

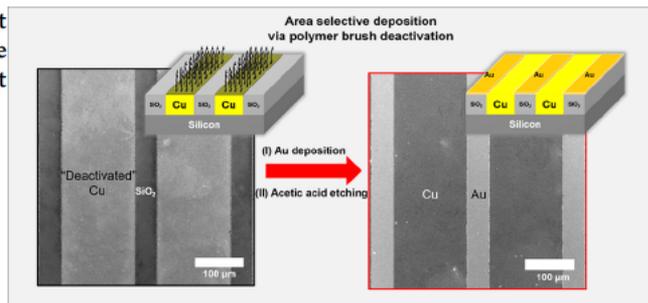
Enabling Large-Area Selective Deposition on Metal-Dielectric Patterns using Polymer Brush Deactivation

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ABSTRACT: Area selective deposition could be an important self-aligning material deposition technique to enable future nanoelectronics by accurately placing active materials at previously defined substrate patterns. We describe a robust self-aligning strategy to pattern uniform gold (Au) thin films on only the dielectric areas of prepatterned copper/silicon dioxide (Cu/SiO₂) substrates. The use of an amine terminated polystyrene polymer brush (i.e., PS NH₂) to selectively block micrometer Cu regions of patterned Cu/SiO₂ substrates is demonstrated. Following thermal evaporation of ~35 nm thick Au films on PS NH₂ modified Cu/SiO₂ surfaces and subsequent acetic acid etching, large area selective patterning of Au films on SiO₂ regions was achieved. We evaluated the influence of the initial PS NH₂ polymer brush film concentration and etching conditions to optimize the process window for the demonstration of highly successful area selective deposition on SiO₂ surface regions. X ray photoelectron spectroscopy and scanning electron microscopy analysis show the high selectivity of the initial polymer brush deposition process. Auger electron spectroscopy and transmission electron microscopy data reveal the distinct interfaces at the substrate surface after Au area selective deposition. The technique is highly reproducible with no discernible deposition of Au on Cu over macroscale areas after etching. The process involves relatively short and inexpensive processing steps compared to previously reported methods. The accuracy and precision exemplified in this work to dictate metal deposition at desired substrate areas make the process appealing for future semiconductor practices.



1. INTRODUCTION

The ability to control and select specific deposition areas of functional material at the macro and nanoscale is important in a number of technological applications. In particular, aligning active device layers might be critical to the fabrication and scaling of circuitry in processor and other electronic device fabrication. As feature sizes approach sub 10 nm, such dense patterning places significant technological and cost stresses on manufacturing practices. Thus, novel methodologies (both schemes and materials) to precisely deposit films on a surface or interface to keep pace with desired integrated circuit scaling milestones are crucial.¹ While traditional top down UV lithography is a cornerstone of silicon patterning, potential complementary techniques are of immense interest including e beam lithography,² directed self assembly of block copolymers,^{3,4} and nanoimprint lithography,⁵ which can produce sub 10 nm features at low cost and reduced process complexity. Similarly, area selective deposition (ASD), a self-aligning patterning process that can dictate material placement through tailored chemical interactions, has emerged as a hot topic for semiconductor processes. The fundamental appeal of ASD is that it allows the creation of new device layers based upon the underlying atomic/molecular architecture and reduces (or

potentially eliminates) repeated etching, deposition, or lithography steps.

ASD is envisaged as a simplified process to achieve sophisticated deposition to satisfy future semiconductor requirements including overlay, edge placement error, etc.⁶ ASD provides an innovative toolbox for one to pattern specific materials at precise locations of a substrate and encouragingly has been extended to 3D architectures of late.^{7,8} A broad range of methods to enhance selectivity have been reported including plasma treatment;^{7,9-11} self assembled monolayer (SAM) deposition;^{12,13} unreactive polymer layers including poly(methyl methacrylate),^{14,15} poly(vinylpyrrolidone),^{16,17} and poly(imide);¹⁸ and chemically amplified photoresist layers.¹⁹ Depending on the chosen approach, ASD can “activate” or “deactivate” a surface region.²⁰ For example, SAMs are the surface modification of choice and in combination with atomic layer deposition (referred to as ASALD) are a powerful platform for self aligned patterning.^{21,22} Bent and co workers have exemplified the use of SAMs including octadecylphos

phonic acid and alkanethiols to block (i.e., deactivate) Cu,^{23,24} thus inhibiting ALD at Cu sites. Similar SAM approaches have been utilized to improve the efficacy of molecular layer doping producing polyurea films,²⁵ including a useful method to enhance selectivity through electrochemically removing SAMs from Cu on a Cu/SiO₂ wafer.²⁶

