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Chemiresistor sensors based on gold nanoparticle composites

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Abstract

On a silicon wafer equipped with interdigital electrodes, gold nanoparticles with an average size of 5 nm are assembled in a thin film using different organic linkers, either manually by layer-by-layer spin coating or automatically by layer-by-layer self-assembly in a microfluidic cell. The composition of the films is analyzed by X-ray photoelectron spectroscopy (XPS). The electrical and chemiresistive sorption properties of toluene, 1-propanol, 4-methyl-2-pentanone and water in the organic/nanoparticles composites are investigated.

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1. Introduction

During the past decades, gold nanoparticles become one of the most relevant topics for scientists [1]. Gold nanoparticles have attracted such considerable interest due to their potential applications in catalysis, bio-labeling, and photonics. Their size, size distribution, and morphology control become the key to the understanding of the optical and surface properties [2, 3]. Due to their unique optoelectronic properties, high surface-to-volume ratio and excellent biocompatibility, gold nanoparticles allow researchers to develop the novel sensing strategies with improved sensitivity, stability and selectivity [4]. According to their tiny sizes (up to 100 nm), new types of nanosensors, which allow detecting of extremely small concentrations of analytes (few parts per billion), have been developed. Several research groups have demonstrated that these films can be used for numerous applications, such as vapor or gas sensors [5-10]. From the other hand, gold nanoparticles are also very suitable for selective coatings

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for strain gauges [11, 12], electrochemical sensors [13, 14], and substrates for surface enhanced Raman scattering (SERS) [15].

In this work, we report on the assembly, the material conductivity, the chemical composition, and the vapor response of the nanoparticle networks interlinked with aromatic, conductive organic molecules. For the films manufacturing, two methods were implemented: manual layer-by-layer preparation with a spin coater and automatic layer-by-layer self-assembly in a microfluidic cell. Additionally, systematic investigations how the molecular structure and composition of oligophenyldithiol-interlinked films depend on the nature of the linker molecule and method of film preparation are performed.

2. Materials and samples preparation

Chemicals were purchased from Sigma Aldrich, Merck, VWR, Technic France, and Honeywell and used as received. 1,4-Benzenedithiol, 1,4-Benzenedimethanethiol, Bipheryl-4,4’-dithiol, and p-Terphenyl-4,4’-dithiol linkers were used as the organic linker molecules (0.5 mmol/L in toluene). For the substrates surface functionalization, 3-Mercaptopropyltriethoxysilane (MPTES) and Aminopropyldimethyl-ethoxysilane (APDMES) were used as silanization agents. The gold nanoparticles (AuNP) were synthesized, as was described by Peng [16], at 20°C. A silicon wafer with a defined thickness of 625±15 μm, obtained through Siltronic AG, was cut to the small pieces with an edge length ca. 15 mm and used as substrates for all measurements. For the sensing measurements, the substrates were equipped with gold finger-electrodes (52 finger pairs, 50 μm width and 5.2 mm length, 100μm gap).

The method of manual preparation of the samples was proposed by Schlicke et al. [17] and used in a modified way, as reported in [18]. The method of automatic layer-by-layer self-assembling was previously described by D. Bethell and co-workers [19]. Firstly, the silicon substrates were cleaned with DI-water and isopropanol and left in the linker solution over the night. Prior to the films deposition, the substrates surfaces were functionalized via gas phase silanisation. Then the substrates were placed to the microfluidic cell, treated for 5 minutes with nanoparticles solution, then washed for 4 minutes with toluene, treated for 5 minutes with linker solution again, and once more washed with toluene (1 deposition cycle). These steps were repeated 15 times. Afterwards, the films were washed with toluene and drying with air for 10 minutes respectively. After the preparation, all samples were placed in a desiccator under argon atmosphere.

3. Results and discussions

3.1 X-Ray Photoelectron Spectroscopy (XPS)

The composition of all films was studied with XPS. Au, C and S were found. During the layer-by-layer preparation of the films, the stabilizing molecules (dodecylamine) of the nanoparticles were completely exchanged by the interlinking molecules. That was indicated by an absence of a peak from nitrogen. As shown in Fig. 1, the number of free thiols in the samples interlinked with 1,4-Benzenedithiol, 1,4-Benzenedimethanethiol, Bipheryl-4,4’-dithiol, and p-Terphenyl-4,4’-dithiol remains higher than the sulphur-to-gold bonds. In the other words, most of the dithiols are bounded only with one end to the gold nanoparticle or are intercalated in the organic matrix instead of being covalent attached to the nanoparticles. The reason for that might be comparative small length of linker molecules and wide distribution of gold nanoparticles. For the sample interlinked with 1,4-Benzenedimethanethiol, the number of free thiols is smaller than sulphur-gold bonds, because of the presence of the aliphatic group in the linker, which makes interlinkage more flexible. In the case of preparation with the microfluidic cell, no oxidation peaks were found, and the level of interlinkage in samples was higher. Thus the automated layer-by-layer preparation with the microfluidic cell is favoured over the manually spin coating process.

3.2 Sensing Properties

The sorption of toluene, 1-propanol, 4-methyl-2-pentanone, and water in the organic molecules-nanoparticles composites was investigated by coating the material on substrates equipped with interdigitated electrodes. The similar vapor pressure of solvents makes them very suitable for studying the chemical selectivity of the sensor materials [4]. For all analytes, concentration dependent measurements of the mass in the range 100 – 5000 ppm were performed. The response traces toward 5000 ppm of the analytes are given in Fig. 2.
Fig. 1. S2p spectra. The degree of interlinkage, represented by the S-Au/S-H ratio is indicated.

Fig. 2. Sensor responses. Concentration 5000 ppm. Preparation with microfluidic cell.
The low level of interlinkage and corresponding high sorption capacity cause relatively high sensitivity of the samples prepared by level-by-level self-assembly. Increasing of resistance during the experiments i.e. positive electrical signal is connected with phenomena of film’s swelling. Decreasing of resistance in the samples 2-4 during the experiments i.e. negative electrical signal can be explained by phenomena of pore filling. With growing of the linker length, an increase in the pore filling effect is observed, while swelling became minor. The selectivity of the analytes uptake of the films is comparable for all materials, as expected due to the similar chemistry of the linker molecules.

In the case of the samples prepared with spin coater, the responses are smaller, slower and not fully reversible. This may be due to the oxidized nature of the film or the enhanced swelling probability due to a lower degree of interlinkage.

4. Conclusions

The possibility of fast response, reversibility and the high sensitivity to volatile organic compounds (VOCs) make noble metal nanoparticle composite films promising materials for sensor applications.

Concerning the fabrication the automated layer-by-layer preparation with the microfluidic cell is favoured over the manually spin coating process.

References