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FTIR study of copper agglomeration during atomic layer deposition of copper

Min Dai,[1] Jinhee Kwon,[2] Yves J. Chabal,[2] Mathew D. Halls,[3] and Roy G. Gordon[4]
[1]Laboratory for Surface Modification, Rutgers University, 136 Frelinghuysen Road, Piscataway, NJ 08854, U. S. A.
[2]Department of Materials Science and Engineering, The University of Texas at Dallas, Richardson, TX 75080, U.S.A.
[3]Materials Science Division, Accelrys Inc., San Diego, CA 92121, U.S.A.
[4]Department of Chemistry and Chemical Biology, Harvard University Cambridge, MA 02138, U.S.A.

ABSTRACT

The growth of of metallic copper by atomic layer deposition (ALD) using copper(I) di-sec-butylacetamidinate ($[Cu(^{s}Bu\text{-}amd)]_2$) and molecular hydrogen (H_2) on SiO_2/Si surfaces has been studied. The mechanisms for the initial surface reaction and chemical bonding evolutions with each ALD cycle are inferred from in situ Fourier transform infrared spectroscopy (FTIR) data. Spectroscopic evidence for Cu agglomeration on SiO_2 is presented involving the intensity variations of the SiO_2 LO/TO phonon modes after chemical reaction with the Cu precursor and after the H_2 precursor cycle. These intensity variations are observed over the first 20 ALD cycles at 185°C.

INTRODUCTION

Atomic layer deposition (ALD) has recently received great interest with the need for new materials and thin-film deposition techniques for device scaling in integrated circuits (IC). The self-limiting growth mechanism of ALD is ideal for producing very thin, conformal films even on surfaces with high aspect ratios with control of the thickness and composition at the atomic level. As the industry heads toward the 22 nm node, the interest in metal ALD is growing, especially for copper interconnects. Cu is replacing aluminum as an interconnect material in ICs due to its lower resistivity ($1.72\times10^{-6}\Omega\cdot$cm vs. $2.82\times10^{-6}\Omega\cdot$cm) and higher melting point (1083 ^{o}C vs. 659°C).[1] For this application, a highly conformal and continuous copper seed layer is required before subsequent electrochemical deposition of copper film with high growth rate.[2]

ALD of non-noble metals, however, has had limited success [3, 4]. One of the reasons for these difficulties is related to a lack of suitable precursors which satisfy stringent requirements for ALD. [5] In addition, the lack of understanding of growth mechanisms of metal ALD hinders the development of suitable precursors.

ALD of Cu has been considered previously. Several copper (I) and copper (II) precursors were commonly used in the past, such as CuCl[4, 6], Cu(II)-2,2,6,6 -tetramethyl-3,5-heptandionate $[Cu(thd)_2]$[7, 8], Cu(II)-1,1,1,5,5,5-hexafluoro-2,4 -pentanedionate $[Cu(hfac)_2]$ [9, 10], and Cu(II) acetylacetonate $[Cu(acac)_2]$ [11, 12], but all suffered from undesirable properties as ALD

precursors.[13] For example, CuCl has very low vapor pressure, and the Cu film deposited by $Cu(hfac)_2$ contains fluorine which reduces the Cu adhesion on the substrate. They all have very low reactivity with low growth rate, so that either high temperature (> 200°C), which is not well suited for smooth Cu growth due to Cu agglomeration and diffusion [13-15], or plasma is needed to enhance the reactivity.

Recently, Gordon et al.[16] reported ALD growth of metallic copper with high conformality and high conductivity using an amidinate precursor (copper (I) di-sec-butylacetamidinate, $[Cu(^{s}Bu\text{-}amd)]_2$) and molecular hydrogen at relatively low temperature (~185°C). One of the advantages of this precursor is its high reactivity with molecular hydrogen at reasonable temperatures. In order to understand the ALD Cu growth mechanisms with this amidinate precursor, we used in-situ Fourier transform infrared spectroscopy (FTIR) to investigate the chemical bonding evolution after each ALD cycle.

