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Experimental and computational investigation of chemical vapor deposition of Cu from Cu amidinate

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ABSTRACT

Experiments and computations are performed for the Cu MOCVD from copper(I) N,N′-di-isopropylacetamidinate [Cu(^{i}Pr–Me–amd)]$_2$ or [Cu(amd)]$_2$ where amd = $CH(CH_3)_2NC(CH_3)NCH(CH_3)_2$. The *a priori* choice of this precursor is dictated mainly by its oxygen and halogen–free ligands allowing co-deposition with oxophilic elements such as Al and by its ability to provide conformal Cu films in atomic layer deposition processes. The nucleation delay and the deposition rate as a function of deposition temperature and the evolution of the deposition rate along the radius of the substrate holder are experimentally determined with depositions performed at 1333 Pa in a vertical, warm wall, MOCVD reactor. With the aim to propose a kinetic scenario for Cu deposition, based on recently published experimental results for the decomposition of [Cu(amd)]$_2$, a predictive 3D model of the process is built, based on the mass, momentum, energy and species transport equations. In agreement with the previously mentioned experimental results, it is demonstrated that a single surface reaction is responsible for the deposition of Cu. Two surface kinetics expressions are implemented depending on the deposition regime; a simple Arrhenius type expression in the reaction limited regime and a Langmuir–Hinshelwood type expression prevailing in the transport limited regime which takes into account the inhibition effects. The two different kinetics designate a modification in the surface reaction mechanism. The results show good agreement between experiments and computations. Complementary computations are performed, in order to compare the deposition rates of the Cu films deposited via the [Cu(amd)]$_2$ and the (hfac)Cu(VTMS) and Cu(hfac)$_2$ so as to determine relative advantages and disadvantages of Cu MOCVD from [Cu(amd)]$_2$.

1. Introduction

Cu deposition from the gas phase often results in a nodular, loose microstructure which can be driven towards either thin films or nanoparticles, depending on the targeted application (often low electrical resistivity [1] and anti-bacterial properties [2], but also ductility, high thermal conductivity and strong resistance to electromigration). Metalorganic chemical vapor deposition (MOCVD) and atomic layer deposition (ALD) are often used for the processing of Cu films, because they ensure film growth on complex surfaces with tunable microstructure and deposition rate.

There are numerous precursors for the MOCVD of Cu but, to the best of the authors' knowledge not many satisfy specifications including low deposition temperature, oxygen and halogen–free ligands allowing codeposition with oxophilic elements such as Al, and ability to provide conformal Cu films. Relatively air-stable copper(I) amidinates were successfully studied as oxygen-free molecular compounds in ALD, aiming at the preparation of pure copper films. Based on the works of Lim et al. [3,4] and Li et al. [5], we recently reported the results on the MOCVD of copper(I) N,N′-diisopropylacetamidinate [Cu(^{i}Pr–Me–amd)]$_2$ or [Cu(amd)]$_2$ (amd = $CH(CH_3)_2NC(CH_3)NCH(CH_3)_2$) [6–8], a Cu(I) precursor. Pure copper films were obtained in the temperature range 200 °C–350 °C at a total pressure of 1333 Pa, under high hydrogen/precursor molar ratio. The process is characterized by a kinetically controlled regime below 240 °C with a predominant surface reaction between molecular hydrogen and the entire precursor molecule, followed by a diffusion limited regime for depositions in the temperature range 240 °C–350 °C. By using [Cu(amd)]$_2$ and dimethylethyl amine alane, we deposited Al–Cu films by sequential deposition followed by post deposition annealing [9,10]. Despite these experimental results there are still no investigations of the surface kinetics prevailing in the MOCVD of Cu from [Cu(amd)]$_2$. The present work aims at further consolidating the deposition of Cu by investigating the process through computational analysis and by comparing theoretical predictions with experimental results.

The article is presented as follows. First, the experimental protocol involving MOCVD of Cu films is presented in detail, followed by the computational aspects of the present work. Then the experimental and theoretical results are presented and discussed. Finally, computations for the deposition rates of two other precursors are presented and compared with [Cu(amd)]$_2$, prior to providing concluding remarks.

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2. Experiments

Growth experiments of Cu films are performed in a vertical, cylindrical, stagnant flow, warm wall, stainless steel MOCVD reactor which has been described in detail in [11,12]. $5 \times 10 \times 1$ mm^3 304 L stainless steel coupons are used as substrates. They are polished with SiC disks to 4000 grit, cleaned in a supersonic bath with acetone and ethanol for 5 min and dried in Ar flow followed by residence in a furnace at 50 °C for 20 min. They are weighted in view of determining the deposition rate based on mass gained during the experiment and immediately loaded in the reactor. In each experiment five substrates are placed at different radial positions on a 58 mm diameter susceptor heated by a resistance coil gyred just below the surface and positioned below a shower plate. Prior deposition, organic pollutants adsorbed on the surface of the substrates are being removed by a (Ar-10% H_2) RF plasma pretreatment [13]. The pretreatment conditions are: Ar-10% H_2 flow rate of 100 standard cubic centimeters per minute (sccm), pressure of 293 Pa, substrate temperature in the range of 200 °C–350 °C depending on the experiment, emitted and reflected power of 80 and 30 W, respectively, and duration of 30 min.

