Trimethylaluminum and Oxygen Atomic Layer Deposition on Hydroxyl-Free Cu(111)

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Supporting Information

ABSTRACT: Atomic layer deposition (ALD) of alumina using trimethylaluminum (TMA) has technological importance in microelectronics. This process has demonstrated a high potential in applications of protective coatings on Cu surfaces for control of diffusion of Cu in Cu2S films in photovoltaic devices and sintering of Cu-based nanoparticles in liquid phase hydrogenation reactions. With this motivation in mind, the reaction between TMA and oxygen was investigated on Cu(111) and Cu2O/Cu(111) surfaces. TMA did not adsorb on the Cu(111) surface, a result consistent with density functional theory (DFT) calculations predicting that TMA adsorption and decomposition are thermodynamically unfavorable on pure Cu(111). On the other hand, TMA readily adsorbed on the Cu2O/Cu(111) surface at 473 K resulting in the reduction of some surface Cu2+ to metallic copper (Cu0) and the formation of a copper aluminate, most likely CuAl2O4. The reaction is limited by the amount of surface oxygen. After the first TMA half-cycle on Cu2O/Cu(111), two-dimensional (2D) islands of the aluminate were observed on the surface by scanning tunneling microscopy (STM). According to DFT calculations, TMA decomposed completely on Cu2O/Cu(111). High-resolution electron energy loss spectroscopy (HREELS) was used to distinguish between tetrahedrally (Altet) and octahedrally (Aloct) coordinated Al3+ in surface adlayers. TMA dosing produced an aluminum oxide film, which contained more octahedrally coordinated Al3+ (Altet/Aloct HREELS peak area ratio ≈ 0.3) than did dosing O2 (Altet/Aloct HREELS peak area ratio ≈ 0.5). After the first ALD cycle, TMA reacted with both Cu2O and aluminum oxide surfaces in the absence of hydroxyl groups until film closure by the fourth ALD cycle. Then, TMA continued to react with surface Al–O, forming stoichiometric Al2O3. O2 half-cycles at 623 K were more effective for carbon removal than O2 half-cycles at 473 K or water half-cycles at 623 K. The growth rate was approximately 3–4 Å/cycle for TMA+O2 ALD (O2 half-cycles at 623 K). No preferential growth of Al2O3 on the steps of Cu(111) was observed. According to STM, Al2O3 grows homogeneously on Cu(111) terraces.

KEYWORDS: Cu(111), trimethylaluminum (TMA), scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), high-resolution electron energy loss spectroscopy (HREELS), atomic layer deposition (ALD), surface science, single crystal

INTRODUCTION

Copper is widely used for a variety of applications including water heat exchangers,1 interconnect and gate electrodes for microelectronics,2,3 and heterogeneous catalysts for reactions including low temperature water–gas shift (WGS)4 and methanol steam reforming.5,6 However, the use of copper in these applications is limited by corrosion in oxidative environments,7 diffusion into adjacent layers in microelectronics,2,3 and particle sintering and leaching in Cu-based catalysts.6 Recently, atomic layer deposition (ALD) of alumina using trimethylaluminum (TMA) has been introduced to form protective coatings on Cu surfaces that prevent corrosion in oxidative environments,8 diffusion of Cu in Cu2S films in photovoltaic (PV) devices,9 and sintering of Cu-based nanoparticles in liquid phase hydrogenation reactions.6,9,10

ALD is a variation of chemical vapor deposition (CVD) based on cyclic, self-limiting reactions of gaseous precursors with a solid surface.11 For binary ALD reactions, each ALD cycle consists of two half-cycles during which the surface is consecutively exposed to a precursor and a coreactant. Between each cycle, the reaction chamber is purged by inert gas or vacuum. TMA is the most widely used ALD precursor for growth of aluminum oxide films, and water is one of the most common coreactants (see, for instance, reference 12 and references therein).

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Though the interaction of TMA with adsorbed hydroxyl functional groups on Al has been studied in depth, the reaction of TMA with air-exposed copper surfaces complicates this ideal ALD picture due to the formation surface oxides at room temperature. Furthermore, this oxide persists and rearranges at 473–623 K to form the ordered “44” structure on Cu(111), a structured CuO overlayer with unit cell size 44 times larger than the Cu(111) unit cell. This temperature range corresponds to processing temperatures for TMA+H₂O ALD with the maximum growth rate. This and other adsorbed oxygen structures persist on the surface until at least 773 K. Hydroxyl formation via water dissociation on copper surfaces is not observed in UHV. No adsorbed hydroxyl species formed following exposure of clean Cu(111) to 1 Torr of water up to 333 K, however, a preoxidized Cu surface readily forms hydroxyls during water exposure at the same conditions. In UHV, exposure of a preoxidized Cu(111) surface to 200 L H₂O at 1 × 10⁻⁶ Torr at 473 K resulted in a surface with both oxide (Cu₂O) and hydroxide patches.

TMA+H₂O ALD performed on oxidized Cu surfaces has resulted in low growth per cycle during the first several cycles. Abdulagatov et al. studied alumina ALD on copper oxide using TMA and water on an in situ copper-plated quartz crystal microbalance (QCM). They observed a nucleation delay at 450 K. The nucleation delay was caused by blockage of the copper oxide surface by carbonaceous species and/or lack of initial hydroxyl groups; however, the cause was not determined due to the lack of chemical information. Lu et al. demonstrated that alumina grows preferentially on step edges of a partially hydroxylated, oxidized Cu(111) surface for TMA+H₂O ALD. They speculated from STM images that TMA reacts with OH but not copper oxide.

In this work, we sought to understand better the reactivity of TMA with copper oxide surfaces. More broadly, we sought to study the reactivity of TMA with copper oxide and alumina in the absence of a source of hydroxyl groups and to examine the resulting surface chemistry and morphology. The reaction of TMA with alumina has received attention in the literature; however, here we used O₂ as the ALD coreactant with the maximum growth rate. This and other adsorbed oxygen structures persist on the surface until at least 773 K. Hydroxyl formation via water dissociation on copper surfaces is difficult. On Cu(111), thermally induced water dissociation was not observed in UHV. No adsorbed hydroxyl species formed following exposure of clean Cu(111) to 1 Torr of water up to 333 K, however, a preoxidized Cu surface readily forms hydroxyls during water exposure at the same conditions. In UHV, exposure of a preoxidized Cu(111) surface to 200 L H₂O at 1 × 10⁻⁶ Torr at 473 K resulted in a surface with both oxide (Cu₂O) and hydroxide patches.

