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Growth kinetics of copper thin films in different MOCVD systems

T. GERFIN, M. BECHT and K.-H. DAHMEN

Laboratorium für Anorganische Chemie, ETH Zürich, Universitätsstrasse 6, 8092 Zürich, Switzerland

Abstract - Thin copper films were grown in two different MOCVD systems using bis-(2,2,6,6-tetramethyl-3,5-heptadionato)-copper, $[\text{Cu}(\text{thd})_2]$, as precursor. The experiments were carried out in a horizontal hot-wall quartz reactor and a vertical cold-wall apparatus of stainless steel. The thicknesses of the films were measured by profilometry, the absorption coefficients k at a wavelength of 1300nm by ellipsometry and the electrical sheet resistances by four-probe measurements. The growth kinetics, which depends on the partial pressure of the precursor, on the reaction gas type and on the substrate temperature, will be discussed. A mechanism will be given for the MOCVD process in the horizontal system.

1. Introduction

Copper is a very promising material for metallization in ultra large scale integrated (ULSI) technology.^[1] In the last two years, there have been many MOCVD investigations using copper(I) or copper(II) precursors, since this growth technique allows selective growth of metallic copper.^[2] Although $\text{Cu}(\text{thd})_2$ is widely used in the preparation of high T_c superconducting films, there are only few reports about metallic copper films prepared from this compound.^[3-6]

Here, we report growth experiments of copper films carried out in two different MOCVD systems using $\text{Cu}(\text{thd})_2$ as precursor.

2. Experimental Part

The horizontal hot-wall quartz reactor (HR) used was described earlier.^[7] Figure 1 shows a schematic picture of the vertical cold-wall apparatus (VR) in which the substrate is heated resistively. The nozzle of this system had a diameter of 20mm and a distance of 5mm to the

Figure 1: Schematic Representation of the Vertical MOCVD System (VR) (TC = Thermocouple)

susceptor whose diameter was 31mm. The experimental parameters used are listed in Table I. The evaporation rate was determined by weight loss of the ceramic boat in the HR system. However, no similar values could be measured in the VR system because of a different evaporation chamber. Comparison of the two systems can only be made on the basis of the evaporation temperatures. The films were investigated by profilometry, ellipsometry ($\lambda = 1300\text{nm}$), X-ray diffraction and four-probe resistivity measurements.

Table I: Experimental Conditions of the Two Different MOCVD Systems

	HR	VR
substrate	quartz	quartz
carrier gas, flow	He, 66 sccm	He 60sccm or H ₂ 30sccm
reaction gas, flow	H ₂ , 108 sccm	H ₂ , 60 sccm
pressure	20 - 25 mbar	1-3 mbar
evaporation temperature	120 - 150°C	105 - 155°C
substrate temperature	275 - 550°C	300 - 500°C
time	5-100 min	5 - 103 min

3. Results and Discussion

In Figure 2, we compare the dependence of the thicknesses of the films on the duration of the experiments using the same evaporation and substrate temperatures in both systems. There are evident differences between them. The huge growth rate of the VR system within the first ten minutes can be explained by the evaporation technique used. After this time both systems have reached a steady state and all results being reported here are measured in this region by making two experiments and correcting the data. The differences in the slope (0.12 ± 0.01 Å/s for the VR and 0.23 ± 0.02 Å/s for the HR, respectively) may be due to different evaporation rates, different pressures or different hydrodynamics of the systems.

Figure 2: Thicknesses of the Films Measured by Profilometry in Dependence on the Duration of the Experiments (VR -○-, HR -●-). ($T_{\text{evap}} = 110^\circ\text{C}$, $T_{\text{sub}} = 450^\circ\text{C}$)

Figure 3.a shows the dependence of the growth rate on the evaporation rate in the HR system and Figure 3.b the dependence on the evaporation temperature for both systems. The curve in Fig. 3.a represents a Langmuir isotherm [8]:

$$G = \frac{a [\text{Cu(thd)}_2]^x}{1 + b [\text{Cu(thd)}_2]^x}$$

The exponent x was fitted to a value of 1.25 ± 0.19 ($a = 0.26 \pm 0.03$, $b = 0.72 \pm 0.08$). The mechanism of a Langmuir isotherm means that the growth is determined by absorption or desorption on the surface of the substrate and not directly by mass flow of the precursor or the reaction gas hydrogen.

There are two points in Figure 3.b which should be noted:

- (1) the absolute values of the growth rates are significantly higher in the HR system,
- (2) the dependence is different for the two systems, i.e., with the VR system a typical linear behavior is observed, which can be explained by mass flow control, whereas with the HR system saturation was found as described above. It can not be excluded that a similar saturation would be found in the VR system at higher growth rates.