$[Cu(amd)]_2$, is synthesized by NanoMePS[1] by appropriately adapting the protocol reported in [4] and is purified by vacuum sublimation at 100 °C before use. Despite its relatively light and air stability, $[Cu(amd)]_2$ is distributed in sealed ampoules and is manipulated in glove box, to avoid gradual degradation and darkening that ambient air can cause, over a period of days [14]. It is loaded in an innovative compact sublimator (useful space is 2.6 cm^3), built from VCR fittings and schematically illustrated in Fig. 1. The thermal regulation of this sublimator is convenient, resulting in reduced risk of side condensation of the sublimed precursor. Its reduced dimensions allow introducing it with its upper and lower isolation valves in a glove box, for air free precursor loading.

Pure nitrogen (99.998%) and a mixture of argon/hydrogen (10% hydrogen, Air Products) are fed through computer-driven mass flow controllers (MKS). Experiments are performed in fixed conditions, namely total pressure $P_{tot} = 1333$ Pa, precursor sublimation temperature $T_{prec} = 95$ °C, and dilution N_2 ($Q_{N2,dilution}$), N_2 flow through the precursor ($Q_{N2,prec}$) and Ar/H_2 ($Q_{Ar/H2}$) flow rates equal to 50, 50, and 225 sccm, respectively. The adopted value of T_{prec} was the one used in the ALD experiments in [14] and corresponds to a saturated vapor pressure P_{sat} of $[Cu(amd)]_2$ of 0.733 Pa [7]. Considering the relation proposed by Hersee and Ballingal [15] these conditions yield a maximum flow rate Q_{prec} of $[Cu(amd)]_2$, and a molar fraction in the input gas equal to 2.7×10^{-2} sccm and to 10^{-4}, respectively. The latter value is relatively low compared with those typically used in CVD protocols, namely 10^{-3} to 10^{-2}. It could be increased by decreasing P_{tot} or by increasing T_{prec}. However, the adopted value of the former is technologically feasible without oversizing the vacuum equipment. Alternatively, the increase of T_{prec} from 95 °C to 110 °C results in a fourfold increase of P_{sat}. In this case we experienced precursor decomposition in the sublimator and in the tubing between the sublimator and the reactor.

Fourteen independent experiments are performed at different temperatures, T_s, in the range 200 °C–350 °C. The deposition time is 4 h in all experiments plus the time required for the nucleation to take place in each T_s. The nucleation delay corresponds to the change of the color of the substrate's surface from gray metallic to red. It is evaluated by visual observation of the illuminated substrate surface through two windows mounted at the deposition chamber. Such observation does not provide precise determination of the nucleation delay. However, it does not lead to strongly erroneous determination in view of the observed time scale. It is worth mentioning that these results are underexploited in the present work. Still, they are useful in the detailed investigation of the surface reaction mechanism.

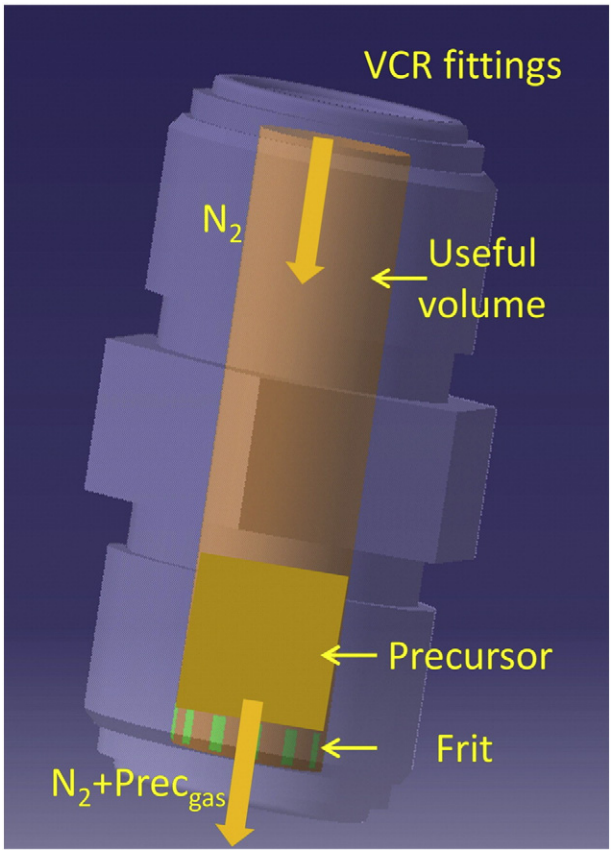

Fig. 1. Schematic of the compact sublimator used for the generation of vapors of $[Cu(amd)]_2$.

The deposition rate is evaluated directly by weight difference of the substrates before and after deposition. Three independent weight measurements are carried out for each substrate before and after the experiment, and an average value is calculated. The maximum deviation from this average value is estimated by the difference between the minimum measured value before the experiment and the maximum measured value after the experiment, while the minimum deviation is obtained by the difference between the minimum measured value after the deposition and the maximum measured weight before the deposition.

3. Computations

Aiming at understanding the mechanisms of Cu films growth, a predictive three-dimensional (3D) model of the MOCVD reactor is built, based on the governing equations describing the transport phenomena and chemical reactions inside the reactor: the continuity, the momentum, the energy and the species transport equation is the set of equations which, augmented with realistic boundary conditions, is discretized in 3D and solved with Ansys/Fluent [16,17]. This set of equation is described in detail in [16] and is omitted for the sake of brevity.

The properties of the individual species and of the mixture are computed as in [16]. The Lennard-Jones (LJ) parameters, namely σ and ε, are the parameters of the LJ potential and are needed for the estimation of the properties in the gas phase of the CVD reactor. σ is the measure of the size of the molecules and ε/k is a measure of how strongly the molecules attract each other. For the unknown species, namely $[Cu(amd)]_2$

[1] www.nanomeps.fr