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Surface-driven, one-step chemical vapor deposition of γ -Al₄Cu₉ complex metallic alloy film

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A B S T R A C T

The present paper is a paradigm for the one-step formation of complex intermetallic coatings by chemical vapor deposition. It genuinely addresses the challenge of depositing an intermetallic coating with comparable contents of Cu and Al. Depending on processing conditions, a pure γ -Al₄Cu₉ and multi-phase Al-Cu films are grown with wetting properties of the former being similar to its bulk counterpart. The deposition process and its parametric investigation are detailed. Two metalorganic precursors are used taking into account their transport and chemical properties, and deposition temperature ranges. On line and *ex situ* characterizations enlighten the competition which occurs at the growing surface between molecular fragments, and which limits growth rates. Notably, introducing a partial pressure of hydrogen gas during deposition reduces Al growth rate from dimethylethylamine alane (DMEAA), by displacing the hydrogen desorption equilibrium. This Al partial growth rate decrease is not sufficient to achieve a Cu/Al atomic ratio that is high enough for the formation of intermetallics with close Al and Cu compositions. A fivefold increase of the flux of the gaseous copper(I) cyclopentadienyl triethylphosphine CpCuPEt₃, whereas the DMEAA flux remains constant, results in the targeted Al/Cu atomic ratio equal to 44/56. Nevertheless, the global growth rate is rendered extremely low by the deposition inhibition caused by a massive phosphine adsorption (-PEt₃). Despite these limitations, the results pave the way towards the conformal coating of complex surface geometries by such intermetallic compounds.

1. Introduction

Coating of complex 3-dimensional surfaces with complex metallic alloys (CMAs) including quasicrystals provides added value materials for innovative applications. Examples are low sticking and low friction glass molds that sustain high temperatures, and porous preforms infiltration for the production of supported catalysts ([1–3], and references therein). CMA coatings show excellent mechanical properties such as low adhesion, anti-fretting, or wear resistance, but the drawback of low adhesion is that it almost always results into auto delamination that can only be overcome by an efficient increase of interfacial accommodation and adhesion. Several solutions have been proposed to face this problem; one being the use of a buffer layer of a material that shows intermediate electronic and structural properties between those of the substrate and the coating [4,5]. The Al-Cu system presents such intermediate phases which have proven their efficiency for accommodating icosahedral Al-Pd-Mn and Al-Cu-Fe quasicrystals [5,6].

Actually, there is no satisfactory technique for the processing of such coatings on complex surfaces. By operating in the surface reaction limited regime, chemical vapor deposition can in principle meet this requirement. In this paper we present for the first time the direct, one-step processing of a pure CMA-containing coating by metalorganic chemical vapor deposition (MOCVD). Specifically, we report on the MOCVD of Al-Cu alloyed coatings, including the γ -Al₄Cu₉ approximant phase with similar properties to the bulk crystal.

Previous CVD co-deposition experiments of Al-Cu films were performed in the early nineties in order to replace pure Al interconnections in very large scale integration technology by α -(Al) solid solutions whose electromigration and resistivity are lower. Tomoharu et al. [7] and Eiichi et al. [8] used dimethylaluminumhydride, DMAH, and copper cyclopentadienyl triethylphosphine, CpCuPEt₃ as precursors for the co-deposition of Al and Cu, respectively. They obtained pure films with homogeneous distribution of Cu in the Al matrix, containing Al₂Cu precipitates typical of hypoeutectic Al-Cu alloys. The major difference between these works and the present one lies in the low concentration of Cu in the former, which is in the order 1 wt %. Processing of films with comparable content of Al and Cu is more constraining because of potential significant gas

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phase and/or surface interactions between the two precursors or their fragments. In a first approach to the MOCVD of Al-Cu coatings, we recently published results on the sequential deposition of Al and Cu followed by annealing. Intermetallics are also obtained but while the method is simpler than the one proposed here, it presents additional steps that are source of films contamination and involve higher thermal load [9].

