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Efficient Process for Direct Atomic Layer Deposition of Metallic Cu Thin Films Based on an Organic Reductant

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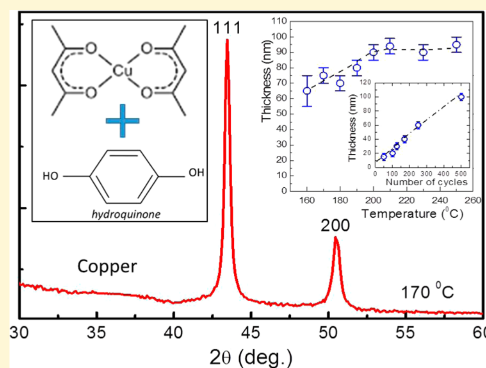
ABSTRACT: We report a promising approach to use an organic reductant for *in situ* atomic layer deposition (ALD) of metallic copper films. The process is based on sequentially pulsed precursors copper acetyl acetonate (acac), water, and hydroquinone (HQ) and yields crystalline copper films at temperatures as low as <200 °C with an appreciably high deposition rate of ~2 Å/cycle. Deposition parameters are explored for the process $m \times [n \times (Cu(acac)_2-H_2O)-HQ]$ with several values of m and n, keeping $m \times n$ fixed to 500. The films are found crystalline with metallic copper as the main phase, but different trace amounts of Cu_2O are observed when the HQ pulse frequency decreases below $^1/_5$. The as-deposited copper films are shiny and specularly reflecting and show metallic-type electrical conductivity. The absolute resistivity of the films estimated at room temperature is in the order of 2−5 $\mu\Omega$ cm, having a sizable contribution, with 0.5 $\mu\Omega$ cm from residual resistivity as a result of impurities and/or imperfections. We believe that the new process could yield benefits in interconnect applications.



1. INTRODUCTION

Copper metal has been an important constituent of our daily life since the prehistoric era, termed "copper age", which paved the way to the development of human technology. Now, in our modern society, almost all electrical devices rely on copper for electrical connections. In the microelectronic industry in particular, copper metal is the most important interconnect material.[1,2] With the boundless desire for further miniaturization and portability of electronic devices, there is a continuous need for advances in the fabrication technologies. These advances have led to the high level integration and complex interconnections in microelectronic chips.[3] However, when we approach from the micro to the nano regime, Joule heating becomes a major concern in all of the interconnect applications. Hence, to keep pace with development, there is an urgent need to deal with the apparent integration and interconnection problems in microelectronic chips and some niche applications.

In interconnect technology, copper is preferred over other elements, owing to its remarkably high electrical conductivity, abundant availability, and relatively good resistance to electromigration.[4−7] However, conformal deposition on the most demanding high-aspect-ratio substrate geometries is still a challenge. Physical vapor deposition (PVD)[8−11] is the most common technique for fabricating thin copper seed layers (<50 nm), but conformity problems limit its application in advanced technologies.

Chemical vapor deposition (CVD) has been considered as a way forward to highly conformal copper coatings. However, the difficulties in controlling nucleation and interfacial adhesion of copper atoms to the common barrier metals, such as TiN, TaN, and WN, on the common semiconducting substrate surfaces and the lack of morphological control for ultrathin films, together with the toxicity, limited availability, and laborious handling of the most promising precursors, have made these efforts a partial success only.[12,13] There is research going on toward finding new precursors[14−16] and new variants of the CVD technique,[17−20] but common to most of these processes is that hydrogen is used as the reducing agent to obtain a metallic film.[21,22] As an alternative, few works have reported the use of alkyl alcohols as co-reactants/solvents to enhance the film growth, where dehydrogenation of alcohols produces hydrogen radicals that reduce copper oxides to pure metal.[23−28]

