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Full Paper

Mass Spectrometric Monitoring of the Gas Phase during the CVD of Copper from Copper Cyclopentadienyl Triethylphosphine**

By *Asiya E. Turgambaeva,* Nathalie Prud'homme, Vladislav V. Krisyuk, and Constantin Vahlas*

Application of mass spectrometry (MS) for the investigation of metal-organic (MO)CVD processes is demonstrated through the example of the deposition of copper films from copper(I) cyclopentadienyltriethylphosphine (CpCuPEt_3). In-situ MS, where a miniature hot-wall CVD reactor built in the time-of-flight mass analyzer, is used to investigate the decomposition mechanism of the precursor during low-pressure (LP) MOCVD. On line MS is used to explore the gas phase upon copper film production as a function of temperature in a cold-wall MOCVD reactor operating under 10 Torr. The two MS techniques provide compatible information which illustrates the vapor behavior of the precursors on the growing surface, and correlates all changes in the composition of the gas phase with the growth rate of Cu films in any stage of the deposition process. In agreement with reported experimental results, a monotonic increase in the intensity of the precursor and a decrease in the intensity of the products are observed with deposition time at low deposition temperature, indicating a gradual decrease in the growth rate. This behavior is attributed to the saturation of the growing surface with adsorbed triethylphosphine which hinders precursor supply to the deposition zone. It is shown, through the example of the co-deposition of Al-Cu films from dimethylamine alane and CpCuPEt_3 , that there is no mutual interaction of the precursors in the gas phase.

Keywords: Copper cyclopentadienyltriethylphosphine, Copper film, Gas-phase monitoring, Mass spectrometry, MOCVD, Thermal decomposition

1. Introduction

Copper-containing coatings are promising materials for numerous applications due to the combination of their chemical and physical properties. Addition of alloying elements enables the tailoring of such properties through the formation of intermetallic phases, also resulting in the modification of the grain size, the crystallographic orientation, and the adhesion to the substrate. In an on-going project we investigate the MOCVD of films containing Al-Cu intermetallic compounds with a view towards potential applications related to tribological properties, tailored wetting, or corrosion resistance.^[1,2] Processing of such coatings by MOCVD allows the functionalizing of complex-in-shape surfaces, provided that suitable co-deposition processes can be managed. Such processes imply the use of compatible precursors for the two elements. In the case of Al-Cu films, specifications for such precursors

include oxygen- and halogen-free ligands, similar deposition conditions, and compatible gas-phase and surface chemistries.

Most of the copper precursors contain oxygen and/or halogens in their ligands, or require oxygen-containing co-reactants for the deposition of copper.^[3] Among the few oxygen and halogen-free precursors, copper(I) cyclopentadienyl phosphine derivatives were investigated in CVD processes.^[3–8] CpCuPEt_3 ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$, $\text{Et} = \text{C}_2\text{H}_5$) was synthesized and characterized in the late 1950s,^[9–11] but it had not been used as a MOCVD precursor until the 1980s.^[7,12] In the 1990s, it was used in combination with alanes for the co-deposition of Cu-Al films,^[5,6] however in these reports copper concentration in the films was low, at the level of 1 wt.-%. We recently investigated the physical and thermal properties of CpCuPEt_3 .^[13] This work concluded that its Clapeyron law in the range 313–343 K is $\log P_{\text{vap}} (\text{Torr}) = 9.671 - 3455/T(\text{K})$, that the compound is stable below 343 K, and that it provides pure copper films in the range 423–563 K without hydrogen as the reducing agent.

The above temperature range matches the one for the deposition of Al from dimethylethyl amine alane, which is the selected precursor for the MOCVD of Al in the present project.^[14,15] Implementation of a sustainable; i.e., reproducible and robust co-deposition process, however, also requires compatible decomposition schemes for the involved precursors both in the gas phase and especially

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on the growing surface, under real technological conditions. While the decomposition mechanism of dimethylethylamine alane is well known,^[15] this is not the case for CpCuPEt_3 . Thus, the subject of the present work is to experimentally investigate conversions occurring in the multi-component system upon Cu deposition and Al-Cu co-deposition. The aim is to reveal decomposition mechanisms, interaction among components of the system, and mutual influence of the precursors. This investigation is based on the interplay between on-line and in-situ MS. The combination of the information obtained by these two techniques, together with that on properties of deposited film (elemental and phase composition, growth rate), provide useful input for the optimization of the co-deposition process.