In a co-deposition process, caution has to be taken regarding compatibility between the selected metalorganic precursors. Compatibility concerns deposition temperatures, chemical composition (O, F, and C contaminants release), chemical interactions, and transport in the gas phase. For this reason, the present work has been preceded by the investigation of the MOCVD of unary films of Al and Cu. Cu is obtained by decomposition of CpCuPEt_3 , a solid precursor, the saturated vapor pressure of which is 0.2 Torr at 60 °C [10]. Its thermal decomposition in the gas phase at 150 °C < T < 270 °C results in the formation of $\text{PEt}_{3\text{gas}}$ and a surface intermediate $\{\text{CuCp}\}_{\text{surf}}$ that rapidly converts into metallic Cu and $(\text{Cp}_2)_{\text{gas}}$. Above 270 °C, the mechanism is presented as follows: $\text{CpCuPEt}_3 \rightarrow \text{Cu}_{\text{surf}} + \text{HCp}_{\text{gas}} + \text{other organic fragments}$ [10]. In vacuum, mass spectrometry experiments show an intensity decrease of the molecular peak at temperature higher than ca. 150 °C, whereas decomposition with hydrogen is somehow stabilized and shifted at approx. $T > 170$ °C. CuCpPEt_3 is therefore suitable for MOCVD in the surface temperature range 150–290 °C. In this range, growth rate increases with increasing precursor feeding rate indicating that deposition takes place in a diffusion controlled regime. Nonetheless, mass spectrometry experiments show that the growing surface saturates with adsorbed phosphine leading to a continuous decrease of the Cu growth rate with deposition time. This can be counterbalanced by increasing deposition temperature above 240 °C in order to desorb by-products and offer enough free surface for precursor adsorption [11].

On the other hand, Al films are obtained by decomposition of dimethylethylamine alane, DMEAA – a liquid precursor. The mechanism attributed to its decomposition at surfaces can be stressed as follows: adsorption, breaking of the Al-N bond, desorption of the dimethylethylamine, cracking of the alane AlH_3 into metallic Al and adsorbed H atoms that recombine to form H_2 gas [12]. Above a substrate temperature of 150 °C, Fourier transform infrared spectroscopy revealed that DMEAA decomposes in the gas phase [13], and chemical kinetic modeling allowed to estimate that only ca. 5% of the precursor participates in the deposition reaction, with a sticking coefficient on Al(111) close to unity [14]. Jang et al. [15] showed that the Al films with the lowest electrical resistivity, highest density, and highest purity, are obtained at a substrate temperature of 160 °C which also corresponds to the highest Al growth rate in the investigated 100–220 °C temperature range.

Obviously, a compromise must be found for co-deposition involving the two aforementioned precursors. Specifically, substrate temperature must be chosen in such a way that growth rates are compatible with the targeted Al-Cu phases' compositions while minimizing homogeneous decomposition of precursors. It is reassuring though that preliminary mass spectrometry experiments during co-deposition show no interactions between precursors [11].

The article is presented as follows. The experimental protocol involving MOCVD of Al-Cu films is presented in details, first. Then, the composition, the obtained Al-Cu phases and the morphology of the films are presented and discussed. Finally, preliminary results of the wetting by water of the $\gamma\text{-Al}_4\text{Cu}_9$ bulk and MOCVD processed phase are presented, prior to providing concluding remarks.

2. Materials and methods

Depositions are performed in the experimental setup described in details and modeled in Ref. [16]. The setup is composed of a stagnant flow, cylindrical, stainless steel reactor. The deposition chamber features a double envelope allowing the monitoring of walls temperature through the circulation of thermally regulated silicon oil. A turbomolecular pump ensures a base pressure of 1.3×10^{-4} Pa. The pumping group is protected from the corrosive by-products by a liquid nitrogen trap. Gas is distributed through a showerhead system, described and modeled in Ref. [17]. Gases are fed through electropolished stainless steel gas lines with VCR fittings and their flow rate is controlled by computer driven mass flow controllers. HF cleaned $10 \times 5 \text{ mm}^2$ silicon coupons are used as substrates. For each experiment, five samples are positioned horizontally on a 58 mm diameter susceptor and heated by a resistance coil gyred just below the surface of the susceptor. DMEAA (Epichem) (99% pure) is used as received and CpCuPEt_3 (Strem) is purified by vacuum sublimation at 70 °C. N_2 (99.9992% pure) and H_2 (99.995% pure) (air products) are fed through electropolished stainless steel gas lines with VCR fittings with a total flux maintained at 325 standard cubic centimeters per minute, sccm. All experiments are performed at 10 Torr; i.e. a reduced, although technologically convenient pressure.

