This is an electronic reprint of the original article.
This reprint may differ from the original in pagination and typographic detail.

Tripathi, Tripurari S.; Karppinen, Maarit

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

Published in:
Chemistry of Materials

DOI:
[10.1021/acs.chemmater.6b04597](https://doi.org/10.1021/acs.chemmater.6b04597)

Published: 14/02/2017

Document Version
Peer reviewed version

Published under the following license:
Unspecified

Please cite the original version:
Tripathi, T. S., & Karppinen, M. (2017). Efficient Process for Direct Atomic Layer Deposition of Metallic Cu Thin Films Based on an Organic Reductant. *Chemistry of Materials*, 29(3), 1230-1235.
<https://doi.org/10.1021/acs.chemmater.6b04597>

This material is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.

Efficient process for direct ALD of metallic Cu thin films based on an organic reductant

Tripurari S. Tripathi and Maarit Karppinen*

Department of Chemistry, Aalto University, P.O. Box 16100, FI-00076 Aalto, Finland

*maarit.karppinen@aalto.fi

KEYWORDS: Atomic layer deposition, metallic copper, hydroquinone, thin films.

ABSTRACT: We report a promising approach to utilize an organic reductant for *in situ* ALD (atomic layer deposition) 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, $m \times [n \times (\text{Cu}(\text{acac})_2 - \text{H}_2\text{O}) - \text{HQ}]$ 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 $\mu\Omega\cdot\text{cm}$ having a sizable contribution, 0.5 $\mu\Omega\cdot\text{cm}$ from residual resistivity due to 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 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 of a partial success only.^{12,13} There is research going on towards 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 in order 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 the β -diketonate family, e.g. $\text{Cu}(\text{acac})_2$ (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-enhanced⁴⁴ and radical-enhanced⁴⁵ 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 wide spread use of the Cu-ALD technology a simple low-temperature ALD process that allows 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 97%) from STREM chemicals and HQ (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 $(Cu(acac)_2-H_2O)$ or $(Cu(acac)_2-H_2O-HQ)$, 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 the basic cycles applied. As common to all ALD processes, every precursor pulse was followed by a subsequent N_2 purge pulse (though not indicated above). The depositions were carried out at various temperatures (160–250 °C) on 35×35 mm² 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 an N_2 working pressure of 2–3 mbar.

The crystal structure of the films was examined by grazing-incidence x-ray diffraction (GIXRD) (PANalytical model X'pert Pro diffractometer ($CuK\alpha$ radiation)). Atomic force microscopy (AFM; TopoMetrix Explorer) measurements we carried out for the determination of film thickness and roughness, and scanning electron microscopy (SEM; Zeiss-Sigma VP, resolution 1.3 nm @ 20 kV) measurements for the film morphology. The 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 one 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 due to oxide formation on the surface. Hence, we carried out all 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 utilized the cantilever tip jump AFM technique for the thickness measurements.^{50,51} As shown in Figure 1, when scanned across the edge 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 scanning electron microscope (SEM) images (not shown) for some films reported in Ref (51). Results were in agreement within 2-5 % accuracy.

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.

We first explored the deposition parameters for our $m \times [n \times (\text{Cu}(\text{acac})_2\text{--H}_2\text{O})\text{--HQ}]$ 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 $\text{Cu}(\text{acac})_2$ / 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 ($1/n$) at 1. From Figure 2, the film thickness first increases with 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.

Figure 2. Film thickness as a function of deposition temperature for our copper metal films obtained from the $m \times [n \times (\text{Cu}(\text{acac})_2\text{--H}_2\text{O})\text{--HQ}]$ process for $n = 1$ and $m = 500$. The left inset shows the essentially linear increase of film thickness with increasing number of deposition cycles, i.e. $m \times n$ (here m , as $n = 1$), at the deposition temperature 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.

