Polymer-metal nanocomposites with 2-dimensional Au nanoparticle arrays for sensoric applications

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Abstract. Sensors for volatile organic compounds (VOC) are of increasing interest for various applications ever since. Here we present a novel method to achieve a fast and reversible response by employing a polymer-metal nanocomposite film with 2-dimensional Au nanoparticle arrays. Our sensors are made out of spin-coated polymer substrates on which we deposit gold clusters with a cluster density near the percolation threshold via thermal evaporation. The sensor operates on the principle of swelling of polymers in the presence of VOC. This leads to a change in the interparticle distance and therefore the conductivity of the composites. The method is fast, easy, precisely to control and the sensor fabrication process produces only a minimum amount of waste (like organic solvents). The degree of swelling primarily depends on the type of polymer and the organic solvent, i.e. solubility parameters of the polymer and the vapor. Therefore, the pattern leads to fingerprints of particular polymers towards different vapors. These fingerprints can be employed as a parameter for detecting different VOCs.

1. Introduction

The use of conducting particles in insulating matrix materials is a well-known basis for chemiresistor vapor sensors. During the last years a number of investigations have been done on nanoparticle-based materials due to their unique properties and potential applications also as chemical sensors. Nanocomposites with dispersed conducting carbon nanoparticles or carbon nanotubes in insulating polymer matrix have been reported for vapor sensors [1],[2]. On the other hand diverse monolayer-protected gold nanoparticles (MPN) were also synthesized and characterized for use as a sorptive layers on chemical sensors [3],[4]. In these materials electron travel progresses from particle to particle, and current can be modulated by the sorption of vapor molecules in the non conducting matrix. Main emphasis was thereby put either on wet chemical approaches with complex organic molecules or on a mixture of inorganic materials (ceramics, carbon black or CNT) with metal particles. In presence of VOC, the flexible network on linked nanoparticles allows a swelling-induced alteration in either length or chemical nature of electron tunneling pathways.

Here, the difference to above described approaches is that we do not use a wet chemical process in order to incorporate metal nanoparticles in the polymer. Our approach is based on the formation of Au nanoparticles on different polymer surfaces by vapor phase deposition of metal atoms. Noble metals exhibit a strong aggregation tendency during deposition on polymers due to the facts that the cohesive
energy of metals is typically two orders of magnitude higher than that of polymers, and that the interaction between moderately reactive metals and polymers is generally very weak in comparison to the strong metal-metal binding forces [5]. For these reasons metals of low reactivity like gold do not wet untreated polymer surfaces and form randomly distributed nanoparticles during vacuum deposition. To avoid various sources of inhomogeneities in particle growth, an Ar\textsuperscript{+} ion treatment of the polymer surface was performed with a low ion dose prior to evaporation. Such a treatment of a polymer surface creates a defined number of surface adsorption sites (nucleation centers). This procedure allows the synthesis of two-dimensional nanoparticle arrays with a well-controlled surface density also near percolation threshold [6].

By using our approach it is possible to monitor the existing organic vapors and their corresponding concentrations by the change of the electrical properties of the material. The properties of this new material system, as indicated by the first results which will be published here, might be promising for future applications in the field of organic vapor sensors.

2. Experimental

Polymer films of thicknesses between 90 and 350 nm were prepared via spin coating on top of glass slides. The polymers of choice thereby were Polymethylmethacrylate (PMMA) with a molecular weight of 20000 g/mol and Polystyrene (PS) with a molecular weight of 21400 g/mol. After the complete removal of the solvent from the film, Au-Pd-contacts of a thickness of 200 nm were sputtered on top of the polymer film. The distance between the contact lines was 0.3 mm and the length of the lines were 10 mm. The 2-dimensional Au nanoparticle arrays were prepared via thermal evaporation of gold atoms on the polymer surface in a vacuum chamber as described elsewhere [6]. During the deposition, the Au built up a regular pattern of nanoclusters on top of the polymer and hence between the contact lines. The morphology of the films was verified by TEM – measurements, for which PMMA and PS films of around 30 nm thickness were deposited on top of copper grids especially made for TEM-measurements. In order to achieve this regular pattern, the polymer was treated beforehand by a bombardment of Ar\textsuperscript{+}-ions which created a controlled pattern of surface adsorption sites on top of the polymer at which the Au clusters could grow much easier than in the surrounding. The conductance of the sample, which increased abruptly at the percolation threshold during the Au deposition, was monitored \textit{in situ} by using a picoampere meter (Keithley Model 6485). This procedure is important to prepare the samples with Au nanoparticles arrays closed to percolation threshold with a resistance ~ 10 M\textOmega.

