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Monitoring microstructure and phase transitions in thin films by high-temperature resistivity measurements[†]

Thomas Duguet,^{a*} François Senocq,^a Lyacine Aloui,^a Fanta Haidara,^b Diane Samélor,^a Dominique Mangelinck^b and Constantin Vahlas^a

We present first experimental results obtained with a newly patented high-temperature resistivity measurement apparatus. This technique is of great interest for monitoring the behaviour of a surface layer submitted to high temperature, either during its processing or while the functional surface is used. The innovation resides in the combination of features that are available commercially or have previously been reported by research groups worldwide, but isolated. Resistivity measurements can be performed under vacuum or controlled atmosphere, from room temperature to 1250 °C, on samples as low as 10 × 10 mm² in size. Technical details about the apparatus are presented. Then, we show that high-temperature resistivity measurements performed on a platinum sheet compare well with available data, and validate the prototype measurement head. Finally, we explore the monitoring of phase transitions occurring in an Al/Cu bilayer processed by metallorganic chemical vapour deposition, while a temperature ramp is applied. The high-temperature resistivity plot is very well explained by the following sequence of phase formation: $\text{Al} + \text{Cu} \rightarrow \theta\text{-Al}_2\text{Cu} + \text{Cu} + \text{Al} \rightarrow \delta\text{-Al}_2\text{Cu}_3 + \gamma\text{-Al}_4\text{Cu}_9 + \text{Cu} \rightarrow \delta\text{-Al}_2\text{Cu}_3 + \gamma\text{-Al}_4\text{Cu}_9 + \text{Cu} + \alpha\text{-(Cu)}$, as determined by high-temperature X-ray diffraction. Copyright

Keywords: resistivity; high temperature; platinum; aluminum; copper; intermetallics; coatings; thin films; metallorganic chemical vapour deposition; MOCVD

Introduction

Insight into the behaviour at high temperature of superficial regions of pieces and parts is of great interest for a variety of applications, which involve either processing and surface treatments at high temperature or operation of functional and structural coatings in severe environments, including elevated temperature. Heat activates phase transitions (formation of oxides, intermetallics, precipitates, and interface interdiffusion) that can be detrimental to their functional properties, such as resistivity in high-power electronic devices, mechanical properties of turbine blades or cutting tools, or transport properties in thermoelectric alloys and oxides. On the contrary, a controlled annealing can be used for the formation of the targeted phases or microstructures.

A convenient method for monitoring structural transitions in thin films is to follow electrical resistivity during a temperature ramp, sometimes called ramped resistance measurements.^[1–4] Compared with high-temperature X-ray diffraction (HT-XRD), high-temperature resistivity shows an instantaneous response to structural changes, which renders reaction kinetics accessible, using the Kissinger method for instance.^[5] The combined use of both techniques provides a comprehensive description of the material's behaviour.

The development of a high-temperature electrical resistivity measurement apparatus is based on the fact that no commercial equipment satisfies the following combination of features: high temperature measurements, controlled environment, and the possibility of characterizing small samples. The present work introduces results obtained with a newly designed and patented high-temperature resistivity apparatus based on the four-probe method.^[6] It provides the possibility of monitoring the resistivity of

metallic and semiconductor thin films, from room temperature to 1200 °C, in a controlled environment.

The instrument will be described first, followed by the validation of its performances through the measurement of electrical resistivity as a function of temperature of a Pt sheet. Finally, results will be presented about the *in situ* monitoring of Al/Cu phase formation in an Al/Cu bilayer processed by metallorganic chemical vapour deposition (MOCVD). Although processing of such coatings by MOCVD is challenging, it is of major interest for the surface treatment of complex-in-shape substrates and of architected surfaces with high aspect ratios. Films and coatings composed of Al/Cu intermetallics present attractive properties such as low resistivity, corrosion resistance, low friction coefficient, and high microhardness.

