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Ultrathin gold nanowires for transparent electronics: breaking barriers

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Abstract

Novel types of Transparent Conductive Materials (TCMs) based on metal nanostructures are discussed. Dispersed metal nanoparticles can be deposited from liquids with moderate thermal budgets to form conductive films that are suitable for thin-film solar cells, displays, touch screens, and nanoelectronics. We aim at new TCMs that combine high electrical conductivity with optical transparency and mechanical flexibility. Wet-processed films of randomly arranged metallic nanowires networks are commercially established and provide a relatively cost-effective, scalable production. Ultrathin gold nanowires (AuNWs) with diameters below 2 nm and high aspect ratios have recently become available. They combine mechanical flexibility, high optical transparency, and chemical inertness. AuNWs carry oleylamine capping ligands from synthesis that cause high contact resistances at their junctions. We investigated different annealing processes based on temperature and plasma treatment, to remove the ligands after deposition and to allow electrical conductivity. Their effect on the resulting nanostructure and on the material properties was studied. Scanning Electron Microscopy (SEM) and optical spectroscopy revealed changes in the microstructure for the different post-treatments. We found that the conductivity and the stability of the TCM depended strongly on its final microstructure. We demonstrate that the best results are obtained using H_2-plasma treatment.

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Keywords: nanowires; sintering; transparent electronics

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1. Introduction

Flexible mobile phones that are unbreakable, foldable tablets that fit in your pocket, or photovoltaic cells that can be rolled out from within a pen – such concepts require replacements for Indium Tin Oxide (ITO) as transparent electrodes that are less brittle. Indium production is energy-intensive, its deposition usually requires vacuum and high temperatures that are not compatible with some organic substrates, but foremost, ITO is brittle ceramic material that will crack under bending loads.[1] Solution-processed metal nanowire (NW) networks are promising alternatives for transparent conductive material. Random silver nanowires networks on polymeric substrates are commercially available today.[2] However, the typical silver wire diameters of 30-80 nm causes scattering and haze already at low wire densities, and silver nanostructures are prone to degradation that limits stability in the final devices.[3]

We use ultrathin gold nanowires (AuNWs) as the basis of transparent conductive materials. With diameters below 2 nm and high aspect ratios, AuNWs exhibit little scattering and mechanical flexibility.[4,5] Gold is stable towards oxidation. AuNWs are capped by an oleylamine (OAm) monolayer during synthesis that provides colloidal stability that is necessary for ink formulation. OAm is a long-chained organic molecule (2.05 nm length) with a high boiling point (350 ºC). It forms insulating barriers between AuNWs that hinder electron transfer and decrease the conductivity dramatically.

Here, we report different methods to remove the OAm while retaining the structure and allowing electrical conductivity through AuNW layers. We demonstrate that the different sintering treatments induce changes in the morphology of the formed layers and we discuss the suitability of them for the production of transparent electrodes based on ultrathin AuNWs.

2. Experimental

2.1. AuNWs synthesis and layer preparation

Ultrathin gold nanowires were synthesized following a modification of the procedure of Feng et al.[6] described in [7] After synthesis, the wires were precipitated with ethanol (2.5 times the reaction volume) and redispersed in n-hexane after supernatant removal. This step was done twice.

Glass slides were cleaned using ultrasonication in different solvents: Milli-Q water, ethanol:acetone (1:1 v/v) and then treated with oxygen plasma for 5 min and silanized by immersion in 5% 3-mercaptopropyltrimethoxysilane (95%, Sigma-Aldrich, Steinheim, Germany) in toluene overnight according to published procedures.[8]

AuNW layers were prepared by manually dipping a glass slide into a 2 mg/mL AuNW dispersion. The process was repeated 5 times to obtain 10 nm thick layers.

2.2. Annealing of AuNW layers

Thermal annealing was carried out by placing the samples on a hot plate (Harry Gestigkeit GmbH, Germany) that was pre-heated to the desired temperature. Plasma treatments were performed in a RF PICO plasma system (13.56 MHz, Diener electronic GmbH & Co. KG, Ebhausen, Germany) operating at 100 W RF power and 0.3 mbar of pure oxygen or 5% hydrogen in argon.

