The growth of Au/Pd on alumina/Cu-Al system

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Abstract. We have studied thin layered Au/Pd/alumina/Cu-Al system by means of synchrotron radiation photoelectron spectroscopy (SRPES), X-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED). Ordered 0.8 nm thick alumina film was prepared by the controlled oxidation of the single-crystalline Cu-9at.%Al(111) support. The Pd and Au layers were prepared afterwards by a step-by-step deposition at room temperature. LEED measurement itself did not confirm epitaxial growth of the metal overlayers. They exhibited a pseudo layer-by-layer growth mode confirmed by work function measurements and the Monte Carlo simulation of the copper XPS peaks attenuation.

1. Introduction
Ultra thin alumina layers are subject to a great number of studies nowadays. Alumina exhibits extraordinary mechanical, chemical, optical and electrical properties. Therefore, it is very popular in many fields of science and industry. The preparation of ultra-thin alumina film is mostly based on controlled oxidation of the metallic substrate containing aluminum [1-3]. Alumina thin films are very suitable for investigation by photoelectron spectroscopy and have superior electrical and chemical resistivity. Due to the low thickness, the film does not suffer from charging effects and it is a perfect candidate for model catalysts support [2,4,5].

Metal-insulator-metal (MIM) systems are widely studied in order to manufacture electron emitter device as well as for other usage in microelectronic industry. Suitable MIM structure should exhibit 2D growth of both insulator and metallic overlayer. The thickness of insulator layer has to be higher if compared to the case of model catalysts studies. Other demand is well-ordering of layers in order to decrease energy losses of tunneling electrons. There are many studies of ultra thin aluminum oxide layer prepared on NiAl(110) surface [6-9]. However, the thickness of this oxide film is not sufficient for using as an insulator in MIM structure due to the reduced band gap of alumina [5]. Moreover, Cu-9at.%Al(111) appears to be the promising substrate [10-12] because of its low misfit with respect to alumina lattice. This enables preparation of oxide layer with less defects and higher thickness (if compared to e.g. alumina layers on NiAl).

Palladium was chosen as a candidate for the top metallic layer in order to create 2D layer. Nearly layer-by-layer growth of palladium was reported on various aluminum oxide substrates using the deposition at room temperature [13-15]. On the other hand, palladium is known for its catalytic
properties and adsorption/dissociation of carbon monoxide [16,17]. Unlike the case of model catalyst studies, highly reactive material is unsuitable for the top layer of the MIM system used in microelectronics. Therefore we have chosen the gold as the topmost metal. The gold is widely used as a protective material due to its stability and inert behavior.

In our work we try to confirm the assumption of pseudo 2D growth of the topmost layer. Examination of work function together with valence band and core level spectra should bring the information on band bending or charge transfer between species.

2. Experimental

All measurements were performed at the Materials Science Beamline, Synchrotron Elettra in Trieste, Italy. Ultra high vacuum chamber has the background pressure of 1.10^8 Pa. The Cu-9at.%Al substrate from Surface Preparation Laboratory Inc. was cut and mechanically polished with accuracy better than 1° with respect to (111) surface plane. Cleaning of the sample was carried out by repeated subsequent Ar⁺ sputtering (1000 eV, 10 minutes, 15 µA/cm²) and heating at 770 K for 15 minutes. For the photoemission measurements, a hemispherical electron analyzer Phoibos 150 (Specs) and either Al anode of the X-ray source (1486.6 eV photons) or monochromatized synchrotron light (106 eV photons) were used giving the total resolution of 1 and 0.1 eV, respectively.

The sample was oxidized at the elevated temperature of 910 K in 8.10^-6 Pa of oxygen for 4.5 hours, which corresponds to an exposure of 1000 L. Palladium was deposited in 10 steps afterwards with LEED, XPS and SRPES measurements performed after each step. The deposition of Au was done in the similar step-wise manner afterwards. The deposition rates were 0.02 nm/min and 0.05 nm/min for Au and Pd, respectively.

