Available online at www.sciencedirect.com

Thin Solid Films 498 (2006) 50 – 55

www.elsevier.com/locate/tsf

Novel slurry solution for dishing elimination in copper process beyond 0.1-μm technology

K.W. Chen [a], Y.L. Wang [b,*], C.P. Liu [c], L. Chang [a], F.Y. Li [d]

[a] *Department of Material Science and Engineering, National Chiao-Tung University, Hsin-Chu, Taiwan, ROC*
[b] *College of Science and Engineering, National University of Tainan, Taiwan, ROC*
[c] *Department of Material Science and Engineering, National Cheng Kung University, Tainan, Taiwan, ROC*
[d] *Department of Chemistry, National Chung-Hsin University, Taichung, Taiwan, ROC*

Abstract

The reduction of the copper dishing was investigated by optimizing the copper CMP processes. The reduction method is a novel copper slurry with the organic passivation agent used during the copper polishing to reduce the copper dishing level. The passivation mechanism of the copper polishing was proposed. With the optimized condition of the copper ECD and CMP, the resistivity deviation of 180-μm square metal pads with 10–80% pattern densities was reduced from over 30% to less than 10%. The amount of the copper dishing was reduced from around 150 nm to less than 30 nm. Finally, 10% increase of wafer yield and better process reliability were achieved.

Keywords: Copper; CMP; Copper slurry; Dishing

---

1. Introduction

While the device size shrinks to sub-0.13-μm and beyond, the copper damascene metallization replaces the aluminum process as the interconnect technology due to higher electric conductivity and electromigration (EM) resistance of copper [1–3]. With higher packing density, the reduction of feature size on the chip puts even more stringent demands on the planarization efficiency to implement high-stacked layers of metallization [3], which results in larger resistance deviation of copper trench than that of metal line made by aluminum, as shown in Fig. 1. It was suspected that the poor non-uniformity distribution of the copper resistance was generated by the overplating phenomena of electrodeposition (ECD) and the narrow overpolishing window of copper chemical mechanical planarization (CMP) processes [4,5]. The overplating behavior with a bump formation over the metal lines was believed due to the bottom-up filling by accelerators [6]. The bump formation was accentuated by the dense neighboring feature and thus influenced on the surface morphology of the deposited films, even to induce a large non-uniformity deviation of step height within the wafer after the CMP process. Furthermore, the high non-uniformity deviation brought more overpolishing to guarantee CMP free of copper residue. The high overpolishing ratio, however, not only resulted in the high dishing amount in the large-size features, but also influenced on the resistance deviation of metal trenches and local topology for lithography process [7,8].

Solutions to overcome the overpolishing issues have been intensively developed, such as the dielectric dummy pattern inserted into larger copper pad, increase in trench depth to compensate the dishing effect, the soft-landing application of CMP, and capping other tungsten or electroless metal over the dishing area [8–11]. However, these methods all brought other side-effects to the device performance and process reliability. For example, the inserted dielectric dummy pattern into the larger copper-filling feature reduced the copper dishing level but rapidly increased the resistance for metal trenches. Furthermore, the

---

* Corresponding author. Tel.: +886 6 5051400x5069; fax: +886 36 5051273.

E-mail address: ylwang@tsmc.com (Y.L. Wang).

0040-6090/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2005.07.061

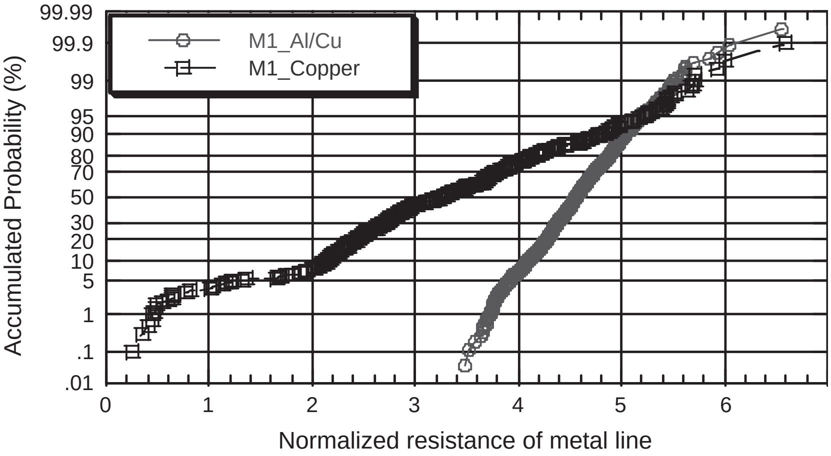

Fig. 1. Comparison of the resistance deviation between copper trench and aluminum metal lines within the same feature size and aspect ratio of the wafer.