A polymer “brush” is a polymer (end) grafted or tethered to an interface, whereby the polymer chains stretch away from an interface.^{27,28} Typically, polymer brushes are anchored covalently to a surface through the grafting to or grafting from approach. The grafting to approach involves the tethering of prefunctionalized polymer brushes with substrate functional groups. The grafting from approach, or surface initiated polymerization method, relies on the polymerization of initiating substrate groups to form polymer layers.²⁹ Using prefunctionalized polymer brushes, such as in the grafting to method, allows thorough characterization of the polymer material prior to attachment and is a key advantage over the grafting from technique.³⁰ For either method, tailoring the chemistry of a polymer brush can lead to intriguing polymer materials that exhibit excellent responsive behaviors depending on their environment. Developing responses modulated by exposure to, for example, light, temperature, or pH variances is possible via polymer brush design.^{31,32} The flexibility that can be endowed through polymer brush synthesis strategies opens a pathway to develop functional surfaces and interfaces exemplified hitherto in biotechnology,^{33,34} nanoelectronics,³⁵ and sensory applications.³⁶ For ASD application, the chemical robustness and short grafting periods offered by polymer brushes make them appealing in comparison to other molecular modification strategies such as SAMs that can take several days to process.²⁹ Moreover, SAM layers typically exhibit defects such as pinholes that do not block or protect a desired film region, allowing nucleation during ALD on protected sites. Polymer brushes can possess high grafting densities that make them an attractive option for activating or deactivating a surface. Our initial work on area selective polymer brush deposition revealed that we could use end functionalized (e.g., -NH₂, -SH) polymer brushes to activate specific surface areas.³⁷

Here, we dictate placement of Au thin films on SiO₂ regions using a short (<1.5 h processing) polymer brush deposition method. We have used the grafting to approach of an amine terminated polystyrene polymer brush (PS NH₂) to Cu regions of patterned Cu/SiO₂ to enable Au ASD on SiO₂ areas. The strategy allows us to (i) protect and deactivate Cu regions and (ii) enable acetic acid etching of CuO_x layer to selectively remove deposited Au material on Cu regions. Low concentrations of PS NH₂ polymer brush worked effectively to remove Au on Cu regions, while denser PS NH₂ films showed an inability to remove the deposited Au. We detail X ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) analysis in order to define an optimized process window. The results show that the process is sensitive to polymer brush solution concentration, and careful attention is required for both the deposition and removal stages of the strategy.

2. EXPERIMENTAL SECTION

2.1. Materials. Patterned substrates with Cu and Si stripe dimensions of ~160 and ~60 μm, respectively, were purchased from Sil’tronix, France. Note that patterned substrates possessed a native silicon dioxide, SiO₂, layer of ~2 nm, as

well as a chromium adhesion layer for Cu. Blanket Si and Cu substrates were also purchased from Sil’tronix for initial assessment studies. An amine terminated polystyrene brush, referred to as PS NH₂ herein, was purchased (number average molecular weight = 9.5×10^3 , polydispersity = 1.16) from Polymer Source, Inc., Canada, and used as received. PS NH₂ solutions (0.25–1 wt %) in toluene were prepared and stirred overnight. Toluene (CHROMASOLV, for high performance liquid chromatography (HPLC), 99.9%) and citric acid monohydrate (ACS reagent, ≥99.9%) were purchased from Sigma Aldrich and were used as received unless stated otherwise. Glacial acetic acid was purchased from VWR International. Deionized (DI) water was used where necessary.

2.2. Surface Cleaning, Polymer Deposition, Metal Deposition, and Acetic Acid Etching. Substrates (Si, Cu, and patterned Cu/SiO₂) were first degreased using ultrasonication in toluene for 10 min followed by drying with N₂ gas. Immersion in 1% aqueous citric acid solution for 5 min was used to remove oxide and artifacts from copper and to passivate the surface as determined by XPS previously.^{37,38} Following this, thorough cleaning of citric acid treated wafers was carried out with DI water followed by drying with N₂ gas. All PS NH₂ solutions were deposited at 3200 rpm for 25 s, with a ramp of 5 s. Samples were immediately placed in a vacuum oven and baked for 1.5 h at 190 °C (463 K). After the bake, samples were sonicated in toluene for 20 min (2 × 10 min) in order to remove ungrafted polymer material, briefly rinsed in toluene, and dried with N₂ gas. A Temescal Evaporation system (FC 2000) was used to deposit Ti/Au (5 nm/35 nm) where Ti is used to “anchor” the gold layer. Acetic acid etching of the CuO_x layer to remove Au deposited on brush modified or blanket substrates was carried out in an ultrasonic bath for 15 and 30 min, respectively, at 19 °C.

2.3. Characterization. Top down scanning electron microscope images were obtained by a high resolution (<1 nm) Field Emission Zeiss Ultra Plus Scanning Electron microscope with a Gemini column operating at an accelerating voltage of 5 kV. For cross sectional SEM imaging, samples were cleaved and placed in a holder in a vertical position with the edge of interest facing the electron gun. Samples were then characterized while tilted at an angle of 15–20°. X ray photoelectron spectroscopy (XPS) was performed under ultrahigh vacuum conditions (<5 × 10⁻¹⁰ mbar) on a VG Scientific ECSAlab Mk II system using Al Kα X rays (1486.6 eV). The analyzer pass energy was set to 100 eV for survey spectra and 20 eV for high resolution core scans. Photo emission peak positions were corrected to C 1s at a binding energy of 284.8 eV. Auger electron spectroscopy (AES) was carried out using a PHI 680 Xi Auger Nanoprobe at Karlsruhe Institute of Technology, Germany. AES analysis conditions were as follows: accelerating voltage (10 keV), current (10 nA), and beam size (40 nm). Transmission electron microscopy (TEM) lamella specimen were prepared using a Zeiss Auriga DB focused ion beam (FIB), where ~100 nm electron beam Pt and ~2 μm ion beam Pt were deposited on areas of interest before FIB milling and lift out. Lamella samples were analyzed by an FEI Titan high resolution TEM operating at an accelerating voltage of 300 kV. Scanning TEM (STEM) mode was used for energy dispersive X ray (EDX) mapping and line scans performed. Feature sizes and channel widths of substrates were calculated using ImageJ analysis of SEM images.

