*Article*

# Morphology Behavior of Copper Films Deposited after Wet Surface Treatment on Polished Alumina

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In this paper, a pre-treatment process for electroless copper (Cu) deposition on the polished alumina ($Al_2O_3$) 99.9% and the behavior of Cu plating by electroless process after $Al_2O_3$ surface treatment were explored. Our work was carried out by changing the roughness of $Al_2O_3$ through micro-etching (coarsening), nucleation its surface by a two-step method (sensitization and activation) and electroless Cu plating deposited using non-commercial solution having formaldehyde as reducer, alkaline pH and operating temperature of 30 ºC. Contact angle system (CA), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), mechanical profilometer (DekTak XT) atomic force microscopy (AFM) and analysis by Gwyddion v2.27 software were used to evaluate the wet treatment and the morphology of the electroless deposition (ED) of Cu on the $Al_2O_3$ surface. The results show that the surface treatment of purity polished $Al_2O_3$ with 0.1% of vitreous materials present into the substrate surface, presents a high performance in ED film at low temperature (30 ºC), during the Cu deposition, obtaining more compact and uniform film, with small grain size, uniform thickness, and a high purity Cu metallic deposit.

**Keywords:** electroless copper deposition, wet surface treatment, surface morphology, alumina, coarsening, nucleation

## Introduction

Electroless deposition (ED) of metals and alloys on non-metallic materials such as ceramics, carbon, plastics, polymers, semiconductors and dielectrics are increasing for a wide range of commercial applications.[1-8] The process is particularly important in the printed circuit industry.[9] For example, polished alumina ($Al_2O_3$) has been used as an interconnect substrate onto which a conductive metal layer, such as gold or copper, can be applied[8] by ED, since it is a low-cost process compared to other methods, such as plasma spraying, physical vapor deposition (PVD) chemical vapor deposition (CVD) or electrodeposition.[10] ED (autocatalytic) plating involves the presence of a chemical reducing agent in solution to reduce metallic ions to the metal state. The name electroless is somewhat misleading, however. There are no external electrodes present, but there is electric current (charge transfer) involved. Instead of an anode, salt supplied the metal. The process takes place only on catalytic surfaces rather than throughout the solution. If the process is not properly controlled, the reduction can take place throughout the solution, possibly on particles of dust or of catalytic metals, with undesirable results like the decomposition of the solution. Autocatalytic plating is defined as the deposition of a metallic coating by a controlled chemical reduction that is catalyzed by the metal or alloy being deposited. Such plating has been used to yield deposits of nickel (Ni), nickel phosphorus (Ni-P), copper (Cu), cobalt (Co), palladium (Pd), silver (Ag) and gold (Au). For Cu electroless deposition, chemical reducing agents have included formaldehyde as the most important (the one originally used by the inventors for Ni and Cu deposition and still the most important and widely investigated).

Among the various engineering ceramics, $Al_2O_3$ is one of the most widely used in the engineering materials due to is good mechanical properties, high hardness and low density.[11] However in some situations, the toughness, electric conductivity and the thermoconductivity of the ceramic need to be enhanced.[12] Electroless Cu films exhibit many advantages such as remarkable electric, magnetic and heat conducting properties.[13] However, $Al_2O_3$ ceramic shows no affinity to a metal plating and simple physical

deposition cannot be effective to complete copper plating on its surface.[14] To reach the required properties of the Cu layer, besides the bulk composition and properties of the Cu materials, the process that occur at the substrate surface before deposition are also important.[15] The cleanliness, the chemical composition of the surface, coarsening and the nucleation influence the initiation and the subsequent adhesion, both during and after deposition.[16,17]

Coarsening (surface modification) is an important step in the process to obtain a surface with a few nanometers of roughness on a polished alumina. So, it is necessary to carry out a sufficient coarsening to allow the pretreatment process with Sn and Pd deposition. Pre-treatment process of Sn-Pd has been used for decades; however, concerns about the low efficiency and risks of contamination remain unresolved. Many attempts were made to find a single-step catalyzing procedure to replace the two-step method with a more efficient method, such as the Pd-Sn colloidal deposition, noble metal prints, and vacuum deposition methods. Nevertheless, these techniques are either costly or require additional processing steps which reduce the efficiency.[8]