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In this work, we sought to understand better the reactivity of TMA with copper oxide surfaces. More broadly, we sought to study the reactivity of TMA with copper oxide and alumina in the absence of a source of hydroxyl groups and to examine the resulting surface chemistry and morphology. The reaction of TMA with alumina has received attention in the literature; however, here we used O₂ as the ALD coreactant rather than H₂O to isolate the interaction with the oxide and to exclude OH groups. We found that low carbon alumina films are possible using TMA+O₂ ALD, and that TMA reacts with oxygen in both alumina and copper oxide. The high growth rate of ~3-4 Å/cycle was achieved on the surface with low carbon content.

O₂ and O₂ plasma are coreactants often used with TMA (see, for instance, reference 20 and references therein). Typically, electronic properties of Al₂O₃ films (charge density, recombination velocity, breakdown field, dielectric constant, etc.) are discussed and the quality of Al₂O₃ films is compared for different oxidants (O₂, O₃ plasma, or H₂O) in the literature. In a few publications, possible chemical mechanisms were discussed for “H₂O-free” ALD with TMA. On the basis of simulations, Elliott et al. supposed that the chemical mechanism of TMA+O₂ involved hydroxyl groups, which were produced on the surface by the oxidation of adsorbed methyl groups by O₂. In situ FTIR studies of TMA+O₂ revealed that O incorporation into the surface results in a stable formate intermediate. Ammonium methoxy, –[Al(OCH₃)]₂, and surface Al−OH−Al linkages formed after O₂ pulses were suggested as reaction sites for TMA. In situ attenuated total reflection Fourier transform infrared spectroscopy data show that both OH groups and carbonates were formed on the surface during the oxidation cycle of TMA+O₂ and TMA+O₃ plasma. OH groups and C-containing impurities were found to be incorporated in the Al₂O₃ film during TMA+O₂ plasma ALD, and the impurity level could be reduced by prolonging the plasma exposure.

To obtain direct chemical information and elucidate the reaction pathways of TMA with copper oxide and alumina without OH groups, we coupled surface-sensitive techniques including X-ray photoelectron spectroscopy (XPS) and high-resolution electron energy loss spectroscopy (HREELS) with scanning tunneling microscopy (STM) and density functional theory (DFT) modeling.

EXPERIMENTAL SECTION

Experiments were performed in an Omicron Surface Analysis Cluster at the Birk Nanotechnology Center (BNC) at Purdue University and at the ISIS beamline at the BESSY II synchrotron in Berlin, Germany. The Omicron Surface Analysis Cluster consists of an ultrahigh vacuum (UHV) preparation chamber and a μ-metal analysis chamber with base pressures of 1×10⁻⁹ and 5×10⁻¹¹ mbar, respectively. The preparation chamber was equipped with a residual gas analyzer, an Ar⁺ sputtering gun, resistive sample heating, and ALD precursor manifolds for precursor dosing, which are connected to the system via leak valves. The analysis chamber was equipped with XPS, HREELS, STM, low energy electron diffraction (LEED), and resistive sample heating. The sample temperature was measured by a K-type thermocouple attached to the sample holder.

STM images were obtained at room temperature in constant current (topographic) mode with electrochemically etched W tips. Etched W tips were conditioned in UHV by electron bombardment. STM images were analyzed using WSXM software. STM height measurement was calibrated by setting the step height of a monatomic step on clean Cu(111) equal to 0.208 nm.

HREELS spectra were acquired using an EL5500 instrument (LK Technologies) in the specular direction with primary beam energy of 5 eV. The resolution, measured as the full width at half-maximum (fwhm) of the elastic peak, was <3 meV (<24 cm⁻¹). All HREELS spectra have been normalized to the elastic peak intensity.

XPS data were acquired using a nonmonochromatic Mg Kα X-ray source (hv = 1253.6 eV) with gun power of 150 W. High-resolution spectra were recorded at constant pass energy of 20 eV. The resolution, measured as the fwhm of the Cu 2p½/2 peak, was approximately 1.2 eV. Photoelectrons were collected at a photo-emission angle of 45° with respect to the surface normal. Energy scale correction was not foreseen by the analyzer manufacturer (the electron energy analyzer, Omicron EAC 125 and the analyzer controller, Omicron EAC 2000); therefore, it was possible only to set the Au 4f½/2 peak at 840.0 eV by changing the spectrometer work function.

The basic design of the experimental apparatus at BESSY II has been described in detail previously. It contains a load lock and in situ analysis cell connected to an energy analyzer spectrometer via differential pumping stages. The experimental procedures for sample preparation, TMA dosing, and data collection have been described in detail in our previous publication.

XPS data were analyzed with CasaXPS (version 2.3.16edv85) software. Cu 3s peaks were fitted using an asymmetric Gaussian/Lorentzian line shape with tail dampening (CasaXPS line shape = LF(1,2, 1.3, 15, 60)). Nonmetallic species of oxygen (O 1s) and aluminum (Al 2s) were fitted with symmetric Gaussian/Lorentzian line shapes (CasaXPS line shape = GL(30) or SGL(20)). The two most intense core level Al peaks, Al 2p and Al 2s, overlapped with the Cu 3p and Cu 3s peaks, respectively, associated with the Cu(111) substrate. Therefore, Al 2s and Al 2p contributions were calculated from the curve-fitting.

To calculate coverage from XPS data, we followed Fadley’s approach, which assumes a nonattenuating adlayer at fractional coverage. Coverage (θ), measured in monolayers (ML), is the ratio...
between the number of adsorbed species and the number of surface Cu atoms on (111) plane, and is expressed in eq 1:

\[
\Theta = \frac{N_l(\theta) \times \Omega_l(E_l) \times A_l(e_{l1}) \times \frac{d_{l1}}{d_{l2}} \times \lambda_{sab}^{sub(E_l)} \times \cos \theta}{N_l(\theta) \times \Omega_l(E_l) \times A_l(e_{l1}) \times \frac{d_{l1}}{d_{l2}} \times \cos \theta}
\]

