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Coupled self-assembled monolayer for enhancement of Cu diffusion barrier and adhesion properties†

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In this work, we have demonstrated chemically coupled (3-aminopropyl)trimethoxysilane (APTMS) and 3-mercaptopropionic acid (MPA) self-assembled monolayers (SAMs) to enhance the diffusion barrier properties against copper (Cu) as well as the adhesion properties towards SiO₂ and Cu electrode. The coupled-SAM (C-SAM) can attach to both Cu and SiO₂ strongly which is expected to enhance both the diffusion barrier and adhesion properties. A carbodiimide-mediated amidation process was used to link NH₂ terminated APTMS to COOH terminated MPA. The resulting C-SAM shows a low root-mean-square roughness of 0.44 nm and a thickness of 2 nm. Time-dependent dielectric breakdown (TDDb) tests are used to evaluate APTMS and C-SAM for their ability to block Cu ion diffusion. The average time-to-failure (TTF) is enhanced over 4 times after the MPA attachment, and is even comparable to TaN barriers. Capacitance–voltage (C–V) measurements are also conducted to monitor Cu ion diffusion. Negligible change in the flatband voltage and C–V curve is observed during the constant voltage stress C–V measurement. Enhancement of the adhesion properties are measured using four-point bending tests and shows that the C-SAM has a 33% enhancement in the adhesion properties between SiO₂ and Cu compared to APTMS. The C-SAM shows potential as an ultra-thin Cu diffusion barrier which also has good adhesion properties.

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1. Introduction

Copper (Cu) is the current mainstream multilevel interconnect material for back-end interconnect scaling in ultra-large-scale-integrated (ULSI) circuits due to its high electrical conductivity and electromigration resistance compared to aluminum (Al).¹ However, Cu is more diffusive than Al in silicon (Si) and silicon dioxide (SiO₂) which can create trap levels in the bandgap that degrade device performance.² Thus, the use of a diffusion barrier for Cu is required to prevent interdiffusion and undesired compound formation with Si, which can lead to device failures, and also promote adhesion to Cu–SiO₂

interfaces.^{1–5} Ta/TaN has been widely used for Cu interconnects due to its stable barrier and adhesion property.⁵ However, according to the International Technology Roadmap for Semiconductors (ITRS) report on 2012, the required barrier thickness for the line-width of 22 nm is less than 2 nm.⁶ Reducing the thickness of Ta/TaN has been a challenging task, as current Ta/TaN barriers suffer from high defect density and ineffective barrier at thicknesses less than 5 nm, which gives rise to the development of new types of diffusion barriers.⁵

Other types of diffusion barriers have been studied as a replacement for conventional Ta/TaN barriers. Self-forming diffusion barriers from CuMn alloys⁷ and seedless diffusion barriers using RuMo⁸ have been studied as alternatives; however, it is still difficult to obtain diffusion barriers under the thickness of 2 nm. Recently, graphene has been demonstrated as a diffusion barrier which shows outstanding performance with only 0.34 nm thickness.⁹ Nevertheless, it still lacks the process technology to grow or transfer high quality graphene to complicated structures. Moreover, the low adhesion between the graphene–Cu¹⁰ can lead to chemical mechanical polishing (CMP) failure commercially used in the dual damascene process.¹¹

Self-assembled monolayers (SAMs) are spontaneously formed two-dimensional structures^{12,13} that have been used to

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prevent wet chemical etching¹⁴ and oxidation in air¹⁵ due to their dense molecular packing. SAMs have also been used as a diffusion barrier for Cu diffusion and as an adhesion promoter by the selection of appropriate terminal groups that can immobilize Cu and bond with both Cu and SiO₂.^{16,17} The use of SAMs as diffusion barriers is of interest due to their few- or sub-nanometer thickness and the simple solution based processing techniques that can be used to form SAMs on complicated nanostructures.¹⁸ It has been found that (3-aminopropyl)trimethoxysilane (APTMS) which has a silane (–Si–) head group and amine (–NH₂) functional group is a promising candidate for diffusion barrier against Cu diffusion and adhesion promoter.^{19–21} However, the NH₂ group demonstrates reduced adhesion properties with Cu compared to the thiol (–SH) group which can also lead to lower Cu immobilization.

In this work, we demonstrate the surface chemical modification of APTMS to enhance the diffusion barrier properties to Cu and enhance the nano-adhesive properties of SAMs to both Cu and SiO₂. Selection of the molecule for APTMS enhancement requires several structural aspects, including reactivity with APTMS, thermal stability, and good adhesion of the terminal group to Cu. Therefore, 3-mercaptopropionic acid (MPA) was selected as the target molecule for attachment to APTMS. With both carboxyl (COOH) and SH functional groups, MPA can form an amide bond with the NH₂ of APTMS and have a strong covalent bond with Cu.²² Through carbodiimide-mediated amidation,^{23,24} the COOH group of MPA was chemically coupled to the NH₂ group of APTMS. Cu diffusion is further prevented due to its covalent attachment of S at the top surface of the bilayer SAM. Detailed comparison were studied for MPA coupled to APTMS with reference sample of APTMS through surface morphological characterization, chemical bonding characterization, electrical reliability test, and adhesion property characterization.

