Study on electrochemical mechanical polishing process of copper circuit on PCB

Nadiia Kulyk*, Chang Yong An*, Jung Hoon Oh*, Sung Min Cho*, Changsup Ryu,
Young Kwan Ko**, and Chan-Hwa Chung*,†**

*School of Chemical Engineering, Sungkyunkwan University, Suwon 440-746, Korea
**Central R&D Institute, Samsung Electro-Mechanics Co., Ltd., Suwon 443-743, Korea

Abstract−As an alternative to conventional chemical mechanical polishing (CMP) for the planarization of copper layers on electronic circuits, the electrochemical mechanical polishing (ECMP) process in alkali-based solution was investigated in this work. The influence of the polishing pad materials on the polishing process was studied, and the hard polyurethane polishing pad was shown to eliminate the "dishing effect". The polishing conditions, such as the pad rotating speed, concentration of H_2O_2, and the amount of BTA additives were optimized to control the planarization performance. As a result, good planarization uniformity was obtained not only in small scale (30 μm) trenches but also in very large scale (a few mm) patterns with a single step ECMP process.

Key words: Electrochemical Mechanical Polishing, Copper, PCB, Planarization

INTRODUCTION

As an interconnect material in printed circuit boards (PCBs), copper has been used for decades because of its high electrical conductivity. The copper layer in PCBs has generally been fabricated by electroplating, and it is usually overgrown to ensure a good electrical connection [1]. The recently developed multilayered PCB structure needs a supplementary copper planarization process due to its higher integration. In the microelectronic industry, the chemical mechanical polishing (CMP) process is widely adopted to polish the overgrown Cu layer, in which various slurries, abrasives, and additives are used [1-20]. Recently, some problems and limitations of this process have been reported, such as scratches, stress cracking, and corrosion of the copper, which are commonly caused by abrasives and additives in the slurries [1,5,9,11,17,20].

More recently, as an alternative planarization process, electrochemical polishing (ECP) was introduced to overcome these problems. Using this process, it became possible to avoid corrosion, scratches, and cracking in the planarized surface, because it is performed in an alkali-based electrolyte and no abrasives are involved. The first alkali polishing electrolyte was proposed by J. M. Steigerwald et al. in 1995 [1], in which no additional voltage was applied to control the surface reaction. Later, the electrochemical mechanical polishing (ECMP) process was proposed [10,21-23], giving the opportunity to better control the surface reactions by applying a voltage drop between the sample and the polishing pad. To obtain uniform planarization on the Cu layer, the current density and the composition of the electrolyte should be optimized. In the case of relatively large patterns, however, it is difficult to overcome the "dishing effect" due to the non-uniform potential distribution and chemical etching effect [21,24].

In this work, we planarized the various pattern-width copper

layers on a PCB with the ECMP process in an alkali-based electrolyte that contains benzotriazole (BTA) as a surfactant. Especially, this BTA additive was used to overcome the "dishing effect" [22]. We attempted to optimize this ECMP process by controlling the process variables such as the current, pad rotation speed, polishing time, and composition of the alkali-electrolyte and additives. The surface of the planarized Cu layer was examined by scanning electron microscopy (SEM) and the chemical state of the copper layer was also monitored by x-ray photoelectron spectroscopy (XPS).

EXPERIMENT SETUP

The ECMP equipment setup used in our experiment is shown in Fig. 1 [23]. The 3 cm×3 cm PCB, onto which a 20 μm-thick copper layer was electroplated, was chucked onto the bottom of the head. The head chuck and pad are rotatable. The anodic potential was applied to the backside of the sample, and the cathodic potential was applied to the Pt electrode on the pad side. Two different kinds of polishing pads were installed: a soft polymer pad consisting of polyvinyl alcohols (PVAs) and a harder polymer pad made of polyurethanes. The rotation was set to a speed of 50-80 rpm in the same
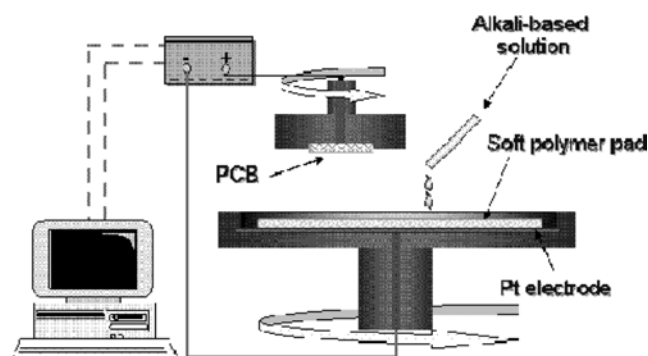

