Electrochemical and Solid-State Letters, **11** (1) D18-D21 (2008)
1099-0062/2007/11(1)/D18/4/$23.00 © The Electrochemical Society

Two-Step Filling in Cu Electroless Deposition Using a Concentration-Dependent Effect of 3-*N*,*N*-dimethylaminodithiocarbamoyl-1-propanesulfonic Acid

Chang Hwa Lee,[a,*,c] Ae Rim Kim,[a] Soo-Kil Kim,[b] Hyo-Chol Koo,[a] Sung Ki Cho,[a] and Jae Jeong Kim[a,,z]**

[a]*Research Center for Energy Conversion and Storage, School of Chemical Engineering, College of Engineering, Seoul National University, Gwanak-gu, Seoul 151-742, Korea*
[b]*Center for Fuel Cell Research, Institute of Science and Technology, Seongbuk-gu, Seoul 136-791, Korea*

This paper describes electroless Cu filling of trenches with different widths ranging from 130 to 300 nm, using a concentration-dependent effect of 3-*N*,*N*-dimethylaminodithiocarbamoyl-1-propanesulfonic acid (DPS). With a fixed DPS concentration, it is shown that these trenches with different dimensions cannot be superfilled simultaneously. This is presumably caused by different surface concentrations of the adsorbed additive, which depends on the feature size and surface area. A two-step filling method is employed to superfill those trenches, which is also effective in control of the deposited Cu amounts to obtain uniform growth front regardless of the trench dimensions.
© 2007 The Electrochemical Society. [DOI: 10.1149/1.2798877] All rights reserved.

Manuscript submitted June 7, 2007; revised manuscript received August 31, 2007. Available electronically November 14, 2007.

Superconformal electrodeposition of Cu using organic additives such as bis(3-sulfopropyl)-disulfide (SPS)-polyethyleneglycol (PEG)-chloride (Cl^-) has been successfully implemented for the metallization of ultra-large-scale integrated circuits.[1,2] Such void-free filling of trenches and vias is quantitatively predicted by the curvature-enhanced adsorbate coverage model, which involves the competitive adsorption between accelerating species (SPS-Cl) and suppressing species (PEG-Cl) coupled with the effect of local area change.[3-6]

However, Cu electroless deposition, for which reducing agents (such as formaldehyde or glyoxylic acid) are used to reduce Cu ions instead of an externally supplied current, has been applied only to the seed repair process for physical vapor deposition (PVD) seeds[7,8] or to the seed layer itself for Cu superconformal electrodeposition, because of its conformal deposition characteristics.[9,10] Recently, however, Cu electroless deposition has been explored as a possibility for direct void-free filling of features covered with barrier layers because it is one approach to solving the pinch-off caused by poor step coverage of PVD seeds, as the feature size shrinks down and the aspect ratio increases. To date, Cu electroless gap filling has been achieved either in the presence of S and/or N bearing sulfonic acid series additives,[11-15] some of which are well known in Cu electrodeposition, or in the absence of deposition-rate-controlling additives.[16-19]

When SPS, a well-known accelerator for superfilling in Cu electrodeposition, was applied to Cu electroless deposition, it was evident that the deposition rate depended on the SPS concentration, namely, accelerating at low concentration and suppressing at higher concentration. The difference of surface concentration between the top and the bottom of 500 nm wide trenches led to bottom-up filling of Cu without seams or voids in electroless deposition, showing the typical overfill bumps.[12,13] Similarly, the use of 3-*N*,*N*-dimethylaminodithiocarbamoyl-1-propanesulfonic acid (DPS), which has a molecular structure similar to 3-mercapto-1-propanesulfonic acid (MPS), also showed the concentration-dependent effect on the deposition rate for the planar substrate and bottom-up filling profiles with smoother surface characteristics than SPS.[14]

Although Cu electroless bottom-up filling was achieved in 500 nm wide trenches using the concentration-dependent bifunctional additives, different kinetics would be anticipated for electroless Cu filling of differently sized features because the variation in the surface concentration of additives would be more strongly affected by the dimension of the trenches.

Therefore, in this article, we investigate how the effect of the concentration-dependent bifunctional additive in Cu electroless filling depends on the trench dimension, especially the widths being <320 nm, through the electron microscopic observation of Cu gap filling using a representative bifunctional additive, DPS. Furthermore, we suggest an effective way to superfill the patterns of various dimensions with uniform growth fronts by modifying the conventional Cu electroless deposition.