Many aspects of nucleation on the substrate surface have been investigated.[18] For the nucleation procedure, a one-step and a two-step process have been distinguished.[19] For the one-step nucleation, samples are immersed in a $SnCl_2$-$PdCl_2$ colloidal solution.[20,21] In the two-step procedure, substrates are sensitized by immersion in a $SnCl_2$ containing solution and activated with a $PdCl_2$ solution.[10,16,22]

According to Svendsen *et al.*,[23] the one-step nucleation procedure is not suitable for alumina substrates. This is confirmed by Honma *et al.*,[24,25] who reported that with a two-step procedure, the adhesion of Cu on alumina is stronger than with a one-step procedure, as measured by the direct pull-off technique.

Generally, three different goals can be distinguished for the pretreatments: first, adsorbed organic contaminations and particles are removed in a cleaning step. Second, by coarsening the substrate, the surface roughness is increased and possible sites for mechanical interlocking are created to improve adhesion. Third, by the nucleation procedure the surface of the substrate was turned catalytic by using the two-step procedure (Sn and Pd) followed by immersion in an accelerator[26-28] for ED deposition.

Copper is a less noble metal, but many studies[29,30] have considered it as a good candidate for the design of new catalysts, especially because of its very remarkable electric conductivity, good stability and low-cost.

Electroless copper deposition is a promising route to realize copper-based catalysts due to is relatively low-cost, simplicity, low processing temperature, good adherence and the high physicochemical properties of the deposit.[31]

This work reports the effect of the treatment performed on the polycrystalline alumina surface by comparing the contact angle (CA) before and after coarsening. The morphology and roughness of the electroless Cu deposition system performed on the alumina coarsened was studied combining atomic force microscopy (AFM), mechanical profilometer (DekTak XT) and scanning electron microscope (SEM). The aim of this study has been, on the one hand, to expand the current knowledge about the process of obtaining a catalytic surface to enable the electroless deposition of Cu on alumina, and on the other, to carry out characterization that can identify the quality of the deposited Cu.

To the best of our knowledge, there have been no previous reports of ED of Cu on polished $Al_2O_3$ 99.9% using wet treatment. This technique, after micro corrosion, allows nuclear (Sn + Pd) on 0.1% of vitreous material incorporated on the substrate surface and practically does not change the roughness of the treated surface. Considering the sub micrometric dimensions of the Cu grains, it favors the application of the film in high-density circuits with interconnection paths with a few microns lines.

## Experimental

Ninety nine point nine percent ADS polished alumina ceramic (CoorsTek, Golden, USA), with dimensions $25.4 \times 25.4 \times 0.6$ mm was used as substrate due to its excellent mechanical properties, low roughness (< 1 μm), excellent corrosion resistance and uniform density $(3.87$ g $cc^{-1})$.[32]

### Cleaning

Under magnetic agitation, samples were cleaned with $H_2SO_4$ (95-97% PA, Merck, Darmstadt, Germany) and nitric acid (62-70% ACS, JT Baker, New Jersey, USA) solution 19:1 (vol%), during 5 min at 60 °C to remove organic contamination and particles remaining from the fabrication polishing, followed by rinsed in circulation de-ionized (DI) water for 2 min and sonicated for 2 min.

### Coarsening

Particles on the alumina surface are activated by coarsening the micron sized $Al_2O_3$ particles into NaOH (PA-ACS, Dinâmica, Indaiatuba, Brazil) solution then, slowly placed on a heating hot plate and remaining for 10 min at 400 °C. In the sequence, it was immersed in $H_2SO_4$ solution at room temperature and washed with DI water.[33]

Coarsening not only improves the mechanical bonding of the metallic seeds with the substrate, but also improves the wetting of the seeding solution.[34]