parasitical capacitance was generated to degrade the device performance [3]. For another example, the method increasing trench depth could compensate the resistance caused by thinning the copper interconnection, but it increased the difficulties during the pattern etching and defect-free gap-filling processes [8]. There are still a lot to be desired for the solutions mentioned above to achieve reliable performance in the shrinkage of the feature size, besides improving the conventional CMP processes. Hence, in this work, we present our current effort to develop the novel slurry method to reduce the dishing level through the novel passivation layer formation in the CMP process.

2. Experimental

A 200-nm blanket silicon dioxide wafer and a patterned wafer with different metal pattern densities were all sputter-coated with 30–50-nm-thick tantalum (Ta) as an adhesion layer, followed by the sputtered copper seed-layer deposition and the copper ECD with total around 1000-nm-thick copper. The ECD process was implemented with the standard electrolyte, composed of 30 g/l $CuSO_4$–5 H_2O (purity ~99%, chloride <10 mg/kg), 275 g/l H_2SO_4 (97%, chloride<0.1 mg/kg), 50–100 ppm chloride ions, and deionized water (~18 MΩ). Moreover, there are several ingredients in the related additives including 15–25 ppmaccelerator of VIAFORM®, 2–10 ppm suppressor of VIAFORM®, and 2–3 ppm leveler of VIAFORM®. An Applied-Material Mirra polisher was used to polish these wafers. Three-step polishing processes were carried out, in the time sequence, the copper polishing, the Ta polishing, and finally the oxide polishing. The copper polishing slurry was prepared with less than 10 wt.% of alumina powders, and an acid solution with pH 3–5, which contained three ingredients including hydrogen peroxide with 8–16% concentration, a surfactant, a complexing agent, and a passivation agent. The copper slurry was designed with high removal selectivity, i.e. lower polishing rate to Ta and oxide than to copper. The selectivity ratio between the copper and the Ta/oxide polishing rate was over 100. After the copper polishing, the Ta thickness remained ~10–20 nm on the dielectric films. While the Ta slurry was designed as medium pH 4–6 solution with alumina powders less than 15%, the oxide slurry was composed of high pH 9–11 solution and silica abrasives. The Ta and oxide slurries had the removal selectivity ratio 0.6–1.0 between the Ta/oxide and the copper polishing rate to compensate the dishing formation during the copper polishing process. After CMP, the condition of copper surface was detected with the X-ray photoelectron spectroscopy (XPS). The analyzed depth for take-off 60° was about 5 nm of copper. Besides, the step heights for various feature sizes and pattern densities were measured with aleph-step profiler. The resistance of the blanket copper film was examined by four-point probe. The resistance of various pattern features was adopted with the wafer acceptance test (WAT) method.

3. Results and discussion

In the CMP process, a novel copper slurry was developed to minimize the dishing effect on the resistance of metal trench with various different pattern densities. The concept was to balance between the mechanical removal rate and passivation layer formation rate. Fig. 2 illustrates the proposed mechanism of the copper polishing. First, copper reacted with the oxidation agent, H_2O_2, to form the porous copper oxide (CuO or Cu_2O). Similar to the convectional method for the copper polishing, the oxidation films would be hydrolyzed easily, and then be removed. As to the new slurry, the oxidation film would simultaneously react with the passivation agent in the slurry to form cross-linked polymeric film on the copper surface. This polymeric film was less porous and could prevent further oxidation of copper. Besides, the polymeric film was unable to be dissolved in the solution and could be removed after abrasion. The passivation agent was generally composed

