Chemical
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Full Paper

Thin, Continuous, and Conformal Copper Films by Reduction of Atomic Layer Deposited Copper Nitride**

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Thin and continuous copper films serve as seed layers for electrodeposition of interconnects in microelectronic devices. Gaps in the continuity of these Cu films must be avoided, because they can generate voids that later lead to failure of the devices. It is difficult to sputter completely continuous copper-seed layers into the increasingly narrow trenches and holes in modern interconnects. Here we report a method for producing thin, completely continuous, and highly conductive copper films conformally inside very narrow holes with aspect ratios of over 40:1. The first step in our process is atomic layer deposition (ALD) of copper(I) nitride, Cu_3N, by the alternating reactions of copper(I) *N*,*N′*-di-*sec*-butylacetamidinate vapor and ammonia on surfaces heated to approximately 160 °C. At this temperature, Cu_3N is thermally stable, but is readily reduced to copper metal by exposure to molecular hydrogen gas (H_2). Copper layers as thin as 0.8 nm (about 3 monolayers) are electrically continuous and show the electrical resistivity predicted by a grain-boundary-scattering model for continuous films of that thickness. 3 nm thick copper films on 2 nm of ruthenium have a sheet resistance of less than 50 Ω/□, a value low enough to serve as seed layers for advanced electroplating techniques.

Keywords: Atomic layer deposition, Copper, Copper nitride, Copper precursor, Ultrathin films

1. Introduction

A number of transition metal nitrides have industrial applications because of their physical, mechanical, and electrical properties, such as high melting points, high hardness, and high elastic modulus.[1] Considerable attention has been paid to fabricating copper nitride (Cu_3N) thin films in recent years owing to possible applications in microelectronic devices and optical data storage. The crystal structure of Cu_3N is cubic anti-ReO_3, where nitrogen atoms occupy the cube corners and Cu atoms lie at the centers of the twelve edges. Additional metal atoms (such as Cu or Pd) can be inserted at the cube center to change the electric conductivity.[2] Copper nitride is a semiconductor with a bandgap at around 1.5–1.9 eV,[3,4] depending on the ratio of copper to nitrogen in the film. Extra Cu atoms can lower the optical bandgap as well as increase the lattice parameter and the conductivity of Cu-rich nitride films.[5] Cu_3N is stable at room temperature and decomposes to make pure copper metal films at temperatures of ca. 250–450 °C.[6,7] The reflectivity of copper nitride to infrared light is smaller than that of pure Cu.[8] The low decomposition temperature and distinct optical properties of the compound compared to those of Cu are applicable for write-once optical recording media by using local laser heating to generate Cu spots on Cu_3N films.[9] Cu_3N films can also be reduced to copper-seed layers for electroplating Cu as the interconnect metal in microelectronics. This method provides advantages over the direct deposition of copper-seed layers because of reduced surface roughness and denser nucleation.

Cu_3N films are usually made by sputtering copper in a nitrogen atmosphere.[10] Sputtering methods, however, make nonuniform coatings inside narrow holes. Atomic layer deposition (ALD) is known to make uniform films even on irregular surfaces and holes with high-aspect ratios, which are encountered more frequently as smaller devices are made in modern microelectronics. Additionally, ALD has better control of thickness (nanometer scale) and stoichiometry. The only previous method for ALD of Cu_3N produced agglomerated films with high contamination by oxygen and carbon.[11]

In this paper we report the ALD of pure Cu_3N thin films from a very stable, low-melting-point, volatile copper(I) amidinate precursor and ammonia. Pure, smooth, continuous, uniform, adherent, and highly conformal copper films were then obtained by reduction of the Cu_3N films with molecular hydrogen.

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2. Results and Discussion

2.1. ALD of Copper Nitride

Substrates at temperatures from 120 to 300 °C were exposed alternately to vapors of copper(I) *N*,*N'*-di-*sec*-butylacetamidinate $[Cu(^{s}Bu\text{-}Me\text{-}amd)]_2$ and ammonia. Films were deposited when the substrate temperature was 140 °C or higher. The stoichiometry and purity of the films were studied by Rutherford backscattering spectroscopy (RBS). Films deposited at 160 °C possessed a N/Cu atomic ratio of 1:3, corresponding to stoichiometric Cu_3N (Fig. 1a). Any carbon and oxygen impurities are very small (<1 at.-%, Fig. 1b). At deposition temperatures over 180 °C, the N/Cu ratio decreased to below 1:3. For temperatures over 280 °C, measurable amounts of carbon (ca. 10 at.-%) were found in the films due to copper-precursor decomposition.