2. Results and discussion

Fig. 1a schematically illustrates the process for coating APTMS and coupling MPA. As-cleaned SiO₂/Si wafers were immersed in APTMS solution to obtain monolayer coverage. Then, the APTMS coated wafers were immersed in an aqueous solution to couple MPA onto APTMS. Fig. 1b shows the detailed chemical reaction for the coupling process. In this report, a carbodiimide-mediated amidation process was used to chemically couple the carboxyl group of MPA to the amine group of APTMS.²³ Initially, 2-(*N*-morpholino)ethanesulfonic acid (MES) is dissolved in deionized water to adjust the pH to an optimal condition.²⁴ The carboxyl group of MPA reacts with the carbodiimide group of *N*-(3-dimethylaminopropyl)-*N*'-ethylcarbodiimide hydrochloride (EDC) to form an unstable ester. EDC is a zero-length cross-linking agent used to couple carboxyl to primary amines. However, the coupling reaction has to be carried out fast, as the reactive ester that is formed can be rapidly hydrolyzed in aqueous solutions. *N*-Hydroxysuccinimide (NHS) is used to increase the stability of this active ester. The addition of NHS stabilizes the amine-reactive intermediate by converting it to an amine-reactive NHS ester, thus increasing the efficiency of EDC-

mediated coupling reactions. The resulting chemical reacts with the NH₂ termination of the APTMS coated SiO₂/Si substrate to form chemically coupled SAMs (hereinafter referred to as C-SAM).

Molecular topography related to the surface roughness was examined by atomic force microscopy (AFM) for the APTMS and C-SAM organic layers. Fig. 2 represents typical AFM images of the surfaces of APTMS and C-SAM coated on SiO₂/Si and their cross-sectional image. The root-mean-square (RMS) roughness of the APTMS surface coating is low as $R_s = 0.40$ nm. We have used low concentration APTMS solution to prevent multilayer or 3-dimensional assembly of the molecules due to the hydrogen bonding of the amine groups to other APTMS molecules or the substrate, which can result in a rough surface.^{21,25} The thickness of the SAM films measured by ellipsometry (not shown here) also indicates the film is well coated. The measured thickness of the APTMS coating is 1.4 nm, which is similar to the experimental values of monolayer APTMS in previous reports.^{21,26} The immersion time for APTMS coating is fixed to 30 minutes at 3 mM to obtain a high monolayer film with partial multilayer film in order to avoid sub-monolayer regions that cannot block the Cu diffusion.²¹ On the contrary, higher degree of multilayer APTMS is also avoided as it may weaken the adhesion property through fracture failure.²¹ There is only a slight increase in the roughness of $R_s = 0.44$ nm after a MPA coupling reaction. Also, the thickness of C-SAM is 2.0 nm based on ellipsometry measurement, which shows a 0.6 nm difference from APTMS alone. This difference is equivalent to the experimental thickness of MPA.²⁷ The cross sectional AFM image shown in Fig. 2c displays the low roughness of the films with a peak-to-valley height less than 2 nm. The results obtained from the AFM and ellipsometry measurements indicate the thin and smooth coating of APTMS and MPA coupling. AFM images obtained from larger area also show the low roughness of the SAM coating (Fig. S1†).

The detailed surface chemistry of the SAM layers was characterized by X-ray photoelectron spectroscopy (XPS) to confirm the changes after carbodiimide-mediated amidation. Fig. 3a–c shows the XPS measurement results of the APTMS and C-SAM layer. The experimental curves are deconvoluted using Gaussian–Lorentzian peaks after Shirley background corrections. The fitted curves are assigned to red and blue which are components from APTMS and MPA molecules, respectively. The XPS spectra obtained from the APTMS film are composed of peaks originating from APTMS. Fig. 3a shows the C 1s core level spectrum which is composed of three peaks. The main peak at 284.6 eV is attributed to C–C bonding, while one smaller peak at 286.1 eV originates from C–N and C–O bonding and another small peak at 287.6 eV originates from C=O bonding.^{21,28,29} The N 1s core level spectrum shows a large main peak at 398.8 eV due to the primary amine peak along with a small amount of hydrogen-bonded amine peak at 400.7 eV as shown in Fig. 3b.^{21,25} The amino groups in the APTMS molecules can interact with each other or the substrate through hydrogen bonding, which leads to a rough surface. The high primary amine percentage of 80% indicates the high quality of the APTMS film which is supported by our AFM results of the APTMS layer with low roughness.^{21,25}