Next, we confirmed the constant growth per cycle (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 the 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 s / 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 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 precursor⁴⁵ and via conventional ALD using copper(I) chloride as the copper source.³⁰

It is well known that the reaction of $\text{Cu}(\text{acac})_2$ with H_2O primarily deposits Cu_2O .^{52,53} Also agreed is that the reaction proceeds through successive ligand-exchange reactions which lead to $\text{Cu}\text{--OH}$ 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 hydroquinone to benzoquinone. This reaction yield hydrogen that could reduce copper oxide on the surface to metallic copper. However, based on their computational calculations Hu et al.⁵⁶ have suggested that $\text{Cu}(\text{acac})_2$ can itself produce reduced copper via successive dissociation when adsorbed on a $\text{Cu}(110)$ surface. Thus, this could also be a possible mechanism in our case but only after few layers of pure copper are formed.

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

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. Firstly, we may conclude that all 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 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 due to the not frequent enough reductant supply. In the lower panel of Figure 3 we investigate the effect of deposition temperature in the range 170–230 °C; $n = 1$ and $m = 500$ for these films. The full width at half maximum (FWHM) of the $\text{Cu}(111)$ peak at 43.45° clearly decreases with increasing deposition temperature indicating enhanced crystallinity. The appearance of the tiny Cu_2O peak may be due to surface oxidation as the GIXRD measurements were performed in 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 RMS roughness values decrease down to ~8 nm for the films deposited at 210 °C.

Figure 4. SEM (left) and AFM (right) images for our copper thin

films deposited at 170 (top), 190 (middle) and 210 °C (bottom) with thicknesses 75 ± 5 , 80 ± 5 and 94 ± 5 nm, respectively.

Finally, in Figure 5 we show the dc electrical resistivity (ρ) of the films plotted as relative resistivity (ρ/ρ_{77}), similar to residual resistivity ratio (or RRR), as a function of 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 at 0 K is estimated. For a single-phase material, the RRR can vary strongly depending on 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 is the sample. The absolute resistivity of the films estimated at room temperature is in the order of ~ 2-5 $\mu\Omega\cdot\text{cm}$, which is quite comparable to the pure copper resistivity value 1.68 $\mu\Omega\cdot\text{cm}$ at room temperature. A perfect metallic conduction behavior ($d\rho/dT > 0$) with linear temperature dependence is seen for all 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 $\mu\Omega\cdot\text{cm}$ for all 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 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/ρ_{77}) as a function of temperature for films deposited at 170, 190 and 210 °C with thicknesses 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 hydroquinone precursors, and yields highly crystalline copper thin films with an appreciably high growth rate of $\sim 2 \text{ \AA/cycle}$ at deposition temperatures as low as $<200 \text{ }^\circ\text{C}$. Apparently the weakly acidic hydroquinone 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 $\sim 2\text{-}5 \text{ }\mu\Omega\text{.cm}$.

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

AUTHOR INFORMATION

Corresponding Author

* E-mail: maarit.karppinen@aalto.fi

Notes

The authors declare no competing financial interest.

Author Contributions

The manuscript was written through contributions of all authors.

ACKNOWLEDGMENT

This work has received funding from the European Research Council under the European Union's Seventh Framework Programme (FP/2007-2013)/ERC Advanced Grant Agreement (No. 339478) and also from the Academy of Finland (No. 296299).