With its self-limiting and sequential surface reactions, the state-of-the-art thin-film technique, i.e., atomic layer deposition (ALD), would in principle be a viable alternative for high-quality conformal copper thin-film deposition. There are indeed several reports on copper thin films deposited by ALD using various copper precursors,[15,29−42] among these are the β-diketonate family, e.g., $Cu(acac)_2$ (acac = acetyl acetonate), appearing the most promising because of its high stability and relatively low vapor pressure. However, the β-diketonate precursors require relatively high deposition temperatures, which is undesirable.[42] Another challenge arises from the difficulty of these precursors to firmly adsorb on pure metal surfaces free from functional groups.[43] To overcome the latter problem, a two-step process has been considered, consisting of (i) the deposition of a CuO layer of the intended thickness first, followed by (ii) its reduction to metallic copper by the reductant (mostly H_2).[15,29,31,38] There are also some plasma-

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enhanced[44] and radical-enhanced[45] ALD processes developed for copper films, but in these processes too, hydrogen is typically used as the reducing agent. The major shortcoming related to the use of hydrogen is the quick recombination of hydrogen atoms on the deposition surface; this limits the usability of the hydrogen-based processes to relatively flat and small-area substrates. Thus, the ALD of metallic copper films on high-aspect-ratio geometries is still in its infancy. For the widespread use of the Cu ALD technology, a simple low-temperature ALD process that allows for the fabrication of smooth, continuous copper films on large and/or complex surface architectures and based on a stable reducing agent would be ideal.

Here, we show that the aromatic diol, hydroquinone (HQ), can be used in combination with the $Cu(acac)_2$−H_2O ALD process as an efficient reducing agent for the *in situ* fabrication of homogeneous metallic copper thin films specular and shiny in appearance at as low deposition temperatures as 170−230 °C. The $Cu(acac)_2$−H_2O ALD process has been previously used for copper oxide thin films,[32,46] whereas HQ has been employed as the organic component in the combined atomic and molecular layer deposition (ALD/MLD) processes for various hybrid inorganic−organic thin films and superlattices.[47−49]

2. EXPERIMENTAL SECTION

The solid precursors were procured from commercial sources: $Cu(acac)_2$ (purity of 97%) from STREM Chemicals and HQ (purity of 98%) from Alfa Aesar. These precursors, $Cu(acac)_2$ and HQ, were sublimated at 140 and 105 °C, respectively, while water was evaporated at room temperature (24 °C). The pulsing sequence of our deposition process could be described as follows: $m \times [n \times (Cu(acac)_2{-}H_2O){-}HQ]$. In other words, a single HQ pulse was applied after n cycles of $(Cu(acac)_2{-}H_2O)$, such that the frequency of the HQ pulse, $1/n$, varied from $^1/_1$ to $^1/_{20}$ in our experiments. Then, the sequence $[n \times (Cu(acac)_2{-}H_2O){-}HQ]$ was repeated m times to obtain a film of the targeted thickness. In this work, we define the basic cycle as $(Cu(acac)_2{-}H_2O{-}HQ)$ and express the so-called growth per cycle as GPC = $t/(m \times n)$, where t is the measured film thickness and $m \times n$ is the total number of basic cycles applied. As common to all ALD processes, every precursor pulse was followed by a subsequent N_2 purge pulse (although not indicated above). The depositions were carried out at various temperatures (160−250 °C) on 35 × 35 mm^2 borosilicate glass and silicon (without removing the native oxide layer) substrates in a commercial hot-wall flow-type F-120 ALD reactor (ASM Microchemistry, Ltd., Finland) operated under a N_2 working pressure of 2−3 mbar.

The crystal structure of the films was examined by grazing-incidence X-ray diffraction (GIXRD) [PANanalytical model X'pert Pro diffractometer (Cu Kα radiation)]. Atomic force microscopy (AFM, TopoMetrix Explorer) measurements were carried out for the determination of film thickness and roughness, and scanning electron microscopy (SEM, Zeiss-Sigma VP, resolution of 1.3 nm at 20 kV) measurements were carried out for the film morphology. The direct current (DC) electrical resistivity (ρ), from room temperature (300 K) to liquid nitrogen temperature (77 K), was measured for the films in a linear four-probe configuration.