Table 1 is an overview of experimental conditions and of results that will be discussed in the following section. The vaporization vessel of DMEAA is maintained at 8 °C, corresponding to a saturated vapor pressure of 0.5 Torr. Transport of DMEAA involves a flow rate of N_2 through the precursor $F_{\text{N}_2, \text{DMEAA}}$, equal to 5 sccm. In these conditions, the maximum flow rate of DMEAA, F_{DMEAA} is calculated as being equal to 0.26 sccm in all experiments [18]. The sublimation vessel of CpCuPEt_3 is maintained at 75 ± 5 °C. Two sets of transport conditions of CpCuPEt_3 are investigated, corresponding to two different flow rates of N_2 through the precursor (30 and 150 sccm). F_{CpCuPEt_3} is estimated from weight loss of the precursor sublimator and using the analytical formula of Refs. [18,19]. Additionally, two substrate temperatures (200 and 260 °C) are investigated as well as deposition with and without H_2 in the input gas.

Electron probe microanalysis (EPMA) is used for determining the atomic compositions of the films, and X-Ray diffraction (XRD) is used for structural investigation. Growth rate (GR) is calculated by weight gain of each sample prior and after deposition over the deposition duration. Table 1 presents GRs and atomic compositions (at $\pm 1\%$) averaged over the 5 samples placed in each experiment. This way to quantify the growth rate does not provide direct access to the thickness of the film. However, it has been adopted since the measurement is straightforward and it is more accurate than investigation of cross sections by SEM due to the roughness and porosity of some samples as will be shown in the next sections. GRs of the individual elements during co-deposition are estimated with the following formulas: $\text{GR}(\text{Al}) + \text{GR}(\text{Cu}) = \text{GR}$

Table 1
Investigated operating conditions and resulting average growth rates (in $\mu\text{g}/\text{cm}^2/\text{h}$), average elemental compositions and structure of the films.

Experiment #	t (h)	T (°C)	H_2 (sccm)	$F_{\text{N}_2, \text{DMEAA}}/F_{\text{N}_2, \text{CpCuPEt}_3}$	F_{CpCuPEt_3} (sccm)	GR	Estimated GR(Al)	Estimated GR(Cu)	Al/Cu (at.%)	Phases
1	2	200	25	5/30	0.07	80	78.1	1.9	99/1	$\text{Al} + \text{Al}_2\text{Cu}$
2	2	260	25	5/30	0.04	30	24.8	5.2	33/67	$\text{Al}_2\text{Cu} + \text{Al}_4\text{Cu}_9$
3	2	260	0	5/30	0.06	50	42.5	7.5	93/7	$\text{Al} + \text{Al}_2\text{Cu}$
4	2.5	200	25	5/150	0.12	25	6.3	18.7	44/56	Al_4Cu_9

and $[GR(Al)/M_{Al}]/[GR(Cu)/M_{Cu}] = [Al/Cu]$ (with M_E molecular mass of element E), using EPMA results. Oxygen has been subtracted from elemental compositions on purpose because systematic monitoring of the gas phase during all experiments by on line mass spectrometry does not show significant amount of oxygen or of water vapors, thus ensuring that all experiments were conducted in the absence of detectable leaks or desorption from the reactor walls.

Wettability by water is performed by the sessile drop method with a GBX Digidrop instrument.