where \(N_l(\theta)\) and \(N_l(\theta)\) are the photoemission peak areas of the adlayer and the substrate at the given photoemission angle, \(\theta\), with respect to the surface normal; \(\Omega\) is the acceptance solid angle of the electron analyzer; \(A_l\) and \(A_s\) are the effective substrate and adlayer area; \((d_{l1})/d_{l2}\) and \((d_{l1})/d_{l2}\) are differential cross sections for the photoemission peaks of the adlayer and the substrate, which are calculated using tabulated Scofield cross sections\(^{32}\) and the Reilman asymmetry parameters:\(^{33}\) \(\lambda_{sab}^{sub(E_l)}\) is the electron attenuation length (EAL) of the photoelectrons originating from the substrate atom that have traveled through the substrate material; \(d_i\) is the interlayer distance of the Cu(111) substrate. The EAL was calculated by NIST SRD-82.\(^{34}\) Overlayer thicknesses were calculated using eq 2:

\[
\frac{N_l(\theta)}{N_l(\theta)} = \frac{\rho_l \times \frac{d_{l1}}{d_{l2}} \times \lambda_{sab}^{sub(E_l)} \times \left(1 - \exp^{-\frac{1}{\lambda_{eff}(E_l) \times \cos \theta}}\right)}{\rho_s \times \frac{d_{s1}}{d_{s2}} \times \lambda_{sab}^{sub(E_s)} \times \left(1 - \exp^{-\frac{1}{\lambda_{eff}(E_s) \times \cos \theta}}\right)}
\]

where \(\rho_l\) and \(\rho_s\) are the atomic densities of the overlayer and the substrate, respectively; \(\lambda_{sab}^{sub(E_l)}\) is the EAL of the photoelectrons originating from a substrate atom that have traveled through the substrate material; \(\lambda_{sab}^{sub(E_s)}\) is the EAL of photoelectrons originating from an overlayer atom that have traveled through the overlayer material; \(\lambda_{sab}^{sub(E_s)}\) is the EAL of photoelectrons originating from a substrate atom that have traveled through the overlayer material; and \(t\) is the overlayer thickness. All other variables are the same as in eq 1. XPS model derivations have been explained in detail in our previous publication.\(^{35}\) eq 2 can be solved for \(t\) using the Thickness Solver tool.\(^{36}\)

A Cu(111) single crystal disk with 10.0 mm diameter, 1.0 mm thickness (Princeton Scientific Corp.), and crystallographic orientation accuracy <0.5° was used. A polycrystalline Cu foil (Sigma-Aldrich, 99.99%) was used for the synchrotron experiments. Both samples were routinely cleaned by repeated cycles of Ar\(^+\) sputtering and vacuum annealing at 1000 K. During the initial cleaning cycles, the Cu(111) crystal was treated in 5 × 10\(^{-6}\) mbar of O\(_2\) at 623–673 K for 20 min to remove adventitious carbon. Single crystal cleanliness was monitored by XPS, STM, and LEED. No impurities (C, O, etc.) were detected by XPS on the Cu foil after cleaning procedures.

The Cu(111) crystal was exposed to TMA (Aldrich, 97%) in the preparation chamber via a leak valve at reported exposure values and temperatures. Prior to dosing TMA, several cycles of freeze–pump–thaw were performed for purification. Dosing lines were heated overnight at 423 K, and the lines were filled with TMA and pumped several times before dosing. Exposure values are reported in Langmuir (1 Langmuir = 1 L = 1 × 10\(^{19}\) Torr-s), and pressures used to calculate exposures are taken from uncorrected ion gauge measurements. During TMA dosing, ionization gauges were left on for pressure measurement. Similar cycles of freeze–pump–thaw were performed on water ("Birck Nanograde Water", as SEMI E12.1 with the total organic carbon (TOC) reduced from 1 to 0.25 ppb). The water mini-cylinder was kept at room temperature during dosing. Separate dosing lines and leak valves were used for water to avoid cross contamination and accidental exposure of TMA to water in the dosing manifold.

**Computational Methods.** DFT calculations were performed by Vienna ab initio simulation package (VASP)\(^{37}\) using projected augmented wave (PAW)\(^{38}\) potential and PW91 exchange-correlation functional.\(^{39}\) A plane wave cutoff of 400 eV was used. Cu(111) was modeled by a three-layer slab with (3 × 3) unit cell. The ordered Cu\(_2\)O layer grown on Cu(111) has a well-defined long-range structure in the literature consisting of Cu–O rings with isolated O located inside each ring.\(^{13,40}\) The presence of this structure is confirmed by our STM images. To model this structure, a ring including 12 Cu and 13 O atoms on two-layer Cu(111) with (5 × 5) unit cell was used (Figure 1). The (4 × 4 × 1) and (2 × 2 × 1) k-point meshes were used to sample the Brillouin zone for Cu(111) and Cu\(_2\)O, respectively. The bottom-layer Cu atoms were fixed and the remaining atoms and adsorbates were relaxed until the residual forces less than 0.02 eV/Å. To prevent artificial interaction between the repeated slabs along the z-direction, 12 Å vacuum was introduced with correction of the dipole moment.

**RESULTS AND DISCUSSIONS**

**Interaction of TMA and H\(_2\)O on Cu Foil.** One goal of this work was to investigate the reactivity of TMA with copper oxide in the absence of hydroxyl groups. This was motivated by our previous research of TMA+H\(_2\)O ALD on Pt(111) and Pd(111).\(^{29,42}\) In that work, aluminum hydroxide species were detected at <573 K in 0.1 mbar H\(_2\)O. These species dehydroxylated at higher temperatures. The hydroxide species gave rise to the Al 2p\(_{3/2}\) XPS peak at 74.9 eV, whereas alumina was characterized by a peak at 74.0 eV. Similarly, for in situ, synchrotron-based XPS of TMA+H\(_2\)O on Cu foil, the Al 2p BE shifted from ca. 75.1 eV after dosing TMA to 74.7 eV after dosing water at 473 K (Figure 2). The Al 2p peak showed the same trend. This BE shift is difficult to explain by the transformation of aluminum hydroxides to aluminum oxide and back: in 0.1 mbar H\(_2\)O, more hydroxide is expected than following TMA exposure, so a higher Al 2p BE under 0.1 mbar H\(_2\)O than after TMA exposure was expected, but the opposite trend was observed. To investigate possible alternative mechanisms of TMA interaction with Cu surfaces, we excluded the source of OH groups (H\(_2\)O) and other possible contaminants in the in situ cell by studying TMA+O\(_2\) ALD under UHV conditions.