Scheme 1. Area Selective Deposition Process Using Polymer Brush Deactivation: (a) As Received Pre patterned Cu/SiO₂ Wafer; (b) After Deposition and Bake of PS NH₂ Polymer Brush; (c) Evaporation of Ti/Au Layer; (d) Etching Process to Achieve Uniform Au Area Selective Deposition on SiO₂ Regions only

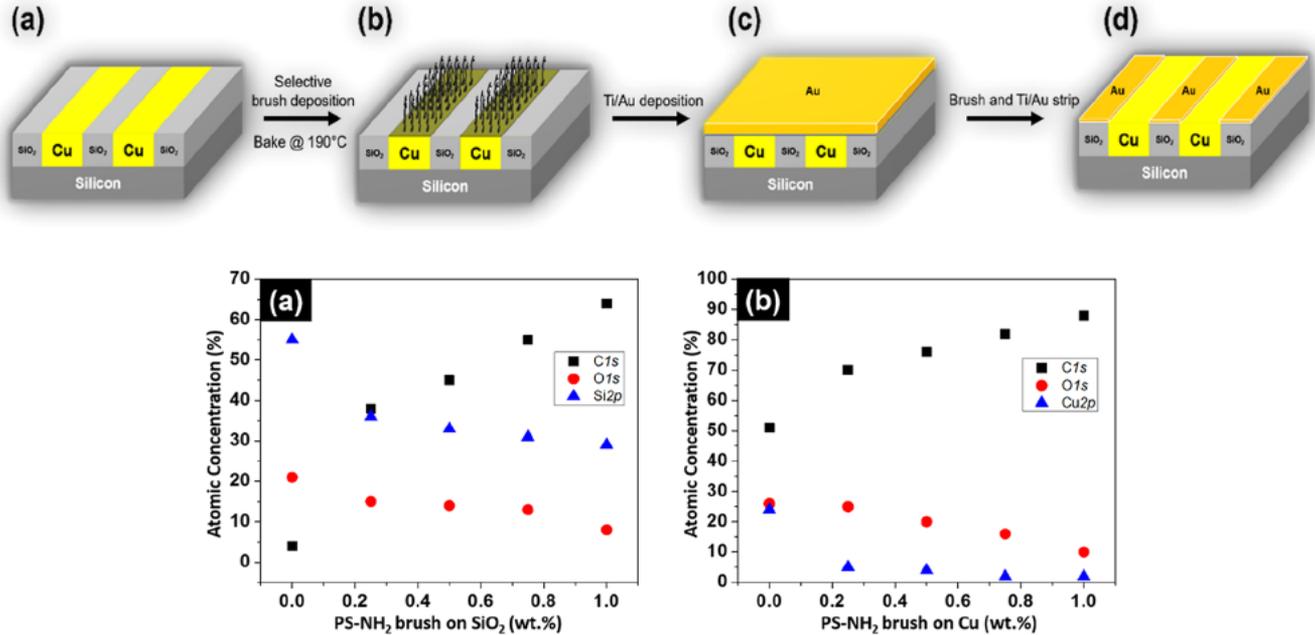


Figure 1. Atomic concentrations (%) of C 1s, O 1s, Si 2p, and Cu 2p following coating of PS NH₂ polymer brush solutions on (a) blanket SiO₂ substrates and (b) blanket Cu substrates. Note that zero on x axis refers to blanket SiO₂ and Cu after citric acid treatment only.