3. RESULTS AND DISCUSSION

Our $m \times [n \times (Cu(acac)_2{-}H_2O){-}HQ]$ process yielded visually homogeneous, shiny, and specularly reflecting copper thin films besides the film deposited at lower temperatures, 160−170 °C. The as-deposited films were electrically highly conducting, but when left in ambient condition for a few days, electrical conductivity decreased as a result of oxide formation on the surface. Hence, we carried out all of the characterizations for freshly deposited films. Even though the as-deposited films were highly crystalline, they did not show the typical fringe patterns in X-ray reflectivity measurements. Thus, we used the cantilever tip jump AFM technique for the thickness measurements.[50,51] As shown in Figure 1, when scanned across the edge

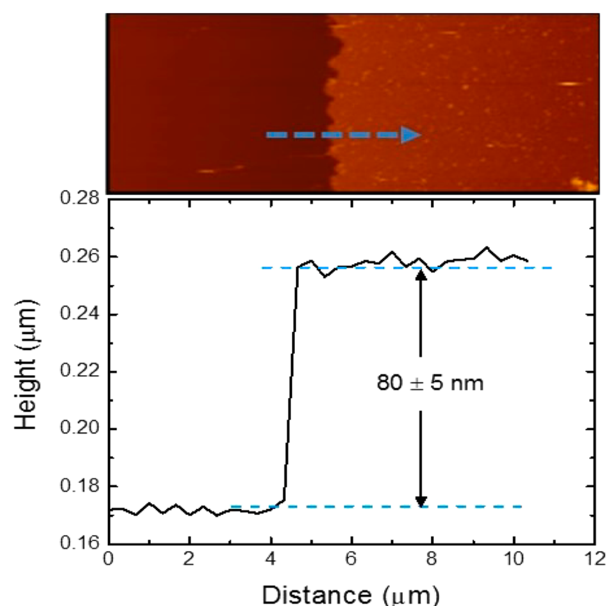

Figure 1. Thickness measurement for a representative copper film sample by the AFM tip jump technique. The arrow points to the direction to which the thickness was estimated.

of a scratch, deliberately scratched on the film using a sharp scalpel, the cantilever tip jump profile gives the thickness of the film. We have verified this method by measuring the thickness from the cross-section SEM images (not shown) for some films reported in ref 51. Results were in agreement within 2−5% accuracy.

We first explored the deposition parameters for our $m \times [n \times (Cu(acac)_2{-}H_2O){-}HQ]$ process, as shown in Figure 2. The main figure presents the film thicknesses for a series of thin films grown at different deposition temperatures from 160 to 250 °C with the following precursor/purge pulse lengths: 3 s $Cu(acac)_2$/4 s N_2−3 s H_2O/4 s N_2−2 s HQ/3 s N_2. The total number of cycles ($m \times n$) was fixed to 500, and the frequency of the HQ pulses ($1/n$) was fixed at 1. From Figure 2, the film thickness first increases with an increasing deposition temperature and then levels off in the temperature range of 210−250 °C. The films deposited at lower temperatures (160−180 °C) appeared more rough and presented remarkably high roughness values (up to ∼50 nm) in AFM measurements.

Next, we confirmed the constant GPC behavior of the deposition process by plotting the film thickness against the number of deposition cycles ($m \times n$), as shown in the left inset in Figure 2. For these experiments, the deposition temperature was fixed to 210 °C. To ascertain the saturative nature of the underlining surface reactions, we varied the individual pulse lengths for all three precursors (and the corresponding purge pulses) one at a time and calculated the GPC values from the resultant film thickness. The results are shown in the right inset of Figure 2, and it is evident that the relatively short precursor/purge pulse lengths of 3 and 4 s are long enough to guarantee the ALD film growth based on successive self-saturative surface reactions of the precursors. Overall, it is important to