Fig. 1. The schematic diagram of ECMP equipment setup [27].

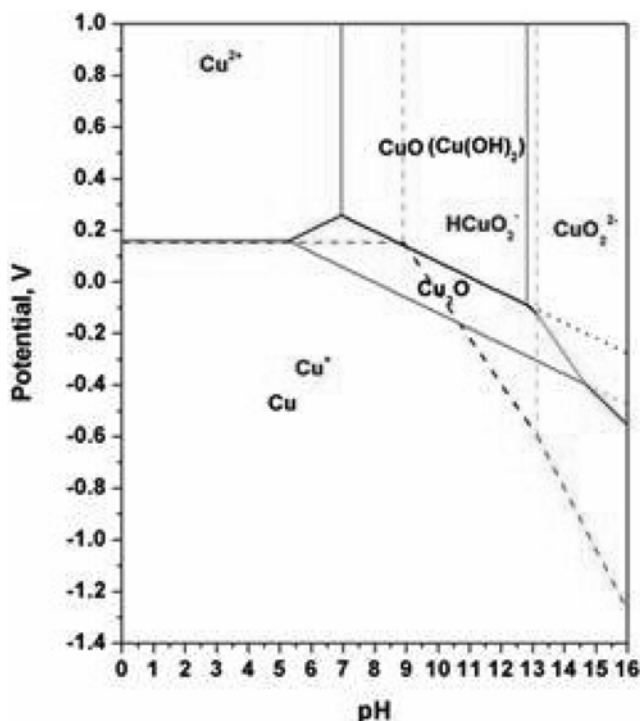†To whom correspondence should be addressed.
E-mail: chchung@skku.edu

Fig. 2. Pourbaix diagram of copper in Cu-H₂O system [25].

Fig. 3. Dependence of the pH value of the electrolyte on the H_2O_2 concentration.

direction for the sample head and the pad. The electrolyte was continuously supplied to the pad with a flow rate of 100 ml/min. A square-type periodic reverse pulsed voltage was applied during the EMCP process, in which the lowest and the highest voltage applied were −0.3 V (of cathodic voltage for 1 second) and 1 V (of anodic voltage for 1 second), respectively. The polishing process time was varied between 10 and 30 min, while the current density on the Cu layer was monitored in the range of −10 mA/cm² for cathodic voltage and 40 mA/cm² for anodic voltage for all experiment conditions with little variations.

The pH value of the electrolyte was controlled to be 14 or higher, because a higher polishing rate is to be expected at higher pH values according to the results of our previous study [23]. This high polishing rate is due to the formation of mechanically soft phases such as $Cu(OH)_2$, $HCuO_2^-$, and CuO_2^{-2} under anodic potentials. On the other hand, as shown in the Pourbaix diagram of Fig. 2, a hard phase of Cu_2O is mainly generated in the pH range of 6-14 at applied volt-
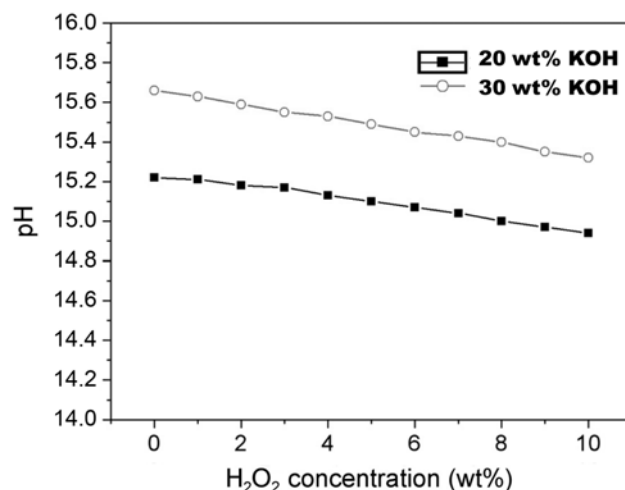
ages of −0.4-0.3 V [25].