3. Results and discussion

3.1. LEED measurement

After the cleaning of the sample, the surface exhibits typical (√3×√3)R30° reconstruction formed by segregated Al atoms after the heating procedure. The diffraction pattern was sharp and contrast, which suggests that the sample surface was clean and well-ordered. After the oxidation, the ultra-thin oxide layer exhibits (7√3×7√3)R30° reconstruction as was described previously [10,12]. The deposition of palladium gave only rise of a diffuse background and no additional diffraction spots were recognized in the pattern. After completing the Pd layer, the diffraction spots both from the substrate and the oxide layer disappeared entirely. After finishing the deposition of Au layer we observed very weak and broad diffraction spots forming a hexagonal pattern. Unfortunately, the pattern has a very intensive background and it is not suitable for the publication. This suggests that even if the Pd and Au layers are not completely well-ordered, there is some long-distance ordering present. Both palladium and gold exhibit fcc lattice and therefore we assume that metals are present in the form of partially ordered layer with the (111) plane parallel to the surface. The results of the work function (WF) measurement encouraged this assumption.

3.2. WF evaluation

The photoelectric WF measurements were performed using synchrotron radiation with primary beam energy of 106 eV. For the WF evaluation we have used the procedure described in [18] with the sample biased to -20 V to observe low energy electron cut-off. The value of WF measured on the clean substrate with (√3×√3)R30° reconstruction was approximately 4.8 eV. After the oxidation, the WF of the sample decreased rapidly. It can be explained by the formation of the dipole layer which decreases the effective WF to 4.2 eV. The results of the measurement during the metals’ depositions are shown in the Fig. 1. Together with the increasing thickness of the Pd layer, the value of the WF rises. The rise is up to the 5.5 eV, which is still below the value of the bulk Pd(111) (5.6 eV [19]). However, the value is still not saturated. By depositing small amount of the gold, the WF value increases but with the further
deposition it starts to decrease and stabilizes at the value close to the one of the Au(111) surface (5.31 eV [19]). The reason for the initial increase of the WF value can be the bimetallic interaction between both metals that is further discussed in the paper [20].

![Figure 1](image1.png)

**Figure 1.** The results of the photoelectric work function measurement during the metals’ depositions.

### 3.3. Growth mode

The palladium and gold growth mode is evaluated by using the XPS intensity of the Cu 2p<sub>3/2</sub> peak. For the determination of the layer growth we have used a simple monte carlo (MC) simulation. We tested the idea that the metallic layer grows in pseudo 2D manner, e.g. that the position of the deposited atoms on the surface is determined only by the random statistical distribution of the atoms and not by any other condition. This means, that the mobility of deposited atoms is so low that it does not influence the position of atoms and they remain at their initial position.

![Figure 2](image2.png)

**Figure 2.** Nominal layer thickness as a function of deposition time. Crosses represent experimental data, solid line shows the result of MC simulation.

The results of the simulation together with the experimental data are shown in the Fig. 2. For better visualization, the intensity of peaks is transformed by an equation for effective layer thickness:

\[ d = -d_{IMFP} \ln(I/I_0) \cos \theta \]

I stands for the XPS intensity of the Cu 2p<sub>3/2</sub> peak, I<sub>0</sub> is its initial intensity, d<sub>IMFP</sub> is the inelastic mean free path of the Cu 2p<sub>3/2</sub> electrons in the covering material (palladium or gold) and \( \theta \) is the electron
emission angle (20° in our case). It can be seen that the experimental data and our simulations are in good agreement, e.g. the effective layer thickness rises linearly. This encourages our assumption of the pseudo 2D growth. The decay of the XPS Cu 2p₃/₂ peak intensity is exponential. If compared to the Frank Van Der Merwe (or layer-by-layer) mode, the envelope of the decay is the same, but in our case we observed no breaks on the intensity curve caused by the completion of each layer.

Our previous results shows the growth of differently prepared Pd-Au system on alumina/Cu-Al system [21]. Palladium and gold were deposited in alternate manner in small steps to enhance their intermixing. Pd and Au form an alloy and the metallic layer grows in the Stranski-Krastanov growth mode. Contrary to it, in this work we deposited Pd on the completed Au layer. It can be seen how the order of the deposition steps can result in a different growth mode.

4. Conclusions
Ultra-thin alumina layer 0.8 nm thick was prepared on single crystalline Cu-9at.%Al(111) substrate. The WF value of the oxide is about by 0.6 eV lower that the one of the substrate. The growth of Pd and Au layers was studied afterwards. From the results of LEED measurement it can be concluded, that metallic overlayers grow in partly oriented manner with the (111) plane parallel to the surface. The results of the WF measurement encourage this conclusion as the WF value attenuates close to the value of Pd(111) and/or Au(111) surface. The layers grow in nearly layer-by-layer, or pseudo 2D growth mode, which was shown by comparison with the MC simulation.

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