Characteristics of copper films produced via atomic layer deposition

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Properties of copper films produced using atomic layer deposition (ALD) were characterized. Composition, morphology, and electrical properties of these films grown on glass, as well as Ta, TiN, and TaN on silicon wafers were examined. The resistivity of films thicker than about 60 nm was near bulk value. Films were deposited using a two-step ALD process in which copper(II)-1,1,1,5,5,5,-hexafluoroacetylacetonate hydrate and water vapor were introduced in the first step and a reducing agent was introduced in a subsequent step. Five reducing agents were evaluated, with the best results obtained using isopropanol or formalin. The optimum deposition temperature with isopropanol was about 260 °C, whereas it was about 300 °C with formalin. These films were also investigated as seed layers for electrodeposition of thicker Cu layers for possible interconnect applications. Excellent fills in high aspect ratio trenches were demonstrated.

I. INTRODUCTION

Electrodeposition of copper for fabrication of microelectronic device interconnects has now become a routine process. Prior to electrodeposition or electroplating, the wafers require a thin layer of Cu, which is called a seed layer. Currently, modified versions of sputtering are employed for deposition of these seed layers. As the device dimensions shrink, one of the challenges faced is finding a way to lay down a uniform seed layer in high aspect ratio trenches and vias of demascene structures. It is important that these layers be highly conformal, continuous, and smooth. To achieve this, we have been investigating use of atomic layer deposition (ALD) for producing thin conformal copper seed layers. Our initial results showing feasibility of this technique were reported recently.¹ Here we present further results, including electrodeposition on ALD Cu seed layers.

Atomic layer deposition is a monolayer stepwise growth process that proceeds by exposing the substrate surface alternately to each precursor followed by a nitrogen pulse to remove the excess species and byproducts of the reaction. Therefore, unlike chemical vapor deposition (CVD), in ALD the precursors are introduced to the substrates separately. Hence with this sequential mode, the duration of each exposure is adjusted so that each surface reaction goes to completion before starting the next reaction. Under properly adjusted experimental conditions all the surface reactions are saturated, making the growth process self controlled. As a result, ALD is capable of depositing conformal films whose thickness can be determined accurately by the number of deposition cycles. In addition, the separate dosing of precursors assures that no detrimental gas-phase reactions will take place. Also in practice, it has been observed that the temperatures needed for depositing high-quality films by ALD are lower than those required by CVD.

The choice of the precursors is critical for the ALD process to work. Although several precursors have been successfully used for Cu deposition using CVD (e.g., see Ref. 2), these sources will not necessarily be suitable for the ALD process, since the latter is driven by sequential surface chemistry. ALD of Cu was first reported by Tuppo et al., who used metallic zinc to reduce copper (I) chloride.³ Subsequently, hydrogen was used as the reducing agent;⁴ however in this case, significantly higher deposition temperature (approximately 400 °C) was required. The higher volatility of the organometallic Cu sources simplifies the deposition process. However, one should note that Cu I sources are generally not well suited for ALD since they tend to be thermally less stable and therefore easily decompose on contact with the substrate. On the other hand, Cu II sources are thermally more stable and hence better suited for the ALD process. Martensson and Carlsson have produced self-limited Cu deposition in the 190 to 260 °C range using Cu

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(II)-2,2,6,6-tetramethyl-3,5-heptandionate or $Cu(thd)_2$ as the Cu source reduced with H_2 .⁵ However, this process requires a layer of platinum/palladium for Cu deposition to occur.

The Cu precursor for our current investigation is copper (II)-1,1,1,5,5,5-hexafluoroacetylacetonate hydrate or Cu $(hfac)_2 \cdot xH_2O$. This source has been examined extensively for CVD deposition of Cu films, with process modifications that include plasma-enhanced CVD and addition of water or ethanol that have lead to significant improvement in the film properties.^{2,6–8} To promote effective reduction of Cu(hfac)₂ molecules into high-purity copper films, the selection of external reducing agents and film deposition conditions play extremely important roles. Application of such reducing agents in CVD metallization process has been shown by Cohen et al. to result in both increased density of Cu nuclei and faster removal of the hfac ligands, thereby allowing for deposition of smoother Cu thin films with excellent step coverage.9