Experimental

The substrates used in the experiments comprised barrier layers of TaN (7.5 nm) and Ta (7.5 nm deposited on SiO_x/Si wafers with lithographically patterned trenches. The trenches covered with the barrier layers had widths ranging from 130 to 300 nm at the bottom and depths ranging from 290 to 300 nm. Their aspect ratios ranged from 1.0 to 2.3 after the barrier layer deposition. Prior to electroless deposition, the substrates were immersed in a mixture of 1% dilute HF solution and 1.4% HNO_3 for 10 min to remove Ta native oxide from the surface. Surfaces were catalyzed by wet Pd activation processes comprising Sn sensitization step and Pd activation step.[10,20]

Cu electroless deposition was carried out in a base electrolyte composed of 0.025 M $CuSO_4 \cdot 5H_2O$, 2.9 g/L paraformaldehyde $[(HCHO)_n]$, 0.054 M ethylenediaminetetraacetic acid (EDTA), and 0.49 M KOH at a temperature of 70°C. In addition, 0.1 g/L 2,2′-dipyridyl as a stabilizer, and DPS as an accelerating/suppressing agent, were utilized for the Cu electroless bottom-up process.

Cu electroless gap filling was performed with two sequential depositions using electrolytes containing two different concentrations of DPS. Between the two depositions, there was a surface cleaning process to eliminate the strongly adsorbed DPS and/or its byproducts from the Cu surface deposited during the first filling step. It was introduced to prevent them affecting the second filling step. The process was done by lightly etching the Cu surface with a dilute NH_4OH solution (1:100) for 1 min. To verify indirectly that adsorbed species were removed, the amount of carbon adsorbed and incorporated in the deposited Cu film was measured by total organic carbon (TOC) method, using 20 mL of a 1/20 diluted solution in which Cu film was dissolved in 10 mL of a 70% HNO_3. The TOC measurement was done three times for each step and the average value was calculated. Deposition profiles for various trench widths were examined using field emission scanning electron microscopy (FESEM, JEOL 6330F). The cross section of the trench was ob-

* Electrochemical Society Student Member.
** Electrochemical Society Active Member.
[c] Present address: Metallurgy Division in Materials Science and Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA.
[z] E-mail: jjkimm@snu.ac.kr

Downloaded 04 Jul 2010 to 147.46.246.152. Redistribution subject to ECS license or copyright; see http://www.ecsdl.org/terms_use.jsp

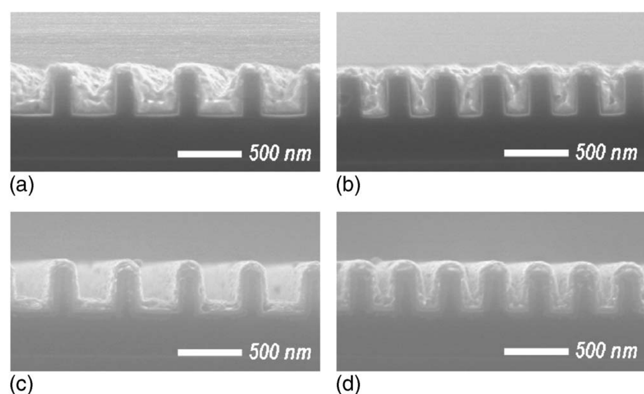

Figure 1. Cross-sectional FESEM images of trenches filled with Cu electroless deposition, using two different concentrations of DPS: 0.5 mg/L in (a) and (b), and 2.0 mg/L in (c) and (d), and with two different trench widths: 300 nm in (a) and (c), and 130 nm in (b) and (d). Deposition time was fixed at 5 min.

served using high-resolution FESEM (Hitachi S-4700), by mechanically polishing and ion milling, to examine the existence of voids in the deposit.

Results and Discussion

There have been several studies on the concentration-dependent effect of the additive in electroless deposition[21-24] as well as in Cu electrodeposition.[25-27] In Cu electroless deposition, the accelerating effect at low additive concentrations is known to be caused by the delocalized π-electron bond in its molecular structure which enhances the reduction of Cu ions,[23] making the breakage of the Cu^{2+}-ligand easier by adsorbing at the surface,[22] or by the electron transfer mechanism through the formation of dimer.[21] Conversely, at higher concentrations, it is significant that the reduction of Cu ions is disturbed by the additive, and the reoriented molecular structure (including dimer or its byproducts) is strongly adsorbed on the active site, where the oxidation of the reducing agent occurs. However, further investigation of the concentration-dependent mechanism for SPS or DPS in Cu electroless deposition is required.