2. Results and Discussion

In-situ MS ensures the tracking of changes in the gas-phase composition during the programmed heating of the precursor in a miniature hot-wall CVD reactor, built in the time-of-flight mass analyzer, under high vacuum conditions, without any sampling effect. It was used (a) to determine the composition of the gas phase during heating of the precursor, (b) to evaluate its vaporization stability, and (c) to investigate gaseous decomposition products. On-line MS was used to explore the gas phase upon the MOCVD of copper in a cold-wall reactor operating under sub-atmospheric pressure. It reproduces the conditions of a real technological process, while in-situ MS ensures the monomolecular decomposition of the precursor on the surface and consequently allowing conclusions to be drawn on the precursor decomposition mechanism.

Figure 1 presents in-situ mass spectra of CpCuPEt_3 recorded at various reactor temperatures, and Table 1 lists some observed peaks of mass spectra and their assignments. The spectrum recorded at 403 K, i.e., far below the threshold of the decomposition of the precursor, reveals no peak in the mass spectrum exceeding the m/z (mass-to-charge ratio) value of the molecular ion $[\text{CpCuPEt}_3]^+$. This result is consistent with reported information, following which the precursor is monomeric both in the solid^[16] and in the gas^[13] phase. Besides the molecular ion, there is another copper-containing peak $[\text{CuPEt}_3]^+$ at m/z 181 for ^{63}Cu which is the most intense metal-containing peak (Table 1). Occurrence

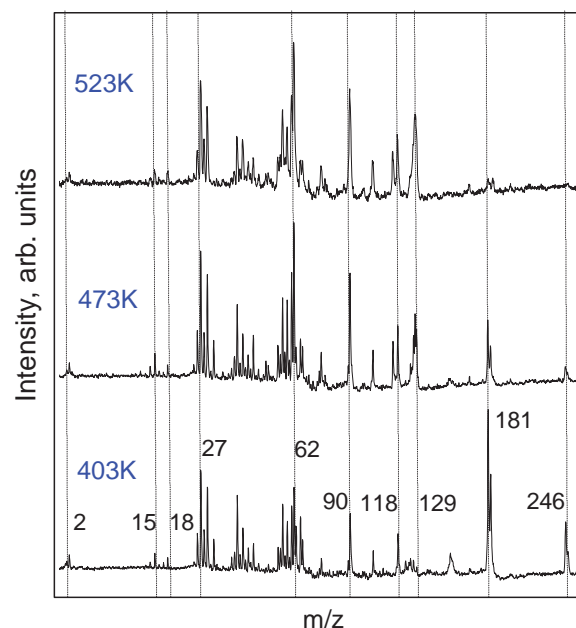


Fig. 1. Mass spectra of CpCuPEt_3 recorded at various temperatures of the reactor.

of low intensity peaks at m/z 126–130 is attributed to dihydrofulvalene $\text{C}_{10}\text{H}_{10}$, which results from the coupling of cyclopentadienyl anions and indicates partial decomposition of the solid compound in the evaporator. This suggestion is supported by data obtained during the experimental determination of the vapor pressure of the compound.^[13] Despite this partial and limited decomposition, no changes in the mass spectrum of the compound were observed during repeated heating (up to 373 K) and cooling cycles in the evacuated evaporator revealing satisfactory vaporization stability.

2.1. MS Study of Gaseous Decomposition Products

Prior to presentation of the results, it is worth recalling the sequence of events which result in the decomposition of the precursor. First, thermal decomposition occurs in the reactor. Then, the reaction mixture, consisting of non-decomposed precursor, gaseous decomposition byproducts,

Table 1. Some observed peaks of mass spectra and their assignments.