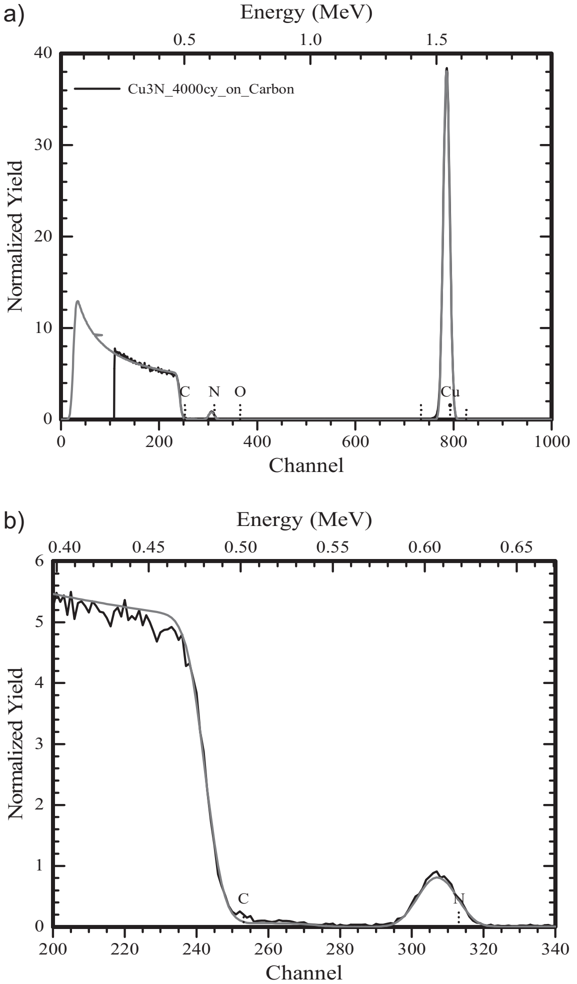


Fig. 1. RBS spectrum of an as-deposited Cu_3N film at 160 °C. a) The gray simulation curve indicates the film stoichiometry is Cu/N = 3:1, with no oxygen in the copper nitride film. b) The enlarged spectrum in carbon and nitrogen region. The gray simulation curve indicates that there is almost no carbon contamination in the copper nitride film. The oxygen and carbon impurities are <1 %.

The simulated X-ray reflection (XRR) spectrum (Fig. 2) shows that the density of the as-deposited nitride film at 160 °C is 5.3 g cm^{-3}, which agrees well with the results from the combination of RBS density and cross-sectional transmission electron microscopy (X-TEM) thickness measurements. The film density is only slightly lower than the bulk value of 5.84 g cm^{-3} for Cu_3N.

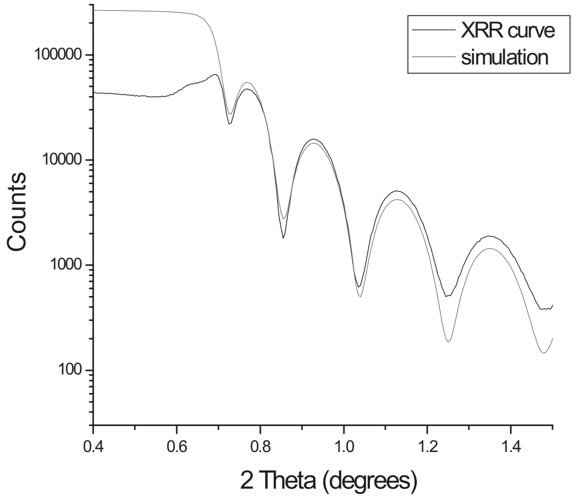


Fig. 2. XRR from a Cu_3N film. The simulation shows the film density is 5.3 g cm^{-3}, which agreed well with the calculation from RBS density and SEM thickness measurement.

The ALD reactions were found to be close to self-limiting both for the metal precursor and for the ammonia. The hallmark of a self-limiting reaction is that the amount of material deposited first increases with exposure to the precursor, but then levels out to approach a maximum amount at large exposures. The exposure is defined as the product of the precursor partial pressure and the time that it is exposed to the surface.[12] The exposure is proportional to the number of collisions of the precursor with the surface. Increasing exposure and greater numbers of collisions of the precursor with the film surface should lead to denser nucleation, smoother and more continuous films, and higher growth per cycle. Changes in the exposure can be made in three different ways: increasing the precursor dose by increasing the precursor bubbler temperature; by using multiple doses at fixed precursor temperature; and by increasing the precursor exposure time in the deposition chamber. Pressure and time were both varied and the growth rate was plotted as a function of their product (Fig. 3a). The growth per cycle increases monotonically with increasing exposure to the copper precursor even though individual points have a variety of pressures and times. Plots (not shown) of growth versus partial pressure or versus exposure time show much more scatter. These results demonstrate that the exposure is the appropriate measure of completeness of reaction, not pressure or time individually. The growth per cycle increases more slowly at larger exposures,