In previous experiments, we have concluded that the bottom-up fill appearing in Cu electroless deposition is due to the concentration difference of additive between the bottom and top surfaces of the trench caused by diffusion of the additive,[12-14] which is significantly affected by the surface area per unit volume.[28]

Cu filling was carried out by electroless deposition in the presence of two different concentrations of DPS of 0.5 and 2 mg/L, on trenches with bottom widths of 300 and 130 nm, as shown in Fig. 1. Interestingly, while the 300 nm trenches were filled with bottom-up shape at 0.5 mg/L DPS, in a manner similar to the previous experiment[14] where successful bottom-up filling was achieved with trenches of 400 nm width and 1000 nm depth, conformal deposition with bottom voids was observed at the 130 nm wide trenches, which have greater surface areas per unit volume than those of the 300 nm wide trenches. However, the 130 nm wide trenches showed V-notches at their centers when 2.0 mg/L DPS was added, which is regarded as proof of bottom-up filling, while a robust suppressing effect appeared on the 300 nm wide trenches. As schematically depicted in Fig. 2, this implies that bottom-up filling does not occur at low DPS concentrations on smaller trenches, due to significant depletion of DPS concentration at the bottom, caused by the increased surface area or by the difficulty of diffusion into the trench.

Although we verified that bottom-up fill could be achieved for smaller feature sizes using Cu electroless deposition, it does depend on the surface area and pattern density. This factor chiefly makes bottom-up fill difficult for trenches of different sizes, when a constant additive concentration is used.

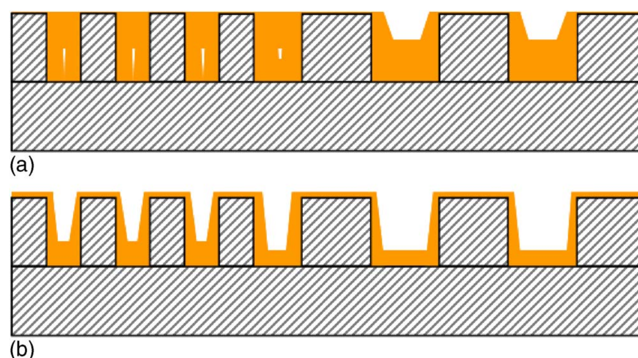

Figure 2. (Color online) Schematics of gap-filled trenches showing the dependency between pattern size and additive concentration: below (a) and above (b) the critical concentration of DPS.

In order to achieve electroless superfilling on different-sized trenches, a two-step filling method was applied. Similarly to the concept proposed for superfilling[27] and leveling[29] in Cu electrodeposition, the process is divided into two filling steps using two different DPS concentration, as outlined in Fig. 3. The first deposition step is to superfill the smaller sized patterns, and the second step is to fill up the highly suppressed regions of the wider trenches, including the remaining parts of smaller trenches. To minimize the impact of accumulated additive on the surface during the two filling steps, two alternatives for removing the adsorbed DPS and its thiolate compounds between the two deposition steps were tried, namely deionized (DI) water rinsing and slight etching of the surface with NH_4OH.

To compare feature filling by the two-step method with conventional one-step filling method, one-step deposition was conducted using 0.5 mg/L DPS for 12 min, which was the same as the total deposition time for two-step filling (5 min for the first step and 7 min for the second step), and presented in Fig. 4a. Despite the deposition time of 12 min, comparison to Fig. 1a and b shows that there was no major difference in the deposited amount, except for a slight increase for smaller-width trenches, which indicates a continuous accumulation of additive on the active site of the Cu surface with time and its resulting suppression effect, even at 0.5 mg/L DPS. The bottom voids generated at the early stage of deposition