Experimental details

High-temperature resistivity apparatus

The high-temperature resistivity apparatus is based on the four-point probe method. Two external pins supplying current (*I*) are

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aligned with two internal pins measuring voltage (V). Thin films and coating resistivities (ρ_s) are thus given by

$$\rho_s = \frac{V}{I} \times C \left(\frac{a}{d}; \frac{d}{s} \right) \times t \quad (1)$$

where C is a constant depending on the sample length parallel to the pin alignment (a), the sample width perpendicular to the pin alignment (d), and the constant spacing between pins (s).^[7] t is the thickness of the coating, film, or sheet. The geometry of the present four-point probe head corresponds to $s = 1.5$ mm, with a tip apex of $40 \mu\text{m}$ in diameter. Figure 1 shows a schematic of the high-temperature resistive meter, along with a photograph of the measurement head. It possesses a working range of regulated current of 100 fA to 100 mA (Keithley, Inc. precision current source model 6220), and the possibility of measuring voltage from 10 nV to 12 V (Keithley, Inc. nanovoltmeter model 2182A/E). Signal acquisition and treatment are driven by a computer program. In the chamber, the base pressure of approximately 10^{-6} torr is obtained through a turbomolecular pumping unit. Additionally, a partial pressure of reactive or neutral gases can be used to mimic the environment of the functional surface. Finally, temperature can be increased up to 1200°C .

This setup is designed for characterizing sample sizes down to $10 \times 10 \text{ mm}^2$. Samples are pressed facedown against the probe, and stabilized with a zirconia slab placed on top. Four independent leaf springs support the four tungsten pins. This mechanical elasticity is beneficial to both the good contact between surface and probe, and the stability of the signals. System temperature is currently controlled through a variable transformer. Although a temperature regulation exists, its use induces measurement perturbations, which suggest that we may have to change the furnace power supply from a.c. to d.c., and implement a d.c. regulator.

MOCVD of Al/Cu coatings

Depositions are performed in the experimental setup described in detail and modeled in the article by Xenidou *et al.*^[8] Al and Cu layers

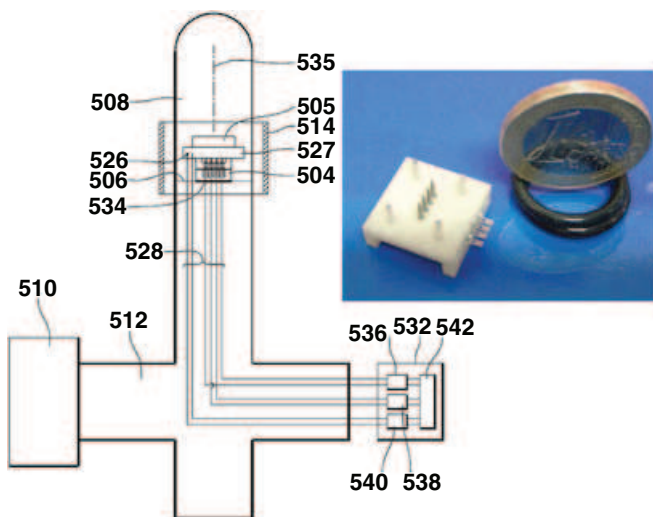


Figure 1. Schematics of the high-temperature resistivity apparatus and photograph of the four-point probe head. Details about numeration can be found in ref.^[6] 535 shows the center of a cylindrical tube (external diameter, 28 mm) that is pumped through turbomolecular pumping (510), and heated through an annular furnace (514). 532 corresponds to control and acquisition of the electrical signals and temperature.

are deposited sequentially in a gas flow of 325 standard cube centimeters per minute (sccm), containing a maximum of either 2 sccm of Adduct Grade dimethylethylamine alane (SAFC Hitech) as Al precursor, or 1.2 sccm of $[\text{Cu}(\text{i-Pr-Me-AMD})_2]$ (NanoMePS) as Cu precursor. Depositions are performed on substrates held at 220°C and 240°C for Al and Cu, respectively. All the samples coated at the same time share close overall atomic composition, as determined by electron probe microanalysis (EPMA), performed with a CAMECA SX-50 apparatus.

In situ XRD measurements are performed during heat treatments under vacuum in a Philips X'pert (Cu $K\alpha$), equipped with an Anton Paar HTK-1200 high-temperature chamber. Surface temperature samples have been corrected through the use of a thermocouple attached to a dummy sample.

Experimental results

To validate the ability of the apparatus to measure resistivity at high temperature, we perform measurements on a Pt sheet and compare accuracy and trend with literature data.^[9] Then, we show how high-temperature resistivity can be used to follow microstructure and phase transitions in an Al/Cu bilayer deposited by MOCVD, and annealed *in situ*. HT-XRD is used to complement and validate our interpretation of the film modifications.