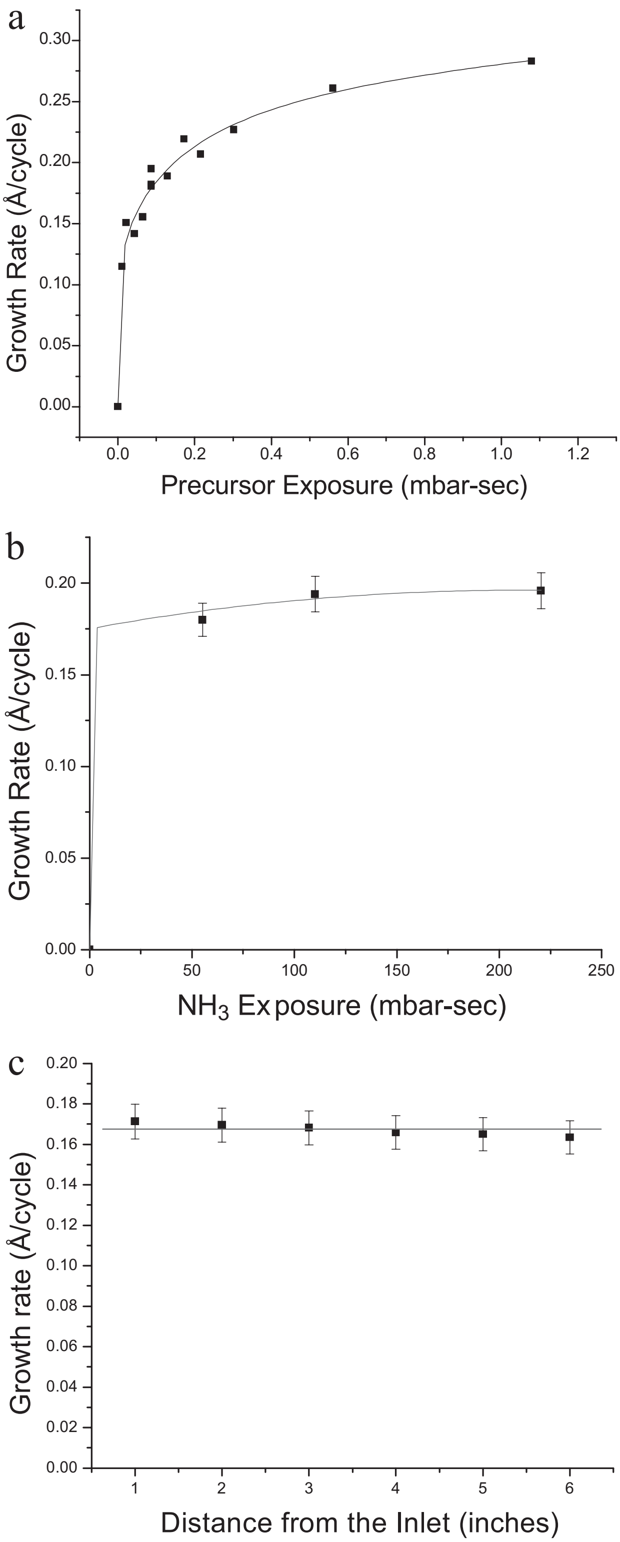


Fig. 3: RBS study of the growth rate as a function of the precursor exposure. The growth rate approaches a saturated value as the exposure of the precursors was increased. The deposition temperature was 160 °C, and the growth rate was based on 600 cycles. a) Cu precursor exposure was varied up to 1.1 mbar s while keeping the NH_3 exposure fixed at 165 mbar s. b) The NH_3 exposure was varied up to 225 mbar s while keeping the metal precursor exposure fixed at 0.2 mbar s. c) Uniform growth over a 6 in. area, keeping Cu precursor exposure at 0.1 mbar s and NH_3 exposure at 165 mbar s.

nearly achieving a constant, saturated value of about 0.3 Angstrom per cycle.

The NH_3 exposure had little effect on the thickness (Fig. 3b). These exposures to NH_3 are hundreds of times larger than the exposures to the copper precursor, leading to completely saturated growth at every exposure of NH_3 tested in these experiments.

ALD can produce conformal and uniform coatings over large areas, even if the flux of vapor is introduced non-uniformly over the surface. The thickness of copper nitride varies by less than 3 % over a 15 cm distance along the direction of the gas flow in the tube furnace (Fig. 3c). The exposures used for these measurements (0.5 mbar s for Cu, 25 mbar s for NH_3) are within the self-limited ranges determined in Figure 3a. The observed thickness uniformity is consistent with the conclusion that the ALD reactions are self-limiting.

The Cu_3N films were highly conformal inside holes in Si with aspect ratios of 42:1. Scanning electron microscopy (SEM) images (Fig. 4) showed cleaved cross-sections of 48 nm thick Cu_3N films on 2 nm ALD tungsten nitride (as an adhesion layer) inside oval holes (diameters 0.14 × 0.17 µm; length 7.1 µm). The thickness of the film on the bottom of the holes is equal to that on the top, confirming the ideal ALD behavior of the reactions.

