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# Cu-Oxide-Assisted Selective Pyrolysis of Organic Nanolayer on Patterned $SiO_2$−Cu Surface

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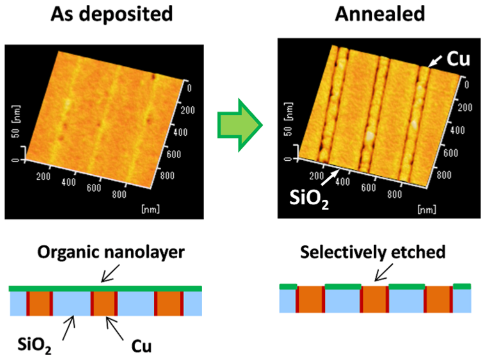
S *Supporting Information*

**ABSTRACT:** Organic nanolayers attract much attention for the isolation and adhesion promotion of the Cu line and insulator in Cu interconnection of microelectronic devices. This paper proposes a strategy for selective formation of adhesion nanolayer on the insulator surface with etching it on Cu surface by Cu-oxide-assisted pyrolysis. After deposition of a uniform polyelectrolyte layer on both $SiO_2$ and Cu surfaces, heat treatment at 350 °C in ambient nitrogen was applied. Then, a larger thickness decrease was observed on the polyelectrolyte layer on Cu when compared to that on $SiO_2$. According to the TDS and XPS analysis, the polyelectrolyte layer was relatively stable on $SiO_2$ up to the intrinsic decomposition temperature of the material, but on the Cu surface it decomposed to volatile small molecules at a lower temperature due to $Cu_2O$-assisted oxidization. This substrate dependent selective pyrolysis was examined for 100 nm width Cu lines and $SiO_2$ spaces, and then a patterned polyelectrolyte layer on the $SiO_2$ surface was obtained with a single nanometer scale edge resolution.



**KEYWORDS:** *selective formation, Cu interconnection, interfacial layer, polyelectrolyte, decomposition*

## INTRODUCTION

In nanotechnology science, control of the surface or interface of the inorganic materials, metals, and their composites has been investigated because they play a significant role in the materials' performance. In most studies, researchers tried to improve their performance by managing the oxidization state, defects, and impurity. Chemical modification by organic nanolayers such as the self-assembling monolayers (SAMs), molecular layer deposited nanolayers (MLDs),[1,2] and polyelectrolyte layer-by-layers (LbLs)[3] can significantly improve all of these materials' performance while adding various functionalities. For example, organic layers play an important role in the control of the dispersion of nanoparticles, stabilization of porous materials,[4,5] adhesion promotion of laminates of metals and/or inorganic films,[6,7] corrosion inhibition of metals,[8,9] wetting control of surfaces, etc. In advanced silicon-based electronic devices, organic nanolayers attract a lot of attention for the fine isolation of the Cu line and $SiO_2$-based interlayer insulator in a single nanometer scale resolution in order to keep its continuous improvement for device performance. In past studies, modification by organic layers was examined for application in Cu diffusion barriers,[10−13] Cu passivation,[8,14] atomic layer deposited barrier metal growth,[15,16] and protection of porous dielectrics from metal penetration or gas adsorption.[17,18] Almost all of these studies were devoted to the optimization of molecular structure for the single blanket film or laminated film performance. To apply these studies for the Cu interconnection integration process, a low-cost and nonlithographic patterning method of the organic nanolayer must developed.

To the best of our knowledge, selective formation or self-patterning is rarely reported for an organic thin film (caulk) derived from poly(*p*-xylene) precursor gas on micrometer scale patterned surfaces,[19] and resist layer on Cu surface from the growth of MLD organic film on $SiO_2$ surface by selective SAM treatment.[20] However, both methods can be realized for the specific chemical composition of precursor monomers, so it is not trivial. Our final goal is to make thin films on specific areas of the metal−insulator pattern with a more versatile method. To realize the selectivity for various kinds of organic materials, other methods must be developed. In this report, a simple and novel technique for the self-selective etching of organic nanolayers on Cu using Cu-oxide catalyzed thermal decomposition while keeping it constant on $SiO_2$ is discussed. Thermal degradation with the help of Cu-oxide is a well-known phenomenon as observed in olefin polymers,[21−25] and at the interface there is degradation of polyimides on Cu substrate.[26−29] However, this work is the first use of the phenomena in patterning of organic films.