**Interaction of TMA with Clean Cu(111).** The interaction of TMA with clean Cu(111) was investigated after TMA exposure by XPS and HREELS. The Cu 2p\(_{1/2}\) and Cu 3s peaks obtained from clean, oxygen-free Cu(111) were located at 932.8 and 122.3 eV, respectively, both within 0.1 eV of literature-reported values for metallic Cu.\(^{43}\) Figure 3 shows the Cu 3s/Al 2s XPS region obtained from the clean Cu(111) surface and following 2000 L TMA exposure at 473 K. No aluminum peaks, Al 2p or Al 2s, were observed by XPS following TMA adsorption on Cu(111). HREELS did not detect any characteristic vibrations of TMA or its fragments.\(^{42}\) The absence of TMA adsorption on clean Cu(111) is in agreement with the findings of Lu et al.\(^{17}\)

DFT calculations are also consistent with the lack of TMA adsorption on clean Cu(111). Figure 4 shows the free energy
The energy loss from the entropy of the gas-phase TMA (g) at 473 K and standard pressure was 0.84 eV and the binding energy of TMA adsorbed on Cu(111) was $-0.28 \text{ eV}$ (computational details regarding entropy changes associated with precursor adsorption can be found in reference 44). Therefore, the difference between the free energy level of TMA (g) and TMA* was $+0.56 \text{ eV}$. This means that TMA adsorption on Cu(111) is endothermic. TMA dissociation on clean Cu(111) was also found to be endothermic: the calculated energies for dissociative reactions of TMA to dimethylaluminum (DMA), DMA to methylaluminum (MA), and MA to Al and CH$_3$ were 0.17, 0.45, and 1.35 eV, respectively.

**Preparation of Cu$_2$O/Cu(111).** Oxygen was adsorbed on Cu(111) by exposure to 4500 L O$_2$ at 623 K. O 1s, Al 2s, and C 1s XPS core-level regions obtained from the Cu$_2$O/Cu(111) surface are shown in Figure 5, and STM images are presented in Figure 6. The O 1s peak was fitted with one component at 529.8 eV, which was assigned to oxygen in the Cu$_2$O layer (assignment made by STM below). Reported Cu$_2$O BEs range from 529.9 to 531.0 eV (see reference 45 and references therein). A high BE shoulder at ca. 936.0 eV was observed in the Cu 2p$_{3/2}$ core-level region following oxygen exposure indicating that some Cu$_2$O was present (data shown in Supporting Information Figure S1). The Cu 3s/Al 2s region was unaffected by the first O$_2$ exposure. Neither XPS nor HREELS of this surface revealed any hydroxyl species (HREELS spectrum shown in Supporting Information Figure S2). It should be noted that Al 2s was used instead of Al 2p for UHV XPS experiments due to the overlap of Al 2p with Cu 3p.

Figure 6a shows STM images of clean Cu(111), and Figure 6b−e shows Cu(111) following oxygen exposure. The step edges of the clean Cu(111) surface are smooth with step height of 0.21 nm. After oxygen exposure at 623 K, a sawtooth pattern is observed on the steps (Figure 6b), and a well-ordered oxide structure is observed on terraces (Figure 6c−e). After annealing oxygen-exposed Cu(111) surfaces at 473−623 K, Matsumoto et al. observed the well-ordered “44” structure, which consists of 7 hexagonal O–Cu–O rings in a unit cell 44 times larger than the $(1 \times 1)$ unit cell of Cu(111). This superficial oxide has stoichiometry Cu$_2$O. A scheme of the 7 rings is shown overlaying our STM image in Figure 6e.

The assignment to Cu$_2$O is based on STM images showing the “44” structure and lack of pronounced O$_2$ XPS shakeup in the Cu 2p region. We cannot rule out the presence of small amounts of Cu$_2^+$ given the surface sensitivity of our instrument. After O$_2$ half-cycles, we do see slight broadening of the Cu 2p peak high BE side (shown in Supporting Information Figure S1), which might be indicative of the formation of some Cu$_2^+$. 

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**Figure 2.** Cu 3p/Al 2p core-level regions obtained during TMA+H$_2$O ALD cycles on Cu foil by in situ XPS. (a) Second TMA half-cycle, (b) second H$_2$O half-cycle, (c) third TMA half-cycle, and (d) third H$_2$O half-cycle. TMA was exposed for 2000 L at ca. 373−473 K for all TMA half-cycles, and H$_2$O was dosed in situ at 473 K at 0.1 mbar for all H$_2$O half-cycles.

**Figure 3.** (a) Cu 3s/Al 2s XPS spectra obtained from clean Cu(111) (open circles) and from Cu(111) exposed to 2000 L TMA at 473 K (filled circles). The expected region for Al 2s is marked by the red bar. The inset shows the magnified Al 2s region.

**Figure 4.** Free energy diagrams of TMA dissociation on Cu(111) and Cu$_2$O/Cu(111). The insets are the optimized most stable structures of adsorbed TMA, dimethylaluminum (DMA), methylaluminum (MA), Al, and CH$_3$, respectively. The orange, green, pink, black, red, and white spheres represent Cu of Cu(111), Cu of Cu$_2$O, Al, C, O, and H atoms, respectively.

**Figure 5.** Cu 3p/Al 2p core-level regions obtained during TMA+H$_2$O ALD cycles on Cu foil by in situ XPS. (a) Second TMA half-cycle, (b) second H$_2$O half-cycle, (c) third TMA half-cycle, and (d) third H$_2$O half-cycle. TMA was exposed for 2000 L at ca. 373−473 K for all TMA half-cycles, and H$_2$O was dosed in situ at 473 K at 0.1 mbar for all H$_2$O half-cycles.
Cu⁺ and Cu⁰ are difficult to separate from the Cu 2p core-level, as their range of reported binding energies overlap.⁴³

First TMA Half-Cycle. Figure 7 shows the HREELS spectrum obtained after Cu₂O/Cu(111) was exposed to 2000 L TMA at 473 K. Major peaks were detected at 608, 747, and 882 cm⁻¹, and weaker peaks were detected at ca. 1480, 1645, and 1750 cm⁻¹. The peak at 608 cm⁻¹ (ν₁) was assigned to the group of stretching vibrations between tetrahedrally coordinated Al³⁺ cations (A₄tet) and their four nearest O²⁻ neighbors, the peak at 880 cm⁻¹ (ν₃) was due to the group of stretching vibrations between octahedrally coordinated Al³⁺ cations (A₆oct) and their six nearest O²⁻ neighbors (ν₃), and the peaks at 1480 and 1750 cm⁻¹ correspond to 2ν₁ and 2ν₃ multiple loss events, respectively.⁴⁶,⁴⁷

