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Atomic layer deposition of copper nitride film and its application to copper seed layer for electrodeposition

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ABSTRACT

We report the formation of smooth and conformal copper seed layer for electrodeposition by atomic layer deposition (ALD) and reducing anneal of a copper nitride film. The ALD copper nitride film was prepared at 100–140 °C using bis(1-dimethylamino-2-methyl-2-butoxy)copper(II) and NH_3, and reduced to metallic copper film by annealing at 200 °C or higher temperatures. The growth rate of ALD copper nitride was 0.1 nm/cycle at 120–140 °C on both ruthenium and silicon oxide substrates, and the thickness of film was reduced approximately 20% by annealing. The resistivity of the 4.2 nm-thick copper film was 30 μΩ·cm. Both the ALD copper nitride and the reduced copper films exhibited extremely smooth surface and excellent step coverage, whereas the copper film deposited using alternating exposures to the copper precursor and H_2 showed a rough surface. The copper film electrodeposited on the copper seed of this study exhibited lower resistivity and smoother surface as compared to the copper film electrodeposited on the ALD ruthenium seed.

1. Introduction

Copper film is grown by electrodeposition into the Damascene pattern to fabricate copper interconnect of integrated circuits. A continuous copper seed layer with good step coverage is essential for a high quality electrodeposition, because it plays an important role in providing a conductive substrate and improving nucleation of copper. Traditionally, the copper seed layer has been manufactured using ionized physical vapor deposition (i-PVD) technique. However, as the feature sizes decrease, i-PVD will soon face scaling problems [1]. Atomic layer deposition (ALD) is an ideal solution to deposit highly conformal seed layer due to its self-limiting growth characteristics [2]. Copper, ruthenium and cobalt have been considered as the potential ALD seed materials [3].

ALD of copper films was studied using organometallic copper compounds, such as copper(II)-2,2,6,6-tetramethyl-3,5-heptandinate [Cu(thd)$_2$] [4], copper(II) acetylacetonate [Cu(acac)$_2$] [5,6], copper(II)-1,1,1,5,5,5-hexafluoroacetonate [Cu(hfac)$_2$] [7] and its hydrate [Cu(hfac)$_2$·xH_2O] [8], copper(I) N,N′-di-sec-butyl-acetamidinate [Cu(^{s}Bu-Me-amd)]$_2$ [9], bis(dimethylamino-2-propoxy)copper(II) [Cu(dmap)$_2$] [10], bis(1-dimethylamino-2-methyl-2-butoxy)copper(II) [Cu(dmamb)$_2$] [11], bis(1-(dimethylamino)propan-2-yloxy)copper(II) [12], and copper(II)(4-ethylamino-pent-3-ene-2-onate)$_2$ [Cu(ethylketoiminate)$_2$] [13]. Reducing agents were hydrogen [4–6,9,13], hydrogen plasmas [6,11], alcohols or formalin [8], diethylzinc (Et_2Zn) [10], and formic acid/hydrazine [12]. Copper(I)(1,1,1,5,5,5-hexafluoroacetylacetonate)(trimethylvinylsilane) [Cu(hfac)(tmvs)], the most popular chemical vapor deposition precursor, cannot be used as the ALD precursor, because its disproportionation reaction is not self-limited. Cu(II) β-diketonate complexes, Cu(thd)$_2$ and Cu(acac)$_2$, have relatively low vapor pressures and low vaporization rates [9]. Fluorinated Cu(II) β-diketonate molecules, such as Cu(hfac)$_2$, exhibit a higher vapor pressure than nonfluorinated Cu(II) β-diketonates; however, the fluorine atoms in the precursor cause poor adhesion of the ALD copper film to tantalum-based barrier metals [14]. Recently, non-fluorinated copper precursors with higher vapor pressures were synthesized. [Cu(^{s}Bu-Me-amd)]$_2$ and Cu(ethylketoiminate)$_2$ showed high vapor pressures and were reduced by H_2 to deposit pure copper film on metallic substrates [9,13]. Cu(dmap)$_2$ and Cu(dmamb)$_2$, which also have high vapor pressures, were studied as the ALD precursor using Et_2Zn or a hydrogen plasma as the reducing agent [10,12]; however, the thermal ALD of copper using H_2 as the reducing agent was not reported yet.

Copper films were also prepared by reduction of copper oxide [15,16] or copper nitride films [17]. The ALD copper oxide film was deposited using bis(tri-*n*-butylphosphane)copper(I)acetylacetonate [(^{n}Bu$_3$P)$_2$Cu(acac)] and wet O_2 at 100–160 °C with low growth rates of approximately 0.01 nm/cycle [15], and can be reduced by the heat treatment in vapors of formic acid at 115 °C [16]. However, oxidizing agent for ALD of copper oxide also oxidizes the barrier metal which is an underlayer below the copper seed layer. The ALD nitride film was