## Nucleation

Several methods for surface activation are reported in the literature,[10,35-37] all based on solutions containing $Sn^{2+}$ and $Pd^{2+}$ species. The first bath is referred as the sensitizer stannous chloride solution ($SnCl_2$), while the second bath is referred as the activator palladium solution ($PdCl_2$). The result of the pretreatment sequence is the formation of finely divided palladium nuclei. The formation of the palladium nuclei is believed to be due to a redox reaction taking place between the adsorbed or absorbed stannous ions on the surface (formation of mechanical bonding) and the palladium ions in the activation solution.[36] The sensitization and activation step can be described by equation 1, as reported in the literature.[23,36-40]

$$Sn^{2+} + Pd^{2+} \rightarrow Sn^{4+} + Pd^0 \tag{1}$$

The composition of the sensitization and activation solutions is given in Table 1.

The process of nucleation occurs in only one face (polished). The other face (unpolished) of the pretreated alumina was wrapped after coarsening with insulating tape (3M, Sumaré, Brazil) to prevent sensitization and activation. The alumina substrate was seeded with palladium by being dipped successively in acid $SnCl_2$ solution followed by acid $PdCl_2$ solution at room temperature. Each dip lasted about 15 to 30 s and was followed by washing, using slowly immersion in distilled water for about 15 s between each dip.

After nucleation, the substrate showed a very light brown color and the tape was removed. After activation

step, an accelerating operation was performed by dipping the substrate in a 10% NaOH.[29] This solution gave the finest remaining particles, which were almost bare active nuclei.[20]

## Electroless

Electroless Cu deposition can be described by two reactions, which occur simultaneously on a catalytic surface, including oxidation reaction of a reducing agent and reducing reaction of Cu ions.[41]

The flow of electrons required for the oxidation-reduction reaction is provide by the species present in the solution.[10] The overall reaction of electroless Cu deposition can be described by the equation 2.[22,42,43]

$$Cu^{2+} + 2HCHO + 4OH^- \rightarrow Cu^0 + H_2\uparrow + 2H_2O + 2HCOO^- \tag{2}$$
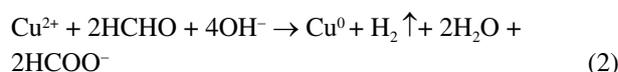
After surface treatment, a non-commercial autocatalytic solution of electroless Cu, similar to that reported by Iacovangelo[44] and Baumgartner,[45] was used (Table 2).

The deposition was performed at $30 \pm 1$ °C, pH adjusted using NaOH to a final value of 12.5 and with stirrer agitation. Under these conditions, the deposition rate is 50 nm min$^{-1}$. Finally, the substrate was rinsed with DI water and dried using gas nitrogen ($N_2$). Stabilizer and buffer were also added to the plating bath to increase the bath stability and to decrease the surface tension of the solution.

Figure 1 shows the scheme of electroless deposition of Cu onto alumina particles using the surface treatment and ED processes.

## Characterization

Surface wettability of the alumina before and after

**Table 1.** Composition of sensitization and activation solution

| Sensitization solution | | Activation solution | |
|---|---|---|---|
| Component | Concentration | Component | Concentration |
| $SnCl_2$ (ACS, Merck, Darmstadt, Germany) | 1 g L$^{-1}$ | $PdCl_2$ (ACS, Merck, Darmstadt, Germany) | 0.5 g L$^{-1}$ |
| HCl (37% ACS-ISO, Merck, Darmstadt, Germany) | 2 mL | HCl (37% ACS-ISO, Merck, Darmstadt, Germany) | 3 mL |

