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Application of imaging spectroscopic reflectometry for characterization of gold reduction from organometallic compound by means of plasma jet technology

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ABSTRACT

This work presents a new application of imaging spectroscopic reflectometry to determine a distribution of metallic gold in a layer of an organogold precursor which was treated by a plasma jet. Gold layers were prepared by spin coating from a solution of the precursor containing a small amount of polyvinylpyrrolidone on a microscopy glass, then they were vacuum dried. A difference between reflectivity of metallic gold and the precursor was utilized by imaging spectroscopic reflectometry to create a map of metallic gold distribution using a newly developed model of the studied sample. The basic principle of the imaging spectroscopic reflectometry is also shown together with the data acquisition principles. XPS measurements and microscopy observations were made to complete the imaging spectroscopic reflectometry results. It is proved that the imaging spectroscopic reflectometry represents a new method for quantitative evaluation of local reduction of metallic components from metaloorganic compounds.
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1. Introduction

The plasma treatment of noble metal precursors was most recently utilized for deposition of noble metal (including gold) layers by plasma-assisted Atomic Layer Deposition [1,2], but also as a method suitable for the synthesis of metal nanoparticles [3–6], or in the field of restoration and preservation of metal corrosion [7]. Those applications usually result in layers or surfaces non-uniform in their parameters along their area. If one of these parameters is reflectance, imaging spectroscopic reflectometry (ISR)[1] could be very suitable to quantitatively characterize this non-uniformity.

In this paper we present a brief description of ISR technique and as an illustration of its application potential we deal with a simple example of detection of area distribution of gold in its oxidation state Au^0 (metallic state). The results achieved by the ISR technique are verified by XPS analysis and optical microscopy observations. Three types of samples were prepared for the experimental comparison. The first sample is a reference sample of a gold layer prepared on a glass sheet by magnetron sputtering. The second sample, which was prepared by the spin-coating method, consists of a layer of the polymer and gold in the form of an organogold precursor. In this case, gold is in the oxidation state of Au^{+I}. The third sample was prepared by the same method as the second sample and it was exposed to the plasma discharge. The radiofrequency plasma jet [8] operated in flux of argon was used for reduction of gold cations within the gold precursor to metallic gold. ISR measurements were performed using an imaging spectroscopic reflectometer (ISRM) developed at The Institute of Physical Engineering at Brno University of Technology [9,10].

2. Experimental

2.1. Samples preparation

The organogold(I) precursor $LAu(PPh_3)$, where L is $[o\text{-}C_6H_4(CH{=}NC_6H_3iPr_2\text{-}2,6)]$ ($M = 723$ $g.mol^{-1}$) was synthesized by the reaction of parent organolithium derivative LLi with

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[1] Abbreviations: ISR – imaging spectroscopic reflectometry; ISRM – imaging spectroscopic reflectometer; VASE – variable angle of incidence spectroscopic ellipsometry; NNSR – near-normal incidence spectroscopic reflectometry.

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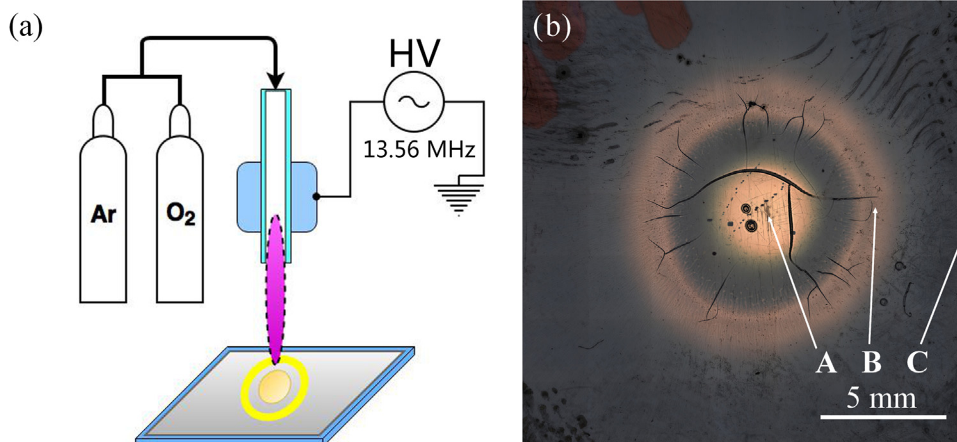

Fig. 1. Schematically set-up of plasma treatment (a) and a picture of treated surface (b) Letters show the regions of XPS analysis: A – center, B – ring, C – border. Picture (b) was taken by a confocal microscope.