The ratio of the peak areas of tetrahedral to octahedral Al³⁺, Altet/Aloct, (Figure 7) was 0.27. The peak at 740−770 cm⁻¹ (ν₂) (and the multiple loss event peak 2ν₂ at 1645 cm⁻¹) was not assigned. Other weak peaks that appeared at 1215 and 2920 cm⁻¹ likely were δₛ(CH₃) and νₛ/as (CH₃) signatures, respectively, of methyl groups attached to the copper surface.⁴⁸,⁴⁹ Indeed, DFT predicted that methyl ligands were transferred from Al center to the copper surface (Figure 4). However, dehydrogenation of the CH₃ ads species could not be ruled out: the peak at 2920 cm⁻¹ was broad and it might be characteristic of other CHₓ ads species such as CH₄ ads and CH₂ ads. The corresponding deformation vibrations, δ(CHₓ), likely overlapped with intense ν₁, ν₂, ν₃ and multiple losses. Nominal carbon coverage was approximately 1.0 ML.

We did not observe a loss peak at ca. 400 cm⁻¹ that has been assigned previously to vertical Al−O vibrations between in-phase alumina layers on different metal surfaces.⁵⁰ This supports the assignment of monolayer growth during the first cycle. As shown in Figure 6, the ratio of ν₁ to ν₃ (tetrahedral to octahedral) peak areas was 0.27.

After TMA was dosed to the Cu₂O/Cu(111) surface, the XPS O 1s peak shifted from 529.7 to 532.1 eV (Figure 5) and the shoulder of Cu 2p3/2 at 936.0 eV disappeared, revealing that oxygen adsorbed on Cu was incorporated into the newly formed adlayer structure. Similarly, surface oxides have been reduced on GaAs and Ge(100) substrates during TMA exposure.⁵⁰,⁵¹ The Al 2s contribution to the Al 2s/Cu 3s

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Figure 5. O 1s, Cu 3s/Al 2s, and C 1s XPS core-level regions obtained (a) from Cu₂O/Cu(111) (4500 L O₂ at 623 K), (b) after the first TMA half-cycle, (c) after the first O₂ half-cycle, (d) after the second TMA half-cycle, (e) after the second O₂ half-cycle, and (f) after four complete ALD cycles. TMA was exposed for 2000 L at 473 K for all TMA half-cycles, and O₂ was exposed for 4500 L O₂ at 623 K for all O₂ half-cycles. The apparent increase in Al 2s peak intensity after O₂ half-cycles relative to TMA cycles is due to the removal of carbon.

Figure 6. STM images of (a) clean Cu(111) and (b–e) Cu(111) exposed to 4500 L O₂ at 623 K. The seven rings of Cu₂O with the “44” structure are shown in image e. Bias voltages were −0.5 V for all images, and tunneling currents were 0.5 nA (images a, b) and 1.0 nA (images c–e). Image e was processed using a wavelet filter in WSxM Software; see the Supporting Information for more details.

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First TMA Half-Cycle. Figure 7 shows the HREELS spectrum obtained after Cu₂O/Cu(111) was exposed to 2000 L TMA at 473 K. Major peaks were detected at 608, 747, and 882 cm⁻¹, and weaker peaks were detected at ca. 1480, 1645, and 1750 cm⁻¹. The peak at 608 cm⁻¹ (ν₁) was assigned to the group of stretching vibrations between tetrahedrally coordinated Al³⁺ cations (A₄tet) and their four nearest O²⁻ neighbors, the peak at 880 cm⁻¹ (ν₃) was due to the group of stretching vibrations between octahedrally coordinated Al³⁺ cations (A₆oct) and their six nearest O²⁻ neighbors (ν₃), and the peaks at 1480 and 1750 cm⁻¹ correspond to 2ν₁ and 2ν₃ multiple loss events, respectively.⁴⁶,⁴⁷

The ratio of the peak areas of tetrahedral to octahedral Al³⁺, Altet/Aloct, (Figure 7) was 0.27. The peak at 740−770 cm⁻¹ (ν₂) (and the multiple loss event peak 2ν₂ at 1645 cm⁻¹) was not assigned. Other weak peaks that appeared at 1215 and 2920 cm⁻¹ likely were δₛ(CH₃) and νₛ/as (CH₃) signatures, respectively, of methyl groups attached to the copper surface.⁴⁸,⁴⁹ Indeed, DFT predicted that methyl ligands were transferred from Al center to the copper surface (Figure 4). However, dehydrogenation of the CH₃ ads species could not be ruled out: the peak at 2920 cm⁻¹ was broad and it might be characteristic of other CHₓ ads species such as CH₄ ads and CH₂ ads. The corresponding deformation vibrations, δ(CHₓ), likely overlapped with intense ν₁, ν₂, ν₃ and multiple losses. Nominal carbon coverage was approximately 1.0 ML.

We did not observe a loss peak at ca. 400 cm⁻¹ that has been assigned previously to vertical Al−O vibrations between in-phase alumina layers on different metal surfaces.⁵⁰ This supports the assignment of monolayer growth during the first cycle. As shown in Figure 6, the ratio of ν₁ to ν₃ (tetrahedral to octahedral) peak areas was 0.27.

After TMA was dosed to the Cu₂O/Cu(111) surface, the XPS O 1s peak shifted from 529.7 to 532.1 eV (Figure 5) and the shoulder of Cu 2p3/2 at 936.0 eV disappeared, revealing that oxygen adsorbed on Cu was incorporated into the newly formed adlayer structure. Similarly, surface oxides have been reduced on GaAs and Ge(100) substrates during TMA exposure.⁵⁰,⁵¹ The Al 2s contribution to the Al 2s/Cu 3s...
A peak envelope was observed at ca. 119.5 eV (Figure 5b). The O 1s (Al−O contribution) and Al 2s peak areas were used to calculate O and Al atomic percentages. The resulting Al:O atomic percentage ratios are plotted for each O2 half-cycle in Figure 8. For the first TMA half-cycle, the Al:O ratio was approximately 0.46. Stoichiometric Al2O3 would yield an Al:O ratio of 0.66. This Al:O ratio of approximately 0.5 suggests the presence of a copper aluminate, for example CuAlO2.

STM images of the TMA-exposed surface (Figure 9) reveal two-dimensional (2D) islands on the surface with an average height of approximately 0.19 nm (a pixel height histogram was used for island height estimation and is shown in Supporting Information Figure S3). No long-range order of the copper surface oxide was observed. The bimodal peak distribution in the height histogram confirmed that the islands are flat with uniform height. Some defects (shown by black arrows in Figure 9b) were observed.