The electrolyte was based on a 20-30 wt% solution of potassium hydroxide (KOH), and it contained 0.5-3 wt% of hydrogen peroxide (H_2O_2) solution and 0.005-0.02 M of BTA, which act as an oxidizer and an additive for uniformity improvement, respectively. Fig. 3 represents the dependence of the pH value on the concentration of H_2O_2 in the electrolyte. As expected, linear dependence was observed for both concentrations of KOH. To prevent the formation of hard Cu_2O phase, the pH value was carefully adjusted by adding phosphoric acid (H_3PO_4) and maintained at 14 or higher under an applied voltage of −0.4-1 V.

Two different Cu/PCB samples were used in this work. The first one has trenches of 150 μm ~ a few mm wide and 35 μm deep, while the second one has trenches of 30 μm ~ a few mm wide and 30 μm deep. Both of them are overfilled with copper by electrodeposition (cf. Fig. 4).

RESULTS AND DISCUSSION

1. Soft and Hard Polymer Pads

First, the influence of the pad materials on the morphology of the planarized samples was investigated, while the other experimental conditions were identical. Fig. 5 presents an SEM image of the
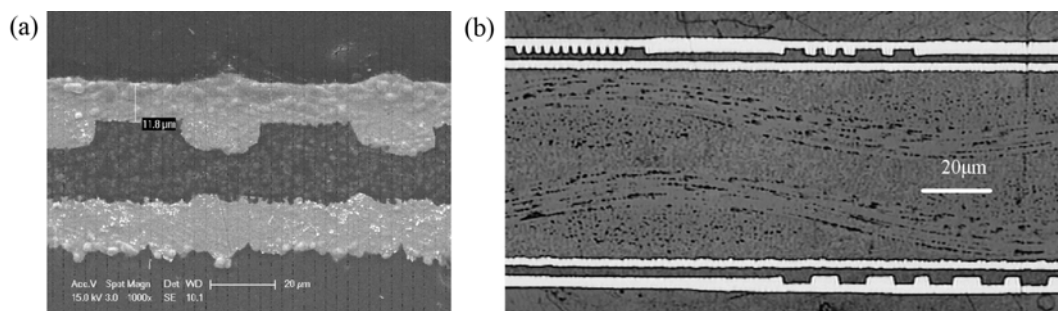