In this work, branched poly(ethylene)imine (PEI) was examined as the nanolayer. PEI has the highest cationic density in existing polyelectrolytes, and it adsorbs on negatively charged −SiOH of $SiO_2$ substrates in solution phase via

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electrostatic attraction forces. It forms a uniform and defect-free single nanometer scale layer on a $SiO_2$ substrate even if its surface is textured. In principle, thanks to the dense amine group and blanket polymer structure, the following benefits can be obtained. PEI shows excellent adhesion promotion at the glass and metal interface. Compared to SAMs, PEI's deposition process with electrostatic adsorption is simple, and a high-quality film is reliably obtained.[3] In this paper, the thickness change of PEI on blanket $SiO_2$ and Cu against thermal treatment was measured by spectroscopic ellipsometer. The mechanisms of thermal properties were studied by thermal desorption spectrometry (TDS) and X-ray photoelectron spectrometry (XPS). Consequently, selective formation was examined on a patterned structure with 100 nm width Cu lines and $SiO_2$ spaces.

## EXPERIMENTAL PROCEDURES

A branched PEI with molecular weight (Mw) ∼50 000−150 000 in deionized water solution (pH ∼ 9.5) was spin coated on a $SiO_2$ or a Cu substrate. The naturally oxidized $SiO_2$ (2 nm thick) on a p-type single crystalline Si-substrate was cleaned by UV−$O_3$ for 5 min before PEI deposition. Its water contact angle was always <5°. Electroplated and chemical mechanically polished Cu (100 nm thick) on a 300 mm diameter Si-substrate was cut into a 2 × 2 $cm^2$ square coupon and kept in a $N_2$ purged box to prevent further oxidation before use. It was dipped into 1 N $H_2SO_4$ solution for 5 min to remove the surface protection layer (i.e., benzotriazole (BTA) treated), and rinsed with deionized water for 5 min. After that, PEI solution was spin coated immediately. With a change in the PEI concentration or spinning frequency (2000−4000 rpm), thickness can be controlled from subnanometer range to a few tens of nanometers range. After deposition of PEI solution on each substrate and rest time for 20 s as is, the sample was rotated to remove excess amount of PEI solution. All of these experiments were performed in clean room conditions. Without any specification, the samples were dried at 125 °C for 1 min on a hot plate to evaporate the water solvent for keeping the initial film thickness. After the sample was dried, PEI film became insoluble against short time water dipping or a rinse in a few tens of minutes. Baking at 150−350 °C was performed for 2 min in pure nitrogen at a reduced pressure (10 kPa) after being pumped down the chamber (0.7 Pa).

The PEI thickness was measured by a UV−vis spectroscopic ellipsometer (Semilab, PS1100). For PEI on $SiO_2$, ellipsometric parameters in 1.26−4.5 eV range were fitted by $SiO_2$/(naturally oxidized $SiO_2$)/Si optical model using WinElli-II program (Semilab). The refractive index of PEI was always assumed to be the same as that of $SiO_2$,[2] in order to obtain numerically stable results. For PEI on Cu, measured ellipsometric parameters in the 2.2−5.0 eV range were fitted by the $SiO_2$/Cu model. The optical parameters of Cu substrate were obtained by measuring bare wafer with the same heat treatment condition. Profiles of thermal decomposition were measured by a thermal desorption spectrometer (ESCO Ltd., EMD-WA1000W/S). The bare Cu substrate was annealed at 600 °C in pure $N_2$ (atmospheric pressure) for 60 min before the PEI deposition to suppress desorption of unspecified volatile species from itself. The surface temperature was corrected by the method of the ref 30. The ramp up rate was 30 °C/min. Surface atomic composition was evaluated by a spectrometer (KRATOS Analytical, Inc., ESCA3400, Mg K$\alpha$ source (200 W), $h\nu$ = 1253.6 eV). Photoelectron was collected at the normal takeoff angle (0°) from sample. Samples were kept in sealed clean box purged with $N_2$ to avoid adsorption of contaminant organics and to suppress the oxidization of Cu samples. Binding energy scale was corrected to Cu(0) peak position at 932.6 eV for Cu samples, and Si(0) peak at 99.5 eV for $SiO_2$ samples. For the quantification of each spectrum peak strength, Shirley background subtraction was performed. Surface morphology of patterned Cu line and $SiO_2$ space wafer was measured by an atomic force microscope (AFM) apparatus of Hitachi High Technologies (SPA400) in dynamic force microscope mode.