m/z	chemical formula	abbreviation	note
246	$\text{C}_5\text{H}_5\text{CuP}(\text{C}_2\text{H}_5)_3$	CpCuPEt_3	
181	$\text{CuP}(\text{C}_2\text{H}_5)_3$	CuPEt_3	Fragmentary ion from $[\text{CpCuPEt}_3]^+$
130	$\text{C}_{10}\text{H}_{10}$	Cp_2 (dihydrofulvalene)	Produces fragmentary ions at m/z 129 (most intensive), 128, 115, etc.
118		PEt_3 (triethylphosphine)	Produces fragmentary ions at m/z 90, 62, etc.
66	C_5H_6	HCp (cyclopentadiene)	Fragmentary ion from $[\text{CpCuPEt}_3]^+$
65	C_5H_5	Cp (cyclopentadienyl)	

and/or carrier gases (if used), enters the ionization chamber. Finally, formed ions enter the mass analyzer. As a result of these events, the recorded mass spectrum is the output of the mass spectrum of the precursor and of the mass spectrum of the thermal decomposition products. In this spectrum, variation of temperature results both in the increase and the decrease in the intensity of the different peaks. Moreover, with increasing temperature, new peaks may appear due to thermal decomposition of the initial compound, as in the case of the dimethylgold diethyldithiocarbamate,^[17] or not, as for most of the beta-diketonates.^[18] Such changes in the intensity of peaks of mass spectra at various reactor temperatures allow unambiguous identification of the gaseous products from the thermal decomposition of the precursor.

The spectrum in Figure 1 (recorded at 473 K) corresponds to the initiation of the decomposition, as witnessed by the decrease in relative intensity of the precursor molecular ion $[\text{CpCuPEt}_3]^+$. The spectrum recorded at 523 K corresponds to conditions of maximum decomposition degree as is indicated by the background level of the intensity of $[\text{CpCuPEt}_3]^+$. No new peaks appear in the mass spectrum, indicating that the composition of both the thermal decomposition products and the products of fragmentation of the molecular ion in the mass analyzer is the same.

Time and temperature dependence of the intensities of ion peaks were derived from the full range mass spectra. Figure 2 presents the temperature dependence of the ion peak intensity of major components of the gas phase obtained by in-situ (bottom) and on-line (top) MS; the intensity of ion peaks $[\text{CpCuPEt}_3]^+$ and $[\text{Cp}]^+$ decreases and, at the same time, the intensity of $[\text{PEt}_3]^+$ and $[\text{Cp}_2]^+$ increases. The trends revealed in Figure 2 can be explained in an idealized scheme, following which, upon reaching the decomposition onset temperature, the intensity of ion peaks $[\text{CpCuPEt}_3]^+$ and $[\text{Cp}]^+$ related to the source compound (precursor), decreases while the intensity of ion peaks corresponding to the products (triethylphosphine and dihydrofulvalene) increases. $[\text{PEt}_3]^+$ ions are, however, generated both from fragmentation of the precursor's molecular ion $[\text{CpCuPEt}_3]^+$ and from ionization of PEt_3 molecules which are produced from the thermal decomposition of the precursor. Therefore, the shape of the temperature dependence curve corresponding to $[\text{PEt}_3]^+$ results from the superposition of two curves related to these two processes. According to in-situ MS results, the decomposition of CpCuPEt_3 is initiated at $T = 443 \pm 10 \text{ K}$.

Data from in-situ MS are obtained by a process which takes place in a hot-wall reactor operating under significantly low pressure (10^{-3} Pa). Under these conditions, decomposition of the precursor occurs on the reactor walls. Such conditions allow unambiguous determination of the composition of the resulting gas phase without any interference due to the recombination of the investigated species, either in the deposition chamber or in the sampling system. Based on this information, and assuming that the

