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# Fast electrical response to volatile organic compounds of 2D Au nanoparticle layers embedded into polymers

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**Abstract** The conductivity of polymer–metal nanocomposites close to the percolation threshold is very sensitive to changes in the metal nanoparticle distances. Here the technical feasibility of a novel type of easy to prepare polymer–metal nanocomposite sensor is explored, which shall be able to detect a unique signal for various volatile organic compounds (VOCs) exhibiting a fast and reversible response. The composite consists of a nearly 2-dimensional Au nanoparticle layer near the percolation threshold thermally embedded into a thermoplastic polymer film. The sensoric response is based on the swelling behavior of the polymeric matrix upon exposure to the organic vapor molecules. Different from conventional nanocomposite sensors that require long-range diffusion of the volatile compound into the bulk of the matrix, the electrical response here only requires the penetration of the VOC a few nanometer below the surface thus causing a rapid detection. The degree of swelling depends on the type of polymer and VOC used as well as on the vapor pressure of the VOC leading to a characteristic response of each polymer to a specific VOC. This enables a "fingerprint" detection of different VOCs by an array of different polymer nanocomposite combined into one sensoric device.

## Introduction

The use of conducting particles in an insulating matrix is a common principle for creating sensitive vapor sensors. During the last years, much research was done on nanoparticle-based materials due to their unique properties and the corresponding possible applications. Nanocomposites which use different carbon nanoparticles like carbon black or carbon nanotubes (CNT) as conducting material have been reported as vapor sensing materials [1–7]. Polypyrrole was also used as conducting filler material [8]. Also quartz microbalances [9, 10] or semiconducting metal oxides [11, 12] have been used for the detection of VOCs.

Another broad area for the detection of VOCs is the use of monolayer-protected gold nanoparticles. These were synthesized and characterized for an application as a sorptive layer on chemical sensors [13, 14]. In these materials, the electron transport is from particle to particle, so that the current can be influenced by the sorption of vapor molecules into the organic non conducting matrix surrounding the particles. Main emphasis was put on wet chemical synthesis approaches using complex organic molecules in combination with suitable metal nanoparticles. In the presence of VOCs, the flexible network of the linked nanoparticles leads to a swelling-induced alteration in the chemical nature and/or the length of the electron tunnel pathways between the nanoparticles.

Common to these sensor materials is their operation principle which is based on a matrix swelling effect to detect the VOCs. The sensors based on CNTs achieve a

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very high sensitivity but show generally a poor reversibility and long term stability of the signal [6, 7], hindering reliable quantification of the VOCs. Monolayer-protected gold nanoparticles like in ref. [13], on the other hand, show a very good reproducibility of the measured signal but exhibit a rather low sensitivity. The composites with carbon black as conducting material achieve also good reproducibility combined with a better sensitivity [5], but require good dispersion of the carbon black in the polymer matrix. They generally exhibit a fairly slow response (on the order of 30 s) due to the required long-range diffusion of the molecules to be detected into the bulk.

Here we use an approach that does not require wet chemical techniques in order to incorporate conducting nanoparticles into the polymer film. Instead the conducting Au nanoparticles are prepared on top of the various polymer films by means of vapor phase deposition. The so prepared nanocomposites also combine good reproducibility with a similar sensitivity as the carbon black sensors, but offer the advantage of simple and reliable preparation and faster response times.

Due to the fact, that the cohesive energy of noble metals is typically two orders of magnitudes higher than the cohesive energy of polymers, there is a strong aggregation tendency of metal atoms deposited on polymers, which is enhanced by the very weak interaction between moderately reactive metals and polymers compared to the strong metal–metal binding forces [15]. Therefore, the polymer surface will not be wetted by the metal but in a self-organization process a 2-dimensional nanoparticle array is formed during vacuum deposition. With predeposited electrodes on top of the polymer film the electrical conductivity of the nanoparticle array can be monitored during metal deposition and a desired range of conductivity for the sensing process can be achieved. Subsequently, the nanoparticles can be embedded just below the surface by heating above the polymer glass transition temperature [16, 17].

Uptake of organic vapors into the topmost few nm of the polymer film will already result in swelling of the thermoplastic polymers in this region and this leads to a change in the interparticle distance of the metal nanoparticles just below the surface. Macroscopically a change in the conductivity or correspondingly the resistance as a function of the vapor pressure of the particular VOC is observed.