REFERENCES

- (1) Norman, J. A. T. Advances in Copper CVD for the Semiconductor Industry. *J. Phys. IV* **2001**, 11(3), 497-503.
- (2) Luo, B.; Gladfelter, W. L. Chemical Vapor Deposition of Metals: W, Al, Cu and Ru, in Chemical Vapor Deposition eds. Jones, A. C.; Hitchman, M. L. *Royal Society of Chemistry* **2009**, 320.
- (3) Rickerby, J.; Steinke, J. H. G. Current Trends in Patterning with Copper. *Chem. Rev.* **2002**, 102, 1525-1550.
- (4) Rosenberg, R.; Edelstein, D. C.; Hu, C.-K.; Rodbell, K. P. Copper Metallization for High Performance Silicon Technology. *Annu. Rev. Mater. Sci.* **2000**, 30, 229-262.
- (5) Kodas, T. T.; Smith, M. J. H. *The Chemistry of Metal CVD*, VCH: Weinheim, **1994**.
- (6) Barriere, C.; Alcaraz, G.; Margeat, O.; Fau, P.; Quoirin, J. B.; Anceau, C.; Chaudret, B. Copper Nanoparticles and Organometallic Chemical Liquid Deposition (OMCLD) for Substrate Metallization. *J. Mater. Chem.* **2008**, 18, 3084-3086.
- (7) Han, B.; Wu, J.; Zhou, C.; Li, J.; Lei, X.; Norman, J. A. T.; Gaffney, T. R.; Gordon, R.; Roberts, D. A.; Cheng, H. Ab Initio Molecular Dynamics Simulation on the Aggregation of a Cu Monolayer on a WN(001) Surface. *J. Phys. Chem. C* **2008**, 112, 9798-9802.
- (8) Czandema, A. W.; Brennan, B. W.; Clarke, E. G. Effect of Water Vapor Exposure on the Epitaxy of Copper Films on Sodium Chloride. *Phys. Status Solidi A* **1971**, 8, K75-K79.
- (9) Pal, A. K.; Sen, P.; Barua, A. K. Electrical Properties of Vacuum-evaporated Copper Films. *Thin Solid Films* **1975**, 25, S25-S28.
- (10) Porteus, J. O.; Choyke, W. J.; Hoffman, R. A. Pulsed Laser Damage Characteristics of Vapor-deposited Copper Mirrors on Silicon Carbide Substrates. *Appl. Opt.* **1980**, 19, 451-454.
- (11) Inal, O. T.; Torma, A. E. Growth Characteristics of Copper of Tungsten Grown through Cementation, Vapor Deposition and Electroplating. *Thin Solid Films* **1979**, 60, 157-164.
- (12) Kim, Y. S.; Shimogaki, Y. X-ray Photoelectron Spectroscopic Characterization of the Adhesion Behavior of Chemical Vapor Deposited Copper Films. *J. Vac. Sci. Technol. A* **2001**, 26, 2642-2651.
- (13) Gandikota, S.; Voss, S.; Tao, R.; Duboust, A.; Cong, D.; Chen, L.; Ramaswami, S.; Carl, D. Adhesion Studies of CVD Copper Metallization. *Microelectron. Eng.* **2000**, 50, 547-553.
- (14) Lim, B. S.; Rahtu, A.; Gordon, R. G. Atomic Layer Deposition of Transition Metals. *Nature Mater.* **2003**, 2, 749-754.
- (15) Li, Z.; Rahtu, A.; Gordon, R. G. Atomic Layer Deposition of Ultrathin Copper Metal Films from a Liquid Copper(I) Amidinate Precursor. *J. Electrochem. Soc.* **2006**, 153, C787-7794.
- (16) Hsu, I. J.; McCandless, B. E.; Weiland, C.; Willis, B. G. Characterization of ALD Copper Thin Films on Palladium Seed Layers. *J. Vac. Sci. Technol. A* **2009**, 27, 660-667.
- (17) Blackburn, J. M.; Long, D. P.; Cabanas, A.; Watkins, J. J. Deposition of Conformal Copper and Nickel Films from Supercritical Carbon Dioxide. *Science* **2001**, 294, 141-145.
- (18) Kim, H.; Bhandari, H. B.; Xu, S.; Gordon, R. G. Ultrathin CVD Cu Seed Layer Formation Using Copper Oxynitride Deposition and Room Temperature Remote Hydrogen Plasma Reduction. *J. Electrochem. Soc.* **2008**, 155, H496-H503.
- (19) Liu, T.; Vilar, R.; Eugenio, S.; Grondin, J.; Danten, Y. Electrodeposition of Copper Thin Films from 1-ethyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide. *J. Appl. Electrochem.* **2015**, 45, 87-93.
- (20) Cabanas, A.; Shan, X. Y.; Watkins, J. J. Alcohol-Assisted Deposition of Copper Films from Supercritical Carbon Dioxide. *Chem. Mater.* **2003**, 15, 2910-2916.
- (21) Bahlawane, N.; Premkumar, P. A.; Onwuka, K.; Reiss, G.; Hoinghaus, K. K. Self-catalyzed Chemical Vapor Deposition Method for the Growth of Device-Quality Metal Thin Films. *Microelectron. Eng.* **2007**, 84, 2481-2485.
- (22) Lay, E.; Song, Y. H.; Chiu, Y. C.; Lin, Y. M.; Chi, Y.; Carty, A. J.; Peng, S. M.; Lee, G. H. New CVD Precursors Capable of Depositing Copper Metal under Mixed O₂/Ar Atmosphere. *Inorg. Chem.* **2005**, 44, 7226-7233.
- (23) Chiang, C. M.; Miller, T. M.; Dubois, L. H. Role of Solvents in Chemical Vapor Deposition: Implications for Copper Thin-film Growth. *J. Phys. Chem.* **1993**, 97, 11781-11786.
- (24) Borgharkar, N. S.; Griffin, G. L.; James, A.; Maverick, A. W. Alcohol-Assisted Growth of Copper CVD Films. *Thin Solid Films* **1998**, 320, 86-94.

