Effect of colloidal silica and copper ions on PVA brush contamination during post-Cu CMP cleaning

Sanjay Bisht[1], Jerome Peter[1], Samrina Sahir[1], Satomi Hamada[2], Young Jung Kim[1], Tae-Gon Kim[1] and Jin-Goo Park[1]
[1]Hanyang University, Republic of Korea, jgpark@hanyang.ac.kr
[2]Ebara Corporation, Japan, hamada.satomi@ebara.com

INTRODUCTION

The stringent requirements to reduce the defectivity and contaminants from the wafer surface, several studies on post-CMP cleaning have been carried out in the literature [1–3]. Most of the studies focus on the effect of chemical delivery, post-CMP cleaning solution and the scrubbing parameters on particle loading and defects on the wafer surface. To meet the current cleaning requirements, it is important to understand the interaction of CMP residues with the PVA brush during the PVA brush scrubbing process. During the post-CMP cleaning process, the pH can affect the brush loading by altering the zeta potential of abrasives and inducing chemical interaction between the brush and the particles. Hence, the understanding of both the CMP residues and the cleaning chemistry during the scrubbing process is crucial to control and prevent defects generation during the post-CMP cleaning process.

The metal CMP slurry consists of a chelating agent, surfactant, abrasives, oxidants, and other additives. Due to the spherical shape, hardness, and stability, colloidal silica is mainly used as an abrasive in slurry preparation for metal and oxide wafer CMP. In post-CMP cleaning such as PVA brush scrubbing the contaminants are removed by the mechanical action of the PVA brush. The particles from the wafer surface are taken up by polyvinyl acetal (PVA) brush nodules due to direct contact with brush nodules and dislodging the contaminants from the substrate surface. However, due to the highly porous structure and hydrophilicity, the contaminants stick to the brush surface and contaminate the wafer in the next cleaning step [4].

PVA brush scrubbing is considered the most effective method to remove these contaminants. Silica particle adhesion on brush surfaces has been studied in the literature with the effect of brush rotation speed, wafer pressure, and friction force analysis [5–7]. However, the physical or/and chemical interaction between brush and particles has not been studied so far. In our experiment, the interaction between colloidal silica and brush at various pH conditions was studied. The interaction between copper ions, colloidal silica, and brush surface was studied for the first time, focusing more on brush loading and cross-contamination.

The adsorption of copper ions on the silica particles can affect the chemical interaction and the adhesion force [8,9]. The concentration of Cu ions also seems to play a significant role in brush loading, i.e., the brush contamination level was drastically increased with an increase in copper ion concentration. This study focuses on the challenges in brush loading for metals post-CMP cleaning for the copper wafer. Our primary concern is the effect of copper ions on colloidal silica after CMP and during the cleaning process. The adsorption of copper ions on the silica particles can alter the surface chemistry of abrasives due to physical and chemical interaction resulting in stronger adhesion with the PVA brush. These contaminants can adhere strongly to PVA brush causing severe brush loading and scratch formation on the wafer surface

BACKGROUND

The Cu post-CMP cleaning process consists of acidic and alkaline chemicals for removing abrasives such as silica, CMP residues like CuO particles, organic residues, and pad debris. The ring-type scratch formation on the copper substrate during the cleaning process is a well-known phenomenon, but no study claims the real cause of scratch formation. The formation of aggregates due to the interaction of colloidal silica and CuO particles with a change in the pH of the cleaning solution was explored by Ping *et al* [10]. Kim *et al.* observed the ring-type scratch formation during Cu post-CMP cleaning, mainly because of the low chemical delivery, less organic residue dissolution, and the hydrophobic nature of residue induces direct contact between wafer and brush [11]. Several cleaning chemicals based on alkaline and acidic cleaning solution are employed to prevent particle and scratch formation [12,13]. These defects can be controlled by

either reducing the post-CMP residues or selecting the proper cleaning solutions. However, developing a brush conditioning solution to prevent particle loading and control cross-contamination can overcome such defects of post-CMP cleaning.