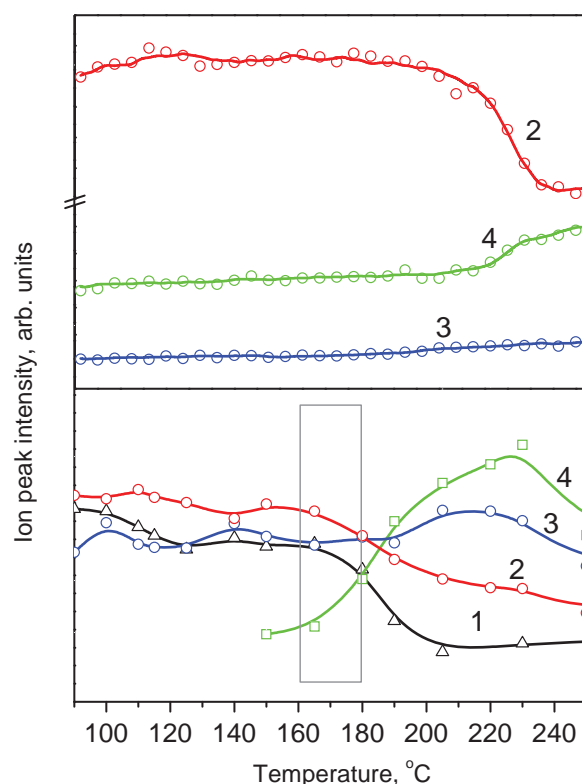
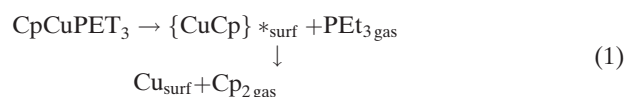


Fig. 2. Temperature dependence of the ion peak intensity of major species of the gas phase obtained by on-line (top) and in-situ (bottom) MS. 1 - $[\text{CpCuPEt}_3]^+$, 2 - $[\text{Cp}]^+$ fragmentary ion from CpCuPEt_3 , 3 - $[\text{PEt}_3]^+$, 4 - $[\text{Cp}_2]^+$. The zone corresponding to the temperature range where decomposition of the precursor is initiated under the investigated conditions is indicated by a rectangle.

Cu-containing species CuCp is a surface intermediate (such a particle was not recorded in the gas phase), the following mechanism (Reaction 1) is proposed for the decomposition on the surface.^[13]



CuCp^* can be presented as an adsorbed Cp radical on the copper surface; it can be recombined to form dihydrofulvalene (Cp_2) or it can react with arriving CpCuPEt_3 precursor molecules to produce Cp_2 , copper, and PEt_3 .^[13] Cp_2 and PEt_3 are recorded in the mass spectra. Thus, in the temperature range of interest for the present study (i.e., 443–543 K), this mechanism can be summarized by the idealized deposition equation, Equation 2.



The proposed mechanism is in a good accordance with the one suggested for CpCuPMe_3 , which is similar to the investigated compound.^[8] According to the suggested

mechanism, decomposition proceeds in a way which is favorable to carbon- and phosphorous-free Cu films, in agreement with deposition experiments.^[13] No difference in the gaseous decomposition products was observed by adding hydrogen to the input gas. This indicates that there is no reduction of the precursor by hydrogen, such as, e.g., for copper(I) *N,N'*-diisopropylacetamidinate,^[19] and indicates that copper reduction proceeds through an intramolecular mechanism.

2.2. Compatibility of Data obtained by In-situ and On-line MS

Comparison between data obtained by in-situ MS under low pressure conditions and those obtained by on-line MS allows a verification of whether the obtained results are representative of the precursor decomposition scheme under CVD conditions of technological interest, namely under higher, typically sub-atmospheric ($\sim 10^{-3}$ Pa) pressure. To this purpose, on-line MS experiments with a programmable heating of the susceptor ($5^{\circ} \text{ min}^{-1}$), similar to the rate in the in-situ MS study, were performed in a cold-wall CVD reactor operating under 1.33×10^{-3} Pa. Comparison of the two diagrams in Figure 2 reveals that both the composition and the thermal behavior of the gas phase are similar in the two operating environments. The decomposition onset is shifted to higher temperatures in on-line MS; this shift can be attributed to the cold-wall configuration in on-line MS, where the residence time in the hot zone for the precursor molecule is shorter. In this way, the established compatibility of the data from both MS techniques allows on-line MS monitoring of copper deposition to be carried out, based on the collection of signals from peaks of the selected m/z .