Using this approach it is possible to detect the type and concentration of different organic vapors simply by monitoring the electrical response of an array of different polymer–metal-nanocomposites. A short first introduction of this approach has been published by our group previously as a conference proceedings [18]. Here a comprehensive description is given how these polymer–metal-nanocomposites can be used to create a reliable and easy to manufacture sensoric device for the detection of different volatile organic compounds. Emphasis here is put on demonstrating the feasibility rather than on producing and testing of sensors in detail.

## Experimental

Polymer thin films of thickness between 10 and 250 nm were produced either via spin-coating or thermal evaporation. Monodisperse poly(methyl methacrylate) with molecular weights of 21.40 (PMMA-1) and 8.07 kg/mol (PMMA-2) and a polydispersity index of 1.07 and 1.06, respectively, was obtained from Aldrich. Also conventional polymers polystyrene (PS, Aldrich), bisphenol-A-polycarbonate (BPA, Bayer) and Polyamide 6 (PA-6, Aldrich) were used. The PA-6 films were deposited by thermal evaporation of the polymer under high-vacuum conditions [19]. All other polymer thin films were produced by spin-coating after dissolving the polymer powders in toluene or dichloromethane. All spin-coated polymer films were dried afterward in a vacuum oven at roughly 50 °C for about 12 h. Gold nanoclusters were formed on top of the polymer samples by means of thermal evaporation. A quartz microbalance was used to follow the amount of gold deposited and a picoamperemeter (Keithley 6485) to monitor the current through the gold nanoparticle film during deposition. With the combination of these two measurements a reliable process control was achieved. The deposition was stopped always, after a desired sheet conductivity of, e.g., $1.5 \times 10^8$ S/□ through the gold nanoparticle film was reached. Note, □ is the ratio of width/distance of the area between the electrodes and accounts for the geometrical setup of the electrodes. The desired sheet conductivity was always reached in a very narrow interval of nominal gold thickness deposited onto the polymer film, largely independent of the type of polymer substrate used. The most sensitive sheet conductivity turned out to correspond to a gold nanoparticle density on the surface that is close to the percolation threshold (see below).

Prior to the gas sensing experiments, the composites were heated up to the surface glass transition temperature of the polymer in order to stabilize the gold nanoparticle array near the surface of the polymer films. This procedure induces an embedding of the metal nanoparticles just below the polymer surface [16–18]. Slightly different embedding depths lead to a minor deviation from a perfect 2-dimensional geometry of the metal nanoparticles. The great benefit of this treatment is that the metal nanoparticles are transferred to a rather stable position in the polymer matrix, and therefore no further movement of the clusters under gas load or slightly elevated temperature will occur. As discussed below, the counteracting contributions of the van der Waals force acting on the particles and an entropical force gives rise to the formation of a local minimum just below the surface [20, 21]. This ensures a stable and reversible electrical ground state prior to contact to any VOCs and also after each and every measurement cycle.

The so treated samples are then exposed to different VOCs at defined partial pressures and the changes in the conductivity (or resistance) were in situ measured against time. The gas load tests were performed in a vacuum chamber with a base pressure of 0.01 mbar and the vapor pressure of the VOC was adjusted by the equilibrium gas pressure above the liquid for a given temperature. Using this setup only vapor pressures above 0.1 mbar could be experimentally tested. The solvent temperature was always kept below the sample temperature to avoid condensation of the VOC on the polymer surface.

## Results and discussion

### Optimization of metal nanoparticle morphology

As mentioned in the introduction the working principle of the desired sensoric device is based on the conductivity response caused by changes in the interparticle distance of the deposited metal nanoparticles. Noble metals like gold show typically Volmer–Weber growth on polymer substrates. In addition, to minimize the gold surface energy the particles first assume a spherical or almost spherical shape without any further treatment [22]. At higher metal coverages nanoparticles start to agglomerate resulting in non-regular shapes (see also Fig. 2).

The conductivity through an array of slightly separated metal nanoparticles is caused by a thermally activated electron hopping process. At a constant temperature the hopping depends exponentially on the interparticle distance related to the electron tunneling character of the hopping process. Therefore, one expects a significant increase in the conductivity, when the distance between the clusters gets just slightly smaller or, vice versa a large decreases in the conductivity when the particle distance increases slightly.