EXPERIMENTAL

The brush contamination level was studied using the dipping experiment at varying pH conditions, as depicted in Fig. 1. The colloidal silica with 20 wt.% concentration and 100 nm particle size were purchased from AceNanochem, Korea. The interaction between the brush and colloidal silica particles was studied using the dipping experiment. In the dipping experiment, the brush nodules of approximately 3 mm were cut from a commercial 200 mm PVA brush (AION Co. Ltd., Japan), followed by dipping in colloidal silica slurry diluted to 0.1 wt.% at three pH conditions (3, 7, and 11). The dipped samples were rinsed with DIW and dried in a vacuum oven at 50 ^{0}C for 24 h. To observe the effect of copper ions on brush loading, the brush samples were dipped in standard copper ions solution (ICP-MS standard solution), with varying concentrations (10-100 ppm) and 0.1 wt.% colloidal silica solution at different pH conditions. The copper adsorption inside the PVA brush was studied by dipping the brush nodules in copper ions solution with a concentration of 100 ppm at varying pH conditions. The samples were rinsed with DIW to observe the absorbed amount of copper inside the PVA brush. The morphology and the level of contamination in the brush nodules were examined through Field Emission Scanning Electron Microscopy (FE-SEM, S4700, Hitachi). The effect on particle size and electrostatic interactions at varying pH was measured using a zeta potential and particle size analyzer (ELS-Z, Otsuka Electronics, Japan). The concentration of copper ions (in ppm) was estimated using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES, Spectro Arcos) analysis.

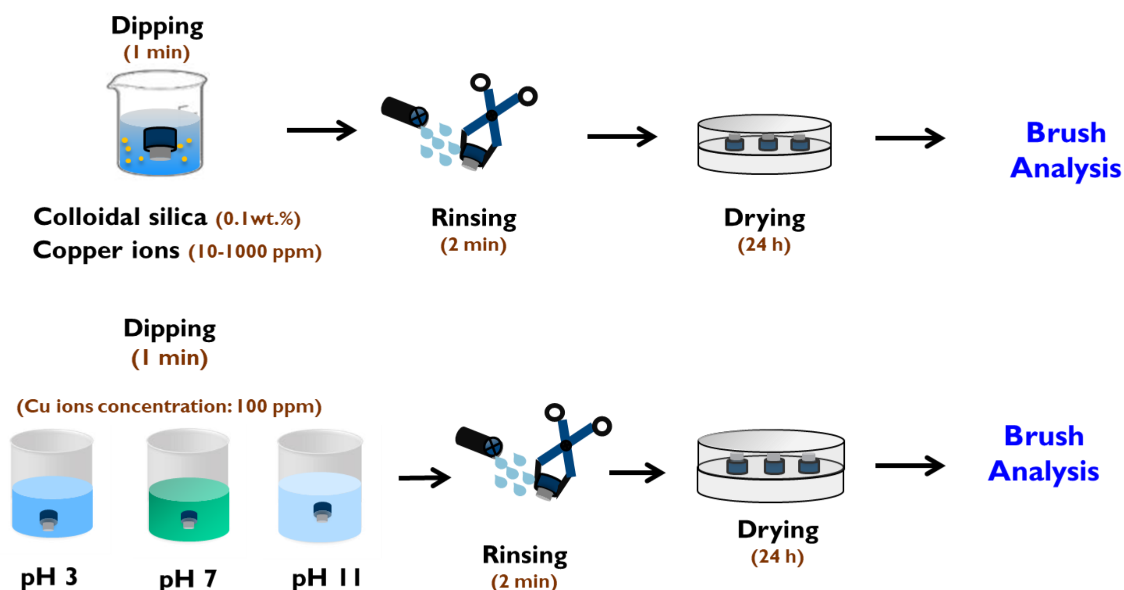

Fig. 1: Experimental procedure for brush contamination using the dipping method

DISCUSSION

1. Interaction between colloidal silica and PVA brush at various pH conditions in dipping experiment

The particle size distribution at different pH conditions was evaluated to confirm the stability of colloidal silica slurry. The average particle size as shown in Fig. 2(a) for the slurries was 140±5 nm at different pH conditions with no particle agglomeration. Thus all slurries were found to be stable at all pH conditions. The zeta potential values of colloidal silica slurry are all negative, as shown in Fig. 2(b). As compared to the zeta potential value of PVA brush at the same pH, the net interaction force between particles is repulsive for pH

greater than 7. As the pH increases, more repulsive forces act between the colloidal silica and brush surface, and we observed minimal brush loading, as depicted from FE-SEM images in Fig. 3. However, at pH 3, we observed high brush loading, which can be explained by attractive electrostatic interaction between the brush and silica particles. The isoelectric point of colloidal silica is between 2-3; at this pH, more hydroxyl groups are present on the silica surface. These groups can also form hydrogen bonding with the brush surface, thus increasing the brush loading.