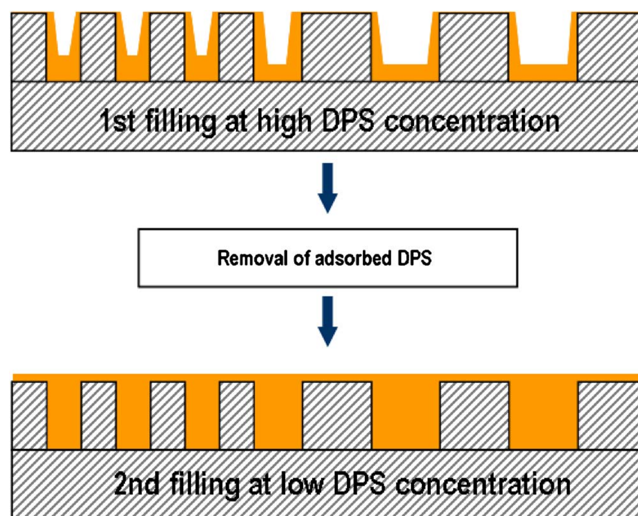

Figure 3. (Color online) The concept of the two-step filling method in Cu electroless deposition.

Downloaded 04 Jul 2010 to 147.46.246.152. Redistribution subject to ECS license or copyright; see http://www.ecsdl.org/terms_use.jsp

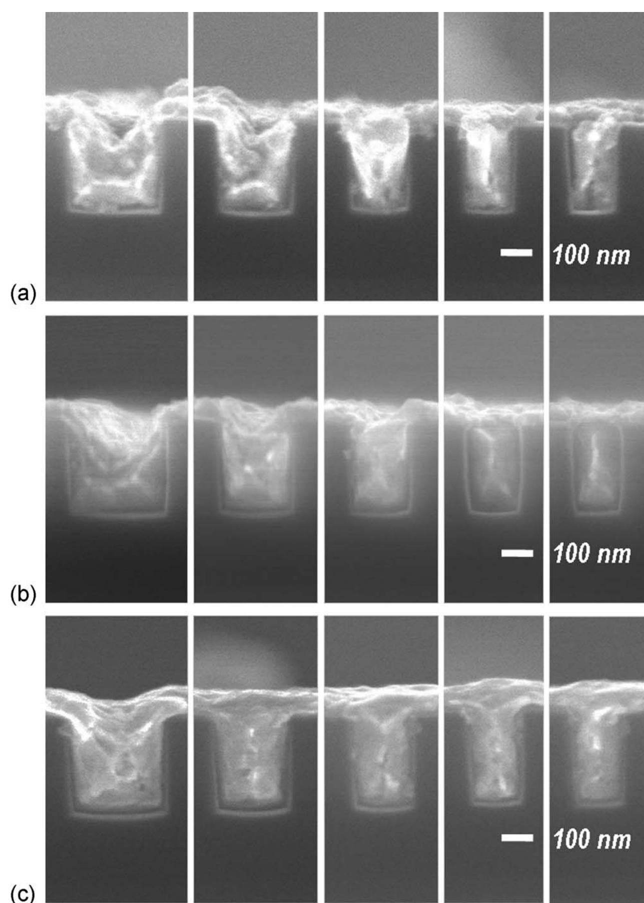

Figure 4. Cross-sectional FESEM images of trenches with various widths (300, 220, 180, 150, and 130 nm) filled with Cu electroless deposition: one-step filling for 12 min in (a), and two-step filling with 5 min for the first step and 7 min for the second step in (b) and (c). Between the two depositions, DI water and a 1:100 NH_4OH solution, in (b) and (c) respectively, were used to remove the adsorbed DPS and its byproducts from the first filling.

were evident for most trench sizes, resulting in further disparity in deposited Cu at the centers of the 300 wide and 130 nm wide trenches.

By contrast, for the case of two-step filling using the DI water-rinsing method to eliminate the adsorbed additive, the bottom voids seen in one-step filling did not appear at all, as shown in Fig. 4b because of the preferential deposition at the bottom of smaller features by control of the DPS concentration. However, the wider trenches, of 300 and 220 nm widths, on which a relatively large amount of the additive would be expected to adsorb, were not completely filled because of the inefficient removal by DI water rinsing. The sulfur-containing additives are attached to metal surfaces with a strong coordinative bond via the deprotonation of the S-H group of thiol molecules.[30,31] The thiolate compounds are incorporated with the forms of Cu sulfides into Cu deposits, which has been observed in the previous result.[12]

In the final experiment, a diluted NH_4OH solution was used to remove the surface-rich DPS and its by-products, by etching the Cu