The conductivity of an gold nanoparticle array on a polymer substrate increases, when the nominal thickness of the gold deposited onto the polymer film increases, because the growth of the gold nanoparticles leads to a decrease of the interparticle distance. Figure 1 shows the change in resistance of a gold/polystyrene composite film as a function of the nominal gold thickness.

There are generally three different regions to be found in such a graph. At low nominal gold thickness there is a plateau exhibiting a high resistance characteristic for the insulating polymeric material. Here the hopping distances between the gold nanoparticles are too large to contribute significantly to the conductivity. On the other side above a nominal thickness of 6 nm gold a thin gold film is already formed exhibiting metallic conductivity. Note, in the graph presented here the resistance does not drop below 3 kΩ, because an additional resistor has been added to the experimental setup to protect the sensitive electrometer against high currents due to shortcuts. Both just described regions are not suitable for sensoric applications because changes in the conductivity of the gold layer upon swelling of the polymer will be rather small.

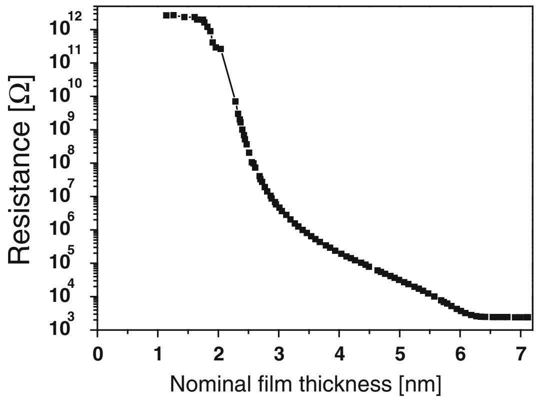

**Fig. 1** Change of the resistance of a poly(methyl methacrylate) (PMMA-1) sample with increasing nominal film thickness of gold. The curve can be split into three regions: insulating up to ca. 2 nm, intermediate from 2 to 6 nm and metallic conductivity above 6 nm. The resistivity drop between the insulating and metallic region is due to changes in the spacing of the nanoparticles which leads to changes in the tunnel probability

The suitable region for vapor sensing is always situated between these two extreme regions. Here a change of the nominal gold thickness of roughly 4 nm causes a drop in the measured resistance over more than 10 orders of magnitude. This drop is explained by the percolation phenomenon. The metal particles grow in size, which leads to a decrease in the spacing between them. Therefore, the tunnel probability between two neighboring gold nanoparticles increases leading to a decrease in the measured resistance of the nanocomposite film. This process proceeds until the first connecting path of gold nanoparticles through the whole nanocomposite film is formed, so that the metallic conductivity through the gold starts to dominate over the hopping conductivity.

In the desired sensor, changes in the conductivity will be generated by small changes in the nanoparticle distance due to swelling of the polymer film upon exposure to VOCs. The optimum response, i.e., the largest relative change of the conductivity, should be achieved when the relative distance change is maximized. This is achieved when the gold nanoparticles are very close to each other, but are not in contact.

By vapor deposition methods the metal nanoparticles formed on a polymer surface are statistically distributed exhibiting a variety of interparticle distances. Therefore, the first task was to find the optimum nominal gold thickness on top of the polymer film. Figure 2 shows TEM bright field images of gold on PMMA-1 with different amounts of deposited gold (2.5–5.4 nm nominal gold thickness). Sensing tests with different VOCs as displayed in Fig. 3, led to the conclusion, that the morphology with a nominal gold thickness of 3.5 nm (see Fig. 2b) shows the largest change in the measurement signal.

The morphology of the nanoparticles in the composites is then such that just a small number of nanoparticles have already made a direct contact (via coalescence) so that only a few short "wires" have been formed. On the other hand, it can be speculated that there are always nanoparticles close to contact in every conduction path, which show a large change in tunneling current upon swelling. This morphology shows a higher sensitivity compared to a morphology very close to the percolation threshold (see Fig. 2c). In the latter with "longer" nanowires formed there are many equivalent ways for the electrons to travel through the composite. If now the whole composite swells up, some of these pathways will show larger gaps, which would increase the resistance of the film. At the same time other pathways would show smaller changes, so that the current can now flow over these "wires" so that in total a smaller relative change in the measured resistance is observed (see Fig. 3). For the morphology in Fig. 2b these competing pathways are not so frequent, so that a swelling of the polymer film leads to a higher increase in the measured resistance of the material. This observation is consistent with calculations made by Kiefer et al. [23]. They pointed out that the percolation threshold, and with this the conductivity of a 2-dimensional composite, is not only dependent on the amount of material deposited on the surface but is also strongly influenced by the morphology of the nanoparticle array formed. The highest sensitivity is expected for a sample with only one dominant conduction path with a very small gap. The more alternative conduction paths in the sample exist the smaller becomes the sensitivity.