**Table 2.** Cu bath composition

| Compound | Function | Concentration / (g L$^{-1}$) |
|---|---|---|
| $CuSO_4.5H_2O$ (PA-ACS, Synth, Diadema, Brazil) | ion source | 8.0 |
| $NaKC_4H_4O_6.4H_2O$ (PA-ACS, Synth, Diadema, Brazil) | complexing agent | 32 |
| HCHO (37% PA, Synth, Diadema, Brazil) | reducing agent | 12 mL |
| $NaHCO_3$ (ACS, Synth, Diadema, Brazil) | buffer | 10 |
| KCN (PA, Merck, Darmstadt, Germany) | stabilizer | 0.02 |
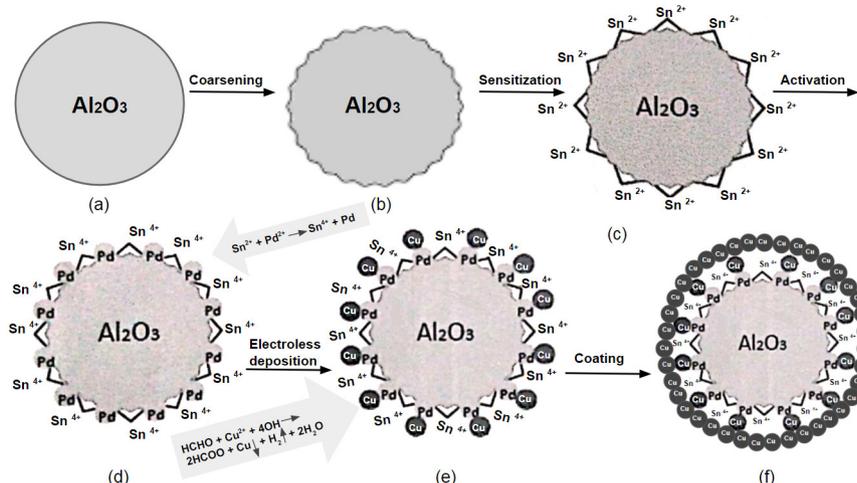
**Figure 1.** Schematic of Cu deposition on the surface alumina particles (adapted from reference 22).

coarsening was evaluated by a contact angle system model OCA 15 plus (Dataphysics Instruments GmbH, Filderstadt, Germany).

Atomic force microscopy (AFM) (Nanosurf FlexAFM model C3000, Liestal, Switzerland), scanning electron microscopy (SEM-FEG) model Mira 3 x MU from TESCAN (Brno, Czech Republic) used at 5 kV, SEM coupled with Bruker Quantax System energy dispersive spectroscopy (EDS) and profilometer DekTak XT (Bruker, Billerica, USA, scan 500 μm, velocity of 30 s) were used to characterize the Cu thin film.

## Results and Discussion

### Surface treatment

Seeds for deposition are necessary in the electroless plating of insulator. There are no metallic bonds between the ceramics and copper coating, but unstable mechanical combination. So, coarsening is carried out to increase the micro roughness of the surface and to obtain a hydrophilic substrate in order to acquire good adhesive coatings on the substrate.[46]

To have a qualitative assessment of whether there was a change in the behavior on the $Al_2O_3$ surface after coarsening, surface wettability was evaluated by a contact angle. Figure 2a showed that the surface of the polished alumina prior to the treatment was very hydrophobic, so the drop of water practically did not spread on the polished alumina surface, unlike the treated alumina surface (Figure 2b) which was quite hydrophilic and where the drop greatly spreads.

This behavior indicates that there was a morphological change on the alumina surface. This change was confirmed by the scanning electron microscopy (Figure 3).
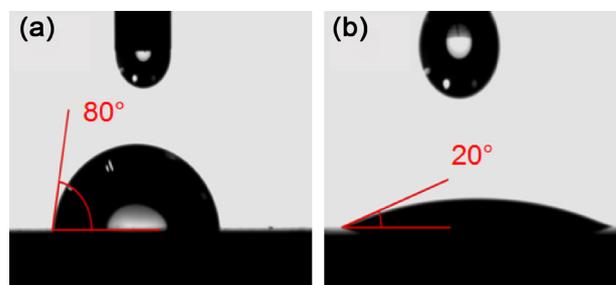


