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Al–Cu intermetallic coatings processed by sequential metalorganic chemical vapour deposition and post-deposition annealing

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ABSTRACT

Sequential processing of aluminum and copper followed by reactive diffusion annealing is used as a paradigm for the metalorganic chemical vapour deposition (MOCVD) of coatings containing intermetallic alloys. Dimethylethylamine alane and copper N,N′-di-isopropylacetamidinate are used as aluminum and copper precursors, respectively. Deposition is performed on steel and silica substrates at 1.33 kPa and 493–513 K. Different overall compositions in the entire range of the Al–Cu phase diagram are obtained by varying the relative thickness of the two elemental layers while maintaining the overall thickness of the coating close to 1 μm. As-deposited films present a rough morphology attributed to the difficulty of copper to nucleate on aluminum. Post-deposition annealing is monitored by in situ X-ray diffraction, and allows smoothening the microstructure and identifying conditions leading to several Al–Cu phases. Our results establish a proof of principle following which MOCVD of metallic alloys is feasible, and are expected to extend the materials pool for numerous applications, with innovative thin film processing on, and surface properties of complex in shape parts.

1. Introduction

Al–Cu intermetallic compounds present attractive properties in applications such as interconnects for integrated circuits [1] or corrosion resistant coatings [2]. Al–Al_2Cu composites feature enhanced Young's modulus, good compressive strength and reasonably good compressive ductility [3]. In addition, Al and Cu are reasonably inexpensive, and easily available.

Processing of Al–Cu and, more generally of intermetallic alloy coatings by metalorganic chemical vapour deposition (MOCVD) is expected to extend their implementation in surface engineering. Especially, thanks to the possibility to operate in surface reaction controlled regime, MOCVD allows surface treatment of complex-in-shape items such as glass moulds, turbine blades and vanes in aeronautic industries, or porous preforms whose internal surface may be functionalized for the preparation of supported catalysts. Versatility, cost effectiveness, environmental compatibility, and the possibility to process films containing thermodynamically metastable phases, are additional advantages of MOCVD processes. Finally, the use of molecular precursors allows operating at low to moderate temperatures, thus extending the targeted applications spectrum so as to cover temperature-sensitive substrates.

The price to pay for this high potential is the need to tackle the challenges imposed by the complex gas phase and surface chemistries. In addition to mastering the deposition reaction, these challenges also concern the design of the precursors upstream the MOCVD process, the engineering of the MOCVD apparatus in terms of precursor vapour generation, energy delivery means, and dynamical in situ and on line diagnostics to monitor gas and surface reactions. The inherent difficulty for the establishment of a robust MOCVD process is further amplified in the case of coatings containing several elements and potentially intermetallic phases, mainly because of the limited width of their stability domains, and the far-from-equilibrium initial state which can lead to unpredicted transitions [4]. Moreover, such a process for the preparation of multimetallic coatings must involve the use of compatible precursors for the deposited elements. The general criteria qualifying an inorganic or molecular compound as precursor for CVD processes were discussed by Maury et al. [5,6]. In the case of the MOCVD of intermetallic compounds there are additional ones such as (a) similar transport behaviours, (b) absence of heteroatoms in the ligands which may react with the other metal, (c) compatible decomposition schemes, and if possible (d) belonging to a common family of compounds. Until now, this situation resulted in limited investigation of MOCVD for the co-deposition of intermetallic alloy films.

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Reports on the MOCVD of Al–Cu were published in the nineties involving aluminum alane and copper phosphine precursors [7,8]. However, they concern films with low copper concentration, at the level of 1 wt.%, targeting the doping of Al-based interconnections in microelectronics rather than the processing of coatings containing intermetallic phases.

The above mentioned constraints can be partially circumvented if the preparation of the coating proceeds in two steps. Namely, sequential deposition of the elements in the form of bi- or multilayers, is followed by an appropriately tuned annealing which leads to the formation of the targeted phases. This latter solution, applied in the processing of Al/Cu bilayers, is adopted in the present study. Optimization of the deposition reactor, processing of the Al and Cu unary films, investigation of their decomposition mechanisms, and kinetic modelling of the MOCVD process are presented elsewhere ([9,10] and references therein).

The article is presented as follows. The experimental protocol involving MOCVD of Al and Cu, and post-deposition annealing is presented in details, first. Then, the microstructure and composition profiles of the as-processed Al-rich and Cu-rich bilayers are compared. Finally, microstructure and phase transitions of the annealed coatings are presented and discussed, prior to providing concluding remarks.

2. Material and methods

Depositions are performed in the experimental setup described in details and modeled in Ref. [11]. 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. [12]. Gases are fed through electropolished stainless steel gas lines with VCR fittings and their flow rate is controlled by computer driven mass flow controllers.