[AuCl(PPh_3)] according to the literature [11]. 2.17 g of the precursor was dissolved in 5 ml of CH_2Cl_2 (Sigma Aldrich) containing a small amount of polyvinylpyrrolidone (0.8 g, K40, Sigma Aldrich) to give solution with c = 0.6 M. The Au layers were prepared by spin coating of as-prepared solution (1 ml per sample) on a microscopy glass using SpinMaster spin coater (Chemat Technology, Inc.) using sequence of two steps – 500 rpm for 1 s, 10 000 rpm for 30 s. After spin-coating, the layers were vacuum dried at 125 °C using vacuum oven at pressure of 1 mBar. The thickness of the as-dried layers was approximately 6 μm (measured by profilometer Dexta XT, Bruker Corp.).

2.2. Plasma treatment

The scheme of set-up used for the plasma treatment of organogold layers in this work is shown in Fig. 1(a). An atmospheric plasma jet driven by 13.56 MHz at 180 W was selected as a plasma source [8]. The powered electrode was separated from the plasma by a silica tube with inner diameter of 2 mm and the discharge is ignited in argon (flow rate 5 slm) and admixture of oxygen (flow rate 0.2 slm) flowing through the tube. Distance between the sample and the end of silica tube was set to 15 mm and the treatment time at 30 s. In the next step, the sample surface was imaged by a confocal microscope Olympus LEXT 4000. In Fig. 1(b) there are clearly visible three different areas, out of which two show a metallic gold appearance. The first area (marked by letter "A") was represented by a circle, and it is an area that appeared directly within the axis of the plasma jet. The second area (marked as "B") was represented by a ring in a distance 3–5 mm from the center of the circle. The third area (marked as "C") was outside the first two areas and it is the farthest area from the intact area of the plasma jet. These areas were then analyzed using an XPS. The ISR measurement was executed in such an area so it will accommodate the three areas.

2.3. Imaging spectroscopic reflectometry

ISR developed at aforementioned institute [9,10,12,13] has been mainly used to evaluate local optical parameters (local thickness, spectral dependences of local refractive index and local extinction coefficient) of non-uniform thin films. In certain cases ISR can be used as a standalone technique, but generally it is worthwhile to combine it with conventional (non-imaging) ellipsometric and spectrophotometric techniques (e.g. variable angle of incidence spectroscopic ellipsometry (VASE) and near-normal incidence spectroscopic reflectometry (NNSR)). Using an appropriate dispersion model of optical constants and structural model of a thin film under study the aforementioned combination of techniques can provide (in principle) maps of further interesting thin film parameters like the band gap, maximum energy limit of the transition of electrons interacting with photons and concentration of electrons taking part in the relevant transition [14,15]. In some cases it is possible to determine also a map of thin film boundary roughness [16]. The utilization of ISR, VASE and NNSR combination was shown also promising in the complicated case [17] when the studied film exhibits an inhomogeneity in refractive index along the direction normal to boundaries of the film. The technique of ISR has been used and verified in many cases for optical characterization of thin films [13,15,16,18–20]. Other approaches to ISR technique, different from the approach presented in this paper, were developed by other groups using different concepts: either combination of imaging and a scanning probe in white light [21,22] or a microscope like device focused on a very high spatial resolution to evaluate electronic devices [23]. Possibilities and limitations of ISR in optical characterization of thin films are transparently presented in the paper [24].

2.3.1. Imaging spectroscopic reflectometer

The set-up of the ISRM we used is presented in Fig. 2:

A source of light for the ISRM is a XeUV broad light spectra arc lamp. Single wavelengths are selected from the spectra by the computer-controlled monochromator. The lamp, the monochromator and the ISRM itself are connected by two identical UV capable optical fibers. The off axis parabolic mirror C with the optical fiber output situated at the focal point of the mirror creates a collimated monochromatic light beam which illuminates (by reflection on the beamsplitter BS_1) perpendicularly a sample in the sample holder SH (it can be assumed that the angle of incidence along the whole sample surface is identical). The sample reflects the light directly back. The reflected light goes through the system of four fused silica wedges BS_1–BS_4 (BS_1 is the aforementioned beamsplitter and it has a beam splitting layer) to a simple spherical mirror IM. This mirror then creates an image of the sample surface on a chip of the CCD camera which records the image. The four-wedge system corrects optical dispersion and removes secondary reflections of the beamsplitter BS_1. The wedge BS_4 also has a beam splitting layer. This wedge allows in axis imaging. The large collimating mirror C ensures good uniformity of the light beam along its cross-section and it also allows utilization of a small part of the measuring camera chip as a reference channel (further called the 2nd channel) of

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