**Figure 2.** Contact angle images of (a) before treatment, (b) after treatment.
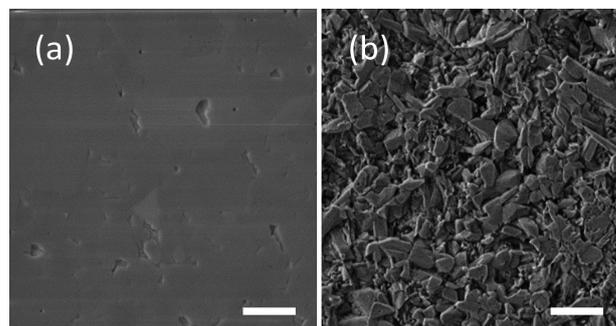


**Figure 3.** SEM images of polished alumina (a) before treatment and (b) after coarsening. Scale bar 2 μm.

Figure 3 shows the surface morphology of the untreated and pretreated polished alumina. The untreated alumina (Figure 3a) comprises uniform, fused $Al_2O_3$ particles with small defects near to 1 μm, which are probably due to the polishing performed in its production. Figure 3b shows the change that occurred after acid-basic coarsening, indicating an increase in roughness. According to Honma and Kanemitsu,[24] the glass phase of the alumina surface was dissolved by coarsening and polar groups were formed (equation 3):

$$Si–O^- Na + H^+ \rightarrow Si–OH + Na^+ \tag{3}$$

Thus, absorption of the catalyst increases the adhesion strength of metals using ED deposition processes.

Figure 4 shows the roughness measured by a profilometer DekTak XT in two points of the sample (P1 and P2). It is verified that the roughness before treatment (black and green lines) is about 25 nm on the polished alumina surface (99.9%). The roughness of the $Al_2O_3$ surface after the treatment (blue and red lines) is in the order of 50 nm. The roughness increase measured on the scan profile confirms the coarsening observed on SEM images on Figure 3 and proposed by Beygi *et al.*[22] (Figure 1). This increase in roughness (25 nm) is already enough to obtain a catalytic surface with the possibility of adhesion of the Cu to be deposited by the ED process.
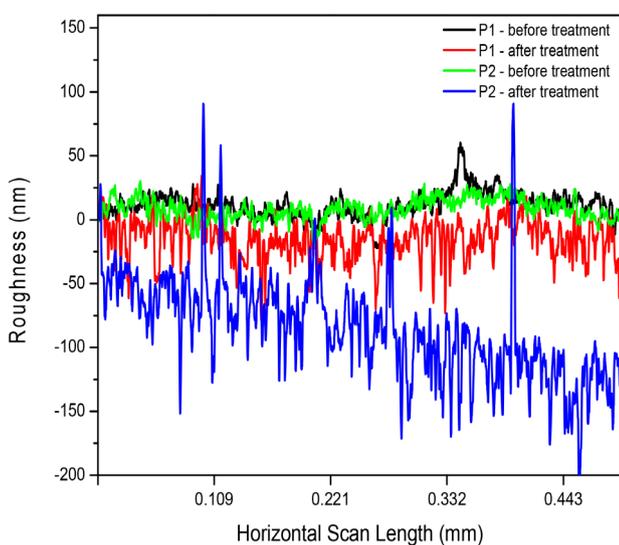


**Figure 4.** Roughness of untreated and treated polished alumina; P1 and P2 are two different areas on the same sample.

## Electroless copper deposition

Electroless deposition of Cu is very popular in printed circuit board (PCB) manufacturing and Cu plating application for features with critical dimensions in the range of 10 μm.[47] Moreover, this process offer several features such as (*i*) high selectivity; (*ii*) uniform thickness, particularly for objects with complex geometry; (*iii*) uniform physical and mechanical properties; (*iv*) high rate of deposition by tuning the solution composition, pH and temperature for commercial applications; (*v*) deposition on non-conducting surface, and (*vi*) very economic cost of tools and materials.[48]

To understand this process in detail, a few fundamental ideas need to be reviewed. Generally, for any electrochemical deposition process, coating bath plays a key role. In the case of ED, the coating bath consist of metal ions, a reducing agent, a complexing agent, a stabilizer and additives.[49]