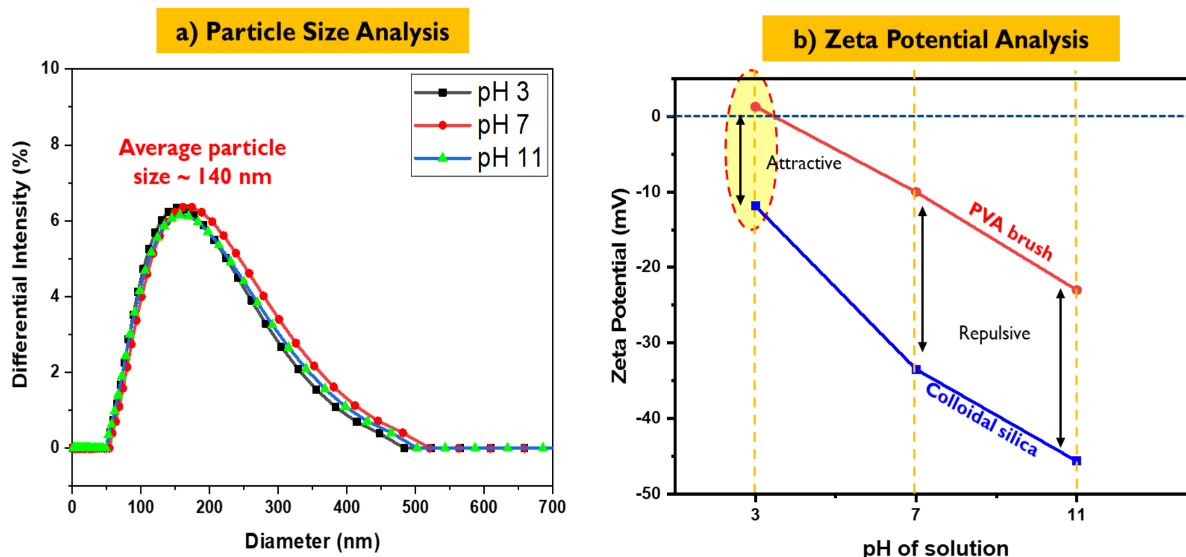

Fig. 2: (a) Particle size distribution of silica slurry at different pH (b) Zeta Potential of silica slurry and PVA brush at different pH conditions

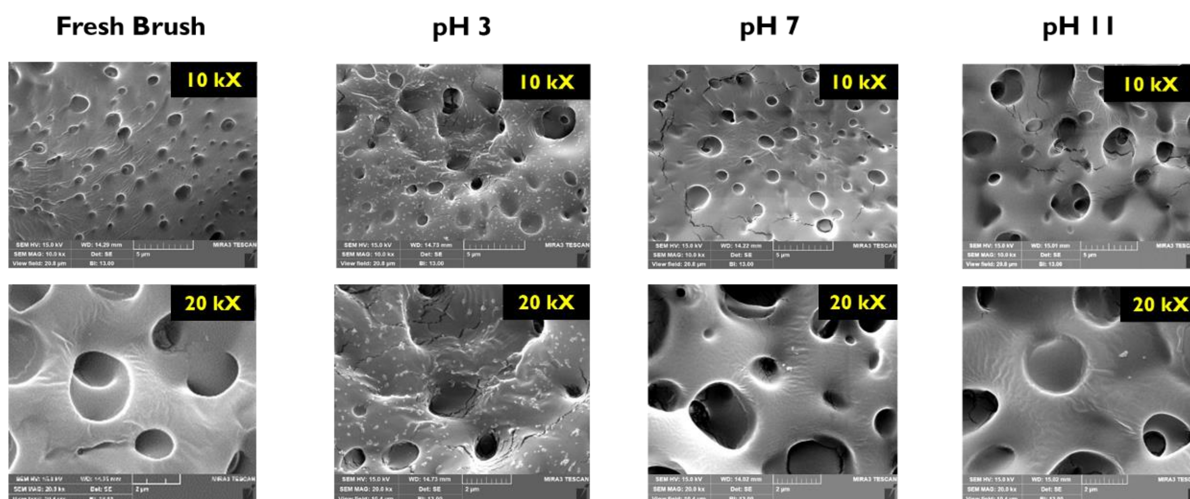

Fig. 3: Colloidal silica loading to PVA brush at different pH conditions

2. Interaction between metal ions and PVA brush at various pH conditions in dipping experiment

The adsorption of copper ions at different pH conditions with the brush was studied by dipping the brush nodules in Cu ions solution at different pH solutions. At pH 3, Cu ions exist as ions due to high stability in the acidic medium. However, some ions can interact with the brush surface and adsorption can occur. With the change in pH, the ions get converted into $Cu(OH)_2$, usually at the transition pH of 6 [14]. Gradually, the formation of CuO occurs with an increase in alkaline conditions. As shown in Fig. 3, the brush surface at pH

3 is clean due to the adsorption of Cu ions (no Cu by-products) on the brush surface. As the pH changes, the ions get converted to $Cu(OH)_2$, and we observed needle-like structures at pH 7 with high brush loading due to the formation of Cu by-products.