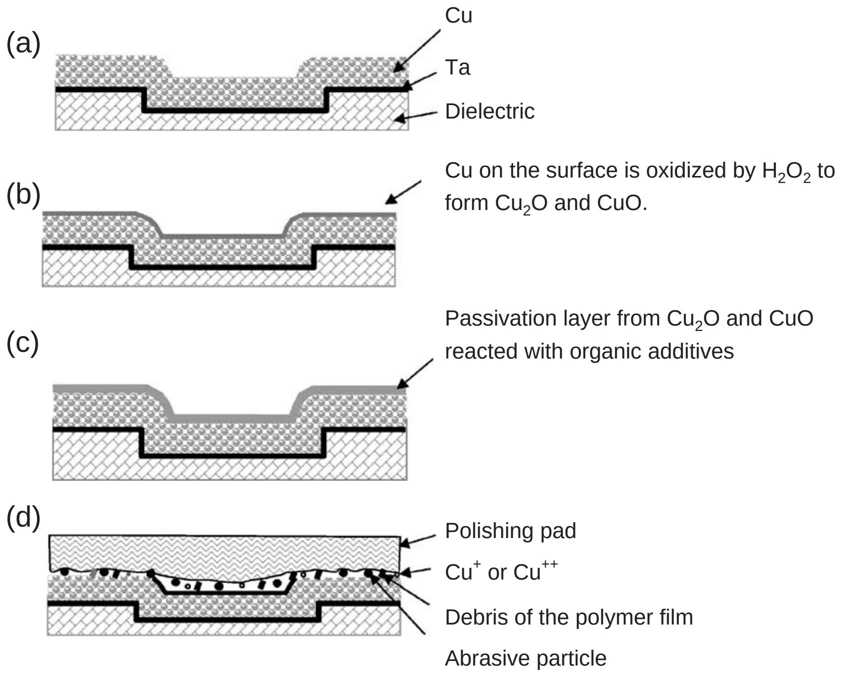

Fig. 2. Proposed mechanism of the copper polishing with the passivation agent in the slurry.

of the azole group, which is characterized by a five-membered ring containing an atom of nitrogen and at least one another non-carbon atom, such as nitrogen, oxygen, or sulphur. It was used as the inhibitor of copper corrosion due to its active adsorption ability on the copper surface to prevent the copper oxidation. For example, the benzotriazole (BTA), tetrazole, and other chemicals containing azole were widely applied in the slurry of the copper polishing [12–14]. In this new slurry, the similar azole component with various long carbon chains, composed of 7–18 carbon atoms, was used as a passivation agent to form the passivation film during the copper polishing. The passivation film also played a role as the abrasion buffer between abrasives and the copper surface, due to the mutually exclusion between the hydrophilic abrasive (Al_2O_3) and the hydrophobic of the long carbon-chain group, which linked azole-group to the copper surface. Hence, as shown in Fig. 3, the removal rate of the copper was not linear with the pressure, due to the passivation film formation in copper surface. A threshold pressure was required to obtain a significant removal rate. As the results, the passivation film at high area of the pattern was removed much faster than that at low area, and Fig. 2(d) depicts this phenomenon. The passivation film at low area of the pattern, therefore, became thicker than that at high area. The material polished away was in form of polymeric debris or copper ions. These copper ions were then complexed by the complexing agent, such as glycine and EDTA, in the slurry to avoid the re-deposition onto the copper surface [15]. The freshly exposed copper surface was oxidized again and the oxidation–passivation–abrasion cycle repeated till the copper polishing process finished. To keep the clean copper surface after the copper CMP process, the passivation

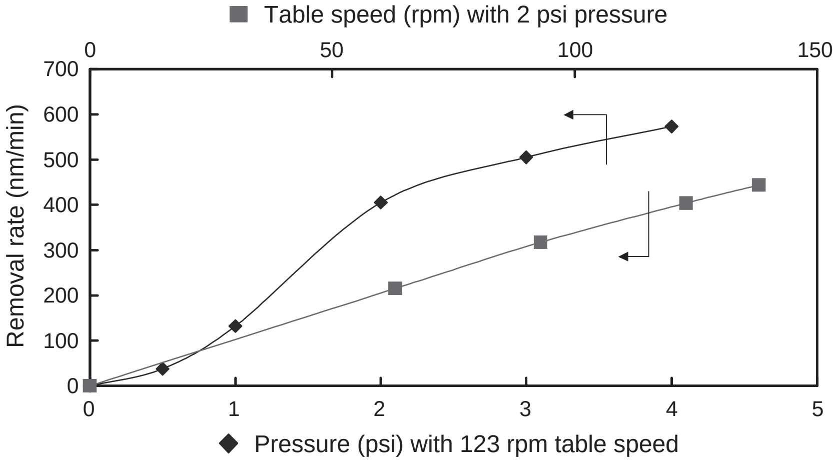

Fig. 3. The behavior of removal rate under various applied pressures and the speeds of the polish table.