II. EXPERIMENTAL

In this investigation, we examined five different reducing agents. These are methanol, ethanol, isopropyl alcohol (IPA), formalin (approximately 37% formaldehyde in 10–15% methanol and water), and carbon monoxide. The carrier gas for the reducing agent and Cu(hfac)₂ was H₂. In the case of Cu(hfac)₂, H₂ was first bubbled through water, which is an important step. Carbon monoxide was delivered as a 30% mixture with H₂ or N₂ (mixtures were supplied by Air Liquide, Morrisville, PA). The Cu films were deposited on 50 × 50 mm substrates that included glass plates and silicon wafers pre-coated with a 500-nm layer of SiO₂, followed by a barrier layer about 6 nm thick. The three different barrier layers examined were Ta, TaN, and TiN.

The Cu deposition was performed in a microchemistry F-120 ALD reactor. A typical ALD cycle consisted of a 1.5-s-long Cu(hfac)₂ pulse, then a 1.2-s N₂ purge, followed by a 1-s reducing agent pulse, and finally another 1.2-s N₂ purge. The Cu source was heated to 75 °C, and the reducing agents were all at room temperature. The chamber pressure was 5 mtorr. Although deposition of Cu was observed in all cases around 230 °C, the results reported here were produced at 300 °C, unless otherwise noted.

III. PROPOSED MECHANISM

As mentioned previously, the carrier gas for the $Cu(hfac)_2$ was H_2 that was first bubbled through water. The importance of water has been studied rather extensively for CVD deposition of Cu from Cu(hfac)₂. The vapor pressure of $Cu(hfac)_2 \cdot xH_2O$ is greater than that of the anhydrous compound. In the absence of added H_2O , dehydration by the dry carrier gas may occur. Thus it is important to add H₂O to the carrier gas stream to maximize the amount of copper delivered per pulse.^{10,11} It has been shown by Lecohier *et al.* that an increased reaction rate occurs even when water vapor is added to the process chamber separately from the copper precursor, so there is an additional benefit beyond vapor pressure enhancements.¹² Awaya and Arita postulated that, in the presence of water, the reaction proceeds by dissociation of water coordinatively bonded to copper, forming oxidized copper and Hhfac, followed by the reduction of copper oxide by hydrogen.⁶ Lecohier et al. observed that both hydrogen and helium carrier gases gave the same reaction rate in the presence of water vapor on Pt seed layer substrates, indicating that the reduction by hydrogen was not important.¹³ They proposed that the ratedetermining step was H-transfer from H₂O to hfac and that resulting OH species could be removed by combination to form H_2O_2 or by reaction with H_2 if present. The film growth rate observed by Lecohier et al. was proportional to the water vapor concentration; i.e., they operated in a regime where water vapor was the limiting reagent. Cohen et al. clearly showed that Cu(hfac)₂ decomposes upon adsorption on a metal surface to form Cu(hfac) and adsorbed hfac, with the latter very likely decomposed.9

Considering the above, we propose a two-step mechanism. In the first ALD step, $Cu(hfac)_2 \cdot xH_2O$ is delivered to the surface with an excess of water vapor, where it is adsorbed and decomposed to $Cu(hfac) \cdot yH_2O$ ($y \le x$) and hfac, followed by reaction to form Hhfac and oxidized copper. The reaction proceeds until the surface is saturated with oxidized copper, hfac, and decomposition products. During the subsequent purge step, there may be some loss of copper by reformation of $Cu(hfac)_2$ on the surface. Hhfac has been shown to effectively react with CuO to form $Cu(hfac)_2$ at 200 °C.¹⁴

Reduction occurs in the second step, where reducing gases such as alcohols transfer hydrogen to hfac on the surface to form volatile Hhfac. They also reduce oxidized copper to metallic copper and water. We observed that formalin and isopropanol produce acceptable copper films even in the absence of hydrogen. Films of about the same thickness and resistivity are achieved on bare glass, Si, and Si coated with TaN when H₂ is replaced with Ar. Use of hydrogen carrier gas gave a somewhat "cleaner" looking film. Previously, in the absence of other reducing agents, it was observed that selective deposition on Pt seeded surfaces occurred with He carrier gas, whereas nonselective deposition occurred with H₂ as the carrier gas.¹² In the present case, the other reducing agents employed gave rise to nonselective deposition, even in the absence of H_2 .