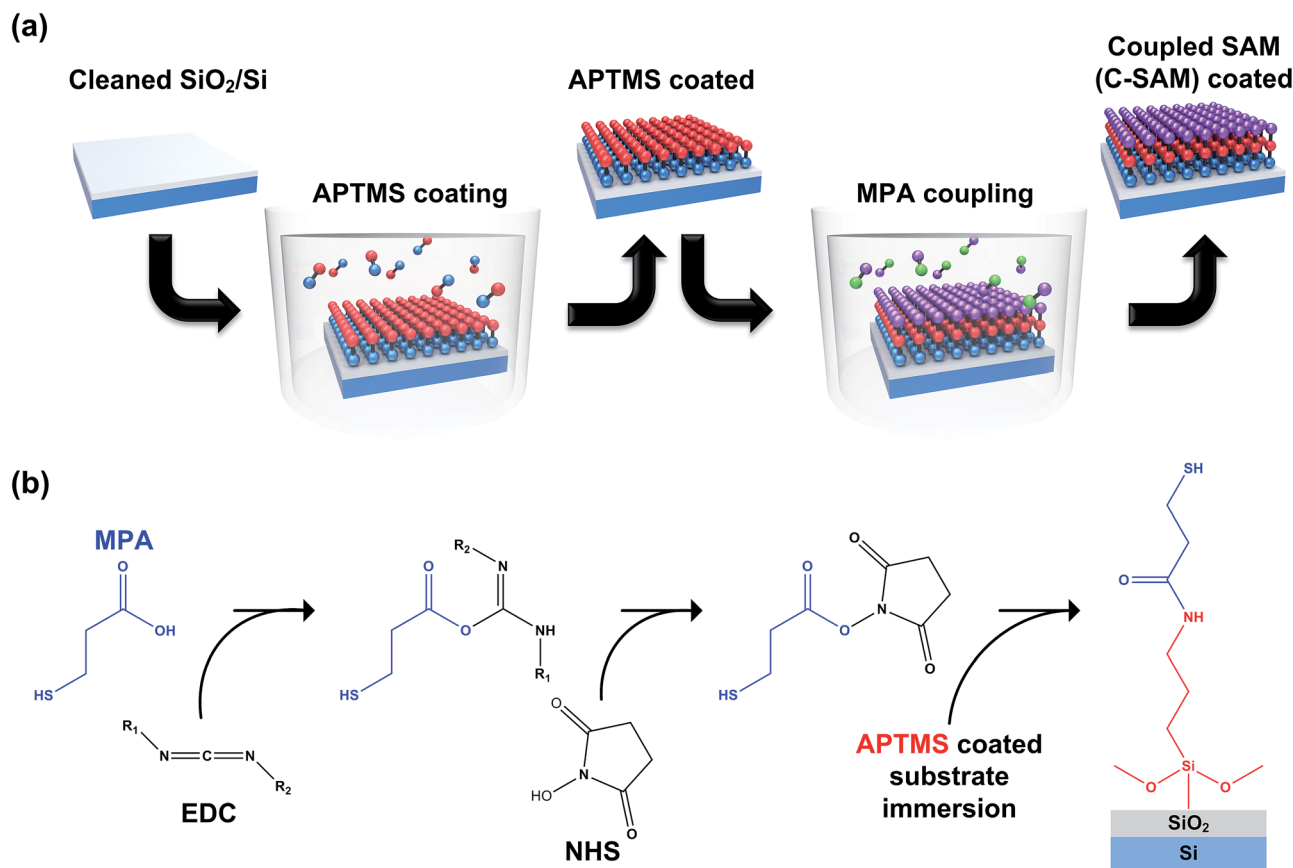


Fig. 1 (a) Schematics of APTMS coating process and MPA coupling process. (b) The detailed chemical reactions for the chemical coupling of MPA onto APTMS.

As shown in Fig. 3c, no detectable peaks were observed in the S 2p core level region due to the absence of S atoms in the APTMS molecule and substrate.

After MPA coupling reaction, additional peaks which are related to thiol or amide groups have appeared. The C 1s core level spectrum of the C-SAM in Fig. 3a shows peaks for C–S at 287.4 eV and O=C–N at 287.7 eV.^{30,31} The N 1s core level region in Fig. 3b shows a large decrease in the primary amine peak intensity along with the appearance of an amide peak at 400 eV (ref. 32) due to the carbodiimide-mediated amidation process. Significant peaks in the S 2p core level region were observed after the MPA coupling reaction as shown in Fig. 3c. The S 2p spectrum shows a doublet structure that was deconvoluted into peaks that originate from S 2p_{3/2} and S 2p_{1/2}. The spectra were fitted using a peak area ratio of 2 : 1 with 1.2 eV spacing.³³ The largest pair was observed at 163.5 and 164.7 eV which is due to unbound thiols (–SH),³³ indicating that the most of the thiols are stable without interaction with other species. Peaks positioned at 161.3 and 162.5 eV are due to atomic sulfur atoms,³⁴ and peaks at 167.9 and 169.1 eV corresponds to oxidized S species.³⁵ Such defects are thought to occur during the chemical reaction of the carbodiimide-mediated amidation process. However, the oxidation of the thiol groups are not a drawback as it can enhance the diffusion barrier properties and bonding strength to Cu compared to unoxidized thiol groups.³⁶