EXPERIMENT

Double side polished, float-zone grown, and lightly doped (~10 Ω·cm) Si(100) with thin thermal oxide (6-10 nm thick SiO_2) is used. The sample is first rinsed by acetone, methanol, and deionized water (DI water, 18.2 MΩ·cm), then standard RCA [17, 18] cleaning is performed followed by thorough rinsing with deionized water and blow-drying with N_2. Then the sample is immediately loaded in the ultra pure N_2 (oxygen impurity < 10^{-3} ppm) purged ALD chamber.

All experiments are done in a home-made ALD system integrated with a Thermo Nicolet 670 interferometer and a MCT/B detector for *in-situ* FTIR measurements.[19] A single-pass transmission geometry is used with an incidence angle close to the Brewster angle to maximize transmission, minimize interference, and increase sensitivity to absorptions below ~1500 cm^{-1}. Distinction of perpendicular from parallel modes to the surface is made by additional normal incidence measurements. Mid-infrared range of 400 - 4000 cm^{-1} is scanned with the resolution of 4 cm^{-1}.

$[Cu(^{s}Bu\text{-}amd)]_2$ is kept at 95-100°C, and purified N_2 is used as the carrier gas to deliver the copper precursor. Cu film is deposited by introducing $[Cu(^{s}Bu\text{-}amd)]_2$ (exposure ~ 10^7 L) and H_2 (exposure ~ 10^{11} L) (ultra high purity, 99.999%, purified by Aeronex Gate Keeper gas purifiers) alternatively into the ALD chamber. During deposition, the substrate temperature is kept at 185°C for optimum Cu deposition. After each precursor dosing, the ALD chamber is N_2-purged thoroughly with pumping.

RESULTS AND DISCUSSION

Figure 1 shows differential IR absorbance spectra of the first cycle of Cu ALD on SiO_2 at 185°C, where the maximum Cu growth rate is observed.[13] Upon the first half cycle when the Cu precursor $[Cu(^{s}Bu\text{-}amd)]_2$ (black) is introduced, the intensity of the transverse and longitudinal optical modes (TO/LO) of SiO_2 at 1075/1247 cm^{-1} decreases. Their intensity loss indicates that the SiO_2 matrix is chemically disrupted due to the reaction of the Cu precursor with surface OH groups. The absorption band at 1010 cm^{-1} corresponds to the formation of Si-O-Cu bonds due to the adsorbed Cu precursor on SiO_2. The reaction scheme is shown as the inset in the right. Upon the H_2 exposure (red), there is a partial recovery of SiO_2 phonon modes (1075/1247 cm^{-1}). The recovery of these modes suggests that after the H_2 dosing, the Cu precursor on the surface is reduced to pure copper atoms which then migrate and self-agglomerate to form copper particles

[13, 21, 22]. As they agglomerate, the chemical bonds established during the first half cycle between Cu and the underlying SiO_2 matrix are broken and rehydroxylated, partially restoring the SiO_2 phonon modes and hydroxyl sites on the surface.