High-temperature resistivity of Pt

The Pt sheet is $300 \mu\text{m}$ thick with a surface area of $15 \times 15 \text{ mm}^2$. The experiment is conducted in high vacuum (base pressure of 10^{-6} torr), from ambient temperature to 800°C . Results are presented in Fig. 2. At 26°C (first diamond), resistivity is $11.9 \mu\Omega \text{ cm}^{-1}$, whereas at 27°C , reference data show $10.8 \mu\Omega \text{ cm}^{-1}$. As expected for a metal, resistivity increases with temperature, with a slope in good agreement with the other data set. Details about the microstructure are not considered in reference data, which renders any further comparison with our Pt sample difficult. Overall, the experimental validation of the high-temperature resistive meter is very satisfactory because this is the first time that an experimental ρ vs T data set is shown for Pt in a unique experiment, and also because agreement with a reference plot (made by gathering different experimental results) is good.

Monitoring phase transitions during annealing of an Al/Cu bilayer

The overall composition of the Al/Cu bilayer as determined by EPMA is 80 atomic % (at.%) of Cu. On the basis of the stable phase

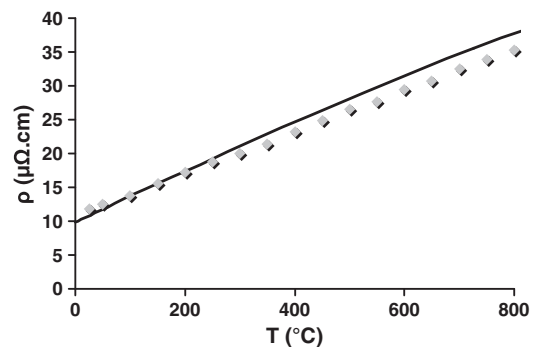


Figure 2. High-temperature resistivity plot of a $300\text{-}\mu\text{m}$ -thick Pt sheet (diamonds). Full line adapted from ref.^[9].

diagram,^[10] phase transitions are expected, with the formation of the gamma-brass phase $\gamma\text{-Al}_4\text{Cu}_9$, the solid solution $\alpha\text{-(Cu)}$ with incorporation of a maximum of 20 at.% Al, and the martensitic phase $\beta\text{-AlCu}_3$, eventually. It is worth noting that those phases correspond to a thermodynamically stable state, whereas the initial state of a thin film is far from equilibrium, and thus annealing can initiate a complex phase transformation path. Figure 3 shows the results of the *in situ* annealing of the Al/Cu bilayer, from ambient temperature to 609 °C (bottom), and back to ambient temperature (top). Current is fixed at 10 mA. The average heating rate is 4.2 K min⁻¹.

Sheet resistance ($R_s = V/I$) is preferred to resistivity because we do not know the thickness and porosity of the bilayer, and because microstructure evolves during heat treatment. Nevertheless, the interpretation is the same because R_s varies as ρ_s does [Eqn (1)]. A change in the resistivity slope means that structural changes occur. Here, the first obvious onset of a change is observed at 457 °C. Around this transition (450–550 °C), the heating rate is constant at 2.7 K min⁻¹. Then, resistivity increases dramatically from 0.05 Ω until it reaches a maximum of 0.33 Ω between 545 °C and 560 °C. The onset of a second transition is observed at 585 °C, slightly decreasing resistivity from 0.32 to 0.29 Ω . While cooling, resistivity increases – as a semiconducting film would do, until a third transition starts at 512 °C. From the end of this transition and down to room temperature, the slope corresponds to a metallic film that cools down.

Because we expect phase transitions during the annealing of an Al/Cu bilayer, we follow the coating structure with HT-XRD on a second sample, originating from the same deposition experiment. To link these two samples together, we perform a postannealing R_s measurement at room temperature (a few months later, stored in ambient conditions). Because both samples show two surface regions, discriminated by different colors (one being light gray, the other being red/orange), we performed three measurements on each sample. Inside the gray region, R_s (gray)=0.56 and 0.55 Ω , respectively. Inside the reddish region, R_s (red)=0.33 and 0.36 Ω , respectively. Finally, across the two surface regions, R_s =0.44 and 0.45 Ω , respectively. Therefore, the final state of the two samples, one after high-temperature resistivity measurement and the other after HT-XRD is the same, allowing one to make a direct comparison of the two experimental results.