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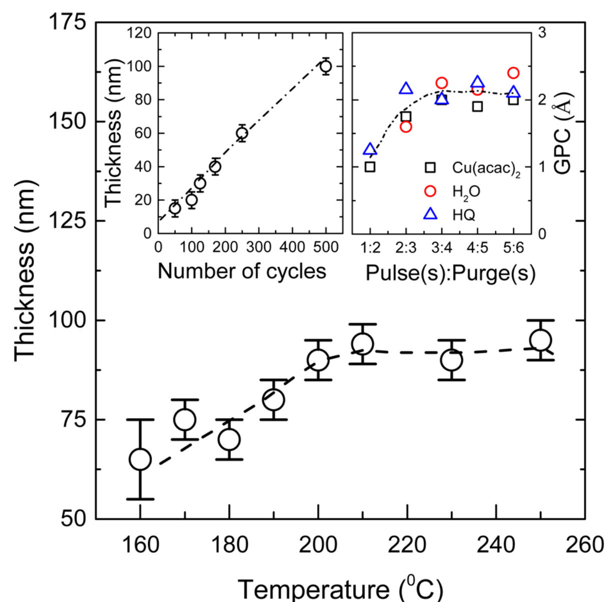

Figure 2. Film thickness as a function of the deposition temperature for our copper metal films obtained from the $m \times [n \times (Cu(acac)_2-H_2O)-HQ]$ process for $n = 1$ and $m = 500$. The left inset shows the essentially linear increase of film thickness with an increasing number of deposition cycles, i.e., $m \times n$ (here m, as $n = 1$), at the deposition temperature of 210 °C. The right inset shows the GPC values for different pulse/purge length ratios of the individual precursors; this is changed for each precursor/purge pair one at a time, keeping others at 2 s/3 s.

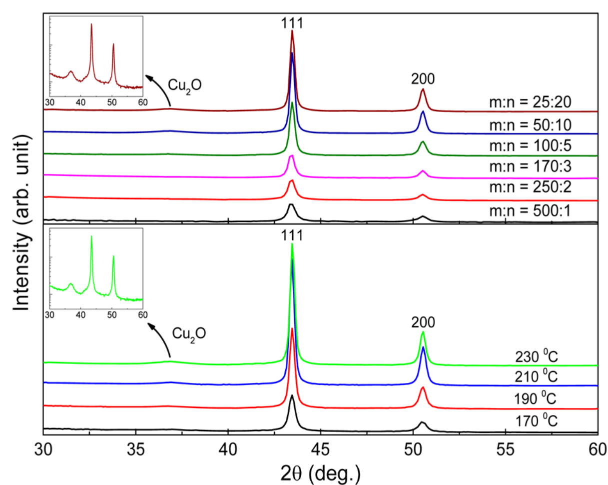

Figure 3. GIXRD patterns for a series of thin films deposited through our $m \times [n \times (Cu(acac)_2-H_2O)-HQ]$ process at 170 °C with different n and m values (upper panel), for ($m = 500$, and $n = 1$) films deposited at different temperatures (lower panel). The indices are for metallic copper. The insets show the appearance of the Cu_2O phase when m/n ratios are reduced below 100:5 and deposition temperatures increased above 210 °C.

emphasize that the GPC values achieved under the aforementioned optimized conditions, i.e., ~2 Å/cycle, are almost an order of magnitude higher than the values reported for the growth of copper films via radical-enhanced ALD using the same precursor[45] and via conventional ALD using copper(I) chloride as the copper source.[30]

It is well-known that the reaction of $Cu(acac)_2$ with H_2O primarily deposits Cu_2O.[52,53] Also agreed is that the reaction proceeds through successive ligand-exchange reactions, which lead to Cu−OH surface groups.[54−58] Then, in the present case, we tentatively suggest that the reduction of copper oxide primarily happens through the oxidation of the weakly acidic HQ to benzoquinone. This reaction yields hydrogen that could reduce copper oxide on the surface to metallic copper. However, on the basis of their computational calculations, Hu et al.[56] have suggested that $Cu(acac)_2$ can itself produce reduced copper via successive dissociation when adsorbed on a Cu(110) surface. Thus, this could also be a possible mechanism in our case but only after a few layers of pure copper are formed.