- (25) Borgharkar, N. S.; Griffin, G. L.; H. Fan, Maverick, A. W. Solution Delivery of $\text{Cu}(\text{hfac})_2$ for Alcohol-Assisted Chemical Vapor Deposition of Copper. *J. Electrochem. Soc.* **1999**, 146, 1041-1045.
- (26) Premkumar, P. A.; Bahlawane, N.; Reiss, G.; Hoinghaus, K. K. CVD of Metals Using Alcohols and Metal Acetylacetonates, Part II: Role of Solvent and Characterization of Metal Films Made by Pulsed Spray Evaporation CVD. *Chem. Vap. Deposition* **2007**, 13, 227-231.
- (27) Premkumar, P. A.; Bahlawane, N.; Hoinghaus, K. K. CVD of Metals Using Alcohols and Metal Acetylacetonates, Part I: Optimization of Process Parameters and Electrical Characterization of Synthesized Films. *Chem. Vap. Deposition* **2007**, 13, 219-226.
- (28) Bahlawane, N.; Premkumar, P. A.; Reilmann, F.; Höinghaus, K. K.; Wang, J.; Qi, F.; Gehl, B.; Bäumer, M. CVD of Conducting Ultrathin Copper Films. *J. Electrochem. Soc.* **2009**, 156, D452-D455.
- (29) Juppo, M.; Ritala, M.; Leskelä, M. Deposition of Copper Films by an Alternate Supply of CuCl and Zn . *J. Vac. Sci. Technol. A* **1997**, A15(4), 2330-2333.
- (30) Martensson, P.; Carlsson, J. O., Atomic Layer Epitaxy of Copper on Tantalum. *Chem. Vap. Deposition* **1997**, 3, 45-50.
- (31) Mane, A. U.; Shivashankar, S. A. Atomic Layer Chemical Vapor Deposition of Copper. *Mater. Sci. Semicond. Process.* **2004**, 7, 343-347.
- (32) Martensson, P.; Carlsson, J. O. Growth and Selectivity in the $\text{Cu}(\text{II})$ -2,2,6,6-tetramethyl-3,5-heptanedionate/ H_2 Process. *J. Electrochem. Soc.* **1998**, 145, 2926-2931.
- (33) Waechtler, T.; Oswald, S.; Roth, N.; Jako, A.; Lang, H.; Ecke, R.; Schulz, S. E.; Gessner, T.; Moskvina, A.; Schulze, S.; Hetschold, M. Copper Oxide Films Grown by Atomic Layer Deposition from Bis(tri-n-butylphosphane)-Copper(I)acetylacetonate on Ta, TaN, Ru, and SiO_2 . *J. Electrochem. Soc.* **2009**, 156, H453-H459.
- (34) Li, Z.; Barry, S. T.; Gordon, R. G., Synthesis and Characterization of Copper(I) Amidinates as Precursors for Atomic Layer Deposition (ALD) of Copper Metal. *Inorg. Chem.* **2005**, 44, 1728-1735.
- (35) Park, J. M.; Jin, K.; Han, B.; Kim, M. J.; Jung, J.; Kim, J. J.; Lee, W. J. Atomic Layer Deposition of Copper Nitride Film and Its Application to Copper Seed Layer for Electrodeposition. *Thin Solid Films* **2014**, 556, 434-439.
- (36) Dey, G.; Elliott, S. D. Copper Reduction and Atomic Layer Deposition by Oxidative Decomposition of Formate by Hydrazine. *RSC Adv.* **2014**, 4, 34448-34453.