## RESULTS AND DISCUSSION

PEI not only adsorbs on $SiO_2$ via electrostatic force between protonated amine groups and deprotonated silanol groups ($SiO^-$), but also adsorbs on Cu via polychelation between amine groups and Cu.[31] The Cu-oxide-assisted selective thermal decomposition of PEI on Cu substrate was examined by baking the blanket PEI/$SiO_2$ and PEI/Cu samples at 350 °C. Figure 1 shows the PEI thickness on $SiO_2$ or Cu after baking at 350 °C under $N_2$ as a function of the thickness before the baking (which was dried at 125 °C). As PEI is deposited, PEI absorbed on both substrates to a similar thickness with the same deposition condition. Drying did not affect thickness. After baking at 350 °C the PEI on $SiO_2$ decreased slightly against the thickness before the baking. The relation was described well by a linear equation $y = 0.85x - 0.75$, where $y$ denotes the thickness after baking and $x$ denotes the thickness before baking.

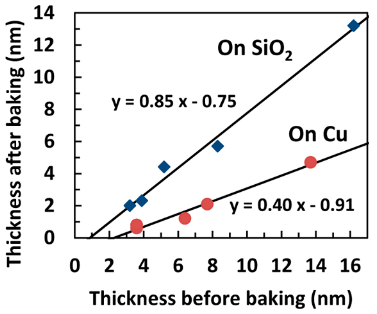

**Figure 1.** Relation between the PEI thickness on $SiO_2$ before baking at 350 °C and after baking (◆). The same relation for the PEI on Cu (●) is also plotted.

On the other hand, an enhanced decrease was observed on PEI/Cu after baking. The thickness relation was described well by an equation: $y = 0.40x - 0.91$. This relation for PEI/Cu had a larger offset than it did for PEI/$SiO_2$. As a result, a large contrast between the thickness of PEI/$SiO_2$ and that of PEI/Cu was obtained after baking at 350 °C in $N_2$ ambient. For example, PEI on $SiO_2$ decreased from 5.2 to 4.4 nm, but PEI on Cu decreased from 6.4 to 1.2 nm. In Figure 1, for thick PEI on Cu before baking (14 nm), the residue after baking was increased to 5 nm. The increased residue is thought to be the lack of oxygen which was necessary to prolong the Cu catalytic oxidation of polymer.[21] We tried to decrease the residue by introducing dilute $O_2$ to the baking chamber; however, it was difficult to control the pyrolysis of PEI on Cu with avoiding the severe oxidization of Cu substrate.

The effect of the baking on the chemical composition of PEI on $SiO_2$ was investigated by Fourier transformed infrared (FTIR) spectroscopy. In Figure 2 the small hump in 3200−3350 $cm^{-1}$ corresponds to the N−H stretching vibrations of primary and secondary amines.[32] The strong peaks in 2920−2802 $cm^{-1}$ correspond to the C−H stretch vibrations.[32] Each normalized spectrum intensity of the C−H stretch was constant against the baking at 350 °C. No other change was detected.