Figure 3 presents the GIXRD patterns for several representative films grown with different deposition parameters/conditions; in each case, the total number of deposition cycles is $(m \times n) \approx 500$, and the film thickness is approximately 100 nm. First, we may conclude that all of the films are crystalline, with metallic copper as the main phase but different amounts of Cu_2O as an unwanted trace. From the upper panel in Figure 3, where the films differ from each other by the frequency $1/n$ of the HQ pulses (deposition temperature of 170 °C), it is seen that essentially pure copper films are obtained even for HQ pulse frequencies down to $^1/_5$. With less HQ pulses (i.e., larger n), the films show increasing amounts of Cu_2O, presumably as a consequence of incomplete reduction of copper oxide as a result of the not frequent enough reductant supply. In the lower panel of Figure 3, we investigate the effect of the deposition temperature in the range of 170−230 °C; $n = 1$ and $m = 500$ for these films. The full width at half maximum (fwhm) of the Cu(111) peak at 43.45° clearly decreases with an increasing deposition temperature, indicating enhanced crystallinity. The appearance of the tiny Cu_2O peak may be due to surface oxidation because the GIXRD measurements were performed in an ambient atmosphere and a couple of hours after films were removed from the reactor. It is well-known that copper films do form surface oxides in ambient conditions.[59,60]

To analyze the surface morphological and topological features, we carried out SEM and AFM measurements, as shown in Figure 4. The SEM and AFM images are well in line with the GIXRD data, confirming that the films deposited at lower temperatures appear rougher than those deposited at higher temperatures. From the SEM images, microagglomerate-like features are seen in the case of the lowest deposition temperature. This is probably because of a low nucleation density on the glass substrate at low temperatures.[12] As the deposition temperature increases, homogeneity improves and the root-mean-square (RMS) roughness values decrease down to ~8 nm for the films deposited at 210 °C.

Finally, in Figure 5, we show the DC electrical resistivity (ρ) of the films plotted as relative resistivity (ρ_T/ρ_{77}), similar to the residual resistivity ratio (RRR), as a function of the measurement temperature (T) to observe the quality of the films. Residual resistivity is usually expressed as RRR, where the ratio of the resistivity of a material at room temperature and 0 K is estimated. For a single-phase material, the RRR can vary strongly depending upon the amount of impurities, grain boundaries, and other crystallographic imperfections. Thus, it serves as a rough index of the purity and overall quality of a sample.[61] The larger the RRR value, the more pure and/or defect free the sample. The absolute resistivity of the films estimated at room temperature is in the order of ~2−5 $\mu\Omega$ cm, which is quite comparable to the pure copper resistivity value of

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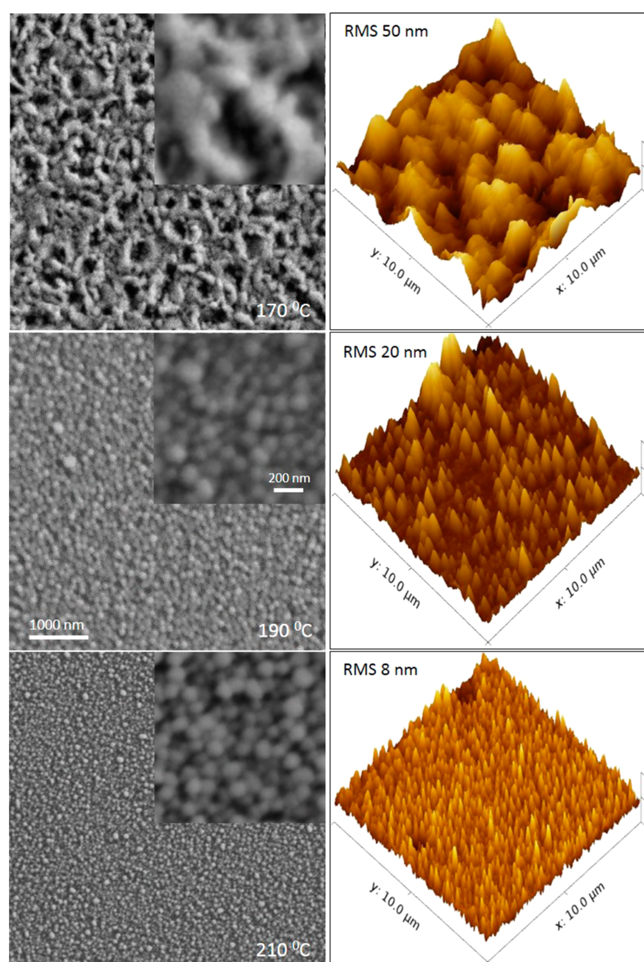