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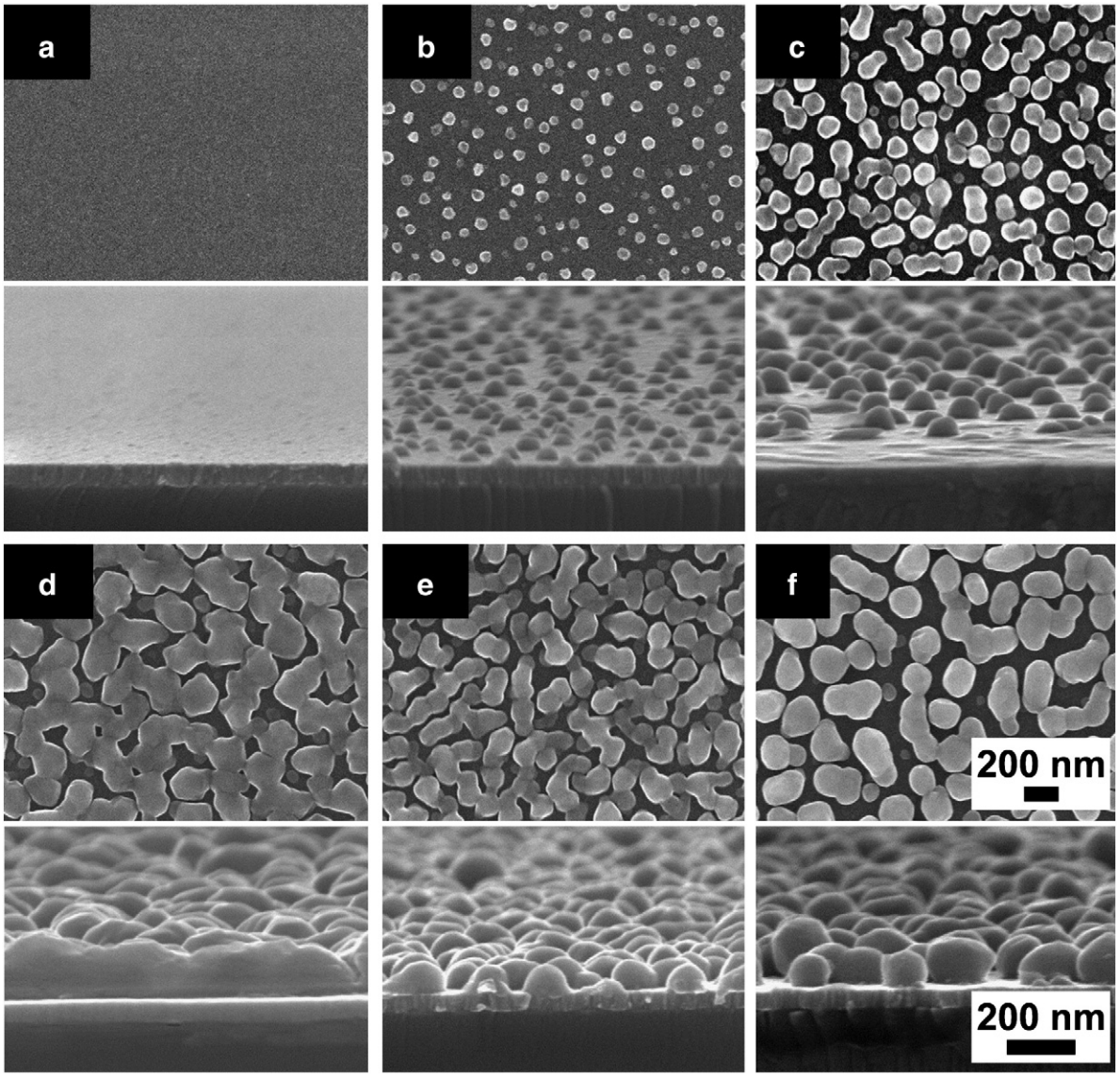

Fig. 1. Plan view and bird's-eye view SEM photographs of the copper films prepared using alternating exposures to $Cu(dmamb)_2$ and H_2: (a) ALD ruthenium substrate; the copper film deposited at (b) 120 °C, (c) 140 °C, (d) 160 °C, (e) 180 °C and (f) 200 °C. The number of ALD cycle was fixed at 100, and the exposures to the copper precursor and H_2 were 3×10^6 and 1×10^9 L, respectively.

deposited using $[Cu(^sBu\text{-}Me\text{-}amd)]_2$ and NH_3, and was reduced to metallic copper by the reducing annealing under 667 Pa of $H_2(10\%)/N_2$ at 225 °C [17]. The surface morphology and resistivity of the copper film reduced from ALD copper nitride were superior to those of the ALD copper film; however, the details of ALD copper nitride process were not published.

In this study, we selected $Cu(dmamb)_2$ as the copper precursor because it is a fluorine-free liquid precursor at room temperature with a high vapor pressure. We compared two different kinds of methods for preparing thin copper seed layers. First one is the deposition of copper film by alternating exposures to copper precursor and H_2, and the second one is the ALD of copper nitride film followed by reducing annealing. The deposition kinetics and film properties, such as surface morphology, optical properties and step coverage were investigated with varying substrate temperatures for the ALD of copper nitride. We also compared the copper film reduced from the ALD copper nitride with an ALD ruthenium as the seed layer for electrodeposition.

2. Experimental details

Copper and copper nitride thin films were grown in a hot-wall tube reactor by alternating injections of $Cu(dmamb)_2$ and the reactant.

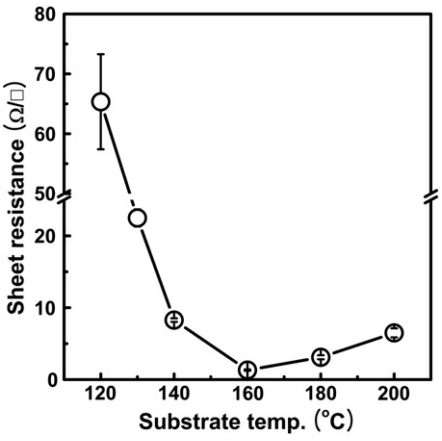

Fig. 2. Sheet resistance of the copper film deposited using alternating exposures to $Cu(dmamb)_2$ and H_2 as a function of the deposition temperature. The films were deposited on ALD ruthenium substrates for 100 cycles, and the exposures to the copper precursor and H_2 were 3×10^6 and 1×10^9 L, respectively.