2.3. Monitoring of the Gas Phase during the MOCVD of Copper

Figure 3 shows the evolution of the main on-line MS peaks of gaseous species as a function of time, for a sequence of various substrate (T_d) and precursor evaporator (T_e) temperatures, during deposition. The diagram is divided into three zones corresponding to three different profiles of T_d and T_e . In zone I, deposition is carried out under steady state conditions at $T_e = 353$ K and $T_d = 473$ K. Initiation of the precursor feeding corresponds to a sharp increase in the precursor intensity, immediately followed by a gradual decrease, and finally by stabilization at a constant value. The decrease in the precursor intensity is accompanied by an increase in the intensity of the main gaseous products Cp_2 and PEt_3 . Zone II shows the gas-phase behavior during the increase in T_d from 473 to 513 K. No considerable change in the intensity of ion peaks is observed indicating that, in this temperature range, precursor conversion is maximal. It is concluded that the growth rate may be controlled by varying

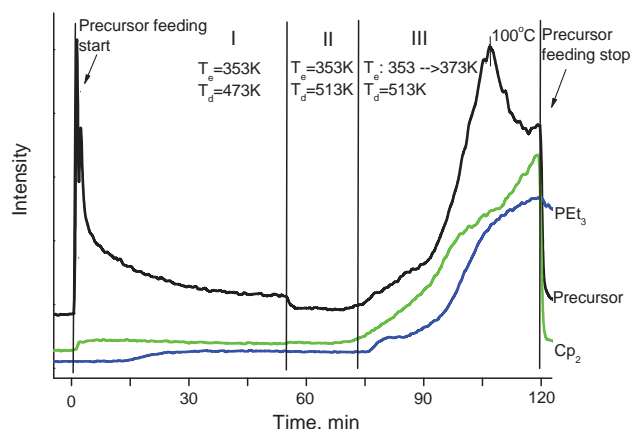


Fig. 3. Evolution of the intensity, as a function of time, of ion peaks corresponding to the precursor (represented by the fragmentary ion at m/z 66) and to the main gaseous products Cp_2 and PEt_3 . Data are collected in the vicinity of the surface by on-line MS, during the MOCVD of Cu. Zones I, II, and III correspond to processing conditions with different substrate and evaporator temperatures.

the precursor concentration in the input gas. In zone III, T_d remains constant at 513 K, while T_e is increased from 353 to 373 K, resulting in a continuous increase in the flow rate of the precursor in the deposition area. Considering the saturated vapor pressure law of CpCuPEt_3 as a function of sublimation temperature^[13] and the adopted operating conditions, the maximum molar fraction of the precursor in the input gas phase increases from 10^{-4} to 10^{-3} . MS signals in zone III reveal a significant increase in the amount of the initial compound, in agreement with its concentration in the input gas. Interesting though, they also reveal a significant and continuous increase in the amount of the decomposition products. This observation is compatible with the conclusions drawn from the observation of zone II; i.e., that growth rate increases with an increase in the precursor feeding rate. The observed behavior and the corresponding conclusions are in agreement with the results obtained in MOCVD experiments, following which deposition under these conditions is subjected to a diffusion-controlled regime.^[13]

To continue, monitoring of the deposition at various temperatures, T_d , is performed. Figure 4 shows the evolution, as a function of time, of the composition of the gas phase during the MOCVD of Cu at two temperatures, 513 K and 493 K. The precursor is represented in the figure by the most intense metal-containing peak $[\text{CuPEt}_3]^+$ at m/z 181. At $T_d = 513$ K, deposition begins just after introduction of the precursor into the reactor; a visible change in substrate color is observed together with an immediate increase in the product intensity after the initiation of precursor feeding. The observed slight monotonic increase in the precursor signal is attributed to accumulation in the reactor. The intensity of the signal corresponding to Cp_2 is almost constant, revealing a constant deposition rate. The profile of the phosphine signal corresponds to the fragmentation of the precursor due to electron ionization and to the

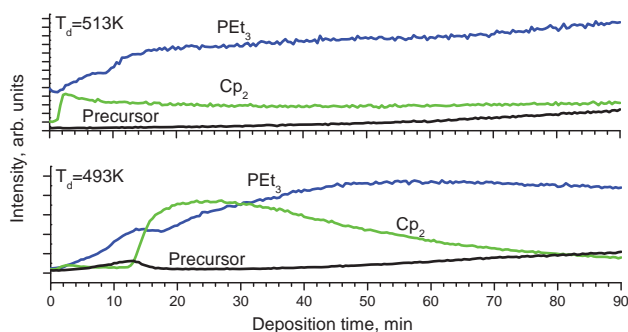


Fig. 4. Time profile of gas-phase composition, illustrated by peaks of the precursor (represented by the fragmentary ion $[\text{CuPEt}_3]^+$ at m/z 181) and of the main gaseous products PEt_3 and Cp_2 , at T_d of 513 K and 493 K (upper and lower diagrams, respectively).

addition of phosphine which is formed as a thermal decomposition product. In addition, desorption of phosphine from the surface also contributes to the signal.