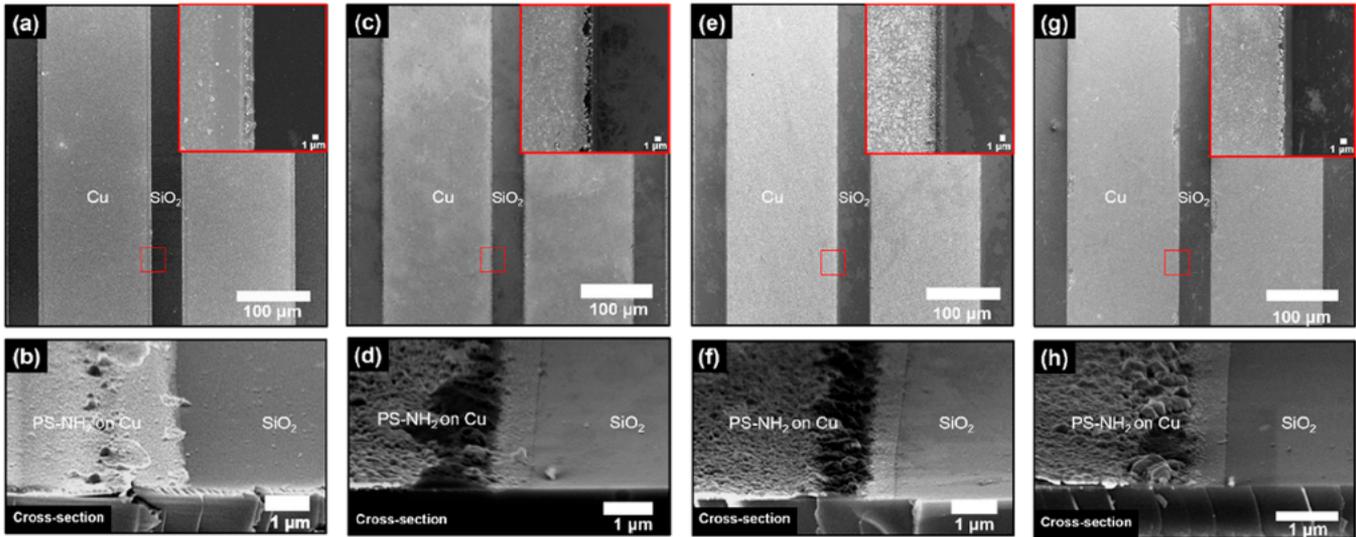


Figure 2. Top down and cross sectional SEM analysis of PS NH₂ polymer brush solutions on patterned Cu/SiO₂ wafers at concentrations of 0.25 wt % (a, b), 0.5 wt % (c, d), 0.75 wt % (e, f), and 1 wt % (g, h), respectively.

3. RESULTS AND DISCUSSION

Scheme 1 depicts the process flow employed here to achieve high quality Au ASD. As received patterned Cu/SiO₂ wafers were initially treated with citric acid (**Scheme 1a**). Following this, a toluene PS NH₂ polymer brush solution was spin coated atop patterned Cu/SiO₂ wafers, and PS NH₂ films were baked at 190 °C in a vacuum oven for 1.5 h after deposition. PS NH₂ grafts to Cu areas as depicted in **Scheme 1b**. Following cleaning to remove ungrafted polymer chains, Ti/Au (5 nm/35 nm) was deposited on wafers (**Scheme 1c**). Finally, acetic acid etching of the underlying CuO_x and PS NH₂ material was used

to remove Au from Cu areas specifically to pattern SiO₂ regions only with Au strips (**Scheme 1d**).

From our initial studies on area selective polymer brush deposition,³⁷ we observed that a PS NH₂ brush deposited selectively on Cu areas as opposed to SiO₂ surfaces. This finding provided an impetus for further investigation to evaluate the possible use of PS NH₂ as a deactivating brush layer material in order to deposit a metal layer on SiO₂. PS NH₂ brush solutions (viz. 0.25, 0.5, 0.75, and 1 wt %) were spin coated on citric acid cleaned blanket Cu and SiO₂ substrates to evaluate the effect of solution concentration on attachment to respective surfaces. Citric acid cleans and