Table I. Result of TOC measurement

	Cu seed only	After first-step deposition and DI water rinsing	After first-step deposition and surface etching
TOC (ppm)	5.54	77.06	6.06

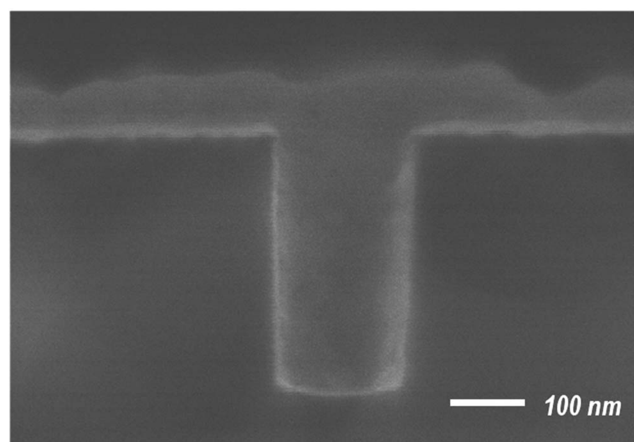

Figure 5. Cross-sectional image of a 150 nm wide trench observed by high-resolution FESEM.

surface with a negligible change of thickness, after the first filling step with 2.0 mg/L DPS. The NH_4OH solution, well known as a Cu oxide etchant, plays a role in etching Cu, even though it increases the surface roughness.[32] From the result of measuring the amount of carbon included in the Cu deposit before and after the surface etching, as presented in Table I, it was confirmed that the surface-preferentially incorporated carbon-containing compounds, such as DPS and 2,2′-dipyridyl, were effectively removed by NH_4OH etching.

Two-step filling using NH_4OH etching revealed that the difference in step height between the different-sized trenches was greatly diminished, as shown by the distinct difference between Fig. 4b and c, and bottom-up filling was successfully accomplished, as evidenced by the bumps in the smaller trenches. In addition, the cross section of one of the trenches was examined by mechanically polishing and ion milling to verify the absence of voids in the deposit. As shown in Fig. 5, in a magnified SEM image of 150 nm wide trench, no voids or seams were observed, even though the surface was slightly rough.

Conclusion

We have found that conventional one-step Cu electroless deposition using the concentration-dependent bifunctional effect of DPS is hard to apply directly to the simultaneous filling of patterns with various dimensions, as the bifunctional effect depends on the effective surface concentration, thus surface area at a given DPS bulk concentration. For void-free electroless gap filling regardless of the pattern size, low concentrations of DPS for wider trenches and high concentrations of DPS for narrower trenches are required. By using a two-step filling process that involves an initial filling for relatively small trenches at high DPS concentration, followed by a second filling for the wide trenches at low DPS concentration, bottom-up filling can be achieved for trenches <300 nm wide simultaneously, without voids. This shows the feasibility of Cu electroless deposition for subquarter-micrometer feature technology.

Acknowledgments

This work was supported by a Korea Research Foundation grant funded by the Korean Government (MOEHRD) (grant no. KRF-2006-352-D00052). The authors are grateful for the support of the Research Center for Energy Conversion and Storage (RCECS), Dongbu HiTek Company, Ltd., and the Institute of Chemical Processes (ICP).

Seoul National University assisted in meeting the publication costs of this article.

Downloaded 04 Jul 2010 to 147.46.246.152. Redistribution subject to ECS license or copyright; see http://www.ecsdl.org/terms_use.jsp