For the investigation of desorption behavior of PEI on both substrates a TDS analysis was performed. Figure 3 shows the TDS of PEI on $SiO_2$ and PEI on Cu. The initial PEI thickness was ∼20 nm to enhance the signal intensity. On the PEI/$SiO_2$,

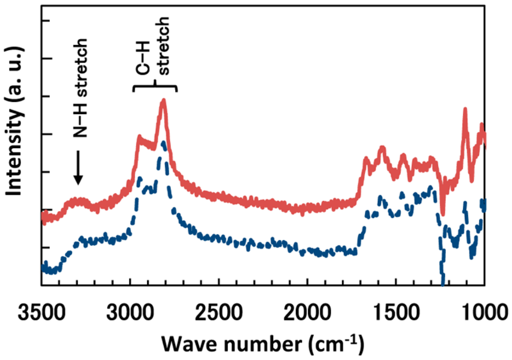

**Figure 2.** Fourier transform infrared spectra of PEI on $SiO_2$ baked at 150 °C (---), and PEI baked at 350 °C (—). Each intensity was normalized to each thickness (9–10 nm).

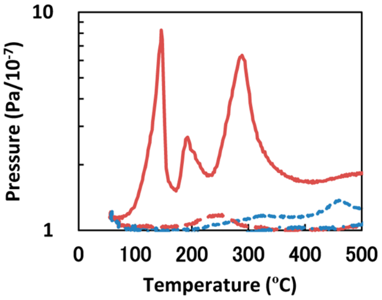

**Figure 3.** Thermal desorption spectra of ~20 nm thick PEI on $SiO_2$ (---) and Cu (—) with drying. The spectra of bare $SiO_2$ (– · –) and bare Cu (– – –).

no desorption was observed up to 315 °C. An apparent decomposition occurred at the 450 °C peak. Specific desorption masses were 2, 16, 18, 28, 30, 42, and 44. It was difficult to specify the molecular structure, but $H_2$, $CO_x$, $CH_x$, $C_2NH_x$, and NO were possible to be desorbed. On the PEI/Cu sample, the decomposition temperature decreased. At 145 °C a strong decomposition spectrum of mass 44 was measured, which corresponds to $CO_2$, $C_2NH_6$, and $CNOH_2$. At 190 °C a sharp peak was measured in the profile of mass 18 and 27, which correspond to $H_2O$ and HCN, respectively. At 285 °C the strongest peak was measured at mass 2, which corresponds to $H_2$. The spectrum intensity of reference bare $SiO_2$ was always negligibly small ($\sim 1 \times 10^{-7}$ Pa or less). That of reference bare Cu was also small ($\sim 1 \times 10^{-7}$ Pa). The small hump at 230 °C in bare Cu was due to desorption of $H_2$, $H_2O$, and $CO_2$. As a result, it was found that the PEI on Cu decomposed to volatile molecules at the lower temperature (145–285 °C) than the decomposition temperature of PEI on $SiO_2$ (315–425 °C). It has to be noted that the detailed decomposition behavior of PEI in TDS analysis and the decomposition behavior at Figure 1 were possibly different from each other because of the different baking condition (chamber pressure and temperature profile).

To validate the accelerated thickness reduction of PEI on Cu of Figure 1, XPS analysis was performed. Figure 4 shows XPS of PEI on $SiO_2$ and PEI on Cu samples. The initial thickness was 5–6 nm. Samples were baked at 150, 250, and 350 °C for 2 min, each under $N_2$ ambient. In the N 1s spectrum on $SiO_2$ (Figure 4a), the intensity was stable against the heat treatment, which was consistent with the thickness change of Figure 1. The other C 1s, O 1s, and Si 2p spectra after baking at 150–350 °C was were same as each other (Figure S1 for Si 2p spectra). The N 1s intensity on Cu (Figure 4b) was decreased with the increase of temperature and was almost eliminated at 350 °C.