5 mm × 10 mm up to 20 mm × 20 mm 304L stainless steel coupons are used as representative of technologically interesting substrates. Thermally oxidized silicon (140 nm SiO_2) coupons are used for the ease of cross sections preparation for observation by scanning electron microscopy (SEM), and for X-ray diffraction analyses (XRD). Substrates are placed horizontally on a 58 mm diameter susceptor standing below the showerhead. They are heated by a resistance coil gyred just below the surface of the susceptor. Stainless steel substrates are polished down to 4000 SiC paper grade and are sonicated in acetone and anhydrous ethanol. Silicon wafers are degreased in a 70% H_2SO_4–30% H_2O_2 solution, rinsed with deionized water and dried under argon stream before use. A set of five stainless steel and five SiO_2 substrates is used in each run. Substrates are exposed to atmosphere for a limited time during their transfer between the preparation lab and their loading into vacuum. Prior to deposition, in situ radio frequency (RF) Ar–10% H_2 plasma etching is applied with input power 40 W at 120 kHz, in conditions 160 Pa and 493 K, for 30 min with the aim to recover an organic-pollution-free steel or silica surface. In all experiments the operating pressure and the temperature of the reactor walls are fixed at 1.33 kPa and 368 K, respectively.

Adduct grade DMEAA (SAFC Hitech) is used as-received in a stainless steel bubbler. It is maintained at 281 K by immersion in a thermoregulated water bath. The corresponding saturated vapour pressure is 99 Pa. The DMEAA bubbler is maintained at this temperature during the entire period of its service in order to avoid degradation of the precursor [13]. 25 standard cubic centimetres (sccm) of 99.9992% pure nitrogen (Air Products) bubbles through the Al precursor. Assuming saturation of the gas phase, these conditions lead to an upper limit of the DMEAA flow rate equal to 2 sccm [14]. The total flow rate is completed to 327 sccm by adding 300 sccm of N_2 as a dilution gas. Deposition temperature is fixed at 493 K. It has been previously shown that in these conditions a mean nucleation delay of 7 min precedes initiation of the growth of Al. Nucleation delay is determined by observation of change of the colour of the surface and is the same for SiO_2 and stainless steel samples. Al growth rate is measured at certain positions over the susceptor, through the weight gain of each sample [10]. Weight gain is preferred to thickness measurement since film porosity and roughness induce an overestimation of the growth rate. For instance, SEM analysis of the cross-section of an Al (resp. Cu) sample showed a 1300 nm (resp. 110 nm) thick film, whereas the thickness determined by weight measurement was 400 nm (resp. 45 nm), only. Al growth rate is mapped as being constant at 12.6 μmol cm^{-2} h^{-1} on the central part of the susceptor and gradually increasing beyond a radius of 15 mm to reach 15.6 μmol cm^{-2} h^{-1} at the edge of the susceptor, averaging 13.3 μmol cm^{-2} h^{-1} on the entire heated surface.

[Cu(i-Pr-Me-AMD)]$_2$ (NanoMePS, www.nanomeps.fr, last accessed October 7, 2011) is used as-received for Cu deposition. This precursor is appropriate for use in a process involving CVD of Al from DMEAA because (a) the two processing conditions windows partially overlap, (b) it contains neither oxygen nor halogens in the ligands, nor it requires oxygen containing co-reactants for the deposition of copper [9]. [Cu(i-Pr-Me-AMD)]$_2$ is manipulated in glove box and is conditioned in a packed bed loaded in a homemade sublimator composed of a full stainless steel body, a frit and VCR fittings. A load of 500 mg of fresh compound is used in each run. During deposition the precursor is maintained at 368 K with thermally regulated heating tapes, this temperature corresponding to a saturated vapour pressure of 36 Pa [9]. 50 sccm of N_2 are fed through the copper precursor corresponding to an upper limit of the flow rate of [Cu(i-Pr-Me-AMD)]$_2$ equal to 1.2 sccm. 50 sccm of 95% pure hydrogen (Air Products) is used as reducing gas. The relatively low purity of H_2 does not impact the purity of the deposited Cu. Similar to the deposition of Al, the total flow rate is completed to 326 sccm by adding 225 sccm of N_2 dilution gas. Cu deposition is performed at 513 K. The mean growth rate of Cu in these conditions was previously determined by weight gain to be equal to 0.3 μmol cm^{-2} h^{-1} [15].

The deposition protocol consists in (a) establishing flow rates in all the gas lines, bypassing the precursor vessels, (b) establishing the targeted temperature at each part of the setup except for the copper sublimator, (c) performing the deposition of Al, (d) bypassing the DMEAA bubbler for 30 min, (e) heating the copper sublimator to 368 K (10 min) and increasing the temperature of the susceptor to 513 K, (f) performing deposition of Cu, and (g) bypassing the precursor vessels while cooling down the susceptor. This protocol presents the drawback of maintaining the free surface of the deposited Al during 40 min (steps (d) and (e)) prior the deposition of Cu, running the risk of contamination of the Al/Cu interface by residual oxygen. However, contamination level is lower than the one obtained if using O-containing Cu precursors.

Several deposition runs are performed in the same conditions, the difference being the durations of the deposition of Al (between 20 min and 57 min) and Cu (between 170 min and 960 min).

Post-deposition annealing is applied to the as-processed Al/Cu bilayers in order to investigate reactive diffusion, and obtain coatings containing different intermetallic Al–Cu phases. In situ XRD measurements in Bragg–Brentano configuration are performed during heat treatments in two instruments, operating with Cu Kα, Ni filtered radiation: a Bruker D8 Advance, fitted with a Vantec Super Speed detector and a Philips X'pert. They are equipped with