Time-dependent dielectric breakdown (TDDB) tests were conducted in order to evaluate the Cu diffusion barrier properties under bias temperature stress (BTS). Al/Ta/Cu stacked dots with 1 mm size were deposited on SAM-coated n^{++} Si with 100 nm SiO₂. The leakage currents of the metal-oxide-semiconductor (MOS) capacitors were measured under constant electric field (2 MV cm^{–1}) at elevated temperature (225 °C). Fig. 4a shows the degradation and breakdown characteristics of SiO₂ during the thermal and electrical stress for each representative sample using APTMS and C-SAM. It should be noted that TDDB results from devices without diffusion barriers were not included due to their breakdown at lower electric field intensity (Fig. S2a†). The time-dependent leakage current has two distinct regions. In the initial state, the current gradually decreased for ~500 and ~1000 seconds for the APTMS and C-SAM, respectively. This initial leakage current is occurred by the Poole-Frenkel tunnelling *via* the trap sites in the SiO₂ insulator, which is further suppressed by the trapping of electrons in the trap sites.³⁷ In the second region, the current starts to increase until it suddenly reaches the compliance current value (1 × 10^{–5} A). The measured time until this event is defined as the time-to-failure (TTF), which is ~2000 and ~7700 seconds for the representative samples. This region strongly indicates the degradation of the SiO₂ layer with trap creation up to the formation of a percolation path for a hard breakdown.

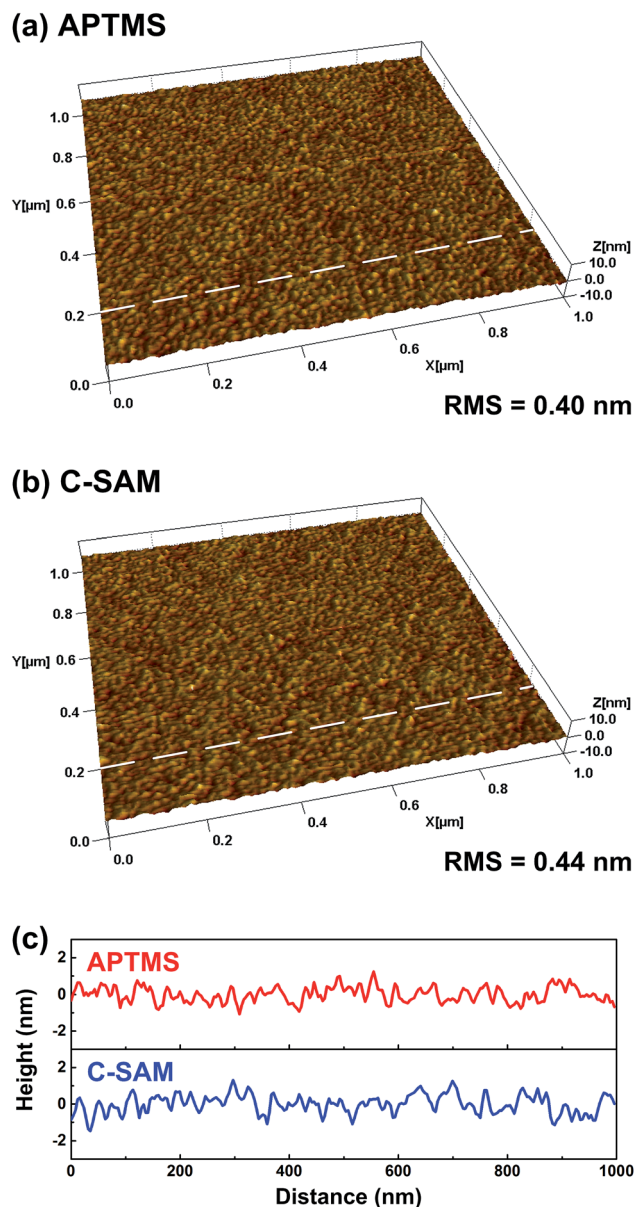


Fig. 2 AFM images of the substrates coated with (a) APTMS and (b) C-SAM and their (c) cross-sectional image.

Such change in the leakage current for TDDB measurements is a typical characteristics of failures due to traps that are newly generated *via* Cu ion migration,³⁸ which modifies the band structure of the MOS allowing Fowler–Nordheim current to flow.³⁷ Such breakdown was not observed when Al was used instead of Cu (Fig. S2b†). The longer TTF shows that the C-SAM exhibits a better Cu blocking property.