References

1. P. C. Andricacos, C. Uzoh, J. O. Dukovic, J. Horkans, and H. Deligianni, *IBM J. Res. Dev.*, **42**, 567 (1998).
2. R. Rosenberg, D. C. Edelstein, C.-K. Hu, and K. P. Rodbell, *Annu. Rev. Mater. Sci.*, **30**, 229 (2000).
3. T. P. Moffat, D. Wheeler, W. H. Huber, and D. Josell, *Electrochem. Solid-State Lett.*, **4**, C26 (2001).
4. D. Josell, D. Wheeler, W. H. Huber, C. Witt, and T. P. Moffat, *Electrochem. Solid-State Lett.*, **6**, C143 (2003).
5. T. P. Moffat, D. Wheeler, M. D. Edelstein, and D. Josell, *IBM J. Res. Dev.*, **49**, 19 (2005).
6. T. P. Moffat, D. Wheeler, S.-K. Kim, and D. Josell, *J. Electrochem. Soc.*, **153**, C127 (2006).
7. T. Andryuschenko and J. Reid, in *Proceedings of the IEEE 2001 International Interconnect Technology Conference*, p. 33, IEEE, New York (2001).
8. E. Webb, C. Witt, T. Andryuschenko, and J. Reid, *J. Appl. Electrochem.*, **34**, 291 (2004).
9. J. J. Kim, S-K. Kim, C. H. Lee, and Y. S. Kim, *J. Vac. Sci. Technol. B*, **21**, 33 (2003).
10. C. H. Lee, S. Hwang, S.-C. Kim, and J. J. Kim, *Electrochem. Solid-State Lett.*, **9**, C157 (2006).
11. S. Shingubara, Z. Wang, O. Yaegashi, R. Obata, H. Sakaue, and T. Takahagi, *Electrochem. Solid-State Lett.*, **7**, C78 (2004).
12. C. H. Lee, S. C. Lee, and J. J. Kim, *Electrochim. Acta*, **50**, 3563 (2005).
13. C. H. Lee, S. C. Lee, and J. J. Kim, *Electrochem. Solid-State Lett.*, **8**, C110 (2005).
14. C. H. Lee, S. K. Cho, and J. J. Kim, *Electrochem. Solid-State Lett.*, **8**, J27 (2005).
15. M. Hasegawa, Y. Okinaka, Y. Shacham-Diamand, and T. Osaka, *Electrochem. Solid-State Lett.*, **9**, C138 (2006).
16. J. H. Lin, Y. Y. Tsai, S. Y. Chiu, T. L. Lee, C. M. Tsai, P. H. Chen, C. C. Lin, M. S. Feng, C. S. Kou, and H. C. Shih, *Thin Solid Films*, **377**, 592 (2000).
17. H.-H. Hsu, K.-H. Lin, S.-J. Lin, and J.-W. Yeh, *J. Electrochem. Soc.*, **148**, C47 (2001).
18. J.-H. Lin, W.-J. Hsieh, J.-W. Hsu, X.-W. Liu, U.-S. Chen, H. C. Shih, *J. Vac. Sci. Technol. B*, **20**, 561 (2002).
19. J. J. Kim, S. H. Cha, and Y. -S Lee, *Jpn. J. Appl. Phys., Part 2*, **42**, L953 (2003).
20. C. H. Lee, S. H. Cha, A. R. Kim, J. -H Hong, and J. J. Kim, *J. Electrochem. Soc.*, **154**, D182 (2007).
21. J. Kivel and J. S. Sallo, *J. Electrochem. Soc.*, **112**, 1201 (1965).
22. L. N. Schoenberg, *J. Electrochem. Soc.*, **119**, 1491 (1972).
23. F. J. Nuzzi, *Plat. Surf. Finish.*, **70**, 51 (1983).
24. F. Hanna, Z. A. Hamid, and A. A. Aal, *Mater. Lett.*, **58**, 104 (2003).
25. C. Ogden and D. Tench, *J. Electrochem. Soc.*, **128**, 539 (1981).
26. K.-C. Lin, J.-M. Shieh, S.-C. Chang, B.-T. Dai, C.-F. Chen, M.-S. Feng, and Y.-H. Li, *J. Vac. Sci. Technol. B*, **20**, 2233 (2002).
27. S. K. Cho, S.-K. Kim, and J. J. Kim, *J. Electrochem. Soc.*, **152**, C330 (2005).
28. R. Akolkar and V. Dubin, *Electrochem. Solid-State Lett.*, **10**, D55 (2007).
29. S.-K. Kim, S. Hwang, S. K. Cho, and J. J. Kim, *Electrochem. Solid-State Lett.*, **9**, C25 (2006).
30. S. A. Sardar, J. A. Syed, S. Yagi, and K. Tanaka, *Thin Solid Films*, **450**, 265 (2004).
31. T. Laiho, J. A. Leiro, M. H. Heinonen, S. S. Mattila, and J. Lukkari, *J. Electron Spectrosc. Relat. Phenom.*, **142**, 105 (2005).
32. J. J. Kim and S.-K. Kim, *Appl. Surf. Sci.*, **183**, 311 (2001).

Downloaded 04 Jul 2010 to 147.46.246.152. Redistribution subject to ECS license or copyright; see http://www.ecsdl.org/terms_use.jsp