As can bee seen from Fig. 1 the electrical resistance measured directly on the sample during deposition is, in the range of interest, a very sensitive function of the nominal gold thickness. Therefore, for practical reasons it is easier to find and adjust to the optimum gold thickness indirectly by deposition of gold up to the optimum resistance of the sample. The particular value is set-up dependent and needs to be determined for each set-up of electrodes on the sample.

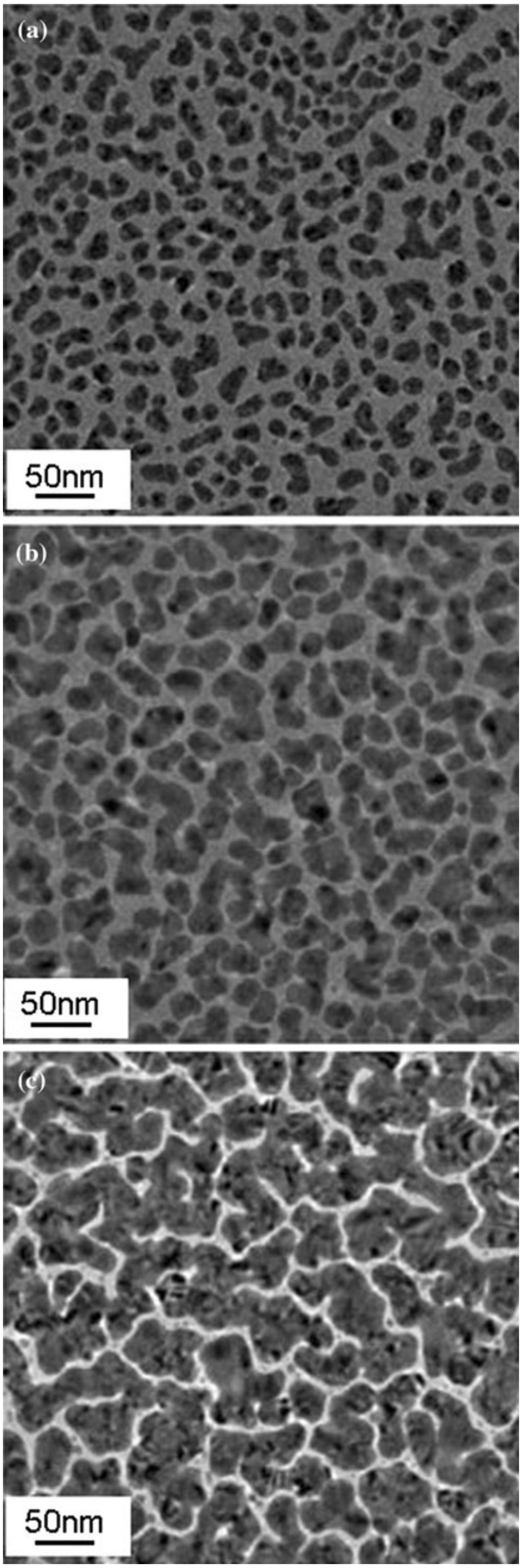

**Fig. 2** Top view transmission electron micrographs of the gold cluster morphology on a PMMA-1 substrate for different nominal gold thicknesses **a** 2.5 nm, **b** 3.5 nm and **c** 5.4 nm

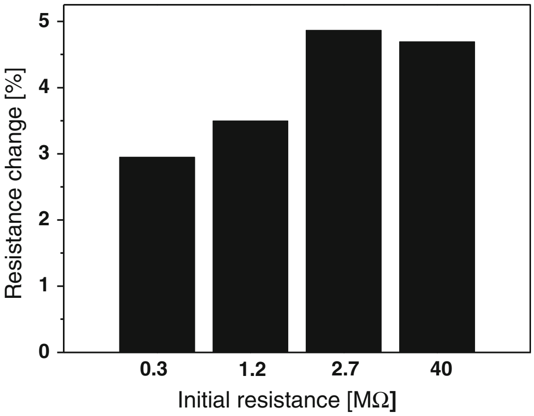

**Fig. 3** Relative change of the resistance of Au/PMMA-1-nanocomposites with different initial resistance (adjusted by differences in nominal gold thickness) upon contact to 30 mbar isopropanol vapor. The maximum response to isopropanol is obtained with a starting resistance of ca. $2.7 \times 10^6\ \Omega$ which represents a sheet resistivity of $1.5 \times 10^8\ \Omega/\square$