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Although CO is a strong reducing agent, the quality of Cu films deposited with it were not as good as with ethanol, IPA, and formalin. The deposition rate with alcohols and formalin was about 0.22 nm/cycle, whereas the deposition rate with CO/H_2 was up to 50% higher. The higher deposition rate with CO is most likely due to a CVD component from residual CO remaining in the reactor between the pulses. This was evident when the pressure in the reactor was monitored. The deposition rate was lower in balance nitrogen than in balance hydrogen (30% CO in either case). The Cu films in both cases were rough and had high resistivity. These films had carbon and oxygen concentrations of about 12 and 14 at.%, respectively, measured by x-ray photoelectron spectroscopy (XPS) analysis. The dark appearance of these films was probably due to the presence of Cu_2O .

Therefore, in summary, the following two-step ALD mechanism is proposed for ALD of Cu. In the first step, $Cu(hfac)_2 \cdot xH_2O$ is transported, followed by adsorption on the surface. Decomposition and then reaction with water follows, giving rise to oxidized Cu and adsorbed hfac. In the second ALD step (after the N₂ purge), oxidized Cu is reduced to metallic Cu and volatile Hhfac is formed. The Ellingham diagram in Fig. 1 illustrates the effectiveness of the various reducing agents. Formaldehyde is not only a strong reducing agent but can also supply H:

$$HCHO + Cu_2O = 2Cu + HCOOH , \qquad (1)$$

$$HCHO + H_2O = HCOOH + 2[H] , \qquad (2)$$

where [H] indicates hydrogen taken up by another species (e.g., hfac). Similarly, isopropanol supplies [H] on reduction to acetone:

$$CH_3CH_2OCH_3 = CH_3COCH_3 + 2[H] \quad . \tag{3}$$

On the other hand, CO is a strong reducing agent but cannot supply [H]. Note also ethanol and methanol cannot reduce H_2O to H_2 at the temperatures of interest, but CO, HCHO, and IPA can. This may indicate that the reason for high resistivity when using EtOH and MeOH is residual H_2O on the surface, presumably leading to oxide formation in the subsequent N_2 purge step.

IV. RESULTS AND DISCUSSION

A. Film properties

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When $Cu(hfac)_2$ and methanol were used as the sources, the Cu films deposited were smooth and conformal. Resistivities of these films tended to be higher; e.g., resistivity of 200-nm thick films was 5.3 $\mu\Omega$ cm. These films appeared reddish probably due to presence of CuO₂. Our efforts in varying the deposition parameters (temperature and pulse time) did not produce

significant improvements in the resistivity of the Cu films. This is most likely due to incorporation of impurities such as carbon and oxygen, resulting either from incomplete dissociation of methanol or partial removal of the hfac ligands from the Cu precursor. XPS analysis showed about 3 at.% carbon and 4 at.% oxygen.

Results with ethanol were significantly better. The films were again smooth and appeared brightly copper colored. Thinner films were mirrorlike; however, thicker films appeared slightly milky due to surface roughness. The best Cu films were produced with IPA and formalin as the reducing agents, with formalin producing slightly better films. These films appeared brightly copper colored and were much smoother than those produced with ethanol. The Cu films discussed below were all produced with the formalin chemistry.

Films with thickness up to about 120 run were mirrorlike. However, thicker films tended to be hazy due to the surface roughness. The adhesion of these films was checked using the Scotch tape pull test, in which the tape was examined for traces of Cu under an optical microscope. The copper films on TiN and TaN adhered well and did not peel off. Adhesion of Cu to Ta and glass was not as good; segments of the film tended to peel off with the Scotch tape. We should note that the Ta-coated wafers were exposed to air for an extended period of time prior to deposition; hence its surface was most likely oxidized. However, Cu deposited at 320 °C had significantly better adhesion on both surfaces.