Fig. 4. Cross-sectional (a) SEM image of copper on PCB filled in narrow trenches and (b) optical microscopic image of copper layer filled in millimeter-scale trenches before ECMP process.
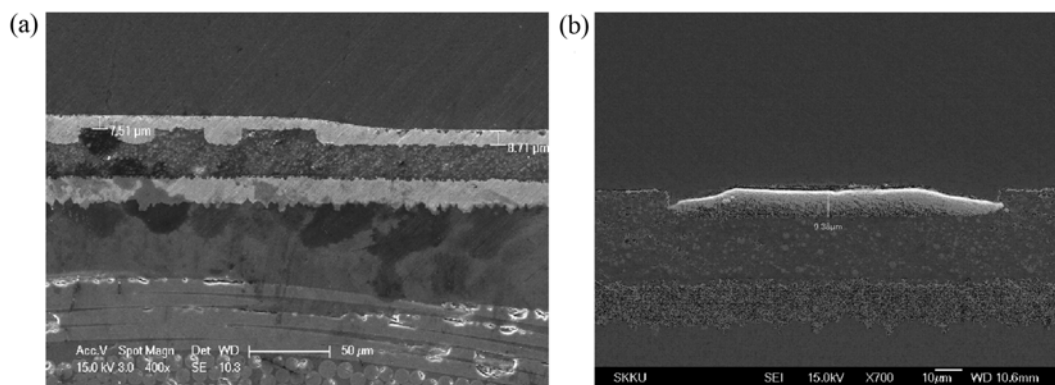
Fig. 5. Cross-sectional SEM images of planarized copper that shows (a) "dishing effect" and (b) "corner over-removal effect". A soft polyvinyl alcohol (PVA) pad was used in this ECMP process.
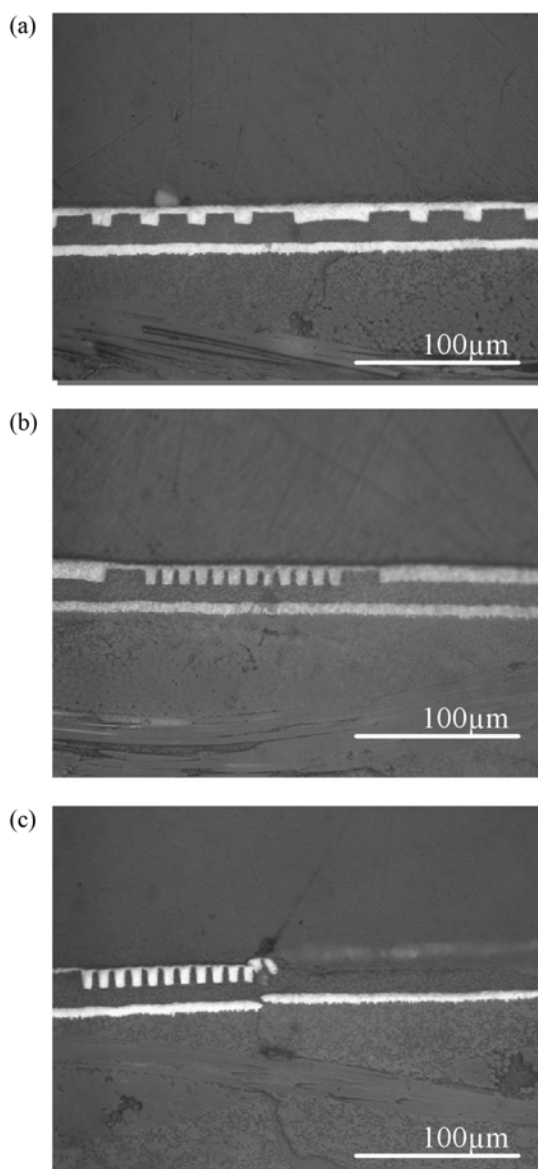

Fig. 6. Images of copper layer obtained after ECMP with hard polyurethane (PU) pad. The electrolyte contained 30 wt% KOH, 0.01 M BTA, and (a) 0.5 wt% H_2O_2, (b) 2 wt% H_2O_2, and (c) 3 wt% H_2O_2, respectively.

sample that was planarized on the soft polyvinyl alcohol (PVA) pad. Two kinds of non-uniformities of the planarization can be clearly seen in the image. The first one is the preferential removal of copper on the edges of the trenches (Fig. 5(a)) and the second one is the "dishing effect" in the center of the wider trenches (such as 100 μm to a few mm scale line widths). Both of these effects are caused by the soft polymer pad. We believe that this result can be explained as follows. The feature of "dishing effect" originates from the initial non-uniformities in the copper layer obtained after the electroplating process. When the copper layer is polished out all the way to the wafer level, the second effect starts to appear, namely the "corner over-removal effect". This effect is caused by the deformation of the soft pad on the copper-PCB board interface, which leads to a higher pressure of pad-copper layer interaction and, as a result, a higher polishing rate in the interface region.

On the other hand, such a preferential removal was not observed in the samples polished with the hard polyurethane (PU) pad. The surface of the hard pad is relatively rigid and cannot easily be deformed, which reduces the "dishing effect" and "corner over-removal effect". The SEM images of the samples planarized with the hard PU pad are shown in Fig. 6. They clearly show uniform planarization performance on the copper layer in both trenches of micrometer and millimeter scale. Due to its superior performance, the hard PU pad has been used in all the other experiments.