The electromechanism of electroless plating is explained by two half reactions: an oxidation half reaction (anodic oxidation of the reducing agent) and a reduction half reaction (cathodic reduction of the metal ions).[50] These half reactions are characterized by redox oxidation or reductions reactions electrode potentials. The redox electrode potential related to the Gibbs free energy (ΔG) and the rate constant of the electrode (K) and these parameters are used to predict the electrochemical reaction tendency.[51] The catalytic activity of the Cu ion promoting oxidation of the reducing agent determines the reduction phenomenon of Cu on the substrate. The ligands developed from chemical reactions can act as accelerators for the deposition process. These complexes facilitate decreasing the reduction potential difference with reducing agents.[52]

Figures 5a and 5b, employed by SEM, showed homogeneous coating over the alumina substrate area with submicron particles of Cu deposited on a smooth rough surface forming a thin nanostructured film.

It can be said that one of the attributions for the Cu film to remain with low roughness and smaller particles is due to the temperature of the solution (30 °C) during the ED deposition of the Cu film.

The uniformity of the Cu film deposition can be better evaluated in Figure 5a, since the analyzed area is 10 μm, while in Figure 5b, the absence of holes and cracks is better observed because the analyzed area is ten times smaller.
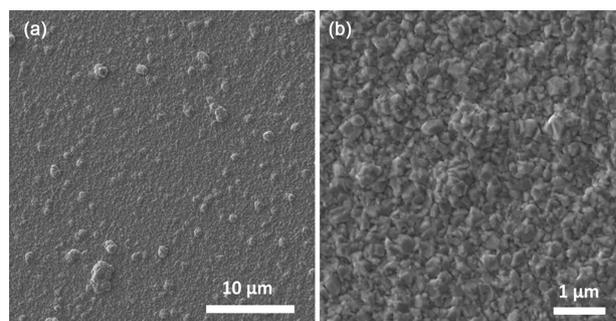


**Figure 5.** SEM images 2D of Cu morphology thin film plating $Al_2O_3$. Scale: (a) 10 μm and (b) 1 μm.

Figure 6a shows the image obtained by AFM of Cu thin film plating $Al_2O_3$ containing four-profile lines (Figure 6b) obtained through analysis by Gwyddion v 2.27 software.[53] The line profile analysis showed an average cluster size of approximately 1 μm. Furthermore, the average roughness (Ra) of 40 nm was also obtained over 10 × 10 μm area (Figure 6a).

Figure 7a shows the analysis obtained by energy dispersive spectroscopy (EDS) coupled with SEM for elemental mapping of Cu thin film plated (Figure 7b).
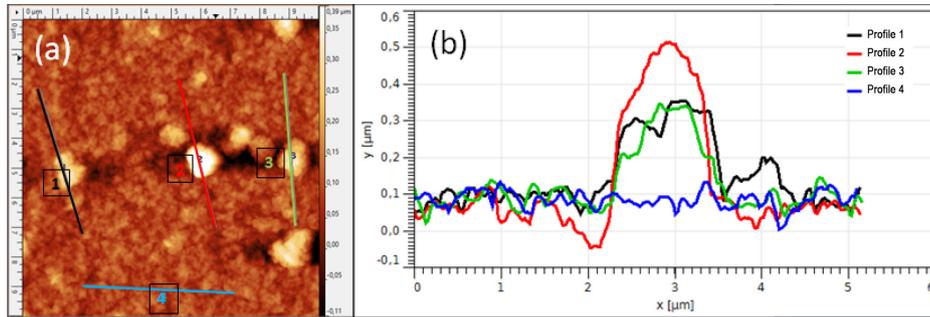
**Figure 6.** (a) AFM image of Cu plating $Al_2O_3$. (b) Line profile graphic showing the surface roughness over four different scans. Analysis obtained by Gwyddion free software.[53]

Through this analysis we observed the high purity (greater than 87%) of Cu thin film after the surface $Al_2O_3$ treatment. In addition, the percentages of Al and O come from the residual reading. On the other way, the percentage of C present in the Cu film (greater than 7%) suggested that during the electrochemical deposition, the chemical reducing agent (HCHO) released C that were incorporated into the Cu plated. As formaldehyde acts directly in the oxi-reduction reaction of copper, it is probably the source of carbon. Natividad *et al.*[10] performed X-ray photoelectron spectroscopy (XPS) analyses and suggested the presence of Pd-Cu alloys after the whole plating Cu process. However, Pd is harder to detect by EDS analyses in relation to the other elements.