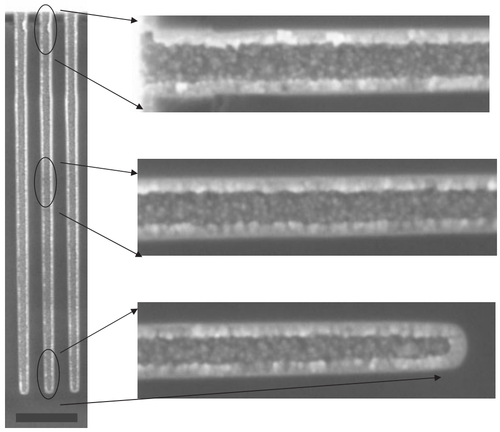


Fig. 4. X-SEM image. As-deposited ALD Cu_3N (48 nm)/WN (2 nm) on Si_3N_4/Si via with width ca. 0.17 µm and length 7.1 µm (aspect ratio 42). Scale bar: 1 µm.

The copper nitride thickness grows linearly with number of cycles on all the substrates tested, including amorphous SiO_2, quartz, UV-ozone treated Si, and metallic Ru, Co, and NiSi. The thickness of Cu_3N on Ru substrates (Fig. 5) is typical. Although these experiments were run at a Cu precursor exposure of 0.06 mbar s, which is less than saturated, the growth is still linear with number of deposition cycles, at 0.15 Å per cycle. These lines pass through the origin, indicating that there is no delay in nucleation on these surfaces.

Completeness of coverage was studied by X-ray photoelectron spectroscopy (XPS). Scans of the Ru 3p region

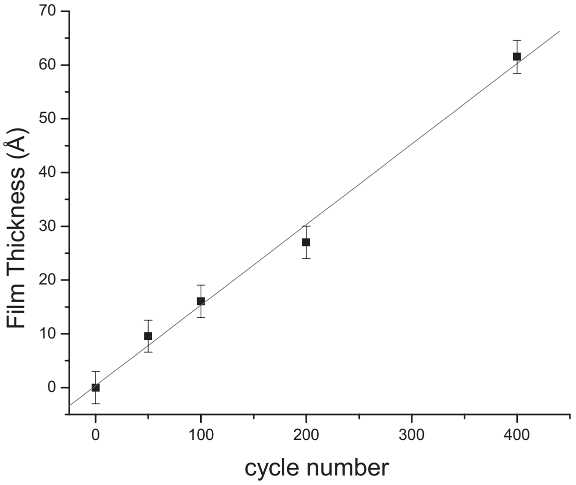
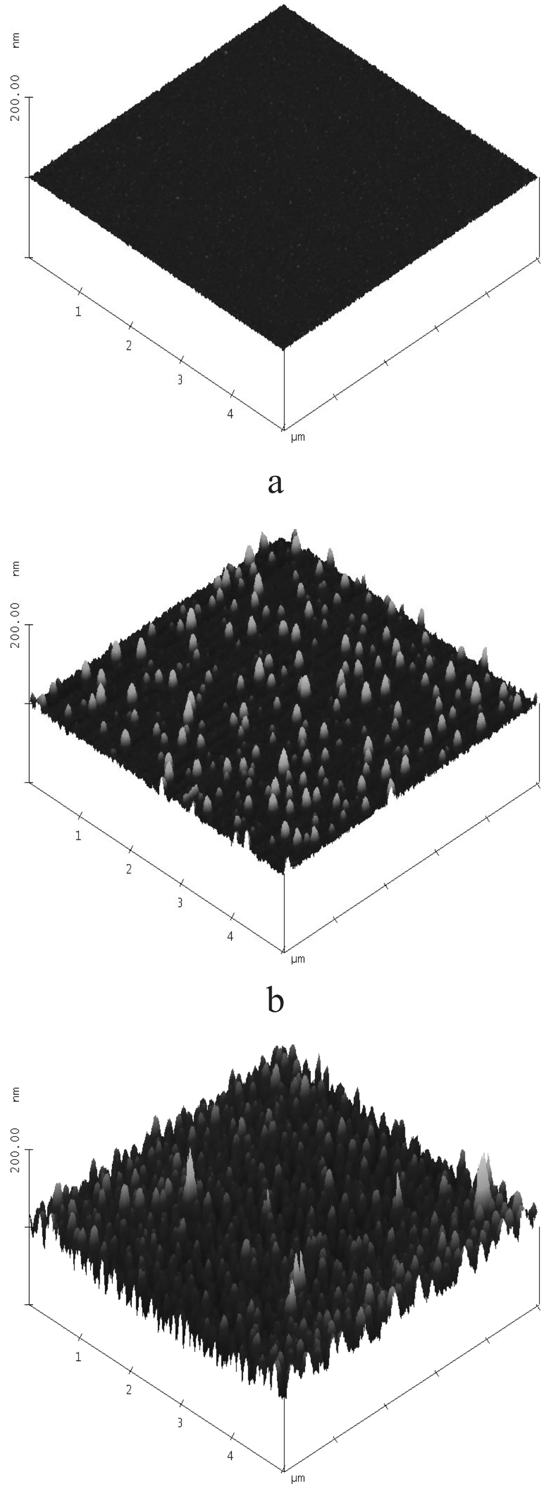