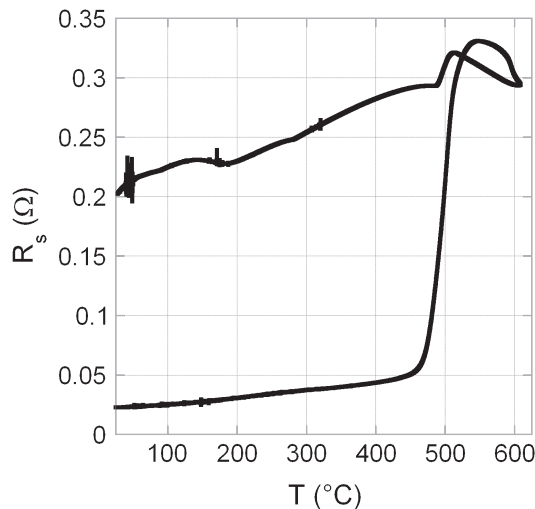


Figure 3. Sheet resistance (R_s) of an Al/Cu bilayer on SiO_2 substrate annealed under vacuum, with an overall atomic composition of Al(20)Cu(80).

Figure 4 shows a selection of X-ray diagrams, from ambient temperature (data not shown) to 650 °C. A constant heating rate of 5 K min⁻¹ is applied.

At 210 °C, the structure of the bilayer corresponds to its initial state, containing *fcc* Al and Cu. Al film is likely textured because the high-angle (200) peak intensity is largely greater than the (111) intensity. *fcc* Al and Cu are still present at 440 °C. The first transition is observed at 458 °C (data not shown) and corresponds to $\text{Al} + \text{Cu} \rightarrow \theta\text{-Al}_2\text{Cu} + \text{Cu} + \text{Al}$. It is followed by the total consumption of Al in the transition $\theta\text{-Al}_2\text{Cu} + \text{Cu} + \text{Al} \rightarrow \delta\text{-Al}_2\text{Cu}_3 + \gamma\text{-Al}_4\text{Cu}_9 + \text{Cu}$, starting at 487 °C. The majority phase is $\delta\text{-Al}_2\text{Cu}_3$, whose main peak reaches a maximum at 550 °C to 575 °C. Then, a decrease of the $\delta\text{-Al}_2\text{Cu}_3$ main peak is accompanied by an increase of the $\gamma\text{-Al}_4\text{Cu}_9$ main peak, and the appearance of an $\alpha\text{-(Cu)}$ solid solution peak (onset at 605 °C). This transition indicates that $\delta\text{-Al}_2\text{Cu}_3$ is partially dissolving, following $\delta\text{-Al}_2\text{Cu}_3 + \gamma\text{-Al}_4\text{Cu}_9 + \text{Cu} \rightarrow \delta\text{-Al}_2\text{Cu}_3 + \gamma\text{-Al}_4\text{Cu}_9 + \text{Cu} + \alpha\text{-(Cu)}$ (boldface font shows main contributions at 650 °C). $\alpha\text{-(Cu)}$ can contain up to 20 at.% Al, corresponding to a 1% increase of its lattice parameter.^[11] Here, the corresponding increase of the Cu lattice parameter would be approximately 1.6%. This error is probably due to thermal expansion at this high temperature of acquisition (650 °C).

The transformation sequence is quite similar to literature results. For instance, the phase sequence reported in Vandenberg and Hamm^[12] is obtained by *in situ* XRD during the annealing of Al/Cu bilayers. For samples with more than 50 at.% Cu, the sequence is summarized as $\text{Al} + \text{Cu} \rightarrow \theta\text{-Al}_2\text{Cu} + \beta\text{-AlCu}_3 + \eta\text{-AlCu} + \text{Cu} \rightarrow \gamma\text{-Al}_4\text{Cu}_9 + \alpha\text{-(Cu)} + \text{Cu}$. Additionally, it is often reported that annealing Al/Cu multilayers first leads to the formation of transient phases,^[12–16] and then (through longer time or higher temperatures) to the phase equilibrium corresponding to the given overall composition.^[17] Transient phases in thin films such as $\theta\text{-Al}_2\text{Cu}$ and $\gamma\text{-Al}_4\text{Cu}_9$ are formed with a relatively low activation energy corresponding to fast diffusion at interfaces and grain boundaries.^[18] The fact that transition temperature is high compared with other works is likely due to a very rough microstructure and to the oxidation of the Al/Cu interface, in the 10-min period of the MOCVD process in which substrate temperature has to be