2. BTA Additive

It is known that benzotriazole (BTA) inhibits the corrosion of metals and reduces the "dishing effect" [5,11,20,26]. We investigated the influence of different concentrations of BTA in the electrolyte on the quality of the planarized film. It was found that by using 0.01-0.2 M of the BTA inhibitor, the planarization performance in our ECMP conditions was proper. On the other hand, the usage of a smaller amount (0.005 M) resulted in the fast corrosion of copper, which leads to fast polishing and the formation of non-uniform defects on the surface. Considering the planarization characteristics and removal rate of copper layer, the best result was obtained with a BTA concentration of 0.01 M.

3. H_2O_2

While keeping the concentrations of KOH and BTA in the electrolyte fixed, the amount of hydrogen peroxide solution was varied in the range of 5-3 wt%. The best result was observed when 2 wt% H_2O_2 solution was used. Fig. 7 shows the SEM images of the copper
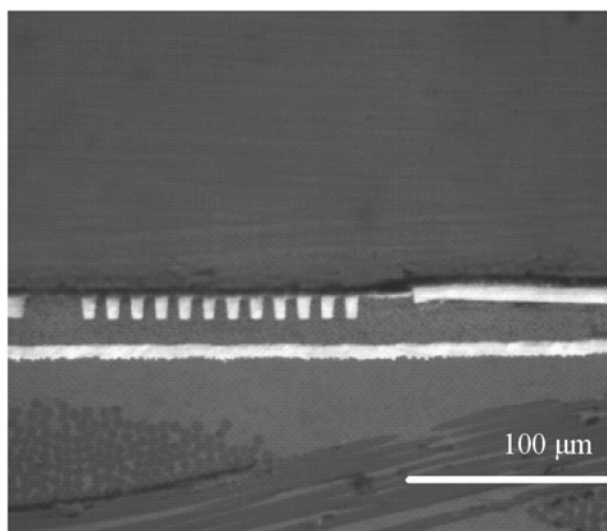
Fig. 7. Optical microscopic images of polished copper layers in micrometer-scale trenches and a millimeter-scale wider pattern obtained after ECMP process for 30 min with 30 wt% KOH electrolyte. The electrolyte contained 2 wt% H_2O_2 and 0.02 M BTA. A hard polyurethane (PU) polishing pad was used and rotated in 50 rpm.

layer obtained after ECMP under the following experimental conditions. Rotating speed of hard PU pad was 50 rpm. The polishing was performed for 30 min in 30 wt% KOH electrolyte containing 0.01 M BTA and (a) 0.5 wt% H_2O_2, (b) 2 wt% H_2O_2, (c) 3 wt% H_2O_2, respectively. One can see that a thick layer of copper has remained after the polishing process with 0.5 wt% H_2O_2, whereas the surface has been a little over-polished with the electrolyte of 3 wt% H_2O_2. When the sample was polished with the electrolyte containing 2 wt% H_2O_2, uniform planarization was obtained without "dishing effect" or other substantial defects. We would like to point out that such a uniform planarization has been performed not only in small scale (30 μm) trenches but also in very large scale (a few mm) patterns with a single step planarization process, which is important for practical application for industrial fabrication process.

To analyze the chemical mechanism on copper corrosion in different electrolytes, XPS analysis was performed. Figs. 8(a), (b), (c) present the short range XPS spectra of Cu 2p3/2, which have been obtained after the ECMP in electrolytes with H_2O_2 solution concentrations of 0.5 wt%, 2 wt%, and 3 wt%, respectively. The KOH concentration was 30 wt% and the BTA concentration was 0.1M, while the pH value was 14. It can be seen that the relative intensity of the Cu 2p3/2 peak from the Cu(OH)$_2$ phase becomes higher with increasing H_2O_2 concentration. The increase of Cu(OH)$_2$ phase results in higher polishing rate in our experiment condition. In this ECMP process, the production of a layer of soft Cu(OH)$_2$ phase on the copper surface is a decisive factor to improve planarization performance.

