



# Fabrication of ultra-pure gold nanoparticles capped with dodecanethiol for Schottky-diode chemical gas sensing devices

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## ARTICLE INFO

### Article history:

Received 1 March 2016

Received in revised form 6 July 2016

Accepted 8 July 2016

Available online 8 August 2016

### Keywords:

Monolayer-capped gold nanoparticles

Advanced gas deposition

Dip-coating

Schottky-diode chemical gas sensors

## ABSTRACT

Ultra-pure monolayer-capped gold nanoparticles for chemical gas sensing devices were prepared by a novel two-step process: a physical vapour deposition technique was first employed to make dispersed ultra-pure size-controlled gold nanoparticles, and this step was followed by a coating process for functionalization of the gold nanoparticles with an organic ligand, specifically dodecanethiol. X-ray photoelectron spectroscopy proved that the nano-assemblies had high purity. Chemical sensing devices based on these nano-assemblies showed Schottky-diode behaviour. We believe this is the first observation of Schottky-diodes fabricated from nanomaterials based on metallic nanoparticles. Gas sensing experiments demonstrated that these devices were suitable for detecting volatile organic compounds.

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## 1. Introduction

Electronic devices with exciting new possibilities for identification and quantification of single- or multi-component chemical and biological species can be developed by immobilising a nanoscale matrix of nanoparticles, provided with appropriate functional terminations, onto the surfaces of the device [1–3]. Monolayer-capped metallic nanoparticles, with nanoparticles connected by linkers of different molecular structures, possess excellent features for identification of target analytes; the capping can employ a wide variety of molecular ligands [4–6]. In these nanoscale sensing assemblies, the molecular functionalities provide sites for the sorption of guest (sensed) molecules, while the metallic nanoparticles give electrical conductivity and allow electron transport through the sensing film [7]. Only a few molecules are sufficient to change the electrical properties of the sensing elements in the electronic transducer, which hence can detect very low concentrations of analytes [1]. Moreover, monolayer-capped metallic nanoparticle-based devices

are superior to the more widely studied metal oxide-based sensors in that they are well suited for room-temperature operation and therefore enable power savings and safe operation even in highly flammable places [5].

Monolayer-capped metallic nanoparticles are generally made by conventional wet-chemistry methodology that uses a two-phase procedure combined, whenever necessary, with ligand exchange [8,9]. However, this procedure employs chemical precursors which leave traces of residual compounds [10,11].

In this study, we introduce a new technique that ensures the fabrication of ultra-pure monolayer-capped gold nanoparticles. This novel approach comprises two steps: (i) physical vapour deposition to make dispersed, ultra-pure, size-controlled, gold nanoparticles (AuNPs), and (ii) coating and functionalizing of the AuNPs with organic ligands.

## 2. Materials and methods

In the first processing step, AuNPs were prepared and deposited onto glass or silicon substrates by use of advanced gas deposition (AGD) [12]. The AGD equipment was adapted, as shown in Fig. 1, to comply with results of our previous studies on the fabrication of thin films of AuNPs [13,14]. For achieving the objective of the present study – i.e., deposition of dispersed (isolated) AuNPs – the nozzle between the evaporation (lower) and deposition (upper) chambers of the AGD equipment was removed in order to avoid the formation of compact gold films, which would otherwise have been

*Abbreviations:* AuNPs, gold nanoparticles; AGD, advanced gas deposition; SEM, scanning electron microscopy; XRD, X-ray diffraction; XPS, X-ray photoelectron spectroscopy; RH, relative humidity; LOD, limit of detection.

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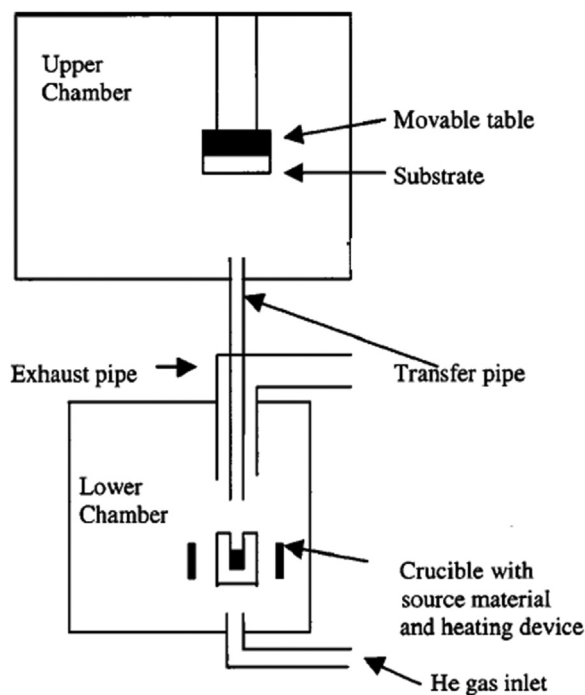


Fig. 1. Configuration of the AGD equipment employed in this study.

favoured by the high speed of the particles driven by the pressure difference between the two chambers in the equipment.