film on the top of copper would be removed during the Ta polishing and the post-CMP clean. Fig. 3 reveals that the removal rate with polishing pressure did not follow the Preston behavior, which the removal rate was proportional to the pressure. The non-Prestonian behavior was not only useful to reduce the dishing level, but also improved the non-uniformity of removal rate and pattern dependency on various pressure distributions. The similar behavior has been reported in an abrasive-free slurry system with BTA [16,17]. However, the polishing table speed did not perform the non-Prestonian behavior, but was positively proportional to the removal rate of the copper polishing, like the oxide polishing with more slipping wear from the abrasive [18].

Fig. 4(a) shows the ratio of O, C, and N to copper concentration on the copper surface under various polishing conditions with the XPS detection. Fig. 4(b) reveals the comparison between C–N/N–H bonding intensity in the various different conditions of the copper polishing. From the summary of these data, increase of the polishing pressure in the copper slurry with the passivation agent decreased the concentration ratio of N to Cu. It indicated that the coverage amount of the passivation films and the passivation agent on the copper surface decreased while the pressure increased, shown in Fig. 4's comparison between the condition **B** and **C**. Besides, the clean copper surface without the passivation film was obtained only after the Ta polishing and the post-clean process, which was corresponding to no C–N/N–H bonding on the copper surface, as shown in Fig. 4(b)'s **E** condition. Fig. 5 demonstrated the passivation agent concentration optimized for the minimum dishing performance. Over 6% passivation agent concentration, the dishing was achieved to the minimum level (<30 nm) for 180-μm square copper pad. However, over-dosage of the passivation agent in the slurry declined the removal