Fig. 4b shows the Weibull plot and the derived parameters of the TTF for more than 15 samples with APTMS and C-SAM barriers. Here, $t_{63.2}$ is defined as the time when 63.2% of the failures occurred and β is defined as the slope of the Weibull distribution obtained from the Weibull plot. TDDB results show a wide range of TTF, therefore statistical analysis is required to confirm that the C-SAM has an improved Cu blocking property and a higher resistivity to breakdown than APTMS.³⁸ Additionally we have presented a clear comparison with as-deposited TaN barriers with a thickness of 25 and 50 nm to the SAM barrier in our work. The $t_{63.2}$ of the APTMS is very low at 0.707 hours, which increases to 2.931 hours after the carbodiimide-mediated reaction to couple the MPA molecules on APTMS. The four-fold increase in $t_{63.2}$ compared to APTMS shows that the barrier property of C-SAM is enhanced, and is even comparable to 50 nm TaN barrier in this experiment. The $\beta > 1$ value of the slope indicates the distribution of the TTF is in a good agreement with other diffusion barriers.³⁹ As a result, the C-SAM diffusion barrier is very promising compared to 50 nm TaN as the thickness of the bilayer of SAMs is very low compared to TaN. The enhancement of the TTF can be attributed to the chemical interaction between S and Cu, which plays an important role in the diffusion barrier,¹⁷ and also the increment in the thickness of the C-SAM layer compared to APTMS alone.

Cu diffusion can degrade device performance when exceeding its critical limit. It is therefore important to employ more elaborate electrical analysis to evaluate the SAM diffusion barrier performance. Capacitance–voltage (*C*–*V*) measurements of MOS capacitors were performed at room temperature to detect the Cu ion diffusion by monitoring the *C*–*V* characteristics. Cu dots with 100 μm size were deposited on SAM-coated p Si with 10 nm SiO₂. Fig. 5a–c shows the *C*–*V* curves of the fabricated devices with (a) bare SiO₂, (b) APTMS-coated SiO₂, and (c) C-SAM-coated SiO₂. The devices were stressed at an electric field of 5 MV cm^{−1} at room temperature and *C*–*V*

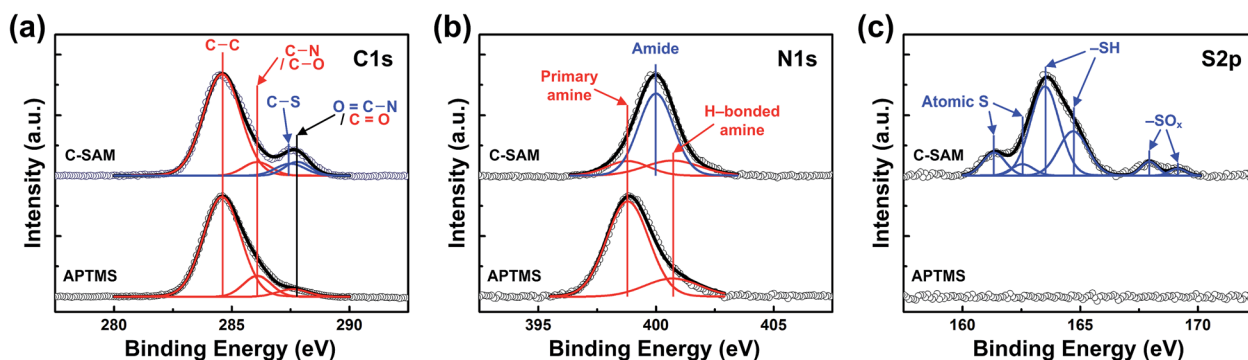


Fig. 3 XPS spectra of the APTMS and C-SAM for (a) C 1s, (b) N 1s, and (c) S 2p.