3. Results and discussion

3.1. Average compositions and growth rates, and crystallographic phases

It is well known that sublimation of a fixed bed is neither a robust nor a reproducible mean for feeding the deposition chamber with vapors of a solid precursor. Indeed, statistical analysis over 10 experiments of Cu precursor sublimation with our reactor demonstrates that it is not possible to discriminate the results #1–3 at the $F_{N_2, DMEAA}/F_{N_2, CpCuPEt_3}$ flux ratio of 5/30 in Table 1. Hardly, we are able to confirm that the 5/150 flux ratio does correspond to a higher feeding rate of Cu precursor (0.12 sccm compared to 0.04–0.07 sccm). An additional reason for this discrepancy is the observed degradation of the precursor on the reactor walls and inside the sublimator because of its reduced stability above room temperature. Moreover, it appears that the elemental composition of the films does not follow that of the gas phase based on the estimation of $F_{precursor}$. Let's consider experiments #2 and #3 at 260 °C in Table 1, for which the only difference lies in the presence of hydrogen or not. The estimations of $F_{CpCuPEt_3}$, at 0.04 and 0.06 sccm, can be considered close values. With (without) hydrogen, the films contain 33 at.% Al (93 at.% Al) and the global growth rate is 30 $\mu\text{g}/\text{cm}^2/\text{h}$ (50 $\mu\text{g}/\text{cm}^2/\text{h}$). A more direct comparison can be done through the individual growth rates. Suppression of H_2 in the input gas leads to doubling GR(Al), whereas GR(Cu) only increases from 5.2 to 7.5 $\mu\text{g}/\text{cm}^2/\text{h}$. We recall that the mechanism of Al deposition from DMEAA involves desorption of H_2 gas from the growing surface, after the alane decomposition. As a rule-of-thumb, we postulate that the increase of the partial pressure of H_2 in the reactor displaces the reaction equilibrium, and therefore decreases the reaction rate of DMEAA at the surface.

The differences observed for experiments #1 and #2 in Table 1 are more straightforward and mainly rely on the deposition temperature. At 200–220 °C, the deposition conditions of Al from DMEAA are optimal. Above this temperature, gas phase reactions consume more than 97% of the precursor and growth rate decreases rapidly [14]. Inversely, increasing T from 200 to 260 °C leads to a higher growth rate of Cu from $CpCuPEt_3$ [10]. Consecutively, the individual growth rates of Cu and Al vary in opposite directions from $T = 200$ °C to $T = 260$ °C; GR(Cu) being multiplied by ≈ 2.5 while GR(Al) is divided by ≈ 3 . However, increasing temperature to 260 °C is not an appropriate option for increasing the Cu content of the film since it drastically affects the global growth rate that decreases from 80 to 30 $\mu\text{g}/\text{cm}^2/\text{h}$. The solution for getting Cu enrichment must come from the gas phase and not from a higher surface temperature.

Therefore, an attempt has been made (experiment #4 in Table 1) with a substrate temperature of 200 °C and a lower $F_{N_2, DMEAA}/F_{N_2, CpCuPEt_3}$ ratio, equal to 5/150. H_2 is also introduced in order to favor Cu deposition at the expense of Al. In these conditions, the estimated Cu precursor flux has increased to 0.12 sccm. The obtained global growth rate of 25 $\mu\text{g}/\text{cm}^2/\text{h}$ is the lowest in this series of experiments, mainly because it is governed by GR(Al) which is low. During Cu unary deposition, it has been demonstrated

by mass spectrometry that PEt_3 is extensively adsorbed on the growing surface with subsequent hindering of precursor supply to the deposition zone, resulting in self-inhibition of Cu deposition and gradual decrease of the growth rate [11]. Here, this situation is valid in all the experiments but we probably attain such a precursor concentration in experiment #4, that inhibiting effects become predominant and affect the deposition mechanisms of Al, as well. Consequently, in addition to the disadvantage of using H_2 , Al deposition rate is further reduced by the saturation of the surface by adsorbed PEt_3 .