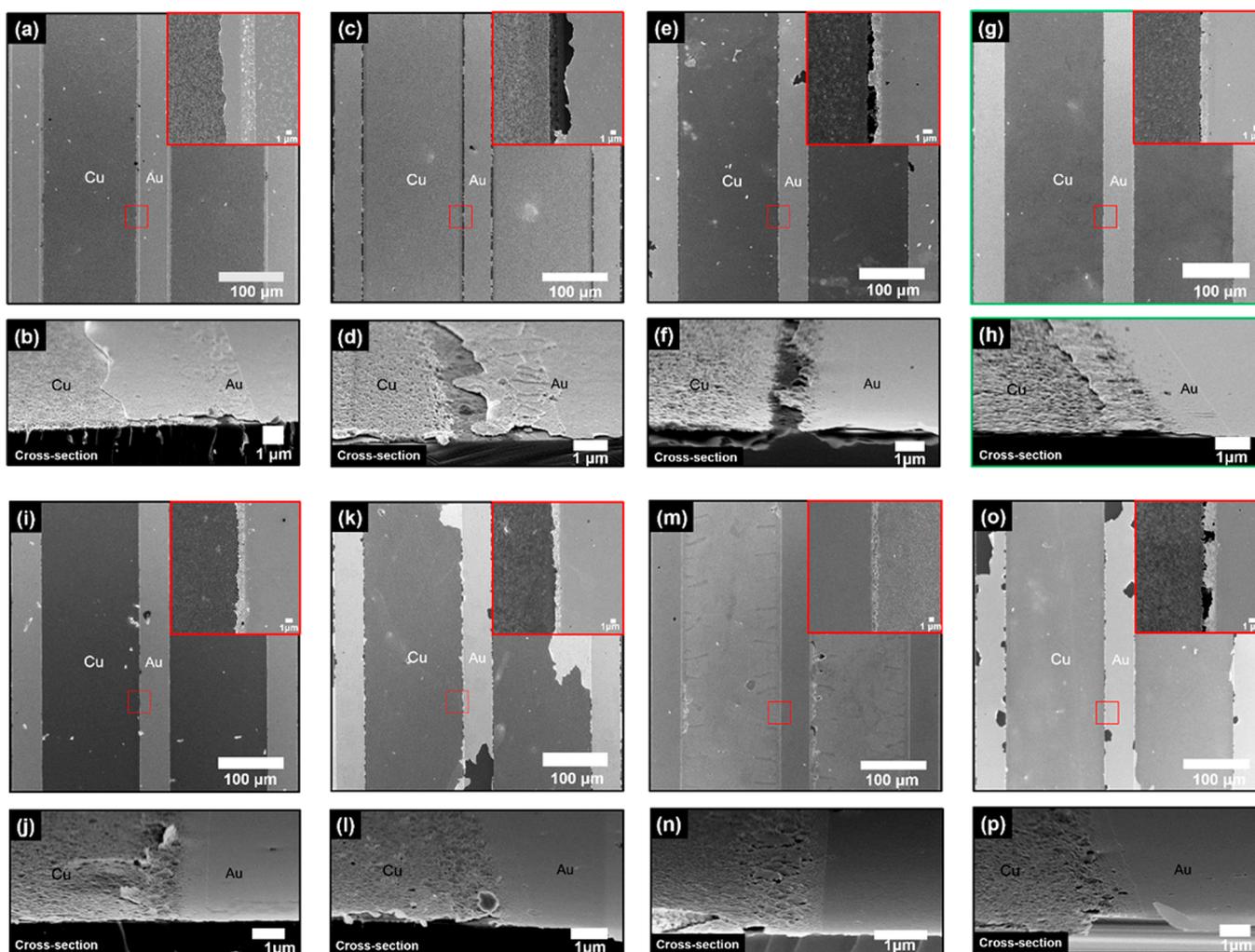


Figure 3. (Left to right) SEM images of Au area selective deposition on Cu/SiO₂ substrates following 15 min acetic etching on 0.25 wt % PS NH₂ modified surfaces (a, b) and 30 min acetic acid etching (c, d). Au area selective deposition on Cu/SiO₂ substrates on 0.5 wt % modified surfaces after 15 min (e, f) and 30 min acetic acid etching (g, h), on 0.75 wt % modified surfaces after 15 min (i, j) and 30 min acetic acid etching (k, l), and on 1 wt % modified surfaces after 15 min (m, n) and 30 min acetic acid etching (o, p), respectively.

passivates Cu, while SiO₂ substrate chemistry is largely unchanged as determined through XPS analysis.³⁷

We used XPS to assess the grafting success of PS NH₂ to Cu over SiO₂, as detailed in Figure 1 (see Figure S1 for all survey spectra). At 0.25 wt % concentration, we observe a significant C 1s atomic concentration on blanket Cu substrates, ~70%, in comparison to C 1s atomic concentration on SiO₂, ~35%; see graph in Figure 1a for SiO₂ surfaces and graph in Figure 1b for Cu surfaces. Moreover, high Si 2p atomic concentration levels, as well as the detection of dopant P 2p and B 1s signals from SiO₂ substrate, reveal that a significant brush layer formation is inhibited at 0.25 wt % PS NH₂ polymer concentration on SiO₂. In contrast, a relatively low Cu atomic percentage was calculated, ~4%, on the 0.25 wt % PS NH₂ coated Cu sample, showing that the PS NH₂ coats the surface uniformly. As the PS NH₂ concentration is increased, we observe an increase of C 1s atomic concentration by up to 10% on SiO₂ surfaces, while marginal increases (~5%) were calculated on Cu surfaces. For example, 0.75 wt % PS NH₂ coated SiO₂ sample had ~55% C 1s while corresponding Cu sample showed ~82% C 1s signal. Figure 1a also shows that Si 2p signal decreased with an increase in PS NH₂ concentration inferring that partial film formation maybe occurring on SiO₂ surfaces. Likewise, we

observed a similar occurrence, i.e., decrease of Cu 2p signal, on Cu surfaces. Notably, O 1s signal decreased in Cu samples with increased PS NH₂ polymer brush concentrations, revealing thicker and denser formation of PS NH₂ polymer brush layers (see cross sectional SEM image in Figure S2).

To elucidate the effect of PS NH₂ brush concentration, we next analyzed films through scanning electron microscopy (SEM) analysis after deposition on patterned Cu/SiO₂ features (see initial characterization of as received Cu/SiO₂ wafer in Figure S3). Figure 2 displays SEM images of PS NH₂ on patterned Cu/SiO₂ samples after deposition of 0.25–1 wt % solutions. As seen in the main SEM images (a, c, e, and g), Cu strips are ~160 μm wide, while SiO₂ regions are ~60 μm wide. Such large feature sizes enable us to use microscopy to assess the initial grafting of PS NH₂ polymer brushes after attachment. After the deposition of 0.25 wt % PS NH₂, it is clear that a film has formed at the interface of Cu and SiO₂ (see cross section in Figure 2b). The SEM images and critically the insets in Figure 2a, c, e, and g show that we retain the Cu/SiO₂ interfaces after deposition of PS NH₂ brushes. As revealed by XPS discussed earlier, the higher wt % solutions create denser films on Cu. This is also confirmed from cross sectional SEM images, as shown in Figure 2 d, f, and g for 0.5, 0.75, and 1 wt