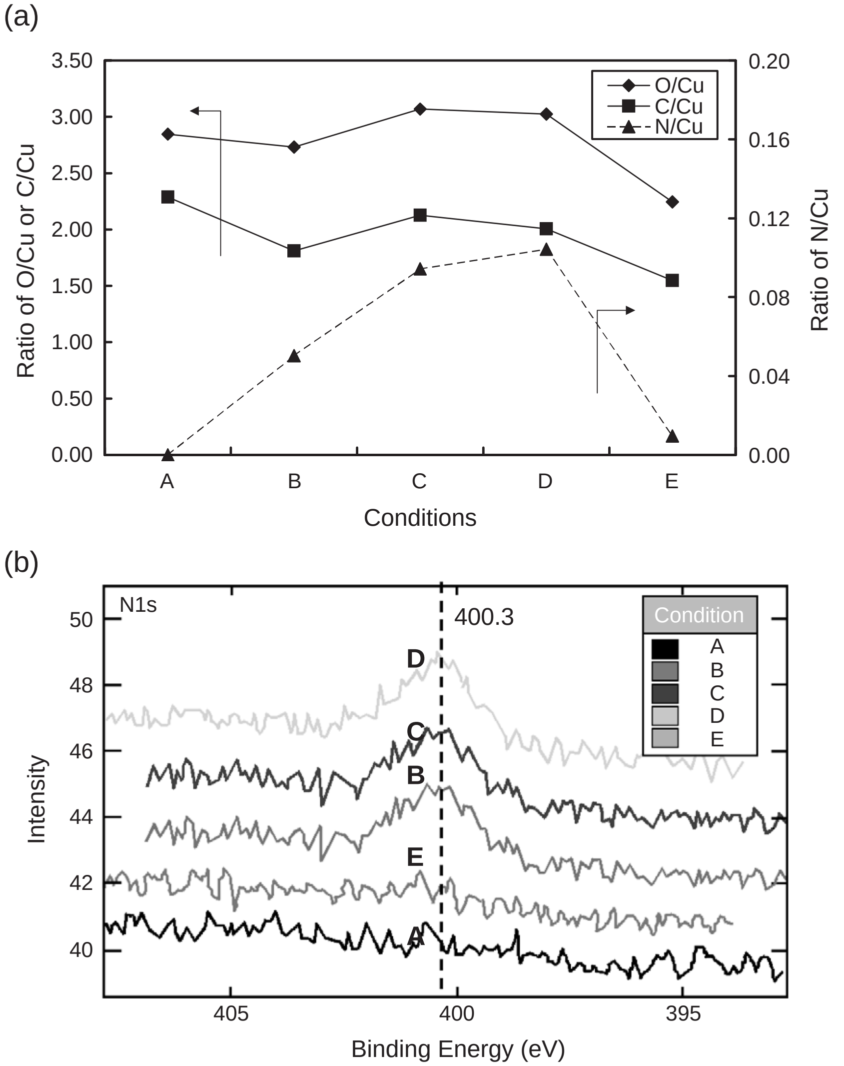

Fig. 4. XPS analysis for surface elements after various different copper slurry polishing conditions*: (a) comparison of the concentration ratio between C, N, O to Cu, (b) C–N/N–H bonding spectra under various conditions. *(**A** was without passivation agent; **B–E** were all with passivation agent, where **B** is with 4 psi pressure; **C** is with 2 psi pressure; **D** is with 2 psi pressure and the concentration of passivation agent is twice of that in **B** and **C**, while **E** is with extra Ta polishing).

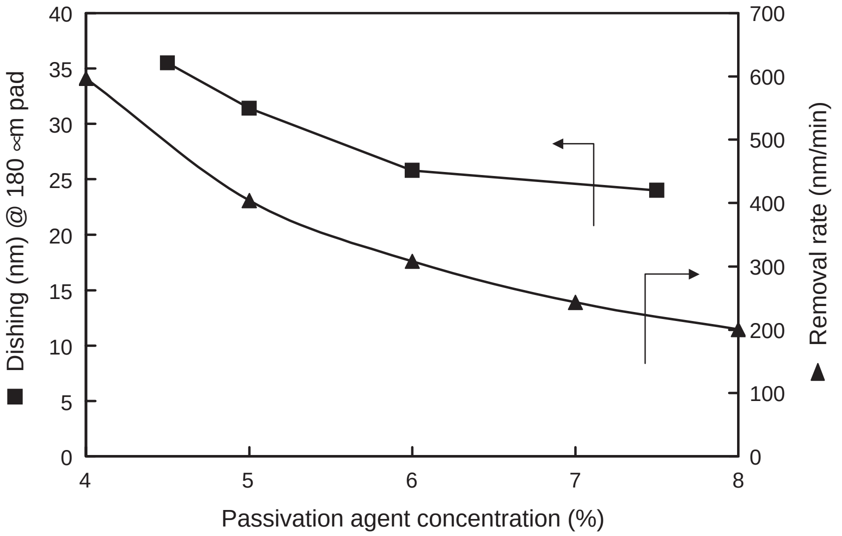

Fig. 5. The performance of removal rate and dishing of 180-μm square pad under various concentrations of the passivation agent.

rate, as shown in Fig. 5, due to the formation of thicker passivation film on the copper surface, corresponding to the **D** condition of Fig. 4(a). Moreover, more pasivation agent would cover at the low area of pattern, then reduce the pressure at the low area for the dishing reduction. This relation also induced the major reason of the non-Prestonian behavior. There was the optimal improvement for the dishing reduction in such a large pad from 150 nm dishing without passivation agent (Fig. 4's **A** condition) to <30 nm dishing with passivation agent (Fig. 4's **C** condition). Hence, the passivation agent played a critical role in reducing the dishing dependency on the pattern density via the non-Prestonian polishing behavior.

Through the passivation agent into the copper polishing, the resistance of copper trenches was improved from over 30% deviation to less than 10% under the 10–80% range of pattern densities, even after the extra 10% Ta and oxide polishing, as seen in Fig. 6. The dishing level and pattern dependency were significantly reduced to achieve the overall planarization for the copper damascene process. In other words, such an overall planarization significantly released the overpolishing window of CMP to compensate high non-uniformity variation induced by the aging of the plating bath and the polishing pad. This method actually improved the product yield over 10% and the stress migration performance.