To further support the above-mentioned assumptions, we now consider *experimentally-determined* growth rates of unary Al depositions. These growth rates are different from the *estimated* GR(Al) reported in Table 1. They result from dedicated Al depositions performed without $H_{2(g)}$ with a flow rate of 0.26 sccm. In co-deposition conditions beneficial to the DMEAA precursor, i.e. either 200 °C or without H_2 , growth rates of experiment #1 (80 $\mu\text{g}/\text{cm}^2/\text{h}$) and #3 (50 $\mu\text{g}/\text{cm}^2/\text{h}$) are similar to *experimentally-determined* Al depositions growth rates (128 and 40 $\mu\text{g}/\text{cm}^2/\text{h}$, respectively). In co-deposition conditions beneficial to the $CpCuPEt_3$ precursor, i.e. either 260 °C (experiment #2) or high $F_{CpCuPEt_3}$ at 200 °C (experiment #4), the pollution of the surface by phosphine results in (i) a low global growth rate, and (ii) a low GR(Al), to be compared with the *experimentally-determined* Al growth rate at 200 °C (128 $\mu\text{g}/\text{cm}^2/\text{h}$). Therefore, the formation of Cu-rich samples is more due to the inefficient deposition of Al rather than to the increase of the growth rate of Cu.

From the results reported above we conclude that we can successfully obtain intermetallic compounds of interest. Despite a major drawback referring to the reduced growth rate and probably the process yield, solutions are available to circumvent those problems which are attributed to the control of the co-deposition by synergetic phenomena. From the analysis of the results reported in Table 1 it appears that better conditions for the growth of Al-Cu compounds from $CpCuPEt_3$ and DMEAA should include: (i) the use of both precursors – but more importantly of $CpCuPEt_3$ – in liquid solution in combination with a regulated delivery system (e.g. direct liquid injection, pulsed injection, . . .), (ii) avoiding the use of H_2 for maximizing Al growth, (iii) determining a couple of $[T; F_{CpCuPEt_3}]$ parameters that allow the proper desorption of PEt_3 from the surface, and prevent the thermal degradation of DMEAA in the gas phase, and (iv) elucidate surface mechanisms that are

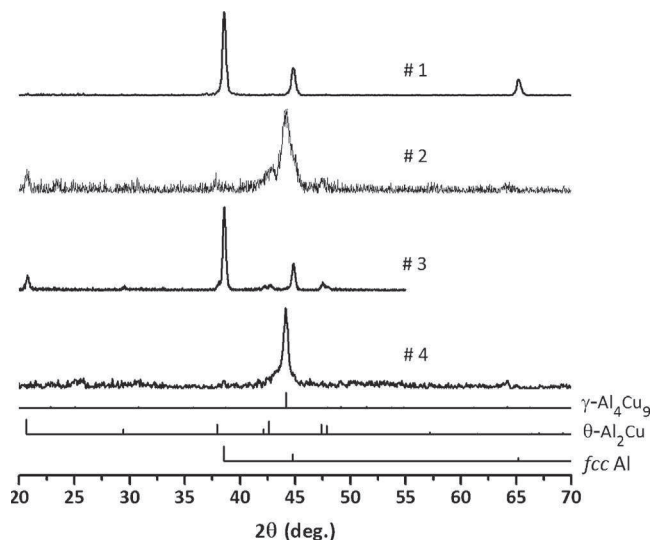


Fig. 1. XRD spectra of samples from experiments #1–4 with given identifications of phases. Phases reported on the right-hand side of the figure where identified with aid of JCPDS #04-0787 for fcc-Al, #25-0012 for θ - Al_2Cu , and #24-003 for γ - Al_4Cu_9 .

responsible for those synergetic effects and tune the substrate reactivity, accordingly.

Fig. 1 shows the XRD pattern for as processed samples of experiments #1–4. The films are composed of 3 different phases: *fcc*-Al, θ -Al₂Cu, and γ -Al₄Cu₉. Comparison of these phases with the Al/Cu ratios shown in Table 1, allows concluding that Al-rich compositions (experiments #1 and #3) correspond to the formation of

either pure Al or of an α -(Al) solid solution plus θ -Al₂Cu, eventually. Indeed, when composition gets richer in Cu (from experiments #1–3) then the contribution of the θ -Al₂Cu phase to the XRD diagram becomes larger. If the composition in Cu is large enough then the targeted γ -Al₄Cu₉ is formed, either pure or with θ -Al₂Cu. Hence, phase formation qualitatively follows the simple mixing rule that can be deduced from the Al-Cu phase diagram. It is worth