Fig. 5. The linear relationship between the thickness of copper nitride on Ru and the number of deposition cycles at 160 °C.



a

b

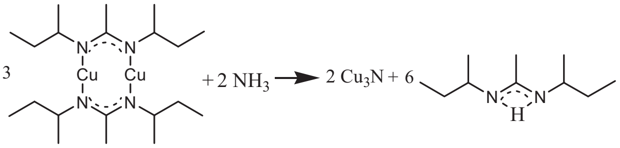
c

Fig. 6. AFM study of the surface roughness of as-deposited films. a) Deposition temperature 160 °C, thickness 6.74 nm, rms 0.70 nm. b) Deposition temperature 180 °C, thickness 7.76 nm, rms 4.47 nm. c) Deposition temperature 280 °C, thickness ca. 5 nm, rms 11.65 nm.

showed no Ru peaks for samples of Cu_3N 6 nm thick on ruthenium substrates (Supporting Information, Fig. S1). This indicates complete coverage of the Ru surface by a 6 nm thick Cu_3N film deposited at 150 °C. When the deposition was performed at 280 °C, mainly yielding Cu films, Ru peaks appeared in the XPS (Fig. S1). Thus the Cu films agglomerated at 280 °C and did not cover the surface completely. Another test of continuity was made by placing films in 30 % hydrogen peroxide solution. Ruthenium films catalyze the decomposition of the H_2O_2, rapidly producing bubbles of O_2 gas. Films of Cu_3N, in contrast, are very poor catalysts for decomposition of H_2O_2, evolving tiny oxygen bubbles very slowly. Similar low rates of catalysis were shown by all Cu_3N films over 3 nm thick, showing that they completely cover the ruthenium surface.

Atomic force microscopy (AFM) was employed to study the surface roughness of the as-deposited Cu_3N thin films. Figure 6 shows an AFM study of the surface roughness of the as-deposited Cu_3N thin films (Fig. 6a). The root mean square (rms) roughness is 0.7 nm for the as-deposited nitride film at 160 °C with thickness 6.7 nm, indicating uniform coverage and no tendency to agglomerate. The smoothness and continuity were confirmed by cross-sectional scanning electron microscopy (X-SEM) (Fig. 4). As the deposition temperature increased to 180 °C (Fig. 6b) small islands, presumably of copper, were formed on the nitride surface, which increased the rms roughness to 4.5 nm with film thickness 7.8 nm. On further increasing the deposition temperature to 280 °C (Fig. 6c), the film is most likely a Cu film with little copper nitride remaining. The surface became much rougher, having an rms roughness of 11.7 nm with film thickness ca. 5 nm.

RBS and NMR spectroscopy were used to study the reaction mechanism. In order to find the source of the nitrogen in the copper nitride film, $^{15}NH_3$ (98 % pure) was used instead of normal NH_3. The RBS spectrum (Supporting Information, Fig. S2) showed that the nitrogen in the film is ^{15}N, indicating that the nitrogen in the film comes from the NH_3 gas reagent and not from the nitrogen in the copper precursor. NMR spectra of the liquid product from reaction of NH_3 with $[Cu(^sBu\text{-}Me\text{-}amd)]_2$ matched exactly free *N*,*N′*-di-*sec*-butylacetamidine.[13] X-ray diffraction (XRD) of the solid, dark-green powder product confirmed Cu_3N formation. These observations suggest the overall ALD reaction chemistry corresponds to the following reaction.



The volatile byproduct, *N*,*N′*-di-*sec*-butylacetamidine, is carried out of the reaction zone as a vapor.

2.2. Reduction of Cu_3N to Cu by H_2

Molecular hydrogen (H_2) was found to remove the nitrogen from Cu_3N films during post-deposition annealing. XRD was used to characterize this reduction process. As-deposited film at 160 °C showed strong Cu_3N diffraction peaks for the anti-ReO_3 lattice structure, mainly oriented in the (100) direction, together with some (111) and (200) (Fig. 7). Rapid thermal annealing (RTA) in the forming gas (5 Torr, H_2/N_2, with 10 % H_2) at 200 °C for 5 min showed a small Cu peak, indicating a little decomposition. Increasing the RTA temperature to 225 °C entirely destroyed the copper nitride peaks, while the copper (111) and (200) peaks strengthened, showing the copper nitride was reduced completely to Cu by the H_2 and heat. The decomposition temperature can be further decreased to 185 °C under pure H_2 at 2 bar pressure for ~30 min, or 160 °C under pure H_2 at 4 bar for ~2 h. RBS confirmed the absence of nitrogen in the annealed films. This agreed with the literature results that with the presence of hydrogen, no copper nitride was formed, even at 150 °C, by sputtering copper in a nitrogen atmosphere.[14]