4. Conclusions

The implementation of the passivation agent in the copper polishing processes significantly reduced the dishing level from original >150 nm to <30 nm on 180-μm square solid copper pads. The reduction of the copper dishing amount showed a weak pattern independency for the resistance variation of different metal densities with different layouts. Especially, the copper removal of the new slurry with the passivation agent, composed of the azole components with long carbon chains, showed the non-linear (Prestonian) behavior with the polishing pressure. There

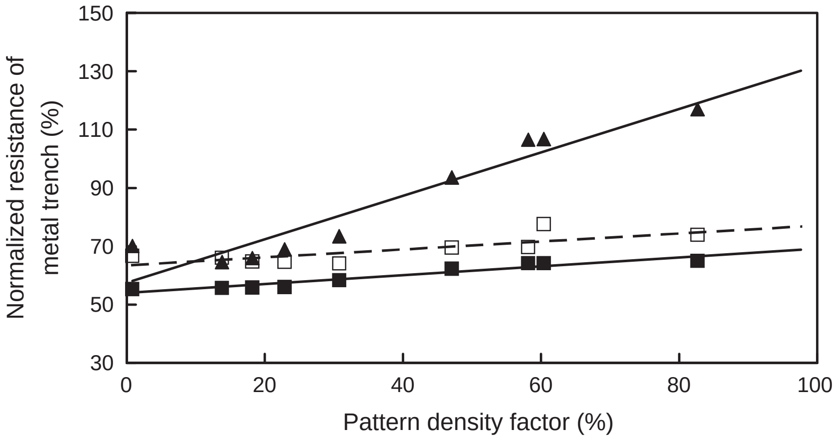

Fig. 6. Relationship between the resistance of copper trench and the pattern density under different copper polishing slurries: ▲ was the conventional copper slurry without passivation agent; ■ and □ were the same copper slurry polished with passivation agent, but □ with extra 10% Ta and oxide polishing.

was a trade-off between the dishing reduction and removal rate with increasing the passivation agent. Finally, the novel slurry solutions of the copper CMP processes achieved the overall planarization, the yield improvement of over 10%, and the better process reliability.

Acknowledgement

The authors gratefully acknowledge the financial support of National Science Council (NSC) of Taiwan for this research project under Contract No. NSC92-2216-E-006-030.

References

[1] P.C. Andricacos, C. Uzoh, J.O. Dukovic, J. Horkans, H. Deligianni, J. Res. Dev. 42 (1998) 567.
[2] J.R. Lloyd, J.J. Clement, Thin Solid Films 262 (1995) 135.
[3] C.K. Hu, B. Luther, F.B. Kaufman, J. Hummel, C. Uzoh, D.J. Pearson, Thin Solid Films 262 (1995) 84.
[4] Q. Luo, S. Babu, J. Electrochem. Soc. 147 (2000) 4639.
[5] S.C. Chang, J.M. Shieh, B.T. Dai, M.S. Feng, J. Vac. Sci. Technol., B 20 (6) (2002 (Nov./Dec.)) 2295.
[6] Y.H. Im, M.O. Bloomfield, S. Sen, T.S. Cale, Electrochem. Solid-State Lett. 6 (2003) C42.
[7] V.H. Nguyen, R. Daamen, H.V. Kranenburg, P. van der Velden, P.H. Woerlee, J. Electrochem. Soc. 150 (2003) G689.
[8] Y. Morand, Microelectron. Eng. 50 (2000) 391.
[9] J.B. Chiu, C.C. Yu, S.H. Shen, Microelectron. Eng. 65 (2003) 345.
[10] E.G. Colgan, Thin Solid Films 262 (1995) 120.
[11] Y. Cao, P. Taephaisitphongse, R. Chalupa, A.C. West, J. Electrochem. Soc. 148 (2001) C466.
[12] Q. Luo, S. Ramarajan, S.V. Babu, Thin Solid Films 335 (1998) 260.
[13] A.T. Al-Hinai, K. Osseo-Asare, Electrochem. Solid-State Lett. 6 (2003) B23.
[14] R. Carpio, J. Farkas, R. Jairath, Thin Solid Films 226 (1995) 238.
[15] S. Aksu, L. Wang, F. Doyle, J. Electrochem. Soc. 150 (2003) G718.
[16] T. Matsuda, H. Takahashi, M. Tsurugaya, K. Miyazaki, T.K. Doy, M. Kinoshita, J. Electrochem. Soc. 150 (2003) G532.
[17] J. Hernandez, P. Wrschka, G.S. Oehrlein, J. Electrochem. Soc. 148 (2001) G389.
[18] J. Luo, D.A. Dornfeld, IEEE Trans. Semicond. Manuf. 14 (2) (2001 May) 133.