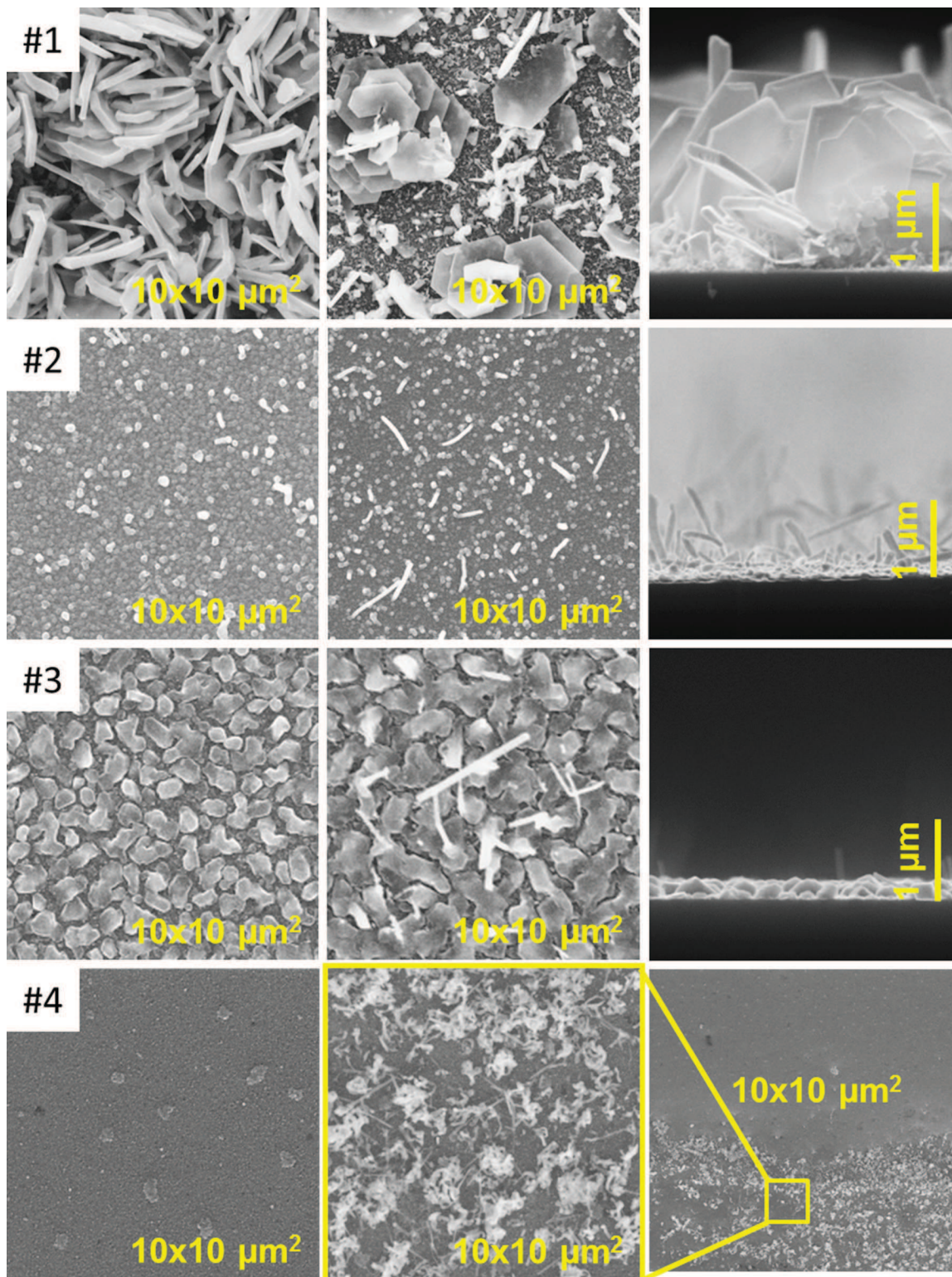


Fig. 2. Surface and cross-section SEM images of samples from experiments #1–4. The Al-Cu film #4 is too thin to achieve a cross section imaging.