## Electrical response to volatile organic compounds

Using the already optimized morphology we studied the response of the sensoric composites to the exposure and subsequent removal of VOCs. Our current experimental setup allows only testing of the feasibility of our composites as sensors for VOCs at relatively high vapor pressures of the VOCs. Still, we believe that these tests are well suited to demonstrate the response behavior of the nanocomposites toward VOCs. The results displayed in Fig. 4 demonstrate the typical response which has been observed for all tested composites. Just the absolute values were different for different composites.

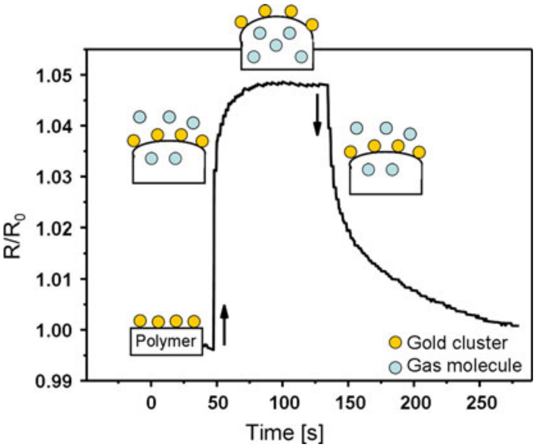

**Fig. 4** General sensor response after contact to VOCs (*arrow pointing up*) and to a degassing step (*arrow pointing down*). After a first steep increase, the slope of the resistance change decrease due to swelling of polymer regions deeper in the film until saturation is reached. In degassing, the same general behavior is observed in opposite direction but with longer time needed to reach the base line again

After exposure to a VOC (indicated by the arrow pointing upwards) there is always an immediate response which leads to a very fast increase in the measured resistance. This increase is caused by swelling of the top region of the polymer film by absorbed VOC molecules. This leads to a relatively large change in the distance between the metal nanoparticles located in the initially affected near surface region of the polymer film.

Subsequently, upon further exposure to the VOC a change in the slope of the response curves in Fig. 4 is observed. This is a result of swelling of polymer regions deeper in the sample giving a less pronounced effect on the measured resistance of the nanocomposite. For obvious reasons the distance change of the metal nanoparticles in the near surface region is smaller if the swelling continues deeper in the polymer compared to swelling of the polymer surface region where the nanoparticles are located.

When the vapors are removed by evacuating the chamber (indicated in the graph by the arrow pointing downwards), the same general behavior only in the opposite direction is observed. First there is a steep decrease in the resistance caused by fast degassing of the top region of the nanocomposite sample. But here the measured signal change is somewhat smaller compared to the change for the uptake of the VOC, because the degassing of the surface near region is incomplete at the beginning. A certain fraction of the VOC molecules removed from the near surface region is replaced by VOC molecules diffused to the surface near region from deeper regions of the polymer film. As expected for this scenario the slower second part of the signal change is more pronounced in the degassing section of the plot. The return of the signal to the initial value as compared to the time to reach the saturation value by taking up the gas is significantly slower. Also the higher stiffness of the polymer chains at the end of the process may contribute to the slower return to the initial value. The stiffness decreases with increasing content of VOC in the polymer, enabling faster diffusion of the VOC molecules into the polymer upon loading, but slowing down the outward diffusion upon removal of the VOC. The modeling of the exact swelling kinetics in thin polymers films is beyond the scope of this study, and the interested reader is referred to the work of Manoli et al. [24, 25].