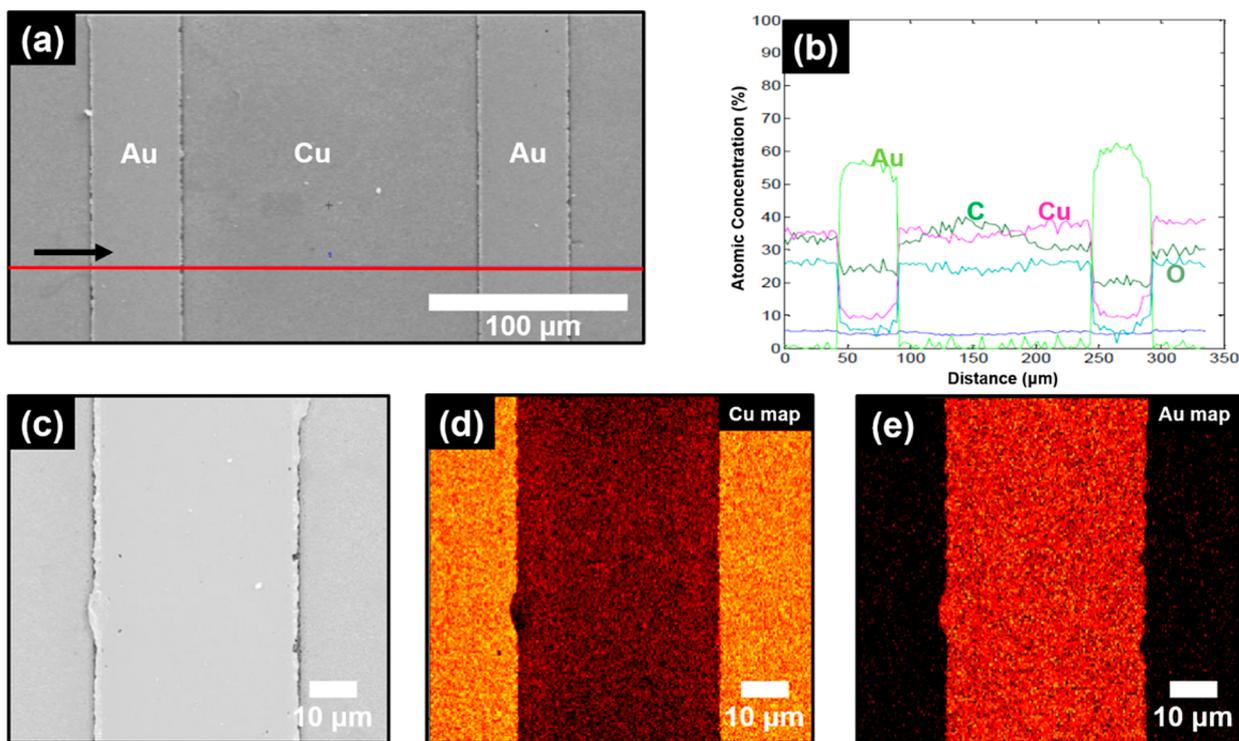


Figure 4. (a) SEM image of Au area selective deposition; red line shows where AES line scan was performed, and arrow shows direction of line scan. (b) AES line scan of area shown in (a). (c) SEM image of Au ASD on SiO₂ between Cu stripes. (d, e) AES maps showing Cu presence and Au ASD, respectively.

% PS NH₂ solutions, respectively. One also observes the accumulation of polymer brush material at the interface of Cu/SiO₂. This presumably occurs due to the affinity of the PS NH₂ brush for Cu over SiO₂, as opposed to a physical edge effect because the topography of Cu and SiO₂ wafer areas is flat following planarization.

These processes (confirmed using XPS and SEM analysis) established a reproducible method to block or deactivate Cu regions versus SiO₂ using varied concentrations of a PS NH₂ polymer brush. Next, we examined the feasibility of our objective to pattern Au on SiO₂ only using such deactivated regions. To achieve Au patterning, Ti/Au (5 nm/35 nm) was evaporated on PS NH₂ modified Cu/SiO₂ substrates. Acetic acid etching of CuO_x and the PS NH₂ used in this work were adapted from a seminal report by Bent and co workers, who used the method in conjunction with SAMs and ALD.²⁴ Our analysis shows that both the initial brush film concentration and the time of acetic acid etching significantly influence the uniformity of Au on SiO₂ regions. Figure 3 displays SEM images of PS NH₂ modified Cu/SiO₂ substrates after the deposition of Ti/Au followed by ultrasonication in acetic acid for 15 and 30 min, respectively. Figure 3a shows selective deposition of Au after modification with 0.25 wt % PS NH₂ brush. The inset in Figure 3a and cross sectional SEM image in Figure 3b show that the Au layer covers the Cu/SiO₂ interface, while this can be removed with extended acetic acid etching as shown in Figure 3c inset and cross section in Figure 3d.