noting however, that the sample of experiment #2 which shows the elemental composition the closest to the theoretical Al_4Cu_9 composition ($\text{Al}_{33}\text{Cu}_{67}$ and $\text{Al}_{31}\text{Cu}_{69}$, respectively) is not the one giving rise to the formation of a single-phase $\gamma\text{-Al}_4\text{Cu}_9$ coating. This is observed for the sample of experiment #4 whose elemental composition is somehow shifted from this ideal composition. This result is in contrast with reports, following which for a given coating composition the corresponding point in the phase diagram can be used to predict the final phase fraction [6,20]. It is rather attributed to partial alloying giving rise to transient phases, mainly $\theta\text{-Al}_2\text{Cu}$ and $\gamma\text{-Al}_4\text{Cu}_9$ because of the relatively low activation energy required for their formation in thin films [9,21]. Moreover, it has been reported that, independently of the Al/Cu ratio, thermal annealing of Al-Cu bilayers first yields $\theta\text{-Al}_2\text{Cu}$ at temperatures as low as 130 °C followed by a small amount of a second phase, AlCu_3 . The subsequent phase formation was found to depend on the Cu:Al atomic ratio. For Cu concentrations higher than 50 at.%, the reaction subsequently proceeds toward the phases $\gamma\text{-Al}_4\text{Cu}_9$ and $\alpha\text{-Cu}$. For Cu concentration lower than 50 at.%, AlCu_3 transforms to a new hexagonal phase Al_xCu which subsequently transforms back to AlCu_3 before the reaction proceeds toward the end phases AlCu and Al_2Cu [22].

EPMA and Rutherford backscattering experiments reveal that oxygen concentration in the films is high, ranging from 13 to 61%. Taking into account that on line mass spectrometry unambiguously shows background level for all oxygen containing species, it is concluded that oxidation of the films occurs *ex situ*. Based on SEM observations illustrated in the next section, the high surface to volume ratio is most likely responsible for surface oxidation in addition to O_2 and water adsorption.

3.2. Morphology

Fig. 2 regroups surface and cross-section SEM images. The first obvious observation is that rough morphologies correspond to Al-rich compositions (experiment #1 and #3) whereas smoother morphologies are found on Cu-rich samples (experiment #2 and #4). However, since Al-rich films are much thicker based on weight gain and on SEM cross-sections analysis, it is unclear whether high thickness or Al growth or the combination of both is responsible for roughness and porosity. A good indication comes from deposition temperatures. The film of experiment #1 was grown at 200 °C whereas the film of experiment #3 was grown at 260 °C. At 200 °C, growth rate is higher because less precursor is consumed in homogeneous reactions. From the surface point of view, it corresponds to a higher flux of precursor. Inversely, a higher temperature results in the combination of a lower precursor flux and higher bulk and surface diffusion rates; both mechanisms are beneficial to the surface smoothness.

The surface of the sample of experiment #2 is composed of a dense film with equiaxed grains on top of which quasi-unidirectional filaments are pointing away from the surface plane. In Fig. 3, similar filaments are found for experiments #2–4. It was not possible to determine their structure and composition due to their size which is not compatible with SEM, XRD or EPMA. Experiment #4 is the most promising application wise: the film is single-phase $\gamma\text{-Al}_4\text{Cu}_9$ (within the limits of XRD characterization) and it shows large surface regions like the one illustrated in Fig. 3 with no parasite filament grains.

This sample provides the first experimental proof of concept according to which MOCVD co-deposition can form a complex metallic alloy coating in one step.