A vapor response measurement was carried out in a vacuum chamber with a base pressure of 0.01 mbar. The sample was exposed to the organic solvent vapours at different partial pressures. The pressure of the test vapours was controlled by the temperature of a liquid solvent source, which provided the vapours by thermodynamic equilibrium of the vapour phase with the liquid phase of the solvent. The solvent temperature was kept at all times lower than the temperature of the substrate and the chamber to avoid the formation of liquid solvent on the surfaces. The electrical response of the sensor setup was measured in situ as described above. Acetone, isopropanol, ethanol and toluene were used as test vapors for our system with partial pressures ranging between 0.28 and 70 mbar. The sensor operates on the principle of swelling of polymers in the presence of VOC. This leads to a change in the interparticle distance and therefore the conductivity of the composites which was measured as function of the VOCs partial pressure. This pressure was controlled by a compact capacitance gauge from Pfeiffer Vacuum.

3. Discussion

During the deposition of gold on the polymer the resistance drops over several orders of magnitude within a region of only 0.2 nm of the nominal film thickness. This is shown in figure 1 in combination with the microstructure of the composites displayed by a TEM micrograph. The top view picture shows spherical metal clusters near to the percolation threshold. As indicated by the arrow in the
figure, this morphology give rise to a resistance of roughly 12 MΩ which turned out to be the position with the highest sensitivity for the sensoric applications.

The conduction mechanism between the metal clusters is electron hopping. This is supported by the observed Arrhenius behavior of the temperature dependence in conductivity in the range from 20-100 °C, which was calculated from the experimental data plotted in figure 2. The data shown in this figure corresponds to the TEM picture shown in figure 1 for a nominal gold thickness of 1.3 nm. This figure has two important regimes, below and above the glass transition temperature of the polymer. Observing the change in the conductivity below \( T_g \) one can clearly see that the conductivity increases with temperature. However, increasing temperature does not only produce an effect of thermal activation of conductivity, but also gives rise to structural changes in the nanocomposite film through embedding of the Au nanoclusters in the polymer film at temperatures above the glass transition temperature of the polymer. This phenomenon has been described in detail in our previous work [7][8].

![Figure 1: In situ measurement of the resistance of the sample during the thermal evaporation of Au on PS thin film. The TEM micrograph shows the cluster morphology at a nominal Au film thickness of 1.3 nm.](image)

![Figure 2:](image)

At \( T_g \) the metal clusters start embedding into the polymer film, which leads to a sharp decrease in the film conductivity. This embedding process is very important to stabilize the composites base resistance after contact with VOCs as seen in figure 2b. The curve for the non-tempered samples does not recover the original base resistance. This indicates that the morphology of the composite is
affected by the swelling process before the metal clusters are embedded into the polymer. The second curve shows the similar measurement for a sample where the Au clusters were pre-embedded at 120°C for 30 minutes. Due to the embedding, the clusters are now localized near the polymer surface and the swelling of the film does not strongly affect the base resistance of the sensor any more. Following this principle, our sensor devices can be used repeatedly with nearly full reversible signal strength.

It is known, that every polymer shows a unique sensitivity to different VOCs [9]. Figure 3 displays the selectivity of our sensors for different VOCs. It can be seen that for PMMA, the general response to the VOCs is higher. But selectivity to different VOCs for PMMA and PS is not the same. The sensor response has a maximum for isopropanol in the case of a PMMA substrate and is different from PS, which is more sensitive to ethanol. Basing on these first results of our sensor devices one can think of an array of sensors made up of several different polymers, which should be able to give information about the presence of different VOCs in just one integrated device.

Surely the detection of tracer amounts is very important in the field of VOC detection. First experiments with our sensors showed that a detection of VOCs down to a partial pressure of roughly 0.1 mbar is easily possible. The measurements showed that there is a trend which can be extrapolated to even smaller amounts of VOCs which still should be detectable.

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