## Optimization of the signal stability

A stable base signal is of fundamental importance for the long time performance of a sensor at least in case of quantitative sensing. Ideally there should be no drift in time independent of the operation of the sensor. This is very often a problem in sensoric systems in particular for the

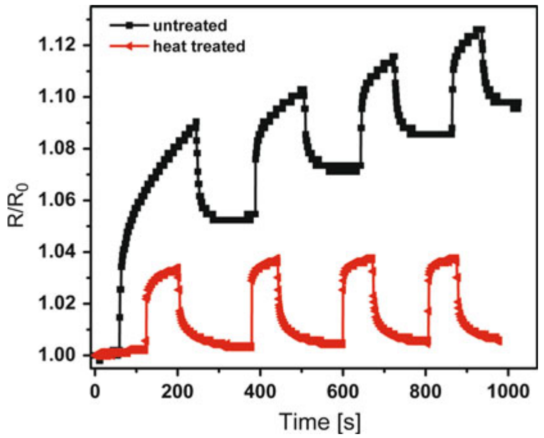

**Fig. 5** Response signal behavior of gas sensing composites (gold on PMMA-1) without and with thermal pretreatment. The sample was repeatedly exposed to 30 mbar isopropanol. Without heat treatment (*black curve*), the base resistance without gas load changes with every cycle. By a heat treatment at the surface glass transition temperature the gold clusters are embedded into the polymer matrix, so that a VOC sensor cycle does not lead to further irreversible changes in the interparticle distance. After the heat treatment the sensor base signal is stable in time

carbon nanotube based sensors. The metal–polymer nanocomposites prior to nanoparticle embedding do not exhibit a stable signal as displayed in the black curve in Fig. 5. The base resistance changes with each measurement cycle to a higher value. This increase of the signal is explained by a gradual embedding movement of the metal nanoparticles into the polymer caused by an increased mobility of the polymer chains upon exposure to VOCs. The driving force for this process is the reduction of the high surface energy of the system by embedding the metal nanoparticles into the polymer matrix. This process is usually thermally induced and has been studied before in detail in several works [16, 17]. At the end of the embedding process the nanoparticles will reach a more stable state just below the polymer surface slowing down further movement. The stable state is due to a minimum of the Gibbs free energy of a particle position just below the polymer surface caused by opposite action of van der Waals energy and the conformational entropy [20, 21]. By a thermal treatment of the metal–polymer nanocomposite at the surface glass transition temperature of the polymer film this process is accelerated very much and after a few minutes the favorable state of embedded nanoparticles is reached. Using this simple thermal pretreatment, a stable base signal of the composite resistance is achieved (red curve in Fig. 5).

At this point it is important to note, that many volatile organic compounds can induce crazing and cracking of glassy polymers [26]. This may actually be regarded as an inherent material weakness of glassy polymers and could also affect the durability of the present sensor in particular if it is exposed to high concentrations of volatile organic solvents for any prolonged time. This, however, is certainly not the typical range of sensor operation. Usually a sensor is operated in the lower partial pressure regime and exposed to the VOC only for a short time. Furthermore, the heat treatment used by us for the embedding will also reduce residual stresses in the polymer and will thus lower the sensitivity toward crazing. Our results show that our type of sensor works reliable and returns to the base value even after several exposures to fairly high partial pressures of different VOCs. Even in a case of a severe accident it will work sufficiently to give a warning signal, but it may be necessary to replace the sensor afterward if it has been exposed to very high partial pressures of VOCs for a prolonged time (similar to other sensors based on swelling of glassy polymers).

## Influence of polymer thickness

Due to the fact, that the polymer film is bonded to a rigid substrate, the swelling behavior of the polymer top layer (in which the metal nanoparticles are situated) should not be independent from the polymer film thickness (as it would be expected in a free standing polymer foil). A supported thin polymer film consists of three regions: The free surface region with larger free volume and enhanced polymer chain mobility, the region which shows bulk like swelling behavior and the interface region to the substrate, where chain mobility and therefore swelling is usually reduced [24]. In addition, the substrate can interact more strongly with the VOC leading to an enrichment of the VOC near the substrate in the interface region. Detailed analysis of the swelling behavior of supported polymer thin films has only be done for a few selected systems and often a rather complex behavior is found [24, 25]. A detailed analysis of the swelling behavior would be necessary for all polymer/VOC combinations to find the optimum film thickness, but this is beyond the scope of this study.