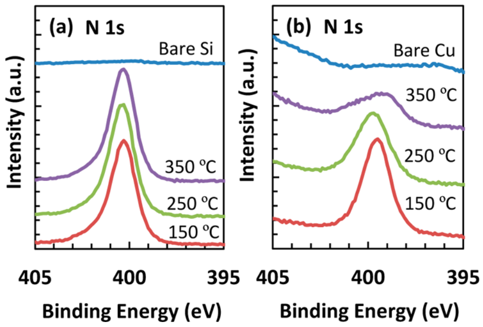

**Figure 4.** X-ray photoelectron spectra of (a) N 1s of PEI on $SiO_2$ and (b) Cu with different baking temperatures. All samples were not dried at 125 °C in air before the baking. Each intensity was shifted in the vertical axis for the plot.

Figure 5 shows the XPS and Auger spectrum of PEI coated Cu samples. In the Cu 2p spectrum (Figure 5a) a strong and sharp peak at 932.6 eV in Cu $2p_{3/2}$ band corresponds to the metallic Cu and $Cu_2O$. The peaks corresponding to CuO at ~933.6 and ~942 eV (shake up) were absent in all samples. The Cu $2p_{3/2}$ peak intensity was increased after the heat treatment and became comparable at 350 °C to that of the bare Cu. The inelastic mean free paths (IMFPs) of common organic polymers are 1.3–1.4 nm at this energy scale (~933 eV),[33,34] and then the film thickness of 350 °C baked film was calculated as ~1.0 nm.[35]

In the Cu 3p spectrum (Figure 5b) the peak at ~75 eV corresponds to the peak of Cu $3p_{3/2}$. The peak intensity was also increased after being baked at 350 °C. The IMFP of organic polymers at this energy is 3.6–3.7 nm. A consistent result (~1.0 nm) was also obtained from the Cu $3p_{3/2}$ peak intensity.[35,38] Therefore, the selective thickness reduction on Cu was also observed. On the pristine Cu surface, there were two kinds of Cu-oxide: cupric oxide (CuO) and cuprous oxide ($Cu_2O$). After the 1 N $H_2SO_4$ cleaning, the CuO was absent from the Cu 2p spectrum, but $Cu_2O$ still existed from the Cu $L_3VV$ Auger spectrum which should grow within the post-water rinse after the cleaning and/or PEI deposition as well as within short time air exposure. Interestingly, without the precleaning, intensity of the CuO was also reduced after PEI deposition. It may be due to the cleaning effect as observed in SAM treatment.[39] In Figure 5c, the heat treatment profile of Cu $L_3VV$ Auger spectrum is shown. The peaks at 916.5 and 918.5 eV are assigned to $Cu_2O$ and metallic Cu (Cu(0)), respectively.[9,39,40] With the increase of temperature, the peak intensity of $Cu_2O$ decreased compared to that of Cu(0), but the Cu(0) peak was enhanced. Because the CuO did not exist, $Cu_2O$ should promote the decomposition of PEI by its catalyzed oxidation. As a result, it was found that PEI on a Cu surface was selectively etched with the acceptable heat treatment condition at the microelectronic device manufacturing process (i.e., <350–400 °C). In addition, with this heat treatment pure Cu with the smaller amount of surface $Cu_2O$ (compared with the amount of $Cu_2O$ in bare Cu sample before baking) was obtained. This is beneficial for the following metallization process if the heat treatment is performed in the same chamber. In addition, we have to mention that all of the above results were obtained in high reproducibility.