Figure 8 shows the 3D surface roughness of alumina after coarsening and the Cu thin film deposited analyzed by atomic force microscopy (AFM). Figure 8a showed the top-view image of polished alumina after coarsening in a $5 \times 5$ μm area and Figure 8b after electroless Cu deposition in a $10 \times 10$ μm area. Figure 8b shows that de Cu coating is homogeneous and uniform. Figure 8c was taken in an area $2 \times 2$ μm and shows the absence of cracks and flaws after the Cu plating. The roughness observed on the $Al_2O_3$

surface after coated with Cu comes from coarsening. The AFM images of alumina after coarsening and electroless Cu deposited on the alumina at 30 ºC, alkaline pH and using HCHO as reducing agent, complement and confirm the results obtained by SEM-FEG and DekTak-XT equipment's.

## Conclusions

In this work, we proposed a surface treatment as low-cost alternative to other more expensive methods, such as chemical vapor deposition (CVD), physical vapor deposition (PVD), plasma spraying or electrodeposition, to obtain a good adherence with metallic film. The four stages treatment process permitted the development of a fully wet Cu deposition process and shows a good alternative to obtain a Cu thin film with low processing cost. The different stages of pretreatment and electroless deposition of Cu on polycrystalline alumina have been studied by means of SEM, EDS, AFM and DekTak XT equipment's and observed high uniformity, absence of holes, cracks and reduced surface roughness in alumina sample coated whit Cu film.
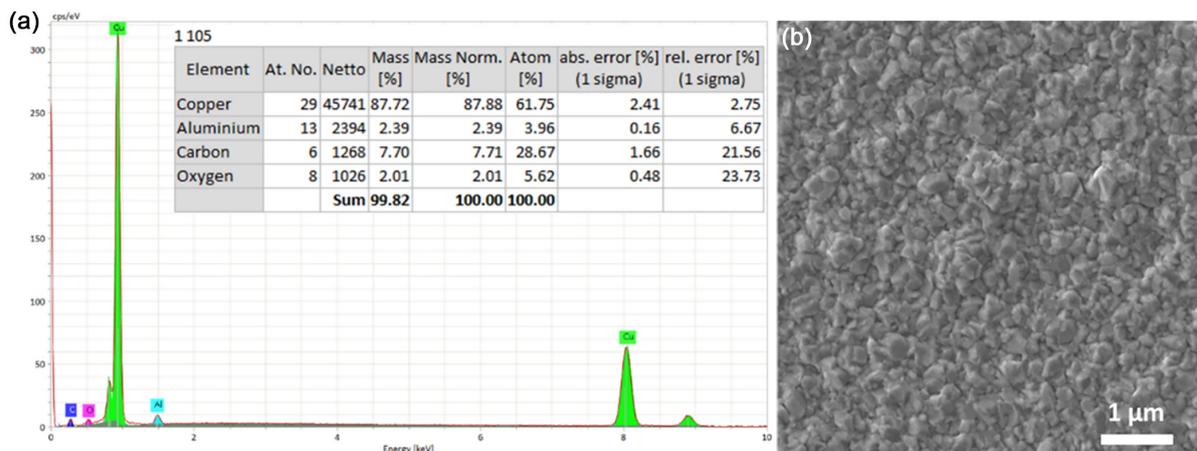


**Figure 7.** EDS elemental spectrum and quantification results of electroless Cu deposition over $Al_2O_3$ substrate (a), obtained by SEM image 2D of Cu morphology (b).