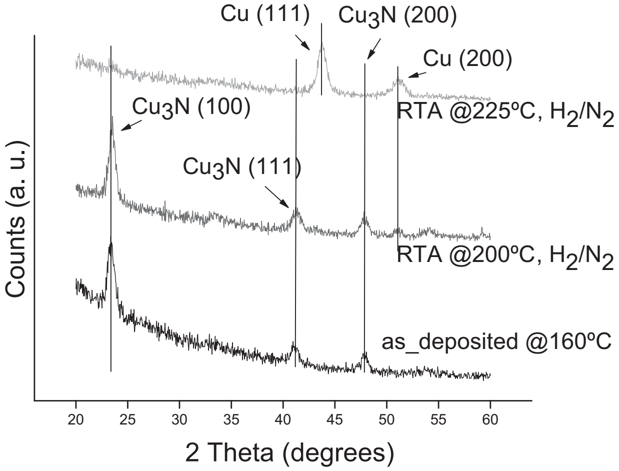


Fig. 7. XRD patterns for Cu_3N. As-deposited (bottom curve); after 5 min anneal under 5 Torr forming gas (10 % H_2) at 200 °C (middle curve) and 225 °C (top curve).

AFM was also employed to investigate the possibility of making smooth Cu films from the decomposition of copper nitride. XRD data showed that Cu_3N can be completely converted to copper film at 225 °C. A Cu_3N film deposited at 160 °C has an rms roughness of 0.7 nm with thickness 6.7 nm (Fig. 8a). After 5 min of RTA at 225 °C in the forming gas, the surface roughness increased to 0.9 nm (Fig. 8b). As a comparison, a Cu film produced using ALD at 160 °C with H_2 in place of NH_3 showed an rms roughness of 1.5 nm with thickness 5 nm (Fig. 8c). Thus the copper film from Cu_3N reduction is smoother than the Cu film with similar thickness produced from ALD.[15]

Even the Cu_3N within the holes with high aspect ratio could be reduced during RTA. The resulting copper thin films remained smooth and continuous on 2 nm ALD WN as an adhesion layer (Fig. 9).[16] Without the thin WN layer, the copper nanotubes remained intact and did not cleave after the silicon around them was cleaved, due to poor adhesion at the Cu/SiO_2 surface.[17]

Film smoothness and continuity were investigated by X-TEM. Figure 10a shows a 13 nm thick Cu_3N film grown on a $Ru/TaN/SiO_2/Si$ substrate. The film is smooth and continuous, with an rms roughness of 0.44 nm. RTA reduction of this sample yielded a smooth and continuous copper film ca. 8 nm thick (Fig. 10b). The interfaces between Cu_3N/Ru (in Fig. 10a) and Cu/Ru (in Fig. 10b) are very sharp, with no evidence for interdiffusion. The dark and light bands that extend from the Ru substrate into the copper layer show that the copper film grew epitaxially on the ruthenium. This epitaxial growth indicates that the Cu/Ru interface is substantially free of contamination by impurities.

Film continuity and electrical conductivity are very important for application of thin copper films as seed layers in microelectronics. Figure 11 shows four-point probe measurements of the electrical resistivity of copper films from reduction of Cu_3N (squares), along with values for very pure copper films sputtered in high vacuum (2 round dots).[18] The good agreement between the conductivity of the Cu films produced by both ALD and PVD indicates that reduction of Cu_3N produced by ALD provides high-quality, Cu metal films having high purity, continuity of structure, and lack of agglomeration.

The resistivity of metal thin films increases with decreasing film thickness owing to several scattering effects: grain-boundary scattering, electron-surface scattering, surface-roughness-induced scattering, and impurity scattering. The curve in Figure 11 is calculated from a simple model that includes only grain-boundary scattering, see Equation 1.[19]

$$\rho/\rho_0 = 1 + 1.5\{R/(1 - R)\}\lambda/g \qquad (1)$$

ρ_0 is the bulk resistance, λ is the electron mean free path (assumed to be 39 nm), g is the average size of the grains