At $T_d = 493$ K, the time profile of the intensity of the main gas-phase components is different from the one described above, prevailing at a higher deposition temperature. At ca. 11 min after the beginning of the precursor feeding, a sharp decrease in the intensity of precursor and an increase in the intensity of Cp_2 product peaks are observed, indicating the beginning of deposition. At the same time, optical tracking of the color change of the substrates reveals the onset of copper film growth. This simultaneous observation indicates that any change in the composition of the gas phase is recorded fast enough and, consequently, there is no significant influence of the sampling set-up on the detection system. The observed induction period is possibly due to the nucleation delay on the substrate at this temperature. The intensity of the Cp_2 peak attains a maximum value immediately after the deposition onset, and then decreases continuously. Based on this behavior, the degree of decomposition of the precursor corresponding to the deposition rate of copper becomes two times lower after ca. 50 min. At the same time, a monotonic increase in the intensity of the precursor is observed, indicating that the growth rate of the film gradually decreases. This observation is consistent with our unpublished results on co-deposition of Al-Cu films from dimethylamine alane and CpCuPEt_3 : An increase in the copper to aluminum precursors ratio in the input gas yields, as expected, Cu-rich films. At the same time, however, the growth rate strongly decreases to a lower value than the sum of the growth rates of the two metals determined individually under the same processing conditions. Such non-steady-state behavior may be attributed to the saturation of the growing surface with adsorbed phosphine which hinders precursor supply to the deposition zone. Indeed, Banaszak Holl et al.^[20] reported that PEt_3 is well adsorbed on the copper surface in the investigated temperature range, and CVD from phosphine-containing precursors should be done at a temperature higher than

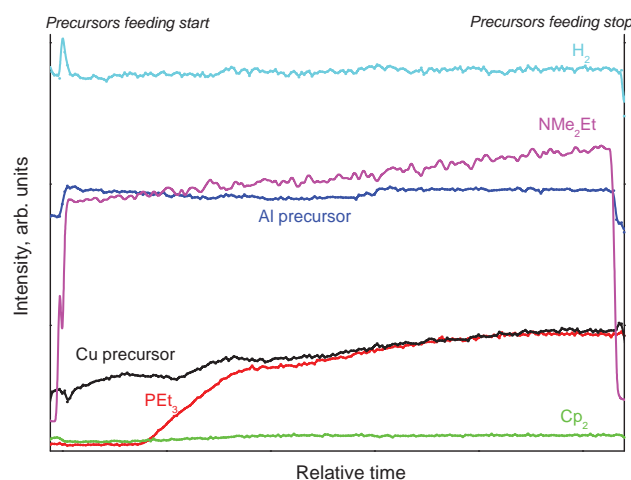


Fig. 5. Time profile of gas-phase composition during Al-Cu co-deposition ($T_d = 533$ K).

520 K, with the aim to desorb the surface-adsorbed PEt_3 . The phenomena observed in our experiments agree with these conclusions; the resulting growth rates appeared to be 398, 1052, and 1544 $\text{nmol cm}^{-2} \text{h}^{-1}$ at deposition temperatures 493, 513 and 533 K, respectively. Such a sharp rise in growth rate is due to desorption of decomposition products, namely triethylphosphine, from the growing surface which maintains the surface nucleation sites available for the film growth process.

Finally, monitoring of the co-deposition of Al-Cu films from dimethylamine alane and CpCuPEt_3 was performed in the temperature range 473–533 K. Figure 5 shows time dependence of the most representative ion peaks recorded during co-deposition at 533 K. Comparison with data obtained during the monitoring of the single-precursor deposition does not reveal any new products or considerable changes in the behavior of the gas phase; simple additive effects take place. It is concluded that there is no chemical interaction between the two precursors in the gas phase during co-deposition.