Grazing incidence x-ray diffraction was used to investigate the structure of Cu films on all four types of substrates. In all cases, the diffraction spectra showed peaks corresponding to (111), (200), (220), (311), and (222) orientations, as shown in Fig. 2. A comparison of the relative intensities of these peaks with powder diffraction standards (JCPDS) data indicates a nonpreferential orientation.



FIG. 1. Ellingham diagram showing the effectiveness of various reducing agents.

2396

J. Mater. Res., Vol. 17, No. 9, Sep 2002

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B. Film resistance

One of the motivations for using copper as an interconnect metal is its low resistivity; hence, the goal of any deposition process is produce Cu films with resistivity as close as possible to its bulk value. Resistivity of the deposited films as a function of their thickness is plotted in Fig. 3. The resistivity was determined by first measuring the sheet resistivity using a four-point probe and multiplying by the film thickness measured using cross-sectional micrographs from a scanning electron microscope. It can be seen that for films of thickness greater about 75 nm, the resistivity was near bulk value (1.68 µm cm). However as the films became thinner, the resistivity increased, which was expected due to interface scattering. We estimated the mean free path of electrons in this film to a first approximation from the film thickness where the resistivity starts to increase rapidly. This estimate gave us a value for the mean free path to be about 50 nm, which is close to the bulk value. Theoretical mean free path of electrons in Cu was calculated to be about 42 nm.¹⁵



FIG. 2. Grazing incidence x-ray diffraction of the ALD copper film.



FIG. 3. Resistivity of the Cu film as a function of thickness.

C. Surface morphology and film composition

The surface morphology of the ALD films was investigated using an atomic force microscope (AFM). An AFM scan of a 80-nm-thick Cu film is shown in Fig. 4(b). As a comparison, the surface roughness of a CVD Cu film (~60 nm thick) deposited independently at a microelectronics company is shown in Fig. 4(a). The CVD film was deposited using Cu(hfac)(tmvs) (tmvs = trimethylvinylsilane) on a similar substrate. The average surface roughness of the ALD film was 4.12 nm compared to 8.35 nm for the CVD film. For electrodeposition, a smooth seed layer is desirable, especially within vias and trenches.

The Cu films deposited using the formalin and IPA chemistries had less impurity incorporation then with methanol and ethanol. XPS depth profiles showed carbon concentration of 1.5 at.%, with only a trace of O and H bonds. Our main concern was F incorporation since it can affect the adhesion of the film to the barrier layer and is believed to reduce the electromigration resistance. Relatively low F concentration of 0.25 at.% was detected, mostly near the barrier layer interface.



FIG. 4. AFM scans showing the surface roughness of copper films deposited via (a) CVD and (b) ALD.

J. Mater. Res., Vol. 17, No. 9, Sep 2002







FIG. 5. Cross-sectional SEM showing (a) the conformality of 20-nmthick ALD Cu film used as a seed layer and (b) electrodeposited Cu on the ALD seed layer.

D. Electrodeposition

As a final test of these seed layers, electrodeposition of thicker Cu films was investigated. The typical thickness of the seed layers was about 30 nm, although layers as thin as 10 nm were also used. A commercial plating solution was used in our electrodeposition cell. Figure 5 shows a scanning electron microscope cross-sectional view of the electrodeposited Cu in trenches. The deposited Cu completely fills these structures and no voids can be observed. The electrodeposited film passed the Scotch tape pull test, indicating good adhesion. The grazing in-

cidence x-ray diffraction pattern of this film was not significantly different from that of the seed layer shown in Fig. 2.

V. CONCLUSIONS

We examined several properties of atomic layer deposited Cu films important for microelectronics applications. It is demonstrated that this is a viable technique for deposition of high-purity copper films with bulk resistivity. The deposited films are smooth and conformal, especially in high aspect ratio structures and hence are well suited as seed layers for electrodeposition. This investigation is still in progress to determine the back-end parameters, such as electromigration resistance. Finally, we also demonstrated atomic-layer etching of copper films using a process that is the reverse of the deposition process discussed above. Details of these results will be presented in the near future.

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