We observed improved resolution of Au features at the Cu/SiO₂ after etching for 15 and 30 min on 0.5 wt % PS NH₂ treated Cu/SiO₂ substrates. Excellent alignment is visible from the top down SEM inset image and cross section shown in Figure 3g and h (outlined in green). A similar result was

attained on 0.75 wt % PS NH₂ treated Cu/SiO₂ substrates after 15 min acetic acid etching (Figure 3i and j).

Conversely, the 30 min acetic acid etching started to reveal large areas of lift off of Au on SiO₂ regions, as displayed in Figure 3k and l. We attribute this to both the extended etch time and the higher concentration of PS NH₂ solution, because such lift off was not observed on 0.25 or 0.5 wt % samples. Interestingly, no lift off of Au was visible on 1 wt % PS NH₂ treated Cu/SiO₂ substrates after 15 min acetic acid etching (Figure 3m and n). This infers that the 1 wt % brush is too thick, and thus, the CuO_x layer and PS NH₂ layer could not be etched significantly to remove Au on Cu regions. The longer 30 min etch time did reveal Au selective deposition on SiO₂ regions; however, both poor selectivity and delamination of the Au film are apparent (see Figure 3o).

Overall, 30 min acetic acid etching of 0.5 wt % PS NH₂ proved to be the optimum conditions for forming well defined Au ASD on SiO₂ (Figure 3g and h). The SEM image in Figure S4 shows a large scale area (~1600 μm × 1200 μm) of successful Au ASD. To clarify the necessity of the PS NH₂ brush modification step to achieve Au ASD on SiO₂, acetic acid etching was carried out on a Ti/Au layer deposited only on untreated Cu/SiO₂ wafers. No lift off or ASD was achieved as shown and discussed in Figure S5, reinforcing the requirement for the deactivating PS NH₂ polymer brush layer to achieve ASD. On this note, it appears that the mechanism here differs slightly from a reported method of ASD utilizing acetic acid.²⁴ The authors discussed (see ref 24) that because ALD had a selective substrate area to deposit upon, protected SAM areas on Cu allow acetic acid to permeate through to etch the CuO_x layer, enabling successful ASD. Because we have deposited a dense uniform Ti/Au layer without any inherent selectivity to the underlying substrate, the

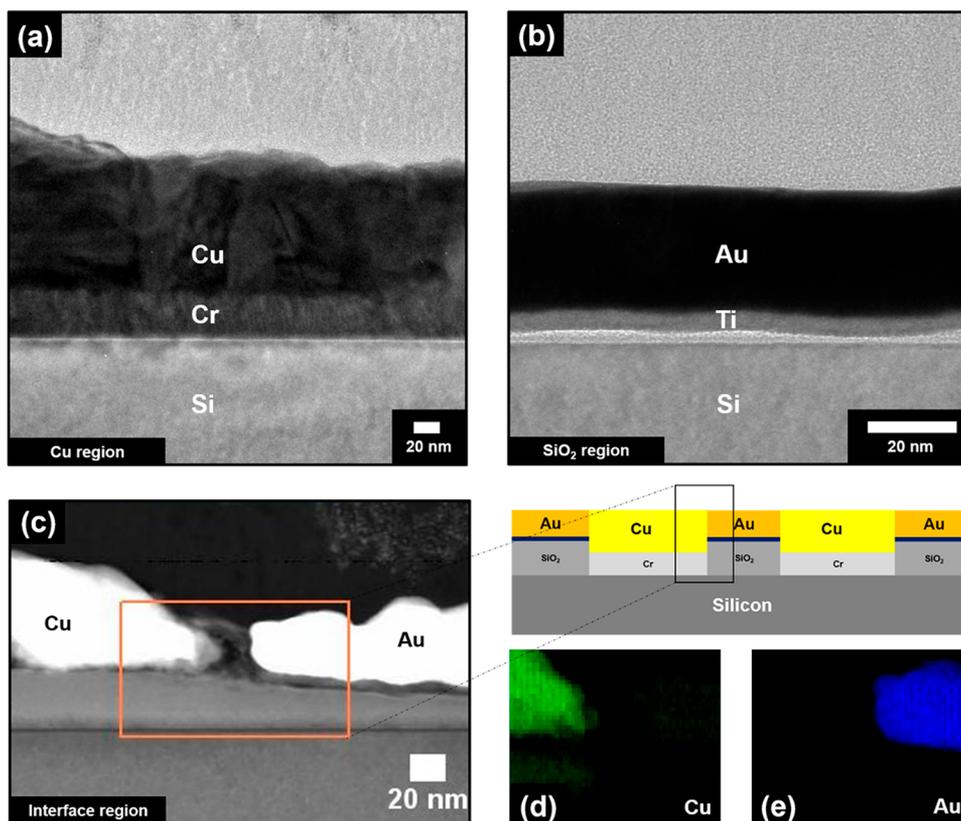


Figure 5. Cross sectional TEM images of (a) Cu film at Cu region only of patterned Cu/SiO₂ wafer following successful Au ASD. (b) Au material on SiO₂ region of Cu/SiO₂ wafer. (c) STEM image of interface region where Cu film and Au ASD are visible. Schematic outlines area of cross section in (c). EDX mapping data revealing the Cu (d) and Au (e) material present at the Cu/SiO₂ interface.

ultrasonication step appears to play a role in enabling acetic acid to permeate through to etch the underlying CuO_x layer. Our work suggests a moderately different etching mechanism for CuO_x but displays similar levels of high quality ASD patterning.