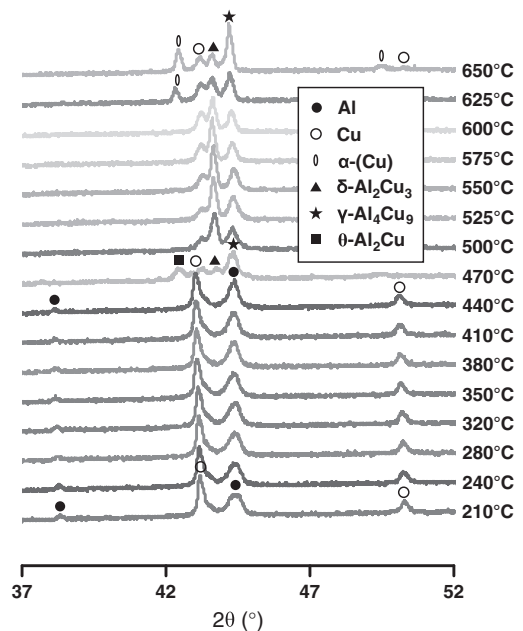


Figure 4. *In situ* X-ray diffractograms of an Al/Cu bilayer during annealing under vacuum. Overall atomic composition: Al(20)Cu(80).

increased, between Al and Cu deposition. This interpretation is supported by elemental depth profiles obtained by glow-discharge optical emission spectroscopy (data not shown).

The combination of high-temperature resistivity and XRD techniques results in the following scenario for the variation of resistivity. For $25^{\circ}\text{C} < T < 457^{\circ}\text{C}$, resistivity corresponds to a bilayer of Al and Cu. The apparent high resistivity for such good conductors is due to the film microstructure and to the oxidation of both the Al/Cu interface and the surface. The first slope change occurs at 457°C and corresponds to the growth of $\theta\text{-Al}_2\text{Cu}$. This dramatic increase of resistivity also includes growth at 487°C of $\delta\text{-Al}_2\text{Cu}_3$ and $\gamma\text{-Al}_4\text{Cu}_9$, whose resistivities are known to be the highest among Al/Cu intermetallics.^[19] The maximum of resistivity is reached between 545°C and 560°C , in agreement with the maximum intensity of the $\delta\text{-Al}_2\text{Cu}_3$ peak in XRD. Then, a solid solution $\alpha\text{-(Cu)}$ is formed at the expense of $\delta\text{-Al}_2\text{Cu}_3$ that dissolves partially. The drop of resistivity observed at 585.2°C corresponds to the vanishing of the very resistive $\delta\text{-Al}_2\text{Cu}_3$ phase, and the occurrence of conducting $\alpha\text{-(Cu)}$. While cooling down, we do not follow crystallographic structure; therefore, we do not give a detailed description of the resistivity behaviour. It is questioning though, that we observe a semiconductor behaviour between $609.4^{\circ}\text{C} > T > 512.3^{\circ}\text{C}$, that is, resistivity increases with decreasing temperature. We can assume that because $\gamma\text{-Al}_4\text{Cu}_9$ is considered as a quasi-crystal approximant with a pseudogap at the Fermi level,^[20] its electrical properties likely follow that of quasi-crystals and complex metallic alloys, that is, increasing resistivity with decreasing temperature. This discussion of the evolution of the resistivity of the film does not explain the third transition observed at 512.3°C , in which the semiconductor behaviour changes again to a metallic one, although the X-ray diagram remains unchanged between 650°C and ambient temperature. This question may be answered in the near future by applying a new ramped resistance measurement to the same sample to observe the electrical properties of an already-annealed coating.

Conclusions

We designed an apparatus for the measurement of electrical resistivity capable of characterizing electrical properties of semiconductor and metallic thin films, coatings and sheets, at high temperature and in a controlled atmosphere (either high vacuum, or neutral or reactive partial pressure). The validation of the apparatus is demonstrated through the measurement of Pt resistivity from ambient temperature to 800°C , in good agreement with available literature data. Then, we show how this system can be used for the exploration of phase

transitions in an Al/Cu bilayer, processed by MOCVD. The combined use of high-temperature resistivity and diffraction techniques provides a deep insight into changes that occur within the coating. This demonstrates that beyond the use of the resistive meter for characterizing electrical properties at high temperatures, this system can also be used for monitoring microstructure and phase transition, with an instant response of the signal, in a variety of environments, for example, in the industry for quality controls of pieces operating at high temperature.

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