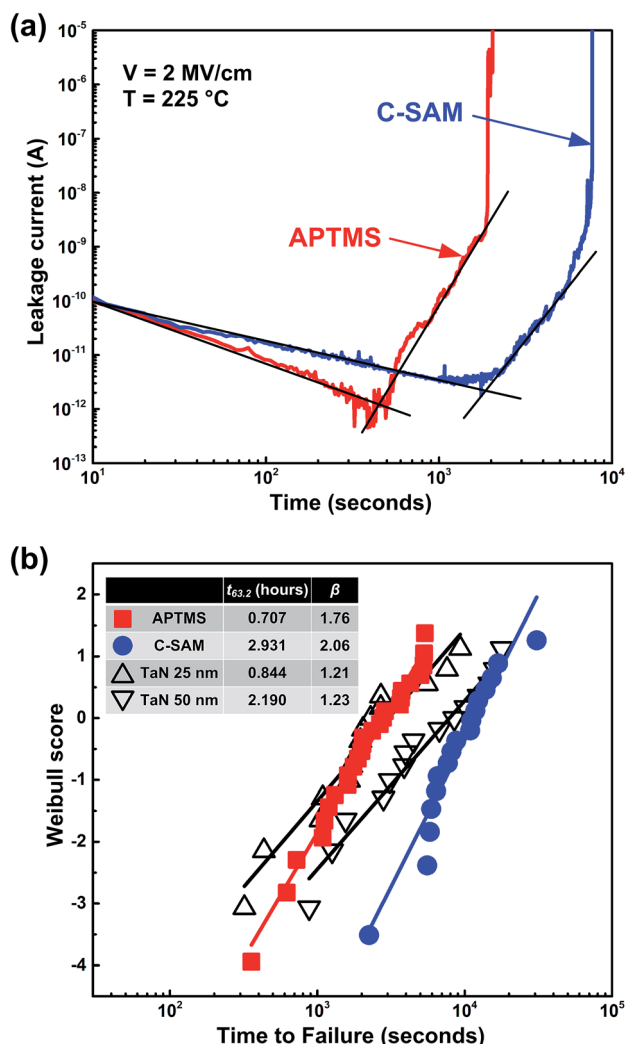


Fig. 4 (a) Representative TDDDB test results for APTMS and C-SAM under 225°C and 2 MV cm^{-1} . (b) Weibull plots and analysis for APTMS, C-SAM, 25 nm TaN, and 50 nm TaN barriers.

characteristics were measured during stress. Bare SiO_2 samples without a diffusion barrier show a negative voltage shift in the $C-V$ curve. The shift in $C-V$ characteristic indicates the diffusion of ionic Cu. The constant voltage stress (CVS) results establish

the effectiveness of SAMs as a diffusion barrier material under different electron injection conditions. Both APTMS and C-SAM layers effectively hinder Cu penetration into underlying SiO_2 and prevent subsequent degradation (Fig. 5b and c) under externally high electron injection compared to the absence of the SAM layer (Fig. 5a). In addition to the shift of the flatband voltage, distortion of the $C-V$ characteristics after extended CVS without a diffusion layer indicates further penetration of Cu ions. The change of the oxide capacitance indicates the diffusion of Cu into SiO_2 as the change in oxide charge is a result of copper diffusion that acts as an interstitial in SiO_2 .

Adhesion properties towards SiO_2 and Cu were also evaluated by using four-point bending tests. The four-point bending test is a widely used method to quantitatively measure the interfacial adhesion energy between two materials.⁴⁰ Fig. 6a shows the representative load and displacement curves obtained from the four-point bending tests of bare SiO_2 , APTMS coated SiO_2 , and C-SAM coated SiO_2 . The samples were annealed in a vacuum chamber at 400°C after Cu deposition to form an annealing-induced siloxane bridge to increase adhesion.^{20,21,41} When force is applied to the sandwiched structure, a linear relation with the displacement is expressed. As the force increases, a pre-crack propagates from the notch to the Cu/ SiO_2 interface and at a critical point of P_C , the force decreases and an interfacial crack initiates with P_{plateau} .⁴² The force during the crack propagation is the factor that determines the adhesion of the Cu film to the oxidized silicon substrate. This force was 4.0, 7.5, and 9.1 N for bare SiO_2 , APTMS coated SiO_2 , and C-SAM coated SiO_2 , respectively. The interfacial adhesion energy is characterized by the critical strain energy release rate defined as the following equation:⁴⁰

$$G = \frac{21(1 - \nu^2)P^2L^2}{16Eb^2h^3},$$

where ν is the Poisson's ratio of the Si wafer, E is the elastic modulus of Si, b is the width of the wafer, h is the thickness of the wafer, P the plateau load, and L is the distance between the loading points at the inner and outer sides.

Fig. 6b shows the converted interface toughness before and after annealing at 400°C with at least 3 samples. Before the annealing step, all of the samples exhibited low adhesion strength of 2.01 ± 0.33 , 2.82 ± 0.39 , and $2.12 \pm 0.11 \text{ J m}^{-2}$ for

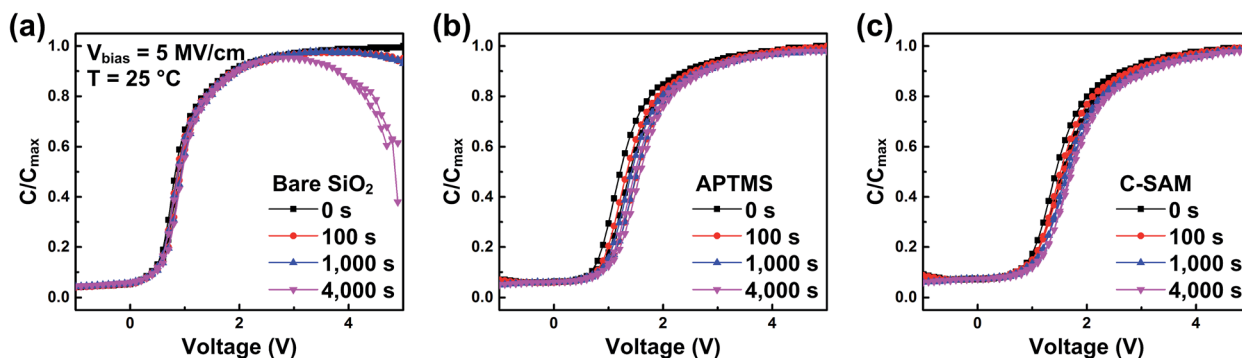


Fig. 5 $C-V$ measurements of the MOS capacitor structure with (a) bare SiO_2 , (b) APTMS coated SiO_2 , and (c) C-SAM coated SiO_2 .