TMA adsorption and dissociation on the Cu2O/Cu(111) surface was found to be exothermic (Figure 4). TMA tends to adsorb at the top position on O in the Cu−O ring via an Al atom with a binding energy of −0.93 eV, which is stronger by 0.65 eV compared to adsorption on clean Cu(111). The free energy for TMA dissociation to DMA is −1.91 eV, and the formed DMA is bound to the bridge site of two adjacent O atoms in the Cu−O ring. DMA dissociation to MA is exothermic by −1.36 eV, and the Al atom of MA coordinates with three O atoms including the isolated O inside the ring. The final step considered, MA dissociation to Al and CH3, is exothermic by −0.09 eV, and the formed Al atom is bound to three O atoms. The exothermicity of dissociative TMA adsorption on the Cu2O/Cu(111) surface is the result of high binding energies of the intermediates on this surface. Compared with clean Cu(111), the binding energies of DMA, MA, Al, and CH3 are stronger on Cu2O/Cu(111) by 2.19, 3.45, 4.35, and 0.54 eV, respectively. In conclusion, DFT calculations predicted no TMA adsorption on Cu(111) but TMA adsorption and dissociation on Cu2O/Cu(111), consistent with experimental data.

Both experiments and first-principles calculations demonstrate that TMA is capable of reacting with a copper oxide surface in the absence of hydroxyl species. The reaction of TMA with the Cu2O/Cu(111) layer is limited by the initial amount of oxygen present in the Cu2O lattice and as trace CuO. TMA consumes oxygen from the surface oxide and...
reduces oxidized Cu to the metallic state, as evidenced by the lack of long-range order in STM images and the shift in the O 1s XPS peak following the TMA half-cycle. Once the substrate is reduced to Cu\(^0\), the surface is inactive for further TMA adsorption and decomposition. As evidenced by the partial monolayer film growth, oxygen must migrate across the surface, forming adlayer islands. On the basis of the Al:O ratio of 0.46, these islands are most likely CuAlO\(_2\). The island height of 0.19 nm is close to the reported Cu–O and Al–O bond lengths of 1.861 and 1.912 Å, respectively, in CuAlO\(_2\) crystalline.

On the basis of the data discussed above, a simplified stoichiometric equation of TMA reaction with on Cu\(_2\)O/Cu(111) can be proposed:

\[
2\text{Cu}_2\text{O} + \text{Al(CH}_3\text{)}_3 \rightarrow \text{CuAlO}_2 + 3\text{Cu} + 2\text{CH}_4 \uparrow + \text{CH}_3\text{ads} \tag{3}
\]

TMA adsorption is limited by the amount of the surface oxygen. The island formation during TMA dosing can be explained by the difference of surface atomic densities of the reactant and products in eq 3. The density of surface copper atoms in the “44” structure is approximately 2 times lower than the corresponding value for Cu(111), meaning that 2 Cu\(_2\)O units cover an area of 8 Cu atoms in the Cu(111) terrace. Three copper atoms and CuAlO\(_2\) cannot compensate the area of 2 Cu\(_2\)O, and this leads to the island formation as shown in Figure 9. The transformation of hydrocarbon products is not straightforward. HREELS revealed methyl groups on the surface. On the other hand, methyl group dehydrogenation could not be ruled out.

**First \(O_2\) Half-Cycle.** Following TMA exposure to the Cu\(_2\)O/Cu(111) surface, \(O_2\) was exposed to the resulting surface for 4500 L at 623 K. The HREELS spectrum obtained from this surface is shown in Figure 7b. Compared to the first TMA half-cycle, the intensity of the peak at 608 cm\(^{-1}\) related to Al\(_{\text{ads}}\) increased, and the Al\(_{\text{ads}}\)/Al\(_{\text{surf}}\) intensity ratio was equal to 0.51 (Figure 7). The \(\delta_\text{CH}_3\) and \(\nu_{\text{asCH}_3}\) vibrations of the CH\(_{\text{ads}}\) groups on Cu(111) disappeared, but a weak C 1s peak slightly shifted to higher BE was detected by XPS (Figure 5). The fact that there was more octahedral Al\(^{3+}\) present after the TMA cycle than after the O\(_2\) half-cycle could be due to the formation of CuAlO\(_2\) after the TMA half-cycle, in which Al\(^{3+}\) cations are octahedrally coordinated.\(^{51}\)

Curve-fitting of the O 1s peak revealed two components: the component at 529.9 eV represents Cu\(_2\)O (19% of the total O 1s area) and the second component at 530.8 eV is from oxygen in the copper aluminate (81% of the total O 1s area) (Figure 5). An O 1s BE of 531.2 eV has been reported previously for thin film alumina on Pt(111).\(^{29}\) The slight Cu 2p\(_{\text{2/3}}\) peak shoulder reappeared at ca. 936.0 eV, consistent with the formation of some CuO (see Supporting Information Figure S1). Cu\(_2\)O was also formed, as evidenced by long-range order observed in STM images (Figure 10b,c). The Al 2s peak is distinguishable from the shoulder of Cu 3s at 118.7 eV (Figure 5). Al 2s shifted by ~0.8 eV to 118.7 eV following \(O_2\) exposure. Lower Al 2p binding energies for aluminum oxides have been attributed to the presence of Al\(^{3+}\) coordinated tetrahedrally\(^{29}\) (see discussion in reference 29). In this case, the Al 2p and Cu 3p peaks overlap, but the Al 2s and Al 2p peaks should exhibit a similar chemical shift in XPS. Here, the shift to lower BE is consistent with the formation of alumina with an increased Al\(_{\text{surf}}\)/Al\(_{\text{ads}}\) ratio following the O\(_2\) half-cycle. A hydroxide-containing species can cause a similar shift of the O 1s and Al 2p (Al 2s) peaks;\(^{56–58}\) however, no O–H stretching vibrations were detected by HREELS after TMA or \(O_2\) half-cycles at ca. 3300–3700 cm\(^{-1}\). The Al:O ratio after the first O\(_2\) half-cycle was approximately 0.53, nearly unchanged from after the first TMA cycle. The resulting Al:O atomic percentage ratios after each O\(_2\) half-cycle are plotted in Figure 8.