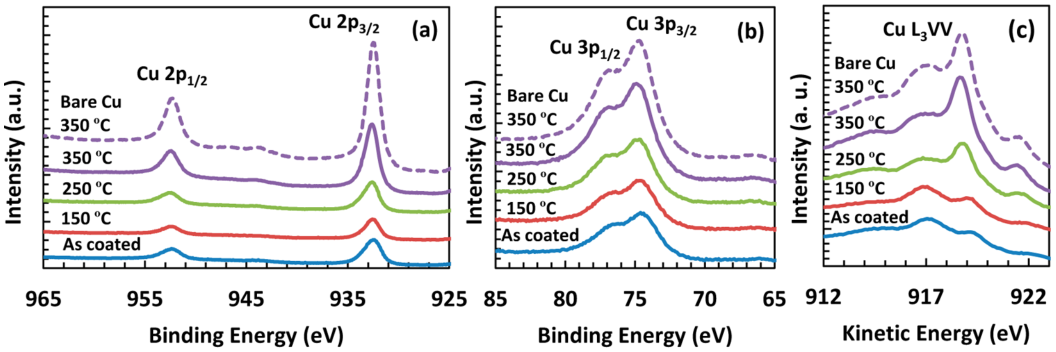

**Figure 5.** X-ray photoelectron spectra of (a) Cu 2p and (b) Cu 3p. (c) X-ray Auger spectrum of Cu $L_3VV$ for PEI on Cu with different baking temperatures. All samples including "as coated" were not dried at 125 °C in air.

Accelerated thermal oxidative degradation of polyolefin in the presence of Cu, Cu oxide, and Cu salt has been reported in previous works. Initial work for the catalytic degradations of bulk polyethylene and polypropylene with the dispersed Cu and Cu compounds was done by Hansen.[21] Allara and co-workers reported the interface initiated degradation of polyethylene film which intimately contact the Cu film.[22−25] There is also work on degradation of polyimide films on Cu.[26−29] In addition, the decreased thermal decomposition temperature of PEI (150−200 °C) which adsorbed on Cu nanoparticles compared to that of PEI (300−350 °C) was reported.[41] Their tendency is consistent with our result. In spite of these many works, there are only a few reports for the catalytic reaction mechanism of Cu[21,42] due to its complex reaction. According to the reports by Hansen, Jellinek, and co-workers,[21,42] the Cu ions (Cu(+1) and Cu(+2)) which are released from Cu-oxide such as $Cu_2O$ react with hydroperoxide (which is present as defective site) in the polyethylene and polypropylene to produce alkoxy radicals which propagate the oxidative chain reaction under air. As a result of the catalytic oxidation, bond breaking of polymer is promoted.

In our case for the PEI on Cu film, decrease of decomposition temperature compared with PEI on $SiO_2$ was also measured as shown above. Unfortunately, its mechanism is uncertain at present. However, speculations are considered as follows. Cu ion was detected from XPS spectrum. Figure 6 shows the Cu $2p_{3/2}$ spectrum of PEI/Cu and bare Cu samples where each intensity was normalized to unity in order to compare the spectrum shape. The spectrum shapes of blank Cu samples were the same independent of the baking temperature. On the other hand, the clear difference was found between the PEI/Cu and blank Cu samples. The higher energy component (broaden tale) was measured in PEI as coated, PEI after 150 °C baking, and PEI after 250 °C baking samples. The higher energy component belongs to Cu(+2). Interestingly, the Cu(+2) peak did not correspond to CuO because its specific satellite peak at ∼942 eV was absent in all PEI/Cu samples. This higher energy component possibly belonged to Cu carboxylate;[10] however, it was difficult to assert the presence of the Cu carboxylate salt from XPS C 1s or O 1s spectrum (not shown). The Cu ion may initiate the bond breaking of PEI by reacting with the contaminant −OOH site of PEI to produce volatile molecules such as $H_2O$, $CO_2$, and $H_2$ as well as $C_2NH_6$, CNH under 350 °C baking temperature. Importantly, in the PEI/Cu sample, the $Cu_2O$ was thought to be reduced to metallic Cu with the reaction products such as $H_2$ in the manner $Cu_2O + H_2 \rightarrow Cu + H_2O$. The reduction is thought to be dominated in the baking around 250−350 °C from Figure 5.