Here we give only one empirical example. As expected the data displayed in Fig. 6 show a dependence on film thickness. Increasing the film thickness from 10 to 50 nm leads to an increase of the response. For a PA-6 substrate and isopropanol vapor at 30 mbar vapor pressure the detected response increases roughly from 10 to 35% of the base value. But increasing the film thickness further to 250 nm leads to a decrease of the response by about 5–10%. Important for the response is the swelling in the lateral direction of the polymer film. It is to be expected that the pinning of the polymer film on the substrate is less significant when the polymer film thickness is increased up to a certain film thickness where pinning becomes negligible. In thicker films the interface between polymer and substrate is still pinned, but the layers between this

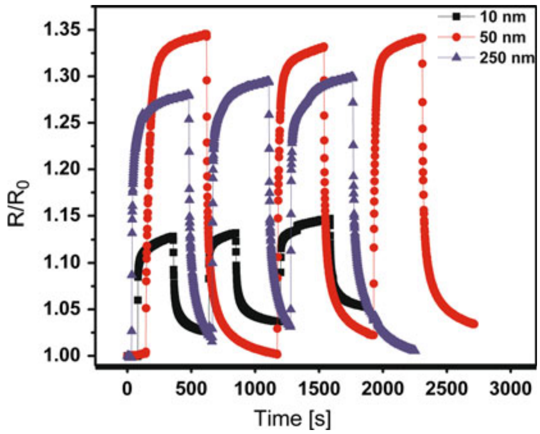

**Fig. 6** Dependence of the film thickness on the vapor sensing properties of PA-6 exposed to 30 mbar isopropanol. PA-6 films with ca. 50 nm polymer thickness are most sensitive to the organic vapors tested. Very thin films show a much reduced sensitivity, for thicker films the sensitivity is only slightly reduced

interface region and the polymer surface can slightly expand also in lateral direction, thus decreasing the pinning effect. This would explain the observed increase of the response signal with increasing film thickness.

For thicker films the vapor molecules will not only stay in the near surface region, but a certain fraction of the molecules will diffuse deeper in the film reducing the actual concentration in the near surface region. For a thinner film the initially reached concentration is higher because the concentration gradient into the film will be much smaller as compared to a thicker film and a smaller fraction of molecules will leave the near surface region. The combination of both effects leads to the optimal polymer film thickness of around 50 nm for the gas sensing properties for the PA-6/isopropanol system. It can be expected that the dependence on film thickness for the other polymer/VOC combinations will be similar, thus the optimum film thickness is expected to be somewhere around 50 nm.

### Identification of VOCs using the selectivity of the gas sensing nanocomposites

After all the optimizations described above a sensor device using a combination of different polymers can be constructed in order to quantitatively detect different VOCs by the characteristic response. Figure 7 shows the response patterns of different composite materials for various VOCs at the same vapor pressure. Each polymer nanocomposite sensor shows a unique signal change by exposure to different VOCs. And vice versa each VOC shows a characteristic response pattern on an array of different nanocomposite sensors, i.e., the ratios of the response signals on the different polymer nanocomposites are characteristic of each VOC. By processing the response signals of several sensor composites in parallel, it will thus be possible to identify the kind of vapor that is present. In addition one can determine the vapor pressure of the so identified VOC by analysis of the absolute response signals. For small partial pressures the response is directly proportional to the vapor pressure of the VOC.

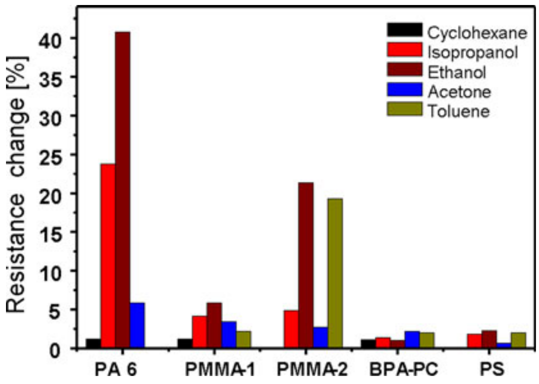

**Fig. 7** Example of a sensor array built up from different polymer–metal-nanocomposites. Every composite shows a different response to a certain organic vapor of 30 mbar. The polymer thickness was 250 nm in each case. The ratios of the response signals are different and characteristic for each organic vapor allowing to detect the kind and partial pressure of a particular VOC simultaneously. Note, the response of Nylon-6 to toluene and the response of PMMA-2 to cyclohexane were not measured

## Conclusions

In conclusion, combinations of 2-dimensional metal-polymer nanocomposites prepared by embedding of gold nanoparticles into different polymers are feasible to build a simple, reliable, stable, and cheap sensor to detect single VOCs. The sensor can be used to detect the type of VOC because the particular VOC present can be identified by its particular response pattern on the different nanocomposit sensors. At the same time its concentration can be determined from the intensity of the signals of the nanocomposite sensors.

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