Figure 10 shows STM images of the copper surface after the first \(O_2\) half-cycle. As evidenced by the well-ordered Cu\(_2\)O structure that can be seen in atomic-resolution images (Figure 10b,c), \(O_2\) exposure reoxidizes the copper surface. Two other features are observed: Aluminum oxide islands that appeared after the first TMA half-cycle with an average height of 0.17 nm (marked by black arrow in Figure 10a), and dark spots appeared on the Cu terrace. Obtaining STM images over regions with a high density of aluminum oxide islands was problematic due to the low density of states for achieving a stable tunneling current and therefore was avoided. Dark spots with a triangular shape are marked inside yellow lines in Figure 10b. As shown by Matsumoto et al.,\(^{13}\) oxygen is capable of abstracting Cu from terraces and leaves behind triangular holes with the 3-fold symmetry. Some of these pits are decorated with bright features (apparent height of ~1.5 nm, Figure 10c,d). These features could be Cu adatoms from the oxide structure that became mobile and diffused across the surface until reaching a low-coordination site such as a hole. The holes detected by STM are likely “mines” delivering copper to the surface, as has been observed for Ag in the Cu/Ag(111) system.\(^{59}\)

A simple mechanism for the O\(_2\) half-cycle can be proposed:

\[
2\text{Cu} + 2\text{CuAlO}_2 + 2\text{CH}_3\text{ads} + 3\text{O}_2 \rightarrow 2\text{Cu}_2\text{O} + \text{Al}_2\text{O}_3 + 2\text{CO}_2 \uparrow + \text{H}_2\text{O}\uparrow \tag{4}
\]
Copper is reoxidized forming the Cu₂O/Cu(111) structure, as shown in Figure 10. Because the Cu₂O structure has a lower density of copper atoms than a Cu(111) terrace, Cu₂O formation results in “swelling” the surface and the islands become masked. The CHₓ,ads species reacts with oxygen and desorbed as CO₂ and H₂O. The recombination of CHₓ,ads to C₂ and C₃ products cannot be ruled out completely, but this process should be unfavorable in the presence of oxygen. The role of copper is to provide dissociation sites for O₂ adsorption and dissociation. The transformation of CuAlO₂ to Al₂O₃ was not confirmed but it can explain the changing ratio of tetrahedral to octahedral HREELS peak areas.

**Second ALD Cycle.** Figure 11 shows STM images obtained after the second TMA half-cycle. Numerous holes were seen on terraces and islands. Terraces were covered with islands having sharp boundaries and a ridge-like structure (marked by a rectangle in Figure 11b,c). These morphological changes reflected the transition from monolayer alumina islands after the first TMA half-cycle (Figure 9) to multilayer islands, as the ridge structure is likely the second alumina layer and/or CuAlO₂. The ridges have an apparent height of about 0.17 nm (Figure 11b), close to the average height for the alumina islands (0.19 nm) after the first TMA half-cycle observed in Figure 9.

Similar to the first TMA half-cycle, TMA consumed oxygen from the Cu₂O structure and reduced Cu oxide to Cu⁰ as evident from the disappearance of long-range ordered Cu₂O structures in STM images. Unlike the first TMA half-cycle, growth is not limited to the copper oxide surface as existing alumina islands can serve as the oxygen source. TMA reduces the aluminum oxide layer wherever the two are in direct contact.

After the second O₂ half-cycle, the Al 2s and O 1s peaks were shifted toward lower BEs at 118.9 and 531.0 eV, respectively (Figure 5). As discussed above, these peaks are characteristic of the alumina structure with the Al₅tet/Al₉oct HREELS peak area ratio of ~0.5 (Figure 7 inset). The Cu₂O contribution in the O 1s peak was one-quarter the size (% of the O 1s area) of the corresponding value observed after the first O₂ half-cycle, which reflected the decrease in the copper surface available for oxygen adsorption. Most carbon was removed after the second O₂ half-cycle (Figure 5), consistent with disappearance of the δ(CH₃) and νas(CH₃) peaks in the HREELS spectrum (Figure 7).

**Subsequent ALD Half Cycles and Film Growth Behavior.** Seven ALD cycles (14 half-cycles of O₂ and TMA) were performed on the Cu₂O/Cu(111) surface (Figure 12). Each TMA half-cycle consisted of 2000 L TMA at 473 K
and each O2 half-cycle consisted of 4500 L O2 at 623 K. Nominal alumina thicknesses calculated from the Al 2s and O 1s peaks are plotted in Figure 12. Roughly linear alumina growth is observed during the first 7 ALD cycles. The nominal calculated thickness gain per cycle using the Al 2s and O 1s peaks, respectively, were 3.0 ± 0.1 and 3.9 ± 0.2 Å. From STM images, we conclude that Al deposition occurred on the surface peaks, respectively, were 3.0 ± 0.1 and 3.9 ± 0.2 Å. From STM images, we conclude that Al deposition occurred on the surface peaks, respectively, were 3.0 ± 0.1 and 3.9 ± 0.2 Å. From STM images, we conclude that Al deposition occurred on the surface.

The water half-cycles were also ineffective for carbon removal. After four ALD cycles the carbon atomic percentage was ~30%. After one H2O ALD cycle at 473 K, the nominal alumina thickness was about 3 Å, and the thickness did not increase for subsequent cycles. It must be noted that carbon removal behavior at the dosing pressures of O2 and H2O used in this study (~10^-6 mbar) may not be representative of the same ALD process carried out in a typical ALD reactor at pressures of a few millibars.29 On the other hand, we observed carbon accumulation on Cu foil during TMA+H2O ALD in situ using synchrotron-based XPS at 473 K and 0.1 mbar H2O pressure.

For ideal alumina ALD using H2O as the coreactant, methyl ligands from TMA are partially exchanged with surface hydroxyl groups and the precursor becomes anchored to the surface during the first TMA half-cycle. Ideally, the coreactant provides the missing element (oxygen), removes the carbon groups via hydrogen transfer to CH3, and functionalizes the surface for the upcoming TMA half-cycle. However, as demonstrated, this ideal picture is not always fulfilled, as TMA fully decomposes and forms an aluminate by losing all its methyl ligands upon deposition on a hydroxide-free Cu2O surface at 473 K. TMA decomposition leaves behind carbon atoms and clusters, and methyl groups attached to the copper surface. Once the copper surface is completely covered, TMA continues to react with hydroxide-free alumina.