Figure 4. SEM (left) and AFM (right) images for our copper thin films deposited at 170 °C (top), 190 °C (middle), and 210 °C (bottom) with thicknesses of 75 ± 5, 80 ± 5, and 94 ± 5 nm, respectively.

1.68 $\mu\Omega$ cm at room temperature. A perfect metallic conduction behavior ($d\rho/dT > 0$) with linear temperature dependence is seen for all of the films investigated. The residual contribution to resistivity estimated from the linear extrapolation of the curves to $T = 0$ K is of the order of 0.5 $\mu\Omega$ cm for all of the films. RRR calculated from this is in the order of ∼4−10, which is substantially less than the values, ∼ 40−50, for pure copper wire. This is also reflected in the relative resistivity of the films that does not change much down to liquid nitrogen temperature. This suggests that the films do have the sizable contribution from residual resistivity, which we believe may be due to the grain boundaries, oxygen impurity, incomplete reduction, and/or presence of traces of the organic precursor in the films. The relative resistivity of the films deposited at 190 and 210 °C is a little less compared to that deposited at 170 °C, which, we believe, may be the contribution from the surface oxide secondary phase, as observed in GIXRD measurements besides the residual resistivity.

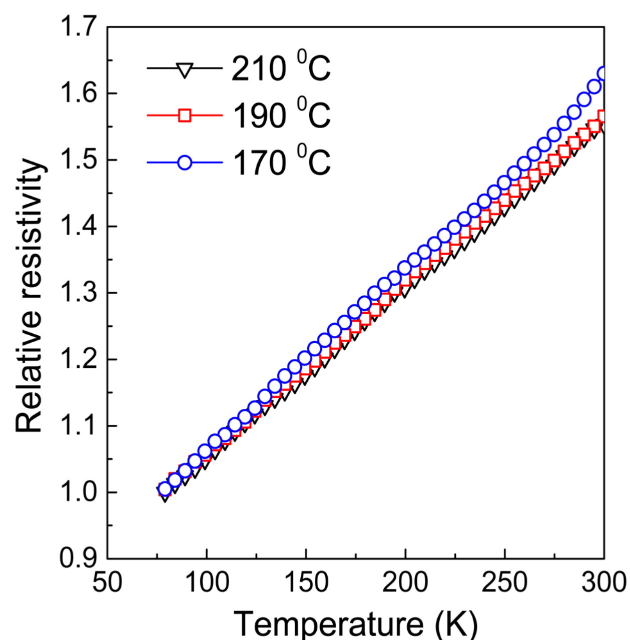

Figure 5. Relative electrical resistivity (ρ_T/ρ_{77}) as a function of the temperature for films deposited at 170, 190, and 210 °C with thicknesses of 75 ± 5, 80 ± 5, and 94 ± 5 nm, respectively.

4. CONCLUSION

We have successfully developed a promising ALD process for the *in situ* deposition of pure copper metal thin films that does not require the use of hydrogen as the reductant. The process is based on sequentially pulsed copper acetyl acetonate, water, and HQ precursors and yields highly crystalline copper thin films with an appreciably high growth rate of ∼2 Å/cycle at deposition temperatures as low as <200 °C. Apparently, weakly acidic HQ works as an efficient reductant in the process. The as-deposited copper films show perfect metallic-type electrical conductivity and room-temperature resistivity values as low as ∼2−5 $\mu\Omega$ cm.

Although further studies are definitely required, our HQ-based ALD process for metallic copper thin films could be beneficial in interconnect applications. Moreover, we foresee that similar ALD processes based on HQ as the reductant could be developed for other metals as well.

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Notes

The authors declare no competing financial interest.

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