- (37) Knisley, T. J.; Ariyasena, T. C.; Sajavaara, T.; Saly, M. J.; Witer, C. H. Low Temperature Growth of High Purity, Low Resistivity Copper Films by Atomic Layer Deposition. *Chem. Mater.* **2011**, 23, 4417-4419.
- (38) Lakmal, C. K.; Scott B. C.; Charles, H. W. Low-Temperature Atomic Layer Deposition of Copper Films Using Borane Dimethylamine as the Reducing Co-reagent. *Chem. Mater.* **2014**, 26, 3731-3738.
- (39) Lee, B. H.; Hwang, J. K.; Nam, J. W.; Lee, S. U.; Kim, J. T.; Koo, S.; Baunemann, A.; Fischer, R. A.; Sung, M. M. Low-Temperature Atomic Layer Deposition of Copper Metal Thin Films: Self-Limiting Surface Reaction of Copper Dimethylamino-2-propoxide with Diethylzinc. *Angew. Chem., Int. Ed.* **2009**, 48, 4536-4539.
- (40) Vidjayacoumar, B.; Emslie, D. J. H.; Clendenning, S. B.; Blackell, J. M.; Britten, J. F.; Rheingold, A. Investigation of AlMe_3 , BEt_3 , and ZnEt_2 as Co-Reagents for Low-Temperature Copper Metal ALD/Pulsed-CVD. *Chem. Mater.* **2010**, 22, 4844-4853.
- (41) Kniley, T. J.; Ariyasena, T. C.; Sajavaara, T.; Saly, M. J.; Winter, C. H. Low Temperature Growth of High Purity, Low Resistivity Copper Films by Atomic Layer Deposition. *Chem. Mater.* **2011**, 23, 4417-4419.
- (42) Utriainen, M.; Laukkanen, M. K.; Johansson, L. S.; Niinistö, L. Studies of Metallic Thin Film Growth in an Atomic Layer Epitaxy Reactor Using $\text{M}(\text{acac})_2$ ($\text{M}=\text{Ni}, \text{Cu}, \text{Pt}$) Precursors. *Appl. Surf. Sci.* **2000**, 157, 151-158.
- (43) Li, Z.; Gordon, R. G.; Farmer, D. F.; Lin, Y.; Vlassak, J. Nucleation and Adhesion of ALD Copper on Cobalt Adhesion Layers and Tungsten Nitride Diffusion Barriers. *Electrochem. Solid-State Lett.* **2005**, 8(7), G182-G187.
- (44) Jezewski, C.; Lanford, W. A.; Wiegand, C. J.; Singh, J. P.; Wang, P. I.; Senkevich, J. J.; Lua, T. M. Inductively Coupled Hydrogen Plasma-Assisted Cu ALD on Metallic and Dielectric Surfaces. *J. Electrochem. Soc.* **2005**, 152, C60-C64.
- (45) Niskanen, A.; Rahtu, A.; Sajavaara, T.; Arstila, K.; Ritala, M.; Leskelä, M. Radical-Enhanced Atomic Layer Deposition of Metallic Copper Thin Films. *J. Electrochem. Soc.* **2005**, 152, G25-G28.
- (46) Kim, H.; Kojima, Y.; Sato, H.; Yoshii, N.; Hosaka, S.; Shimogaki, Y. *Mater. Res. Soc. Symp. Proc.* **2006**, 914, 167-172.
- (47) Sundberg, P.; Karppinen, M. Organic and Inorganic–Organic Thin Film Structures by Molecular Layer Deposition: A Review. *Beilstein J. Nanotechnol.* **2014**, 5, 1104-1136.
- (48) Yoon, B.; Lee, B. H.; George, S. M. Highly Conductive and Transparent Hybrid Organic–Inorganic Zinc Oxide Thin Films Using Atomic and Molecular Layer Deposition. *J. Phys. Chem. C* **2012**, 116, 24784-24791.