These observations can only be stated, but there are no simple explanations for them because of intrinsically different hydrodynamics and differences in the experimental parameters.

Figure 3: Growth Rate of Copper Films at a Substrate Temperature of 450°C. Figure 3.a Shows the Dependence of the Growth Rate on the Evaporation Rate in the HR,. Figure 3.b Shows Its Dependence on the Evaporation Temperature in Both Systems (VR -o-, HR -•-)

No growth is found in the HR and VR system below 270°C and 350°C, respectively. In Figure 4, the growth rate is shown as a function of the substrate temperature in the HR system. Two regions can be distinguished in this diagram, i.e. a strongly temperature dependent region below 290°C ($1000/T_{\text{sub}} \approx 1.7 \text{ K}^{-1}$) with kinetically controlled growth and a high temperature region above 290°C in which the surface is the limiting factor. Even though the curve fits the data quite well, significant deviations can be found at about 350°C. Further investigations with different mass flows will give more insight into this interesting

Figure 4: Growth Rate of Copper Films in the HR System With an Evaporation Temperature of 135°C

temperature behavior. Unfortunately, no comparable results are available at the moment for the VR system.

As can be seen in Figure 5.a, the behavior of the room temperature sheet resistances shows a sharp transition from insulating or semiconducting to metallic. It was not possible to determine more values in the insulating part, because those were higher than we were able to measure. The transition temperature is dependent on the evaporation rate or the growth rate, respectively. A similar effect is observed for the absorption coefficient k measured by ellipsometry at a wavelength of 1300nm^[9], shown in Figure 5.b. X-ray investigations proved that the high temperature films are single phase metallic copper and the low temperature films a mixture of copper and copper(I)oxide.

P.M. Jeffries et al.^[10] investigated the growth of copper oxides and metallic copper using $[\text{Cu}(\text{O}-t\text{-Bu})_4]$ as precursor. They found that it is possible to grow either the metal or the oxide depending on the substrate temperature. The phase deposited seems to be controlled by the substrate temperature. Our results can be explained in the same way, as will be discussed later.

Two groups increased the growth rate with $\text{Cu}(\text{hfa})_2$ (hfa = 1,1,1,5,5,5-hexafluoroacetylacetone) by mixing water or alcohols into the reaction gas flow.^[11, 12] Our investigations of hydrogen and hydrogen/ethanol(0°C) reaction gases showed no influence on the growth rate with $\text{Cu}(\text{dpm})_2$. However, Figure 6 shows the sheet resistances depending on the substrate temperature with these two gases. Using ethanol copper films are formed at all temperatures above 260°C (onset temperature for growth). Thus, it is possible to grow

Figure 5: Room Temperature Sheet Resistance of Films Grown in the HR System with an Evaporation Temperature of 125°C, 130°C, 135°C (a.). Room Temperature Sheet Resistance and Absorbtion Coefficient k Deteremined by Ellipsometry at 1300nm of Films Grown with an Evaporation Temperature of 130°C (b.) .

Figure 6: Sheet Resistances Depending on the Substrate Temperature for Hydrogen and Hydrogen/Ethanol as Reaction Gases (HR).

copper films with a low sheet resistance of $3.6\mu\Omega/\square$ at substrate temperatures of only 270°C.

All results can be explained by following scheme:

The growth rate is determined by k_{ads} and k_{des} via a Langmuir isotherm. Reaction (1) and (5) are probably very fast and thus they have no influence on the observed kinetics. The reduction of copper(I) to copper(0) can proceed thermally or by reaction with H_2 or alcohols. At low substrate temperatures (growth of oxide films) the reaction rate k_3 is too small for complete reduction of Cu_2O and a mixture of this oxide and copper is formed. At high substrate temperatures k_3 increased significantly because of its exponential dependence on the temperature and now the reaction is fast enough for almost 100% conversion into copper(0). Ethanol opens a new pathway to copper via reaction (4) which seems to be quite fast even at very low temperatures of 270°C . More investigations are in progress in both MOCVD systems to verify this mechanism.

4. Conclusions

It was shown that the growth kinetics of copper and copper oxide films depend on the MOCVD system (horizontal or vertical), on the substrate temperature and on the reaction gas. The dependence of the growth rate on the partial pressure of the precursor is surface limited with a Langmuir isotherm for the horizontal MOCVD system and mass flow controlled for the vertical system. When the experiments were performed under hydrogen, a sharp transition from non-conductive to metallic was seen at temperatures that were dependent on the evaporation rate or the growth rate, respectively. Ethanol as an additive to hydrogen improved the electrical properties of the films significantly and allowed growth of metallic copper films at 270°C . A reaction mechanism is given to explain the results.

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