Others have studied the reaction of TMA with oxide-terminated alumina. Dillon et al.18 observed the appearance of IR features assigned to CH3 stretching following a saturation exposure of TMA to a porous alumina membrane previously annealed to 1000 K. These IR features had an integrated absorbance equal to 72% of the same features following exposure of an alumina surface with a saturation amount of hydroxyl. These CH3 stretching features attenuated upon annealing between 300 to 860 K.18 Puurunen et al.19 found that TMA reacted between 353 and 573 K with alumina pretreated at 473 K, and decomposed above 600 K. Assuming that all TMA reacts with hydroxyl groups, releases methane, and forms OAIME species, the amount of carbon observed on the alumina with the highest pretreatment temperatures was higher than expected based on this assumption, suggesting that TMA adsorbs dissociatively on coordinatively unsaturated Al. They found that the amount of methyl groups present on alumina pretreated at 1073 K was 15% less than on alumina treated at 473 K. Elliott et al.14 showed with first-principles calculations that TMA will chemisorb on both bare alumina and hydroxylated surfaces, that hydroxyl coverage does not affect site density, and that adsorbed TMA dissociates to form AlMe3, AlMe, and Me on both surfaces. However, the hydrogen in OH− reacts with methyl groups and CH4 is evolved, so the ALD rate, which is affected by steric hindrance of CH3 groups, is greater on hydroxylated surfaces. The findings shown here agree with the above authors.

The temperature of the surface during oxygen exposure plays an important role in the carbon removal and alumina growth behavior. Incorporation of impurities including carbon is a major concern in oxide dielectrics where an ultrathin film (<10 nm) is deposited by ALD. This application requires a carbon-free oxide film to achieve high-quality microelectronic devices.51

**Figure 12.** BEs of O 1s (red outlines) and Al 2s (solid black) peaks after each half-cycle of TMA or O2 half-cycles. Squares were data points taken after TMA half-cycles, and circles were data points taken after O2 half-cycles. Seven cycles in total were performed. The starting surface was the Cu2O/Cu(111) surface.

Figure 13 plots O 1s and Al 2s BEs after each TMA and O2 half-cycle. The common behavior of the O 1s and Al 2s peaks was the shift to higher BE values after TMA half-cycles and the shift to lower BE values after O2 half-cycles. On the basis of HREELS data from the first two cycles, these changes resulted from the transition between the octahedral and tetrahedral coordination of aluminum cations. The Al contribution increased during TMA half-cycles, and the Al contributions increased during O2 half-cycles.

**Figure 13.** BEs of O 1s (red outlines) and Al 2s (solid black) peaks after each TMA or O2 half-cycle. Squares were data points taken after TMA half-cycles, and circles were data points taken after O2 half-cycles. Seven cycles in total were performed. The starting surface was the Cu2O/Cu(111) surface.
As shown in Figure 8, the Al:O ratio is close to 0.5 for the first 3–4 ALD cycles before increasing and remaining steady at about 0.66. This transition in stoichiometry corresponds to the film closure. As shown in the O 1s region in Figure 5, the Cu=O peak from the Cu₂O surface oxide is no longer present after 4 ALD cycles. In the first several ALD cycles, the Al:O stoichiometry of 1:2 is due to the presence of CuAlO₂. There is more octahedral alumina after the early TMA cycles, because Al occupies the octahedral sites in CuAlO₂. The presence of copper in the first few cycles forces Al into the octahedral positions. As the film closes and Cu is covered, the stoichiometry shifts to that of alumina, Al₂O₃. Alumina interacts with Cu at the interface. Though HREELS data for cycles beyond the second cycle were not collected, amorphous alumina is likely formed by ALD at these conditions.

Finally, we must note that the growth rates measured for TMA+O₂ ALD in this study are likely to differ from growth rates for the same process carried out at millibar pressures in a flow reactor. Because the focus of this study is on the first several ALD cycles, the Cu substrate may affect film growth even after film closure. The cleanliness of surfaces studied here is likely superior to those used for a typical ALD flow reactor, where contaminants may block ALD nucleation sites and often surface sensitive techniques to measure contaminant levels are not available. Finally, the high vacuum dosing pressures used in this study could alter the growth rate.

■ CONCLUSION

We have shown with surface sensitive characterization techniques and DFT calculations that TMA does not react with or adsorb on metallic Cu(111), but that TMA adsorption and decomposition to Al are thermodynamically favorable on Cu₂O. During the first half-cycle, TMA reacts with O adsorbed on Cu(111), depositing Al in the form of single layered aluminate islands. This reduces surface copper not bound to the aluminate to the metallic state, which does not interact with TMA. Therefore, the amount of adsorbed O limits the growth of Al during the first half-cycle.

From XPS and HREELS, TMA half-cycles favor production of octahedrally coordinated alumina, whereas O₃ half-cycles at higher temperature favor production of alumina in tetrahedral coordination. During the first ~3 cycles while Cu is still exposed, XPS can differentiate between O in Cu₂O and CuAlO₂, and TMA interacts with both Cu₂O and the aluminate. TMA continues to interact with the aluminate/alumina once Cu is completely covered.

The choice of processing conditions in high vacuum determines the extent of carbon incorporation in the ALD film. Dosing TMA at 473 K and O₂ at 673 K results in a film with less carbon than when H₂O is used instead of O₂ at the same temperature, and for O₂ at 473 K. These alternative processing conditions result in increasing C deposition with each ALD cycle and little or no Al adsorption after about the third ALD cycle.

We have demonstrated that TMA readily reacts with oxide surfaces even in the absence of coadsorbed hydroxyls. For ALD applications on an air-exposed Cu surface, large domains of oxides might still exist. This is of great importance to thin film applications like microelectronics and catalysis where only a few ALD cycles are desirable. In general, TMA–ALD processing of thin alumina films on initially preoxidized copper substrates using O₂ half-cycles instead of H₂O offers a route to well-defined, carbon depleted, and dehydroxylated films. The high growth rate of ca. 3–4 Å/cycle was observed for TMA+O₂ ALD (O₂ half-cycles at 623 K, the surface with low carbon content).

■ ASSOCIATED CONTENT

Supporting Information
Cu 2p₃/₂ core level region for first 4 half-cycles, HREELS spectrum of Cu₂O/Cu(111) surface, pixel height histogram for STM images after first TMA cycle on Cu₂O/Cu(111), and explanation of image processing used in Figure 6. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b03598.

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■ ABBREVIATIONS

ALD, atomic layer deposition
HREELS, high-resolution electron energy loss spectroscopy
STM, scanning tunneling microscopy
TMA, trimethylaluminum
XPS, X-ray photoelectron spectroscopy

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