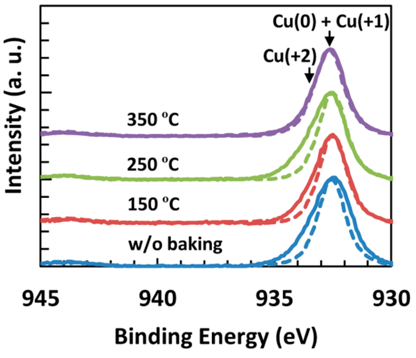

**Figure 6.** Cu $2p_{3/2}$ spectrum of bare Cu and PEI/Cu samples with different baking temperatures. Each spectrum after Shary background subtraction was normalized so the Cu $2p_{3/2}$ peak intensity became unity. Dashed lines represent the spectrum of the bare Cu sample, and solid lines represent those of PEI/Cu samples.

In the case of polyolefin, to prolong the Cu-catalyzed oxidation reaction, reoxidation of Cu or Cu(+1) with ambient $O_2$ is necessary.[21,42] Figure 7 shows the Cu XPS spectrum of bare Cu samples. In our experiment, oxidation of Cu was not promoted in the temperature range (150−350 °C) under pure nitrogen ambient with the absence of PEI. With samples undergoing 250 °C baking, all spectra were approximately the same. After 350 °C baking, the $Cu_2O$ was partially reduced, and the metallic Cu peak intensity increased from the Cu $L_3VV$ spectrum. This reduction may be assisted with the surface contaminant carbon which is frequently observed even with clean room conditions. Therefore, the oxygen source was restricted so that it was originally contained in the PEI/Cu samples in our experimental condition, and then the catalytic oxidation was thought to be limited.

The area selective etching of PEI on Cu was examined for the 100 nm width Cu lines and the 200 nm width $SiO_2$ space patterns. Figure 8 shows atomic force microscope images of the patterned wafers. After the deposition of PEI, both the Cu and $SiO_2$ surface were covered uniformly with PEI (Figure 8b). After samples were baked at 350 °C for 2 min, the Cu line and the PEI/$SiO_2$ space pattern were clearly observed with a single nanometer scale edge resolution as shown in Figure 8c. The surface morphology of $SiO_2$ space after the baking may indicate the existence of PEI.

As shown in Figure 9, after baking, the height difference of the $SiO_2$ surface relative to that of the Cu surface increased by

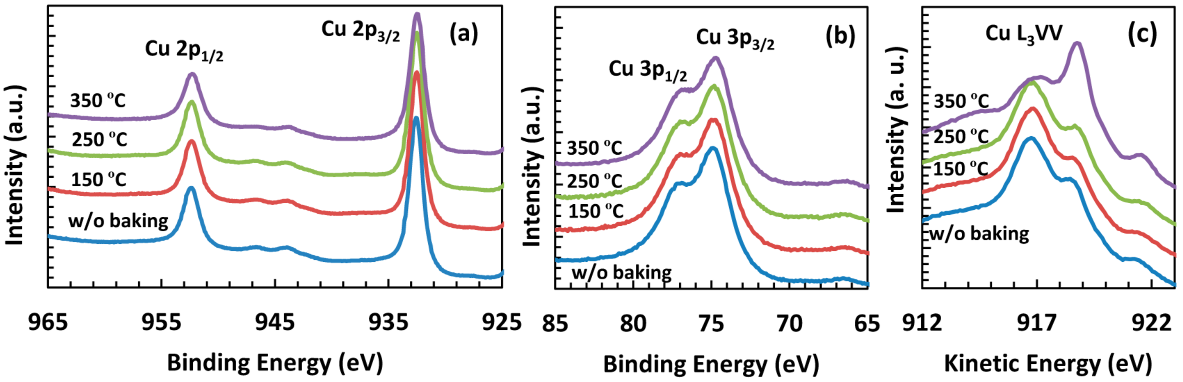

**Figure 7.** Cu 2p, Cu 3p, and Cu L$_3$VV spectra of bare Cu without baking and the same with baking at 150−350 °C for 2 min under pure N$_2$ (10 kPa). All samples including "w/o baking" were not dried at 125 °C in air.