3.3. Wetting of $\gamma\text{-Al}_4\text{Cu}_9$ surfaces by water

The use of MOCVD films containing approximant phases as buffer layers for the interfacial accommodation and adhesion between a metallic substrate and a quasicrystalline coating is subjected to their surface energy, which in turn impacts their wetting by liquids, e.g. water. It is well known that in ambient air, typical values for a quasicrystal of high lattice perfection like an annealed single grain icosahedral Al-Pd-Mn are in the range $90^\circ < \theta < 100^\circ$, whereas pure aluminum metal shows values around 70° [23]. In this context, it is expected that a $\gamma\text{-Al}_4\text{Cu}_9$ single-phased surface should present a contact angle with water between 70° and 90° . In order to verify this point a series of wetting experiments were performed with ultrapure water (resistivity 18.2 MOhm/cm) on the surface of sample #4 (pure $\gamma\text{-Al}_4\text{Cu}_9$) and on the surface of a pure $\gamma\text{-Al}_4\text{Cu}_9$ bulk sample. Before wetting experiments, the surface of the bulk sample was polished with SiC disks. Three surface finishes were obtained with 600, 2400 and 4000 grit, providing surfaces with mean roughness R_a of 246 nm, 16 nm and 7 nm, respectively. Four measurements of contact angle with water were performed on each surface finish. The obtained values are 82° , 84° , and $87 (\pm 2^\circ)$ from the rougher to the smoother surface. These results confirm the intermediate value of the contact angle with water on the surface of the $\gamma\text{-Al}_4\text{Cu}_9$ approximant between those obtained on the surface of aluminum metal and of icosahedral crystals. They are also consistent with Wenzel's theory, following which an intrinsically hydrophilic surface becomes more hydrophilic when its roughness increases [24]. Following the same protocol, four measurements of contact angle with water were also performed on the surface of the MOCVD processed pure $\gamma\text{-Al}_4\text{Cu}_9$ film. The obtained mean value is $89 (\pm 2^\circ)$. Taking into account that R_a of the latter sample was measured to be 5 nm, this result is to be compared with the one of 87° obtained on a bulk $\gamma\text{-Al}_4\text{Cu}_9$ surface with comparable roughness. It is concluded that MOCVD processed approximant phases present similar surface characteristics to those of equivalent bulk crystals. In a more prospective view, it is possible to engineer the surface energy of MOCVD Al-Cu film by proper selection of deposition conditions leading to a mixture of intermetallic phases including approximant ones.

4. Conclusions

We present a one-step process for the deposition of Al-Cu intermetallic coatings by metalorganic chemical vapor deposition. Dimethylethylamine alane (DMEAA), a liquid precursor, and copper(I) cyclopentadienyl triethylphosphine (CpCuPEt_3), a solid precursor, are chosen as precursors for the co-deposition of Al and Cu because they contain no oxygen, they are chemically compatible, and their deposition temperatures are similar.

The elemental composition of the films does not follow that of the gas phase. The presence of hydrogen gas plays an important role in the co-deposition process by displacing the reaction equilibrium of DMEAA at the surface, therefore decreasing the Al growth rate. Additionally, when the CpCuPEt_3 gas flux is high enough for achieving Al/Cu compositions of interest, the experimental growth rate of Al-Cu films is limited by the adsorbed phosphine originating from CuCpPEt_3 decomposition on the growing surface. Encouragingly, solutions are available to circumvent those problems which are attributed to the control of the co-deposition by synergetic surface phenomena.

The single-phase $\gamma\text{-Al}_4\text{Cu}_9$ is formed when the Cu composition in the Al-Cu films is high enough. The surface roughness of such films is very low, with a R_a value equal to 5 nm. Wetting measurements with water on this surface provide a contact angle of $89 \pm 2^\circ$; i.e. roughly the same as the one on a bulk polycrystalline $\gamma\text{-Al}_4\text{Cu}_9$ of similar roughness. It is concluded that MOCVD-processed $\gamma\text{-Al}_4\text{Cu}_9$

approximant phase present similar surface properties with those of equivalent bulk crystals and can, therefore be used as interfacial layer between metallic substrates and quasicrystalline coatings accommodating the mismatch of surface energy between them.

The present work demonstrates that it is possible by MOCVD to process in a single step and at relatively low temperature, films containing intermetallic phases including approximant ones. This work may be considered as a preliminary approach paving the way to the conformal coating of complex surface geometries by such intermetallic compounds.

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