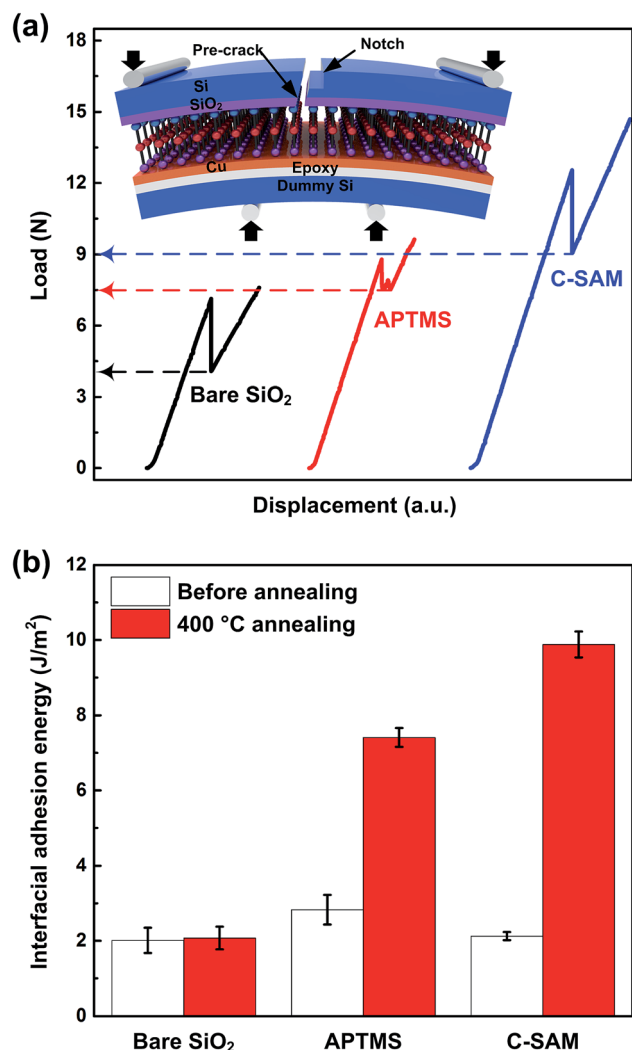


Fig. 6 (a) Load–displacement measurements from four-point bending tests of bare SiO₂, APTMS coated SiO₂, and C-SAM coated SiO₂ after 400 °C annealing. The inset shows the schematic illustration of the four-point bending test sample and measurement system. (b) Bar diagrams of the converted interfacial adhesion energies for the samples before and after annealing.

bare SiO₂, APTMS-coated SiO₂, and C-SAM-coated SiO₂, respectively. Before the annealing step, siloxane bonds formed by the dehydration of silanol groups are strained and tend to rehydrate, and revert to silanol when the samples cool down. However, after the annealing step, irreversible dehydration between the siloxane groups and SiO₂ surface occurs which is a covalent bond.²¹ After the annealing step, the adhesion of the SAM-coated layers increased. The bare SiO₂ samples still showed a very low adhesion of $2.07 \pm 0.30 \text{ J m}^{-2}$, indicating that Cu and SiO₂ have low interaction. APTMS shows increased interfacial adhesion energy of $7.41 \pm 0.25 \text{ J m}^{-2}$, which demonstrates a similar value to previous reports of APTMS on SiO₂.²⁰ In our study of C-SAM, the interfacial adhesion energy increases to $9.88 \pm 0.34 \text{ J m}^{-2}$, which indicates a 33% increase compared to APTMS. Since the fracture mechanism after dehydration of APTMS is due to the Cu–amine interface,²⁰ a tail

group with a stronger bonding strength with Cu is needed to enhance the adhesion properties. Thiols have a binding energy of 48 kcal mol^{-1} on Cu (111),²² which is stronger than that of amine–Cu at approximately $9.4 \text{ kcal mol}^{-1}$.⁴³ The obtained interfacial toughness for C-SAM is higher than as-deposited and H₂ plasma-treated TaN_x, and is even comparable to rapid thermal annealing-treated TaN_x.⁴⁴ This value is sufficient to prevent delamination and cracking during CMP commercially used in the dual damascene process.¹¹

3. Experimental section

APTMS coating process

All of the chemicals were purchased from Sigma Aldrich and used without any further treatment. Pieces of (100) Si wafer with 10–100 nm SiO₂ were successively cleaned by ultrasonication in acetone, isopropanol, and deionized water for 10 minutes each and dried under nitrogen blowing followed by oxygen plasma at 100 W for 3 minutes. The substrates were then immersed in anhydrous toluene with 3 mM APTMS for 30 minutes and then rinsed in pure toluene, a 1 : 1 mixture of toluene and methanol, and pure methanol to eliminate excessive APTMS residues.