- (49) Tynell, T.; Terasaki, I.; Yamauchi, H.; Karppinen, M. Thermoelectric Characteristics of $(\text{Zn}, \text{Al})\text{O}/\text{Hydroquinone}$ Superlattices. *J. Mater. Chem. A* **2013**, 1, 13619-13624.
- (50) Tan, L. K.; Liu, B.; Teng, J. H.; Guo, S.; Low, H. Y.; Loh, K. P. Atomic Layer Deposition of a MoS_2 Film. *Nanoscale* **2014**, 6, 10584-10588.
- (51) Giedraitis, Z.; Lopez-Acevedo, O.; Leal, L. A. E.; Pale, V.; Sainio, J.; Tripathi, T. S.; Karppinen, M. Three-Dimensional Uracil Network with Sodium as a Linker. *J. Phys. Chem. C* **2016**, 120, 26342-26349.
- (52) Lee, C.; Lee, H. H. A Potential Novel Two-Step MOCVD of Copper Seed Layers. *Electrochem. Solid-State Lett.* **2005**, 8, G5-G7.
- (53) Vestal, C. R.; DeVore, T. C. Mechanism for the Formation of Copper From the Reaction Between bis-(2,4-Pentanedionato) Copper and Water Vapor in CVD Processes. *Proceedings of the Conference on High Temperature Corrosion and Materials Chemistry, Electrochemical Society*, Opila, E. J.; McNallan, M. J.; Shores, D. A.; Shifler, D. A. eds. Electrochemical Society, PV 2001-12, Washington DC, 2001. pp. 285-295.
- (54) Huo, J.; Solanki, R.; McAndrew, J. Characteristics of Copper Films Produced via Atomic Layer Deposition. *J. Mater. Res.* **2002**, 17, 2394-2398.
- (55) Pinkas, J.; Huffman, J. C.; Baxter, D. V.; Chisholm, M. H.; Caulton, K. G. Mechanistic Role of H_2O and the Ligand in the Chemical Vapor Deposition of Cu , Cu_2O , CuO , and Cu_3N from Bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)copper(II). *Chem. Mater.* **1995**, 7, 1589-1596.
- (56) Hu, X.; Schuster, J.; Schulzab, S. E.; Gessner, T. Surface Chemistry of Copper Metal and Copper Oxide Atomic Layer Deposition from Copper(II) Acetylacetonate: A Combined First-Principles and Reactive Molecular Dynamics Study. *Phys. Chem. Chem. Phys.* **2015**, 17, 26892-26902.
- (57) Puurunen, R. L. Surface Chemistry of Atomic Layer Deposition: A Case Study for the Trimethylaluminum/Water Process. *J. Appl. Phys.* **2005**, 97, 121301-121301-52.

- (58) Shirazi, M.; Elliott, S. D. Multiple Proton Diffusion and Film Densification in Atomic Layer Deposition Modeled by Density Functional Theory. *Chem. Mater.* **2013**, 25, 878-889.
- (59) Knorr, D.B.; Tracy, D. P. A Review of Microstructure in Vapor Deposited Copper Thin Films. *Mater. Chem. Phys.* **1995**, 41, 206-216.
- (60) Li, J.; Mayer, J. W. Oxidation and Reduction of Copper Oxide Thin Films. *Mater. Chem. Phys.* **1992**, 32, 1-24.
- (61) Ashcroft, N. W.; Mermin, N. D. *Solid State Physics* **1976**, Publisher: Holt, Rinehart and Winston, New York.