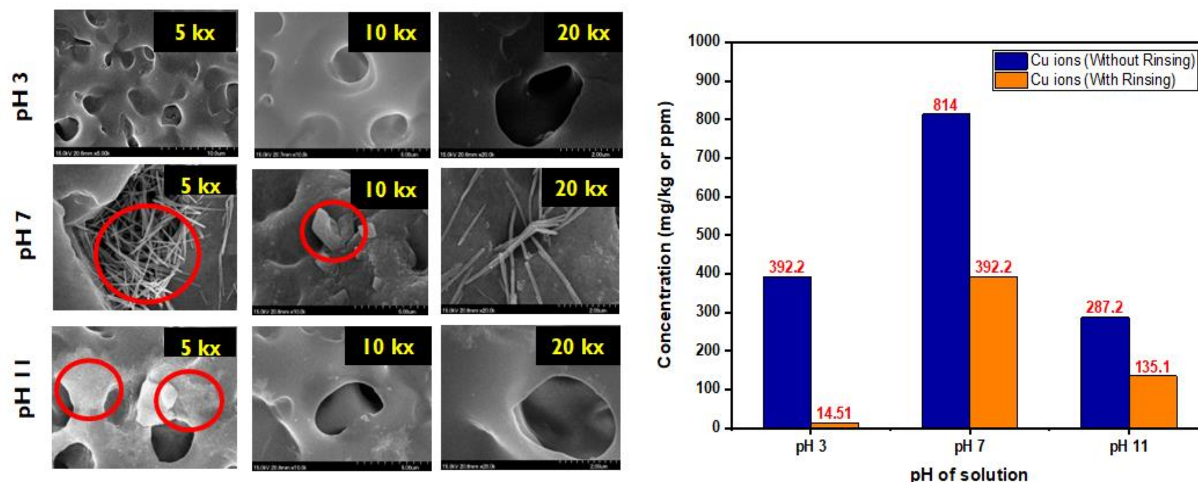

Fig. 4: (a) Brush loading by dipping in Cu ions solution at various pH and (b) ICP-AES analysis of Cu contaminated nodule with and without rinsing with DIW

The $Cu(OH)_2$ changes to stable CuO on further increasing the pH, and big particles are observed on the brush surface. The ICP-AES analysis of Cu-contaminated nodules shows a high concentration at pH 7, followed by pH 3 and 11, as shown in Fig. 4(b). On rinsing the contaminated nodule with DIW, the copper concentration reduces significantly for pH 3.

