Detection of organic vapors on sputtered and annealed thin Au films

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Abstract. Unique optical properties of metal nanostructures enable construction of new types of chemical sensors. Nanostructures composed of Au on glass substrate were prepared by annealing of 2-20 nm thick sputtered Au films at 300 °C for 1 h. The annealing leads to transformation of the as sputtered continuous Au layers to a nanoisland structure. The forming nanostructure shows a strong, well defined surface plasmon resonance absorption band in UV-Vis spectrum, which is useful for construction of a chemical sensor. The samples were used to detect vapors of acetone and water in an experimental testing apparatus. The achieved signal-to-noise ratio was 583 and 386 for acetone and water vapors, respectively on the nanostructure prepared from 4 nm thick Au layer. The nanostructured sensitive layers, however, showed poor signal stability; therefore a polymer overlayer was introduced to protect it. The employed polystyrene film prepared by spin-coating improved sensitivity and selectivity of the sensor, while the dynamic properties of the sensing influenced only slightly.

1. Introduction

Metal nanostructures are recently a highly sought after material thanks to their unique properties. Decreasing the dimensions of structure of a material to nanoscale level leads to changes of its properties. A nanomaterial then possesses different properties than a bulk material of the same chemical composition. This phenomenon is caused by effects of two categories – the surface effects and the quantum-size effects. Surface effects are related to increasing ratio of surface atoms in the material with decreasing particle size. The surface atoms have generally higher energy than those in a bulk of a material, are bonded more weakly to the material and are usually more reactive [1]. In sensor technology, the increasing surface to volume ratio with decreasing particle size is also desirable because of bigger area of interaction of the material with the analyte. The quantum-size effects originate in changes of the electron energy levels is the nanomaterial. As the particle size decreases the density of electron states decreases, which leads to disruption of the energy band structure of the material [2]. A manifestation of this in the case of metal nanostructures is evolution of surface plasmon resonance (SPR) absorption band in their optical absorption spectrum [3].

Thanks to their electromagnetic nature, the plasmon states are dependent on the optical parameters of the environment, which has been used in construction of sensor devices. SPR sensors are employed to detect molecular interactions on a surface of a continuous metal layer. The most significant application of these sensors is in biosensing and analysis of interactions of biomolecules bound to the metal surface [4]. A certain disadvantage of the method is its dependence on a specific transducing medium and an optical aperture to introduce the analytical beam into the metal layer. For a more
general use as a chemical sensor, localized SPR (LSPR) sensors seem to be more practical. The LSPR sensors exploit metal nanostructures to make use of non-propagating – localized – surface plasmons [5]. Thanks to the nature of the nanostructure, there is no need for the optical aperture and transducing medium [6].

The usual methods to achieve a metal nanostructure on solid substrate include either some sort of lithographical process on a continuous layer or anchoring of pre-prepared metal nanoparticles [7,8]. A simple method to transform a continuous metal layer to a nanostructure is solid-state dewetting, which utilizes a configuration, where the interfacial energy between the metal and the substrate is high. With usual physical vapor deposition methods the film growth speed is quite high and the metal atoms are not able to migrate over the surface to occupy the lowest energy positions. As such, the as deposited metal film is usually continuous, but metastable and its annealing leads to its transformation to a configuration with lower total surface energy [9]. In case of noble metals on glass substrate the interfacial energy is high and the lowest energy configuration according to the Young equation is where the metal and the glass are in as low contact as possible. Therefore, with annealing of such structure at sufficient temperatures, where surface diffusion is enabled, the morphology of the metal layer transforms from continuous coverage to a structure of isolated islands [10,11].

In this work, we employed the method of solid-state dewetting to prepare nanostructures of Au on glass substrate from thin Au films produced by cathode sputtering. The successful formation of nanostructures was monitored by atomic force microscopy (AFM). UV-Vis spectroscopy was used to observe the appearance of SPR absorption bands necessary for the samples to be used as sensitive layers for chemical detection. The samples of the Au nanostructures were then tested for their sensitivity to presence of vapors of acetone and water in an experimental sensor testing apparatus.