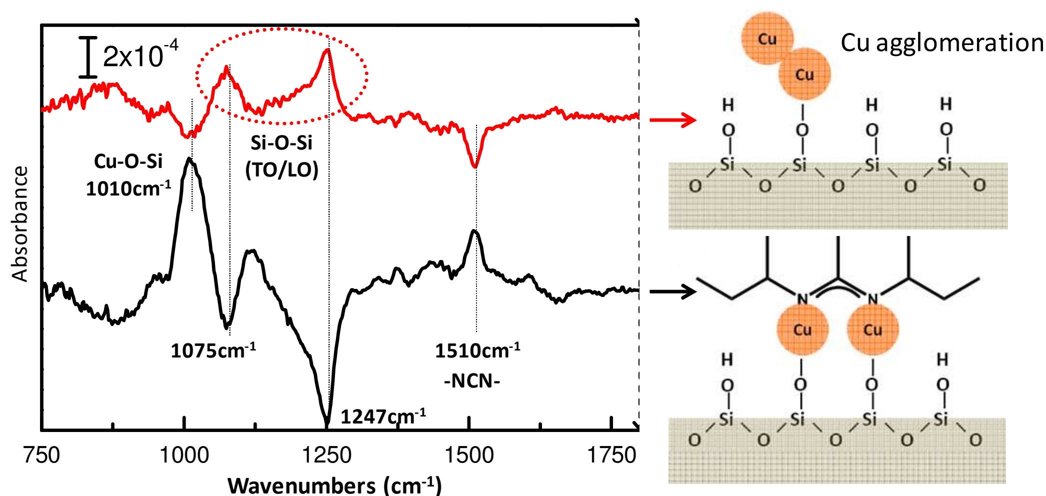

Figure 1. Differential IR absorbance spectra of the first cycle of Cu ALD on SiO_2 measured after the Cu precursor (black) and H_2 (red) dosing. Each spectrum is referenced to the spectrum of the previous treatment and the bottom is referenced to initial oxide surface. The incident angle of IR beam is 74°. The inset in the right shows a schematic of surface reactions corresponding to observations in each spectrum.

In addition, the removal of the ligands by H_2 reduction opens more reaction sites which were initially blocked by the intact ligands. In addition to the repetitive change of SiO_2 phonon modes, the surface Si-O-Cu bonds at 1010 cm^{-1} follows the similar pattern of gain and recovery after Cu precursor and H_2, respectively. This process is again schematically illustrated in the inset of Figure 1. The repetitive loss and gain of SiO_2 modes are observed for the 20th cycle, implying that the surface is not saturated and Cu atoms still agglomerate after 20 ALD cycles. This observation is consistent with the high percolation thickness for Cu on glass reported previously.[13]

In Figure 1, the mode at 1510 cm^{-1} is assigned to ν(N-C-N) of the intact ligand attached to Cu atoms on the surface. Along with CH_x stretching modes at 2800-3000 cm^{-1} (not shown), their intensity increases after each copper precursor and decreases after each H_2, confirming the ALD process through ligand exchange.

Cu agglomeration (i.e. formation of Cu structures with substantially thicker diameter than the average Cu thickness) is also observed in the shape of Rutherford backscattering spectroscopy (RBS) of Cu in Figure 2. The areal density of Cu atoms is measured by ex situ RBS with 2 MeV He^+ ions. The detector is placed at 160° backscattering angle.

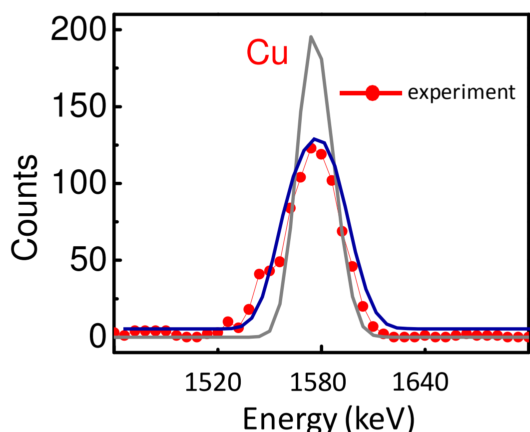

Figure 2. RBS spectrum (red dots) after 10 ALD cycles and simulations assuming uniform Cu coverage (gray) and non-uniform Cu coverage (blue). The detector is placed at a grazing angle of 160° backscattering angle.

The FWHM of the simulation assuming uniform coverage of Cu atoms on the surface (gray) is narrower than that of the experimental RBS data (red dots). The blue line shows the simulated result after taking into account agglomerated Cu atoms of an island structure on the surface. The simulation of non-uniform Cu coverage is reasonably well fitted to the RBS data, confirming the agglomerated Cu on SiO_2.

CONCLUSIONS

The surface reaction and the growth mechanism of Cu ALD with a liquid amidinate Cu precursor ($[Cu(sBu\text{-}amd)]_2$) and molecular hydrogen on oxidized Si surfaces (6-10 nm thick SiO_2) have been investigated by using in situ FTIR spectroscopy and ex situ RBS. The agglomeration of Cu atoms on SiO_2 was shown to have a significant effect on the evolution of SiO_2 phonon modes. The hydrogen reduction of the surface ligand is observed through the modes attributed to CH_x and -NCN- bonds, confirming ALD process through ligand exchange. The Cu agglomeration on the oxide is also confirmed by a broader RBS spectrum of Cu.

ACKNOWLEDGMENTS

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