For the fabrication of the AuNPs, a piece of high-purity gold (99.999%) was placed on a carbon crucible inside the evaporation chamber, and both chambers of the AGD unit were evacuated until their pressure reached  $\sim 0.02$  mbar to ensure clean deposition conditions. A copper induction coil surrounding the crucible provided the heating necessary to melt and evaporate the gold. A laminar flow of high-purity He ( $201 \text{ min}^{-1}$  flow rate) was introduced underneath the heated gold piece, and this gas flow, with upward direction, transported the metal vapour while cooling it down so that initially clusters of Au atoms, and subsequently single Au nanoparticles, were condensed. The pressures in the evaporation and deposition chambers were set to  $\sim 0.8$  mbar and  $\sim 88$  mbar, respectively. A transfer pipe (3 mm diameter) connecting the two chambers of the equipment, was positioned in the vapour region where the individual AuNPs were formed. Because of the pressure difference between the two AGD chambers, the gold nanoparticles were transported rapidly to the deposition chamber, thereby avoiding agglomeration. In this way, individual AuNPs with a narrow size distribution could be transferred to the upper chamber and deposited onto a substrate placed on a movable support table.

In the second processing step, the AuNPs were capped with dodecanethiol. This organic compound contains a thiol group, which is likely to bind strongly to the AuNPs because of the strong affinity of sulphur to gold [15]. The choice of dodecanethiol was founded on previous reports which showed that chemical gas sensors based on AuNPs functionalized with dodecanethiol have promising features for the detection of volatile organic compounds (VOCs) such as acetaldehyde, formaldehyde, etc. [16,17].

In order to accomplish the functionalization, we dissolved  $200 \mu\text{l}$  of dodecanethiol in ethanol. The selected solvent is conveniently volatile and evaporates quickly at low temperature; it is therefore excellent for applications that require high-purity upon evaporation [18]. Stirring for 30 min at room temperature ensured homogeneity of the solution. Samples with pre-deposited AuNPs were immersed in the solution for 1 h, and the solvent was sub-

sequently evaporated by heating the samples at  $50^\circ\text{C}$  for 1 h in a conventional oven.

### 3. Results and discussion

The morphology of the AuNPs fabricated in the first processing step by AGD was governed by the speed of the movable support (set to its minimum value of  $0.04 \text{ mm s}^{-1}$ ) and the number of deposition cycles, as apparent from Scanning Electron Microscopy (SEM) (see Fig. 2). Thus, a single deposition cycle led to isolated gold nanoparticles (Fig. 2a). When the number of deposition cycles was increased to two, the AuNPs started to agglomerate in small clusters (Fig. 2b), while a compact thin film of AuNPs was formed when eight deposition cycles were employed (Fig. 2c).

Electrical resistance measurement between electrodes proved that no electrical contact was formed for the AuNPs samples shown in Fig. 2a and b, which hence consisted of isolated Au nanoparticles and isolated AuNPs clusters, respectively. The electrical resistance measured for the AuNPs samples shown in Fig. 2c was of the order of a few  $\Omega$ , thus indicating the formation of a continuous film of AuNPs, which is inadequate for gas sensing applications.

In order to prevent any influence from the substrate, the physical properties of the AuNPs were investigated on the film shown in Fig. 2c. The crystal orientation of the AuNPs was characterised by X-Ray Diffraction (XRD), as shown in Fig. 3. A strong diffraction peak at  $38.3^\circ$  was attributed to Au (111) planes parallel to the surface of the glass substrate. The other three diffraction peaks, attributed to Au (200) at  $44.4^\circ$ , Au (220) at  $64.8^\circ$  and Au (311) at  $77.6^\circ$ , exhibited weaker relative intensities than for Au (111). The diffraction pattern is in good agreement with that of elemental gold and shows no evidence for contamination or the formation of an any secondary gold phase. The mean crystallite size  $D$  of the AuNPs was calculated from Scherrer's formula (Eq. (1))

$$D = K\lambda / (\beta \cos \Theta), \quad (1)$$

where  $K$  is Scherrer's constant,  $\lambda$  is X-ray wavelength,  $\beta$  is peak width at half maximum, and  $\Theta$  is diffraction angle. Applying this formula to the (111) peak gives  $D \approx 11 \text{ nm}$ , which is in good agreement with the particle size seen from SEM images in Fig. 2a ( $\approx 10 \text{ nm}$ ). This result ensures that the AuNPs are single crystalline. Importantly, the number of cycles used during AuNPs deposition did not have any direct influence on particle size despite the fact an increased number of deposition cycles led to AuNPs aggregation in clusters or to the formation of a thin film of AuNPs.

Functionalization of the isolated AuNPs shown in Fig. 2a with the organic ligand led to linking of the AuNPs, which aggregated into chains forming uninterrupted paths (Fig. 4). This process did not alter the size of the AuNPs, as it can be observed in Fig. 4.

Gas sensing devices were next fabricated on a 2-inch,  $p$ -type,  $10\text{--}20 \Omega$ , (100) oriented,  $275\text{-}\mu\text{m}$ -thick, single-side polished silicon wafer. A  $200\text{-nm}$ -thick  $\text{SiO}_2$  layer was first grown on top of the silicon wafer by dry thermal oxidation at  $1100^\circ\text{C}$ . Two parallel gold electrodes that are  $30 \mu\text{m}$  apart were then patterned using thin positive photoresist and laser lithography. A  $200\text{-nm}$ -thick gold film was sputtered on the  $\text{SiO}_2$  surface, and a lift-off process with acetone was finally employed for removing the gold outside the electrodes area. Fig. S1 from the Supplementary material shows the sensor layout.

Prior to the deposition of the AuNPs by AGD, the sensing devices were treated successively for 5 min in propanol and for 5 min in acetone in an ultrasound bath at room temperature. As a final step, the devices were rinsed with deionised water for removing the impurities.

The electrical resistance of the monolayer-capped AuNP sensing films shown in Fig. 4 ranged between hundreds of  $\text{k}\Omega$  to several

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