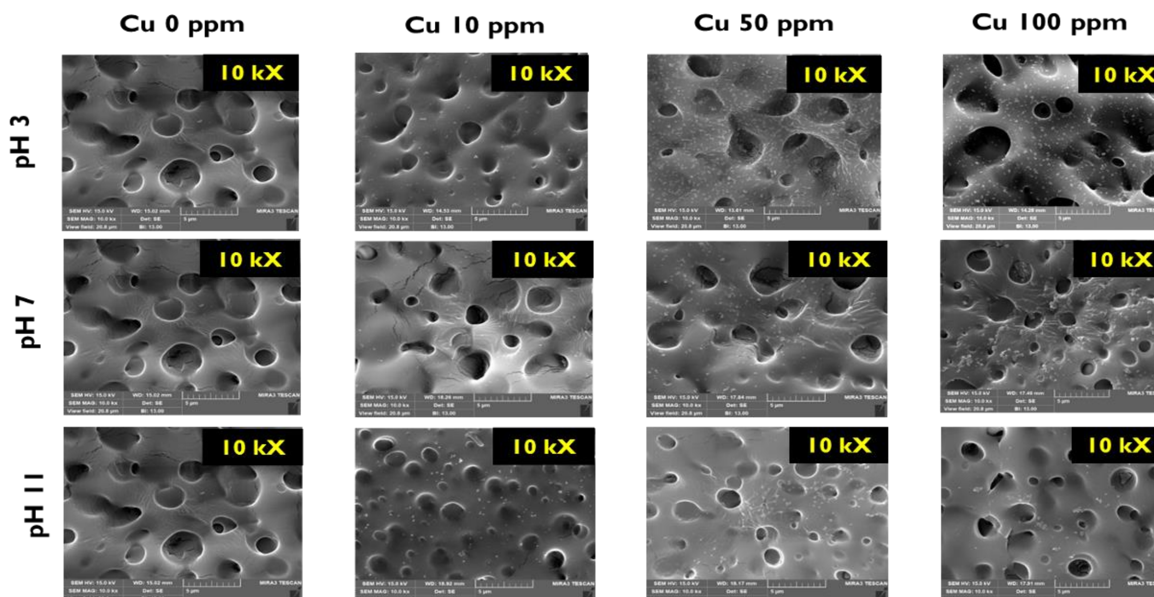

Fig. 5: Brush loading in the presence of copper ions at different pH conditions

However, for pH 7 and 11 contaminated nodules, a large amount of absorbed Cu was still inside brush nodules. This might be due to the formation of the Cu(II)-PVA complex formation inside the brush [15]. Hence, the brush could be severely contaminated with copper impurities in neutral and alkaline conditions.

3. Interaction between colloidal silica, metal ions, and PVA brush at various pH conditions in dipping experiment.

The effect of colloidal silica, copper ions, and PVA brush at different concentrations was studied using the dipping experiment. As shown in Fig. 5, the brush loading is observed to increase with the increase in Cu ions concentration for all pH conditions. High particle loading increases gradually from 10 ppm Cu ions concentration and becomes severe at Cu ion concentration higher than 100 ppm.

In the case of the brush dipped in only colloidal silica at pH 7 and 11, no contamination was observed but, in the presence of copper ions, significant brush loading appears on the brush surface. Hence, not only electrostatic interaction but chemical interactions might play a dominant role in brush loading in such conditions. This phenomenon can be explained by the destabilization of silica particles due to interaction with copper ions. The silica particles can interact with Cu ions via a metal bridging mechanism, also known as the inner-sphere mechanism as shown in Fig. 6 [9]. The adsorption of Cu ions onto the silica surface could result in a Cu(II)-silica complex that might have stronger interaction with the PVA brush.

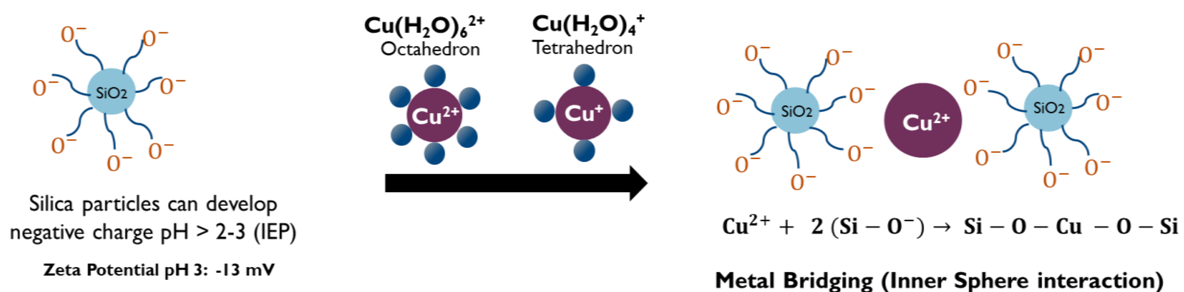

Fig. 6: Proposed Mechanism of the interaction of Cu ions and silica particles

CONCLUSIONS

Our study discussed the interaction between silica and copper ions and its impact on PVA brush loading using FE-SEM, zeta potential, DLS analysis and ICP-AES. The brush loading in presence of only silica was high at pH 3 compared to other pH conditions. The brush loading was also affected by the presence of copper ions in the slurry. With the increase in copper ions concentration, brush loading was significantly increased. The study also shows that particle formation can also take place without the presence of abrasives. Cu ions loading can occur inside the PVA brush at pH >7. Hence, it is essential to understand the chemical interaction between the copper ions, silica, and brush surface to prevent high brush loading during copper post-CMP cleaning.

REFERENCE

[1] J.G. Park, A.A. Busnaina, Adhesion and removal of silica and alumina slurry particles during Cu CMP process, Proc. - Electrochem. Soc. 26 (2003) 312–320.