We performed Auger electron spectroscopy (AES) analysis on the optimized Au ASD sample (0.5 wt % PS NH₂ on patterned Cu/SiO₂) to confirm the presence of Au and Cu at specific sites. Figure 4a shows an SEM image of Au lines on SiO₂ between pristine Cu strips. An AES line scan performed across this region, as shown in Figure 4b, confirms conclusively that we have indeed achieved large area Au ASD at the anticipated sites. Moreover, and encouragingly, we have retained a uniform Cu layer as confirmed through AES mapping displayed in Figure 4d. Figure 4e displays the precision of Au deposition on a SiO₂ region with a defined interface. It is important to preserve a pristine Cu layer given its function in integrated circuit manufacture, where its inherent conductive properties must be retained. We note that discussion on this topic is absent in previous studies related to ASD development.

Here, we have shown that the Cu material maintains its uniformity after several processing steps. Cross sectional transmission electron microscopy (TEM) was also carried out to clarify this. Focused ion beam (FIB) lamella samples were prepared from Cu and SiO₂ regions of patterned Cu/SiO₂ wafers after successful Au ASD. Moreover, a lamella sample was prepared from the Cu/SiO₂ interface. Cross sectional TEM, STEM, and EDX mapping are displayed in Figure 5. Figure 5a shows the excellent uniformity of the Cu

layer (and Cr adhesion layer) after removal using acetic acid etching of the 0.5 wt % PS NH₂ layer and the Au material. It is noteworthy that there is no evidence of a PS NH₂ or Au layer on Cu, emphasizing the efficacy of the acetic acid etching approach. XPS carried out on a blanket Cu substrate modified with 0.5 wt % PS NH₂ after the removal of an Au film using acetic acid etching shows a passivated Cu surface (see Figure S6). The ~35 nm Au layer deposited on SiO₂ also reveals high uniformity after acetic acid etching for 30 min (see Figure 5b). The Ti adhesion layer is also visible from the TEM image. The schematic representation of the Cu/SiO₂ wafer in Figure 5 shows the reader the region of interest where the lamella was prepared at the Cu/SiO₂ interface specifically. The cross sectional TEM image in Figure 5c reveals the roughness of the Cu and Au material following acetic acid etching at the interface.

While we partially expected this result given the crude nature of the metal deposition technique, we foresee improved line edge definition using an ALD approach, and this work is currently underway and will be reported in due course. We envisage the expansion of the “deactivation” polymer brush strategy used here to other surfaces and deposited materials (via ALD or otherwise), e.g., Al₂O₃, ZnO, which can open up new applications. This is possible given the rich nature of polymer brush materials available. Future work will be focused on elucidating a wider library of polymer brushes where activated sites on metal or dielectric can be infiltrated in a simple manner. Moreover, further impetus is required to develop ASD processes on the nanometer scale regime to

provide a reliable complementary method for future semiconductor processing.

4. CONCLUSIONS

In conclusion, we have demonstrated a new strategy enabling large scale area selective deposition using polymer brush deactivation. Polymer brushes allow us to dictate polymer layer positions at specific surface sites through chemical interactions. This is a new approach for area selective deposition application, which is relatively short and avoids complex etching, lithographic, or deposition steps. XPS studies on blanket substrates showed the preferential attachment of PS NH₂ polymer brush to passivated Cu surfaces over SiO₂, indicating its potential for surface deactivation. We subsequently exploited this surface deactivation using Au evaporation on modified Cu/SiO₂ line patterns as a means to examine the usefulness of the PS NH₂ at Cu surfaces specifically. Finally, an acetic acid etching procedure was employed to remove CuO_x material and PS NH₂ at the surface. By tuning the polymer brush concentration, as well as the acetic acid etching time, uniform Au ASD on SiO₂ was enabled over large areas of patterned Cu/SiO₂ stripes. AES confirmed the excellent alignment and well defined Au material on SiO₂ regions specifically. Moreover, TEM revealed that the uniform nature of the Cu surface was retained, which is of importance for further processing steps in electronic device development. Cross sectional data showed slight distortion of Cu and Au materials and reaffirm the need for more detailed analysis of interfaces in the ASD field. Overall, we have described a simple yet effective method using polymer brush deactivation to selectively pattern large areas of metal dielectric regions and suggest that the methodology has significant potential to impact future processing of electronic device layers.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b04092.

XPS survey spectra, cross sectional SEM images of PS NH₂ on blanket Cu, SEM and AES line scan and maps of as received patterned Cu/SiO₂ wafer, SEM of large scale area of Au ASD, SEM images of patterned Cu/SiO₂ without brush treatment and after deposition of Ti/Au and acetic acid cleaning, and high resolution XPS scan of Cu 2p region after acetic acid treatment (PDF)

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The authors declare no competing financial interest.

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