CONCLUSION

The electrochemical mechanical polishing (ECMP) process was investigated in detail for the purpose of improving the uniformity in planarization of the Cu layer on PCBs. The influence of soft polymer and hard polymer pads on the morphology of the planarized
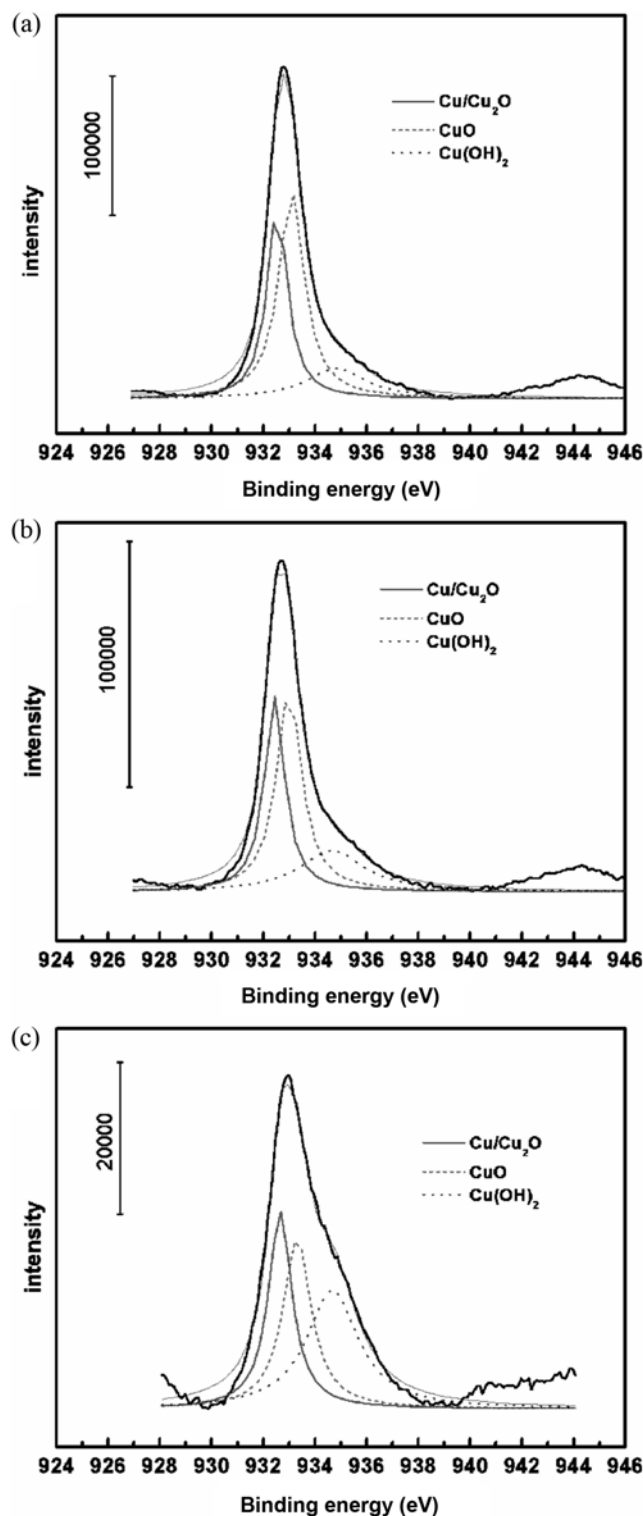

Fig. 8. The XPS spectra of Cu 2p3/2 obtained from copper layer after ECMP process in electrolytes containing (a) 0.5 wt% H_2O_2, (b) 1.5 wt% H_2O_2, and (c) 3 wt% H_2O_2, respectively.

copper surface was investigated. It was found that the "dishing effect" could be eliminated by using a hard polyurethane pad and BTA additive. Moreover, the composition of electrolyte was optimized to diminish the "dishing effect". XPS analyses were also performed and we found that the polishing rate is increased with production

of Cu(OH)$_2$ on copper layer by applying anodic potential in alkaline electrolyte of KOH containing H$_2$O$_2$. The planarized copper surface was uniform in thickness and free from significant defects in both micrometer and millimeter scale patterns.