[2] X. Liu, Y. Liu, Y. Liang, H. Liu, Z. Zhao, B. Gao, Effect of slurry components on chemical mechanical polishing of copper at low down pressure and a chemical kinetics model, Thin Solid Films. 520 (2011) 400–403. https://doi.org/10.1016/j.tsf.2011.06.050.

[3] S.N. Ramakrishna, L.Y. Clasohm, A. Rao, N.D. Spencer, Controlling adhesion force by means of nanoscale surface roughness, Langmuir. 27 (2011) 9972–9978. https://doi.org/10.1021/la201727t.

[4] J.H. Lee, M.K. Poddar, K.M. Han, H.Y. Ryu, N.P. Yerriboina, T.G. Kim, Y. Wada, S. Hamada, H. Hiyama, J.G. Park, Comparative evaluation of organic contamination sources from roller and pencil type PVA brushes during the Post-CMP cleaning process, Polym. Test. 90 (2020) 106669. https://doi.org/10.1016/j.polymertesting.2020.106669.

[5] K. Xu, R. Vos, G. Vereecke, G. Doumen, W. Fyen, P.W. Mertens, M.M. Heyns, C. Vinckier, J. Fransaer, Particle adhesion and removal mechanisms during brush scrubber cleaning, J. Vac. Sci. Technol. B Microelectron. Nanom. Struct. 22 (2004) 2844. https://doi.org/10.1116/1.1815319.

[6] H.J. Kim, G. Bohra, H. Yang, S.G. Ahn, L. Qin, D. Koli, Study of the cross contamination effect on post CMP in situ cleaning process, Microelectron. Eng. 136 (2015) 36–41. https://doi.org/10.1016/j.mee.2015.03.033.

[7] M. Kobayashi, A. Takahara, Tribological properties of hydrophilic polymer brushes under wet conditions, Chem. Rec. 10 (2010) 208–216. https://doi.org/10.1002/tcr.201000001.
[8] A. Marie, A.A. Atia, T.M. Elgogary, A.M. El-Nahas, Adsorption of Cu2+ and Mg2+ ions on silica gel derived from rice hulls ash: Experimental and theoretical studies, J. Theor. Comput. Chem. 18 (2019). https://doi.org/10.1142/S0219633619500263.
[9] N.P. Bansal, Influence of Several Metal Ions on the Gelation Activation Energy of Silicon Tetraethoxide, J. Am. Ceram. Soc. 73 (1990) 2647–2652. https://doi.org/10.1111/j.1151-2916.1990.tb06741.x.
[10] P. Hsu, R. Luo, P. Berar, Understanding the formation of circular ring defects in post-CMP cleaning, Solid State Phenom. 219 (2015) 153–156. https://doi.org/10.4028/www.scientific.net/SSP.219.153.
[11] H. Kim, S. Hong, Y. Jin, D.H. Lim, J. Kim, H. Hwang, T. Kim, Investigation of Copper Oxide Ring Formation during Post Chemical Mechanical Polishing Cleaning of Cu Interconnect, ECS J. Solid State Sci. Technol. 6 (2017) P542–P546. https://doi.org/10.1149/2.0191708jss.
[12] I.H. Sung, H.J. Kim, C.D. Yeo, First observation on the feasibility of scratch formation by pad-particle mixture in CMP process, Appl. Surf. Sci. 258 (2012) 8298–8306. https://doi.org/10.1016/j.apsusc.2012.05.044.
[13] T.Y. Kwon, M. Ramachandran, J.G. Park, Scratch formation and its mechanism in chemical mechanical planarization (CMP), Friction. 1 (2013) 279–305. https://doi.org/10.1007/s40544-013-0026-y.
[14] P. Gao, D. Liu, Facile synthesis of copper oxide nanostructures and their application in non-enzymatic hydrogen peroxide sensing, Sensors Actuators, B Chem. 208 (2015) 346–354. https://doi.org/10.1016/j.snb.2014.11.051.
[15] N. Hojo, H. Shirai, S. Hayashi, Complex Formation Between Poly(Vinyl Alcohol) and Metallic Ions in Aqueous Solution., J Polym Sci Part C, Polym Symp. 307 (1974) 299–307. https://doi.org/10.1002/polc.5070470135.

Corresponding Author:
Jin-Goo Park
Tel: +82 31-400-4080
E-mail: jgpark@hanyang.ac.kr
Department of Materials Science and Chemical Engineering,
Hanyang University, Ansan 15588, Republic of Korea