2. Materials and Methods

2.1. Sample preparation methods
Au films of thickness 2-20 nm were prepared by cathode sputtering from Au target of 99.95 % purity (Safina) on SCD 050 sputter coater (BalTec) at 20 mA for 10-100 s on 18×18 mm² borosilicate glass substrates of 0.13-0.16 mm thickness (Menzel-Gläser) rinsed in methanol and dried in a stream of nitrogen gas before the deposition process. The pre-deposition vacuum was 2 Pa, the deposition was carried out at Ar work gas pressure of 5 Pa (99.99 % purity, SIAD Czech). The Au films were subsequently annealed at 300 °C for 1 h in FED 23 oven (Binder) and cooled in air to room temperature. Polystyrene (PS) overlayer of 200 nm nominal thickness was prepared by spin-coating method from a 5 % solution in toluene (PS powder supplied by Goodfellow) at 2000 rpm. A reflective ca 100 nm thick Ag mirror was prepared on the backside of the samples for the gas sensing studies by cathode sputtering at 40 mA for 200 s on the SCD 050 device.
2.2. Methods of analysis

Optical properties of the nanostructured Au samples were studied by UV-Vis spectroscopy on Lambda 25 spectrophotometer (Perkin-Elmer) in 10×10 mm$^2$ area. The optical absorption was measured in 300-800 nm spectral range at 240 nm·min$^{-1}$ scanning rate and 1 nm data collection interval with halogen (350-800 nm) and deuterium (300-350 nm) lamps. The absorption of the glass substrate was subtracted from the spectra of the samples.

Surface structure was observed by AFM on Digital Instruments CPII microscope (Bruker). Silicon P-doped probes RTESPA-CP with spring constant of 20-80 N·m$^{-1}$ were used in tapping mode. Area of 2.4×2.4 μm$^2$ was scanned at 512×512 px resolution. The obtained morphological scans were used for arithmetic average surface roughness ($R_a$) calculation.

![AFM images](image.png)

**Figure 2.** AFM images of as deposited (RT) and annealed (300 °C) Au layers 2-20 nm thick, values of average surface roughness ($R_a$) in nm are provided.

The prepared Au nanostructures were tested for their optical response to introduction of vapors of acetone, water, ethanol and toluene in an experimental apparatus (Fig. 1). The gas circuit of the apparatus was designed to push dry air (80:20 mixture of N$_2$ and O$_2$) from the air supply with aquarium pump at the rate of 35 ml·min$^{-1}$ alternately directly through the sample chamber and through a bubbler with the analyte and the sample chamber using computer controlled valves. The flow of the gas was controlled in each part of the apparatus with adjustable flowmeters FLDA3428ST (Omega Engineering). The optical system was designed to guide light beam with optic fibers from the halogen lamp of DH-2000 source (Ocean Optics) to the sensitive layer placed in the sample chamber, where it reflected from the backside Ag mirror and to the RedTide USB650 (Ocean Optics) detector, which analyzed the modified emission spectrum of the light source in real time. The regulatory valves were controlled by PC with control software self-designed in LabView environment and the system was set...
to change the atmosphere from air to the analyte and vice versa every 10 min. The system was
designed for the spectra evaluation as well. Signal was obtained as the area under the detected light
intensity spectrum in the wavelength range of 475-575 nm, where the SPR peak of the Au
nanostructures is located and where the greatest variation of the signal with introduced analyte was
identified. The analytes employed in this study were acetone and water.

3. Results and Discussion

Morphology of the thin Au films as observed by AFM is in Fig. 2. Surface roughness of the as
deposited films increases with increasing film thickness, but the surface still remains relatively smooth
and the Au layers are continuous. Annealing leads to a dramatic change of the surface structure. Due
to the high interfacial energy between glass and the Au and the metastable nature of the as deposited
Au films, the continuous Au coverage transforms into an island-like structure (this process is called
“solid state dewetting”). This structural transformation is more apparent in the case of the thicker
layers since a more homogeneous Au layer is formed during the deposition. The surface roughness
increases significantly and as the isolated Au islands are formed the underlying glass substrate gets
exposed in certain areas.