| Element | At. No. | Netto | Mass [%] | Mass Norm. [%] | Atom [%] | abs. error [%] (1 sigma) | rel. error [%] (1 sigma) |
|---------|---------|-------|----------|----------------|----------|--------------------------|--------------------------|
| Copper | 29 | 45741 | 87.72 | 87.88 | 61.75 | 2.41 | 2.75 |
| Aluminium | 13 | 2394 | 2.39 | 2.39 | 3.96 | 0.16 | 6.67 |
| Carbon | 6 | 1268 | 7.70 | 7.71 | 28.67 | 1.66 | 21.56 |
| Oxygen | 8 | 1026 | 2.01 | 2.01 | 5.62 | 0.48 | 23.73 |
| | | Sum | 99.82 | 100.00 | 100.00 | | |
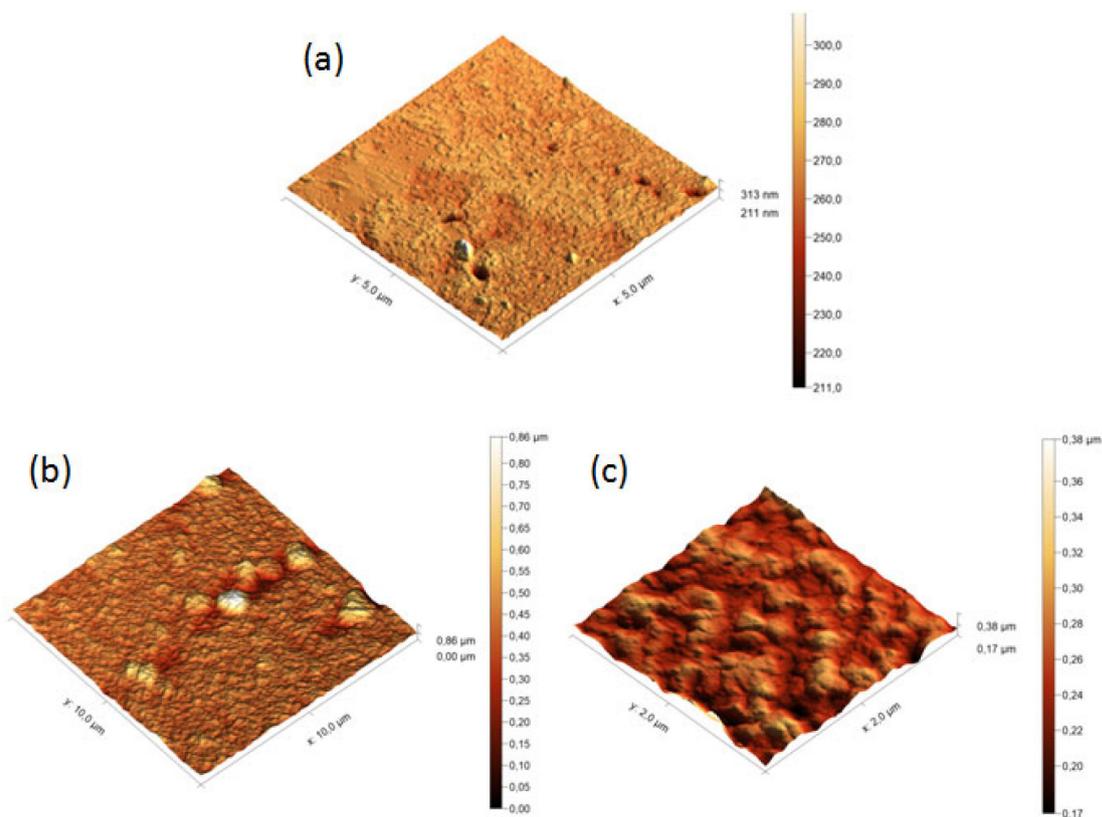
**Figure 8.** Images of 3D surface roughness of (a) alumina after coarsening in 5 × 5 μm area; (b) and (c) after Cu ED in a 10 × 10 and 2 × 2 μm area, respectively.

The surface treatment also showed a high performance in the Cu ED film at low temperature (30 ºC), obtaining more compact and uniform film, with small grain size and a high purity Cu metallic deposit. From the results obtained in this study, we can conclude that the sequence of metallization of high purity and polished $Al_2O_3$ substrate (99.9%) was established, based on autocatalytic (electroless) techniques of film deposition.

## Acknowledgments

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