3. Conclusion

In-situ and on-line MS were synergistically used to investigate the heterogeneous thermal decomposition mechanism of CpCuPEt_3 , an oxygen free precursor for the MOCVD of Cu and of Al-Cu alloy films. In-situ MS was performed under high vacuum in a miniature hot-wall CVD reactor built in the time-of-flight mass analyzer to detect primary decomposition products. On-line MS was used to monitor the composition of gas phase in the vicinity of the substrate during Cu deposition under real technological conditions (1.33×10^3 Pa). The MS quadrupole was connected with the CVD chamber through a capillary system without using any skimmer.

Results obtained by in-situ and on-line MS are compatible; they reveal all changes of the composition of the gas phase corresponding to different regimes of the growth rate of copper films in the CVD process, and demonstrate complete adequacy of the adopted experimental approach.

The different fragments revealed in both configurations correspond to a clean decomposition of the precursor providing pure Cu films, in agreement with our previous results on the MOCVD of Cu.^[13] An evolution of the composition of the gas phase at various deposition temperatures under steady state conditions was illustrated to follow the change in growth rate. Obtained data enabled the specification of the temperature conditions for copper CVD processes from this precursor.

Finally, no chemical interaction between the precursors in the gas phase and on the surface takes place during co-deposition of Al-Cu films from dimethylamine alane and CpCuPET₃.

4. Experimental

An in-situ study of copper deposition from CpCuPET₃ was investigated in a set-up imitating a miniature CVD equipment consisting of an evaporator and a temperature-controlled cell imitating the deposition chamber. The latter was connected to a time-of-flight mass spectrometer (MS) through an effusive orifice. Ionization was performed by electrons with energy ca. 70 eV. The system is detailed in the literature^[21]. The operating procedure consisted of positioning a sealed glass ampoule with ca. 2 mg of precursor in the evaporator maintained at constant temperature of 368 K under dynamic vacuum conditions. In-situ breaking of the ampoule enabled the reactor to be supplied with precursor vapors through a heated membrane valve. During the experiment the reactor was heated from 378 to 573 K with a heating rate of 5° min⁻¹. The reaction mixture entered directly into the MS ion source through the 0.2 mm effusive orifice of the reactor. Full range mass spectra were recorded each 10° during the reactor heating; experiments were performed with and without hydrogen in the input gas. Hydrogen was introduced directly into the reactor. Data collection and processing were performed using National Instruments Corp. hardware and software.

An on-line MS study of deposition was performed using an experimental set-up consisting of a stagnant-flow, vertical, tubular, cold-wall reactor connected to a quadrupole MS. The reactor is described in details in the literature^[14]. The gas phase containing the precursor vapor, decomposition by-products, and nitrogen was continuously sampled from the CVD reactor by using a glass-lined, capillary tubing of internal diameter 0.8 mm. The capillary tube was heated typically to 368 K by circulating silicon oil through a double envelope over its entire length. One end of the tube was positioned at 5 mm above the centre point of the susceptor. The other end was connected to a microvalve which allowed regulation of the gas flow. Gas-phase analysis was performed using a Balzers-Pfeiffer quadrupole MS positioned after the microvalve. It was composed of a QMA430 mass analyzer and a QMH400-5 RF box connected to a QMG422 controller. Ionization electron energy was ca. 70 eV. The vacuum chamber of the MS was thermally regulated with

heating tapes to avoid condensation. Secondary electron multiplier detection was used to measure ion intensities. Data collection was performed using the Quadstar software package.

Gas-phase sampling was realized during deposition experiments performed under the following conditions; $T_e = 273$ K, T_d in the range 473–533 K, total pressure 1.33×10^3 Pa, molar fraction of the precursor in the input gas in the range 10^{-4} – 10^{-3} , total flow rate of carrier and dilution gas (99.998% pure nitrogen, Air Products) 325 standard cubic centimeters per minute (scm). Cu films were deposited on 10 mm × 5 mm (100) silicon wafers subjected, prior to loading in the reactor, to a typical cleaning procedure to eliminate the native oxide.

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