, 227 (2000).
- 16. M. Georgiadou, D. Veyret, R. L. Sani, and R. C. Alkire, J. Electrochem. Soc., 148, C54 (2001).
- 17. T. P. Moffat, J. E. Bonevich, W. H. Huber, A. Stanishevsky, D. R. Kelly, G. R. Stafford, and D. Josell, J. Electrochem. Soc., 147, 4524 (2000).
- Y. Jin, K. Kondo, Y. Suzuki, T. Matsumoto, and D. P. Barley, Electrochem. Solid-18. State Lett., 8, C6 (2005).
- 19. M. Hasegawa, Y. Negishi, T. Nakanishi, and T. Osaka, J. Electrochem. Soc., 152, C221 (2005).
- 20. K.-C. Shim, H.-B. Lee, O.-K. Kwon, H.-S. Park, W. Kob, and S.-W. Kang, D. Josell, S. Kim, D. Wheeler, T. P. Moffat, and S. G. Pyo, J. Electrochem. Soc.,
 21. D. Josell, S. Kim, D. Wheeler, T. P. Moffat, and S. G. Pyo, J. Electrochem. Soc.,
- 150. C368 (2003)
- 22 T. P. Moffat, B. Baker, D. Wheeler, J. E. Bonevich, M. Edelstein, D. R. Kelly, L. Gan, G. R. Stafford, P. J. Chen, W. F. Egelhoff, and D. Josell, J. Electrochem Soc., 149, C423 (2002).
 23. B. C. Baker, M. Freeman, B. Melnick, D. Wheeler, D. Josell, and T. P. Moffat,
- J. Electrochem. Soc., 150, C61 (2003).
- E. J. Ahn and J. J. Kim, Electrochem. Solid-State Lett., 7, C118 (2004).
- Z. Hu and T. Ritzdorf, in Electrochemical Processing in ULSI and MEMS, H. Deligianni, S. T. Mayer, T. P. Moffat, and G. R. Stafford, Editors, PV 2004-17, p.13, The Electrochemical Society Proceedings Series, Pennington, NJ (2005). D. Josell, C. R. Beauchamp, D. R. Kelly, C. A. Witt, and T. P. Moffat, *Electrochem.*
- Solid-State Lett., 8, C54 (2005).
- L. W. Graham, Ph.D. Thesis, Rensselaer Polytechnic Institute, New York (1999). 27
- C.-J. Zhong and M. D. Porter, J. Am. Chem. Soc., 116, 11616 (1994). 28. 29. M. D. Porter, T. B. Bright, D. L. Allara, and C. E. D. Chidsey, J. Am. Chem. Soc., 109, 3559 (1987)
- 30. C. D. Bain, E. B. Troughton, Y.-T. Tao, J. Evall, G. M. Whitesides, and R. G.
- Nuzzo, J. Am. Chem. Soc., 111, 321 (1989).
- 31. C. D. Bain and G. M. Whitesides, J. Am. Chem. Soc., 111, 7164 (1989). J. J. Hickman, P. E. Laibinis, D. I. Auerbach, C. Zou, T. J. Gardner, G. M.
- Whitesides, and M. S. Wrighton, Langmuir, 8, 357 (1992).
- 33. C.-J. Zhong and M. D. Porter, Anal. Chem., 67, 709A (1995).
- 34. H. Rieley and G. K. Kendall, Langmuir, 15, 8867 (1999).
- T. Ritzdorf, D. Fulton, and L. Chen, in Advanced Metallization Conference (AMC)/ 35. 1999, M. E. Gross, T. Gessner, N. Kobayashi, and Y. Yasuda, Editors, p. 101, Materials Research Society Conference Proceedings, Warrendale, PA (2000).