![Figure 3. UV-Vis spectra of as deposited (RT) and annealed (300 °C) Au layers 2-20 nm thick.](image)

The structural transformation of the Au layer has a great impact on the optical properties of the
samples as well (Fig. 3). The as deposited layers show UV-Vis spectra characteristic for bulk Au with
absorption minimum close to 525 nm, where the gap between plasmonic and interband transition
absorption lies. Only in the case of the thinnest studied layers a somewhat defined SPR peak forms.
With increasing thickness of the film, the values of absorption generally increase as the analytical
beam passes through more material. With annealing the values of absorption generally decrease,
because of the decreased effective coverage of the substrate in case of the isolated Au islands. The
character of the spectra changes dramatically as well. A well-defined SPR peak forms, which confirms
the formation of nanostructures. Maximum of the SPR peak lies at ca 530 nm in the case of the thinner
films and shifts towards higher wavelengths with increasing film thickness as a result of the increasing
size of the Au nanostructures. The well-defined nanostructure with strong SPR absorption bands is a
vital requirement for utilization of the Au nanostructures as sensitive layers for chemical sensors since
the absorption of the SPR band is highly sensitive on variation of refractive index of the medium
surrounding the nanostructure.

Figure 4. Sensorgrams of response of 2-8 nm thick Au nanostructures to acetone vapors.

Figure 5. Sensorgram of response of 4 nm thick Au nanostructure with PS overlayer to acetone vapors.

The results of the sensitivity tests of the Au nanostructures against acetone vapors are in Fig. 4. Nanostructures prepared by annealing from films of various thicknesses were tested. The comparison of the sensitivities of the different thicknesses showed the highest sensitivity for the samples with the 4 nm thick Au layer. As the refractive index of the medium around the sensitive layer increases with introduction of the acetone vapors, the signal on the optical detector decreases, because the absorption of the SPR band of the sensitive layer is higher. The sensitivity towards the acetone vapors expressed as signal-to-noise ratio (SNR) reached the value of SNR(acetone) = 583. In case of the water vapors
the sensitivity was somewhat lower at SNR(water) = 386. The response of the sensor is quite slow, after 10 min of analyte exposure the signal values still seem to be quite far from the minimal value. On the other hand, the regeneration of the layer after re-introduction of air is quicker and the signal reaches plateau within the 10 min set in the valve program. The dynamic properties of the sensor could be improved by increasing the temperature. The measurements were carried out at standard laboratory conditions, in case of an elevated temperature the sorption/desorption process of the analyte would be accelerated. The value of the signal in the sensorgram seems to be decreasing with ongoing measurement cycles. This is a problem since the layer is probably degraded during the detection process.

To improve the durability and time stability the thin Au films were covered by a PS overlayer. The overlayer changes the optical properties of the structure, naturally. The sensorgram for acetone vapor detection on this sample is in Fig. 5. Due to the PS having higher refractive index than air and the analyte absorption effectively decreasing it, the introduction of the analyte in this case leads to increase of the value of the signal on the optical detector. The sensorgram clearly shows the stability of the sensitive layer during the sensing process increases considerably with the dynamic characteristics not being influenced too much. The PS layer even leads to increased sensitivity at SNR(PS, acetone) = 706. The polymer overlayer could be as well used to improve selectivity of the sensor as it modifies affinity of the sensor surface to various analytes.

4. Conclusions
Nanostructures of Au on glass substrate were prepared by solid-state dewetting of sputtered thin films. The post-deposition annealing leads to formation of well-defined structure of Au nanoislands, which shows strong SPR absorption bands in UV-Vis spectrum. That is a good presumption to use the structures as sensitive layers in chemical sensors. In an experimental apparatus the samples showed sensitivity towards presence of acetone and water vapors. From testing different sizes of the Au nanostructures the samples prepared from 4 nm thick Au films appeared to be the most sensitive to presence of the vapors. The achieved SNR was 583 and 386 for acetone and water vapors, respectively. Furthermore, we used a PS overlayer, which seemed to improve sensitivity and stability of the Au layers, with mostly indistinguishable impact on dynamic parameters. The polymer overlayer could be also used to improve selectivity of the sensor. In future, we would like to build on the achieved results and test the samples against more analytes and use various overlayer polymers.

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