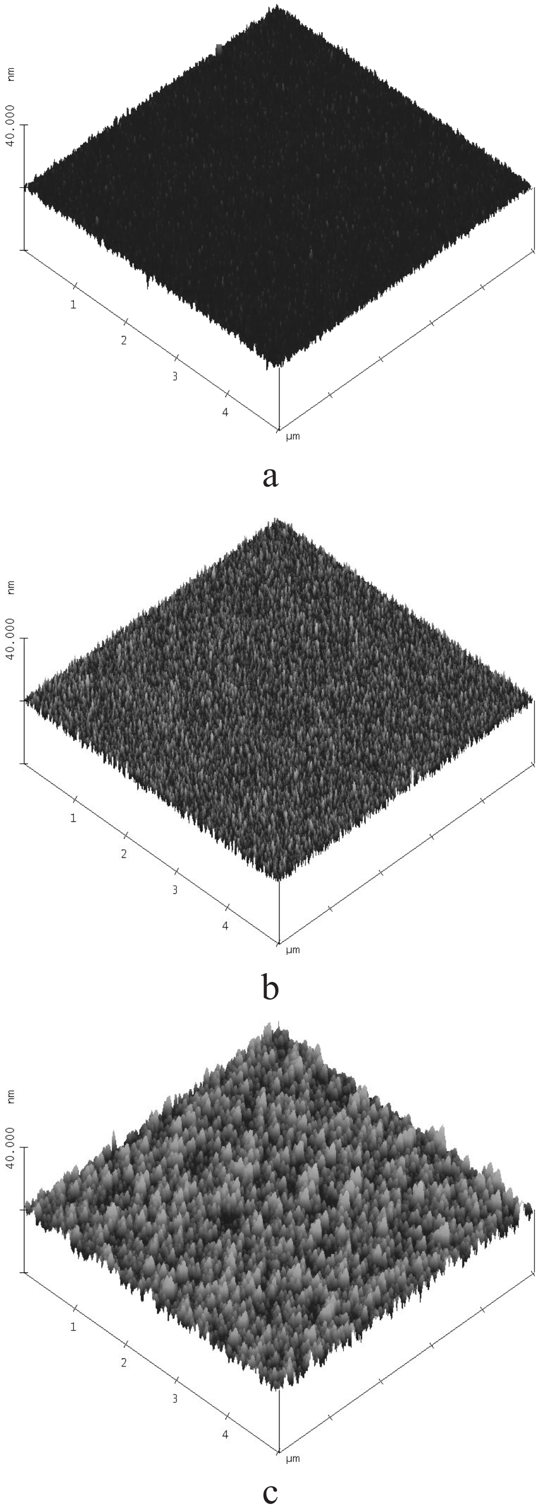


Fig. 8. AFM study of the surface roughness of Cu_3N and its reduction to Cu films. a) Deposition temperature 160 °C, thickness 6.74 nm, rms 0.70 nm. b) Cu films from reduction of Cu_3N sample, film thickness shrinks to ca. 4 nm, rms 0.91 nm. c) As-deposited Cu film produced by ALD at 160 °C, film thickness 5.04 nm, rms 1.52 nm.

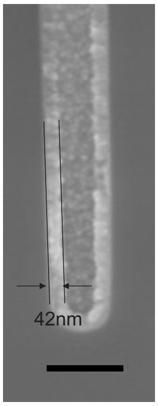


Fig. 9. SEM image of copper formed by anneal (5 min in the forming gas at 250 °C) of Cu_3N deposited inside holes as shown in Figure 4 (bottom part of via). The film thickness shrank to 42 nm after reduction of Cu_3N to copper. Scale bar: 200 nm.

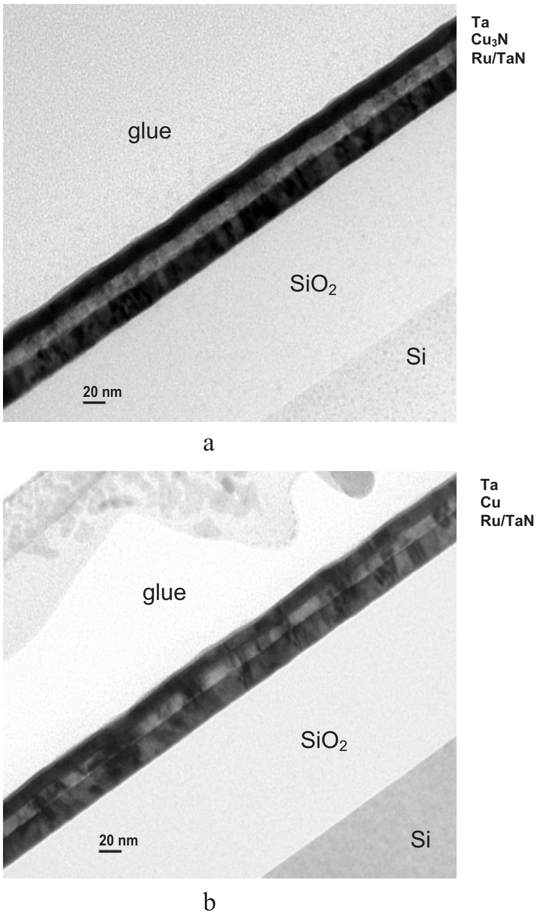


Fig. 10. X-TEM study of the film conformality and continuity, for both Cu_3N and Cu samples; a few nm Ta was sputtered on top of the samples as a protective layer during TEM sample preparation. a) 13 nm Cu_3N deposited on $Ru/TaN/SiO_2/Si$ substrate. b) Cu_3N reduced to Cu (8 nm) on $Ru/TaN/SiO_2/Si$ substrate.