Coupling process

The coupling reaction of MPA to APTMS was performed by immersing the APTMS-coated wafer in a mixed solution. 390 mg of MES was dissolved in 20 mL deionized water to adjust the pH for optimal conditions. Then 20 μL of MPA was added followed by the addition of 192 mg of EDC and 116 mg of NHS. The resulting solution was mixed and the APTMS-coated wafer was immersed for 2 hours, followed by deionized water rinsing and nitrogen blowing.

Characterization

$1 \times 1 \text{ cm}^2$ pieces of (100) n^{++} Si wafer ($0.001\text{--}0.003 \Omega \text{ cm}^{-1}$) with thermally-grown 100 nm thick SiO₂ were used for characterization. AFM images were obtained using XE-BiO (Park Systems) in a tapping mode with a resonance frequency of 298 kHz. Silicon tips with a radius of $<10 \text{ nm}$ were used in the AFM system. Ellipsometry was performed using Elli-SE (Ellipso Technology). XPS spectra were obtained using a K-alpha instrument (Thermo Scientific) equipped with a monochromated Al K α X-ray source (1486.6 eV). The X-ray power was 12 kV and 3 mA with a spot size of 400 μm diameter and pass energy of 50 eV.

TDDB test

$2 \times 2 \text{ cm}^2$ pieces of (100) n^{++} Si wafer ($0.001\text{--}0.003 \Omega \text{ cm}^{-1}$) with thermally grown 100 nm thick SiO₂ were used for the TDDB test. APTMS and C-SAM samples were fabricated using the same procedure, and TaN was deposited using reactive DC magnetron sputtering. The substrates were annealed at 200 °C to enhance the bonding of the SAM to the substrate followed by thermal evaporating 300 nm thick Cu dots with a 1 mm diameter through a stainless steel shadow mask. An additional 20 nm Ta and 100 nm Al was deposited using a DC magnetron

sputtering system to prevent oxidation of the samples. The native oxide on the backside of the substrate was etched using diluted HF followed by 200 nm thick Al deposition using DC magnetron sputtering for the backside contact electrode. TDDB tests on the MOS capacitors were conducted at 225 °C and 2 MV cm⁻¹ using a low leakage multimeter (Kiethley™ 237).

C–V measurement

2 × 2 cm² pieces of (100) p Si wafer (1–20 Ω cm⁻¹) with plasma enhanced atomic layer deposition grown 10 nm thick SiO₂ were used for the C–V measurements. The MOS capacitor devices were made using the same procedure as the TDDB test samples, except that the Cu dot diameter was 100 μm without Ta and Al. The C–V measurements were conducted at room temperature using a C–V analyzer (Kiethley™ 590).

Four-point bending test

3.5 × 3.5 cm² pieces of (100) n⁺⁺ Si wafer (0.001–0.003 Ω cm⁻¹) with thermally grown 100 nm thick SiO₂ were used for the 4 point bending test. Cu (300 nm) was deposited on bare SiO₂, APTMS-coated SiO₂, and C-SAM-coated SiO₂ using a thermal evaporation system. Some of the substrates were annealed in a vacuum chamber at 400 °C for 30 min under Ar 50 sccm and H₂ 50 sccm. The resultant sample was attached to a dummy Si wafer substrate using adhesive epoxy (Araldite Rapid) and cured for 12 hour at room temperature. The sandwiched Si/epoxy/Cu/SAM/SiO₂/Si samples were diced to 3 × 30 mm² and a 400 μm notch was formed in the middle of the samples. Fracture energy measurements were performed at a 0.08 μm s⁻¹ strain rate.

4. Conclusions

In conclusion, we have demonstrated chemically coupled APTMS and MPA, *i.e.* C-SAM, as a Cu diffusion barrier and adhesion promoter. The C-SAM was synthesized by simple solution processes at room temperature using a carbodiimide-mediated process. Results from AFM, ellipsometry, and XPS indicate that the APTMS and MPA molecules are bonded and C-SAM has a 0.44 nm RMS roughness and 2 nm thickness. TDDB measurements conducted at 2 MV cm⁻¹ stress under 225 °C indicate that the average TTF was four times greater after combining MPA and was comparable to TaN barriers. C–V measurements after different CVS times at 5 MV cm⁻¹ stress further confirms that Cu ion diffusion, which acts as interstitial defects in SiO₂, can be restricted by incorporating a C-SAM barrier. The enhancement of the Cu–SiO₂ adhesion property was measured with the four-point bending test, indicating a 33% increase after the coupling process. The C-SAM is a promising Cu diffusion barrier with only a 2 nm thickness that also meets the adhesion property requirements for CMP used in the dual damascene process.

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