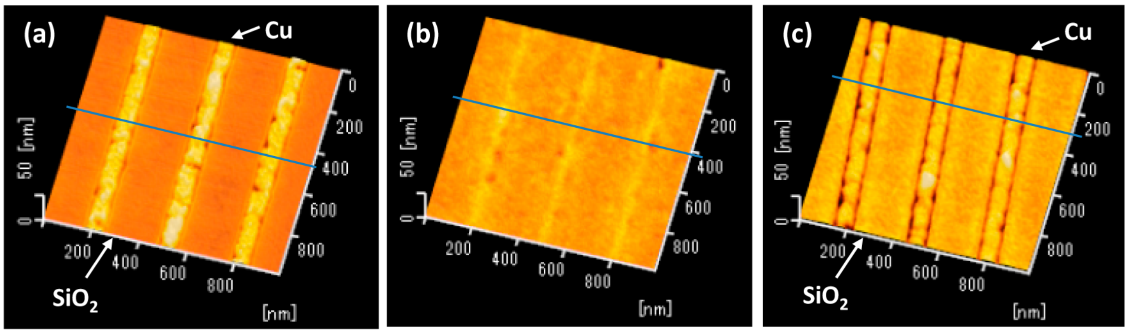

**Figure 8.** Atomic force microscopic image of the 100 nm width Cu line and 200 nm width SiO$_2$ space: (a) without PEI deposition, (b) with PEI deposition, and (c) after PEI deposition and baking at 350 °C. As a barrier for Cu diffusion into the SiO$_2$, 5 nm TaN and 8 nm Ta were embedded between these interfaces.

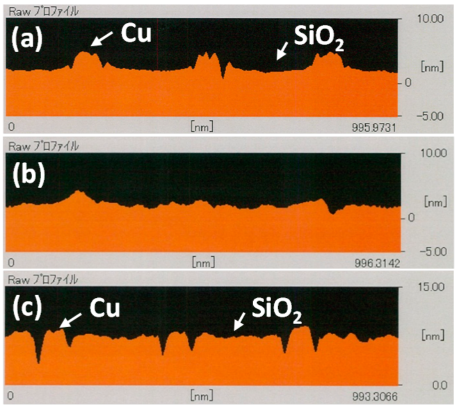

**Figure 9.** One-dimensional atomic force microscopic image across the 100 nm width Cu line and 200 nm width SiO$_2$ space along the cross sectional guide line which is depicted in Figure 8. Descriptions are the same as those in Figure 8.

~2 nm compared to that before the PEI deposition. This result may indicate that the selective etching of PEI on Cu surface was successfully achieved. This patterned structure was also measured in the other patterns such as the 100 nm Cu lines and the 100 nm SiO$_2$ spaces with the same edge resolution.

## ■ CONCLUSION

In conclusion, a new strategy for the area selective etching of an organic nanolayer on Cu surface while keeping it on SiO$_2$, which is applicable for multilevel Cu interconnections, has been shown. The PEI on the Cu surface was selectively decreased by heat treatment at 350 °C, while PEI on SiO$_2$ was relatively stable. It was also shown that the PEI on the Cu was thermally decomposed to volatile small molecules due to the acceleration by surface Cu$_2$O catalyzed oxidation. When the as coated PEI was sufficiently thin (<5 nm), the residue on Cu surface was decreased to ~1 nm. The PEI on Cu surface in a Cu interconnection was also successfully decreased after heat treatment at 350 °C. Our simple and novel technique is applicable for a variety of organic nanolayers on patterned Cu and dielectric surfaces by carefully selecting material, in which the intrinsic decomposition temperature of the material has to be larger than the process temperature but the decomposition temperature on the Cu substrate must be the smaller. This newly developed method will shed light on the continuous improvement of electronic devices.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b03835.

Si 2p spectra of PEI/SiO$_2$ samples after 150, 250, 350 °C baking showing tht they are identical to each other (PDF)

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### Notes

The authors declare no competing financial interest.

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