(approximated as the film thickness), and $R \sim 0.3$ is the grain-boundary-scattering coefficient.[20] It is remarkable that the data for copper films produced by ALD fit this model down to thicknesses below 0.8 nm, or only about three monolayers of copper atoms. This agreement between the measured conductivity and the model suggests

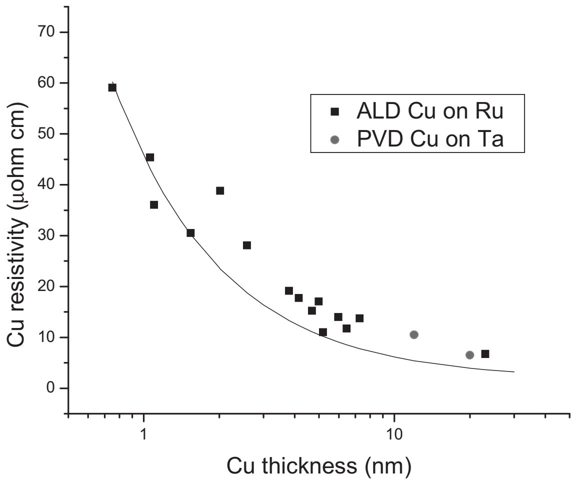


Fig. 11. The resistivity of Cu thin films from reduction of Cu_3N, as a function of Cu film thickness on Ru substrates. Black squares are data from this study, gray dots are data from sputtered Cu [18].

that the copper film must be continuous and nearly uniformly covering the ruthenium surface, even at a thickness of only three atomic layers.

3. Conclusions

Pure films of copper(I) nitride were deposited from vapors of [Cu(^{s}Bu-Me-amd)]$_2$ and ammonia. These are the first high-purity, Cu_3N thin films produced by ALD. They are polycrystalline with fairly smooth surfaces. The films are conformal inside holes with high aspect ratios. The as-deposited copper nitride films are stable below 160 °C, but can be reduced to copper metal by H_2 and heat. The conductivity of the resultant Cu is equal to that of very pure, sputtered Cu. This process is very promising for making thin Cu seed layers for electroplating.

4. Experimental

Copper nitride thin films were formed by complementary, self-limiting reactions from copper(I) *N,N′*-di-*sec*-butylacetamidinate ([Cu(^{s}Bu-Me-amd)]$_2$) with ammonia as the other reagent. [Cu(^{s}Bu-Me-amd)]$_2$ was synthesized from the metathesis reaction of *N,N′*-di-*sec*-butylacetamidinato lithium with copper(I) chloride. The detailed synthesis and characterization of the precursor's properties have been published elsewhere [21]. The compound is dimeric, with a planar structure. The two copper atoms are each bound to two amidinate ligands, which makes this precursor very stable. An NMR study showed that its half-life in C_6D_6 is around one month at 190 °C, which is higher than the deposition temperature. The vapor pressure of [Cu(^{s}Bu-Me-amd)]$_2$ is 0.23 Torr at 95 °C over the liquid phase. It reacts with hydrogen to produce metallic copper films, or with ammonia to generate copper nitride films.

The ALD equipment consists of a tube-furnace into which pulses of vapor were fed from a bubbler containing the copper precursor, into which measured doses of nitrogen carrier gas were metered. Bubbler temperatures were typically 100 to 120 °C. The doses of mixed copper-precursor vapor and nitrogen in the headspace of the bubbler were led separately into one end of the previously evacuated tube furnace by air-actuated valves. Another air-actuated valve between the tube furnace and the vacuum pump confined the vapor mixture for a specific time before opening and a flow of purge nitrogen swept the gaseous by-products and unreacted precursor out of the deposition zone. The ammonia doses from a measured volume were flowed into the evacuated deposition region, in which they were also confined for a time period before purging.

The liquid by-product of the reaction was collected and analyzed by contacting ammonia gas with the liquid precursor at 120 °C. The resulting suspension was mixed with a liquid mixture of deuterated tetrahydrofuran (THF-d_6) and deuterated methanol (CD_3OD), and filtered to remove the precipitated Cu_3N. The ^1H NMR spectrum of the solution was recorded with a Bruker AM-500 spectrometer in the mixed solvents of THF-d_6 and CD_3OD at 25 °C.

The sheet resistance was measured by four-point measurement using a Veeco FPP-100. The sheet resistance of Cu films was calculated assuming parallel connection between Cu layer and underneath substrate containing conductive Ru/Ta. The total sheet resistance of the stack Cu/Ru/Ta/SiO_2/Si was first recorded as ρ_{st}. Nitric acid was then applied to etch away the surface copper layer. RBS measurement confirmed the etching of Cu film, but not the substrate Ru/Ta/SiO_2/Si. The sheet resistance of the remaining substrate was measured as ρ_{ssb}. The Cu sheet resistance ρ_{sCu} was then calculated from $1/\rho_u + 1/\rho_{ssb} = 1/\rho_{st}$. Resistivity was calculated as the product of the sheet resistance and film thickness. In order to separate the conductivity of the substrate Ru layer from that of top copper layer, various Ru thicknesses were used, providing different sheet resistances of the substrates. The resulting Cu resistivity was constant within a range of 13 % error, for Ru thicknesses of 2, 3, 5, 10, and 20 nm. This excluded any possible effect of the conductive substrate on the measured conductivity of the copper films and confirmed the validity of the parallel conductivity calculation.

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