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REFERENCES

1. J. M. Steigerwald, S. P. Murarka, R. J. Gutmann and D. J. Duquette, *Materials Chemistry and Physics*, **41**, 217 (1995).
2. R. Carpio, J. Farkas and R. Jairath, *Thin Solid Films*, **266**, 238 (1995).
3. Z. Stavreva, D. Zeidler, M. Plotner and K. Drescher, *Applied Surface Science*, **91**, 192 (1995).
4. M. Fayolle and F. Romagna, *Microelectronic Engineering*, **37-38**, 135 (1997).
5. M. T. Wang, M. S. Tsai, C. Liu, W. T. Tseng, T. C. Chang, L. J. Chen and M. C. Chen, *Thin Solid Films*, **308-309**, 518 (1997).
6. Z. Stavreva, D. Zeidler, M. Plotner, G. Grasshoff and K. Drescher, *Microelectronic Engineering*, **33**, 249 (1997).
7. Z. Stavreva, D. Zeidler, M. Plotner and K. Drescher, *Applied Surface Science*, **108**, 39 (1997).
8. Z. Stavreva, D. Zeidler, M. Plotner and K. Drescher, *Microelectronic Engineering*, **37-38**, 143 (1997).
9. D. Ernur, S. Kondo, D. Shamiryan and K. Maex, *Microelectronic Engineering*, **64**, 117 (2002).
10. G. Xu and H. Liang, *Journal of Electronic Materials*, **31**, 272 (2002).
11. T.-H. Tsai and S.-C. Yen, *Applied Surface Science*, **210**, 190 (2003).
12. K. Noh, N. Saka and J. H. Chun, *CIRP Annals - Manufacturing Technology*, **53**, 463 (2004).
13. V. H. Nguyen, R. Daamen and R. Hoofman, *Microelectronic Engineering*, **76**, 95 (2004).
14. T. Du, A. Vijayakumar and V. Desai, *Electrochimica Acta*, **49**, 4505 (2004).
15. P. Bernard, P. Kapsa, T. Coude and J. C. Abry, *Wear*, **259**, 1367 (2005).
16. K. W. Chen, Y. L. Wang, C. P. Liu, L. Chang and F. Y. Li, *Thin Solid Films*, **498**, 50 (2006).
17. W. Che, A. Bastawros, A. Chandra and P. M. Lonardo, *CIRP Annals - Manufacturing Technology*, **55**, 605 (2006).
18. Y. Wang and Y. Zhao, *Applied Surface Science*, **254**, 1517 (2007).
19. Y. N. Prasad and S. Ramanathan, *Electrochimica Acta*, **52**, 6353 (2007).
20. H. Lee, B. Park and H. Jeong, *Microelectronic Engineering*, **85**, 689 (2008).
21. P. C. Goonetilleke and D. Roy, *Materials Chemistry and Physics*, **94**, 388 (2005).
22. P. C. Goonetilleke and D. Roy, *Applied Surface Science*, **254**, 2696 (2008).
23. Y.-J. Oh, G.-S. Park and C.-H. Chung, *Journal of the Electrochemical Society*, **153**, G617 (2006).
24. S. Sato, Z. Yasuda, M. Ishihara, N. Komai, H. Ohtorii, A. Yoshio, Y. Segawa, H. Horikoshi, Y. Ohoka, K. Tai, S. Takahashi and T. Nogami, in *Electron Devices Meeting, 2001. IEDM Technical Digest. International*, 441 (2001).
25. M. J. N. Pourbaix, *Atlas of electrochemical equilibria in aqueous solutions*, Pergamon Press, Oxford (1966).
26. Q. Luo, D. R. Campbell and S. V. Babu, *Thin Solid Films*, **311**, 177 (1997).
27. Y.-J. Oh and C.-H. Chung, *Thin Solid Films*, **515**, 2137 (2006).