3. Results and discussion

Figure 1(a) shows a transmission electron microscopy image (TEM, JEM 2010, JEOL, Germany) of the as-synthetized AuNWs. The diameter was 1.6 nm; the length could only be estimated to be several microns. The distance between the surfaces is due to the OAm interdigitation between the monolayer of each wire (see scheme in Fig. 1(b)).

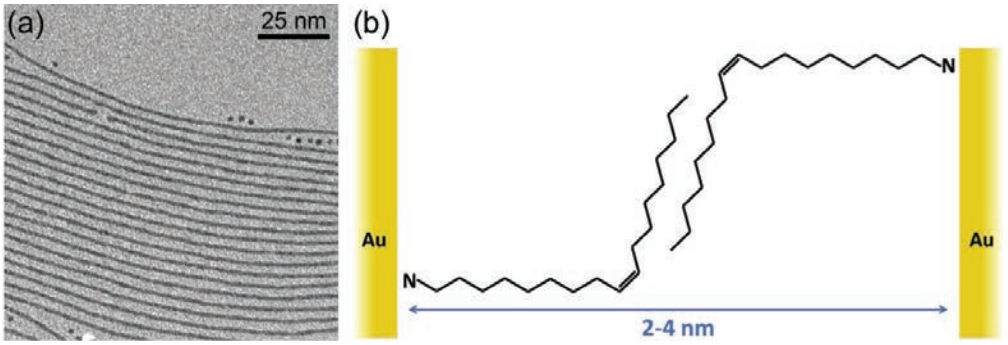

Fig. 1. (a) TEM image of the as-synthetized AuNWs. (b) OAm interdigitation between AuNWs.

The deposition was performed by manually dipping glass slides into the AuNWs dispersion. After deposition, the substrate acquired the dark red that is characteristic of the surface plasmon resonance of these gold nanostructures. Photographs of the sample and normalized UV-vis spectra recorded in transmission (Cary 5000, Varian) are shown in Fig. 2.

The as-deposited AuNW layers exhibited sheet resistances above 40 MOhm/sq. In order to remove the OAm attached to the surface of the wires, we placed the samples on a hot plate at 400 ºC. The samples turned blue-green after 2 s and pink after 2 min. (Fig. 2). None of these samples was conductive after annealing.

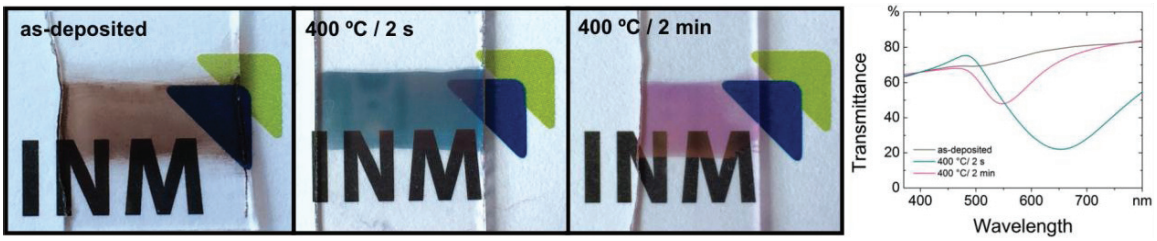

Fig. 2. From left to right: photographs of the as-deposited AuNW layer, after 2 s, and after 2 min at 400 ºC, and normalized UV-vis spectra of the samples.

The characteristic surface plasmon resonance of metal nanoparticles strongly depends on the size and shape of the nanostructures,[9] indicating changes in structure during annealing. We investigated the layers by scanning electron microscopy (SEM, Quanta 400 ESEM, FEI, Germany) and found drastic structural changes (Fig. 3). Bundle-like superstructures had formed from the AuNWs during drying. After 2 seconds at 400 ºC, the AuNWs fragmented into small spheres with plasmons shifted towards the red and a broader band in the UV-vis spectrum. The close packaging of particles found for this sample intensifies the plasmon shift. Longer annealing at 400 ºC led to further coarsening. The blue shift in the spectrum is probably due to the particle spacing caused by Ostwald ripening (see Fig. 3c).

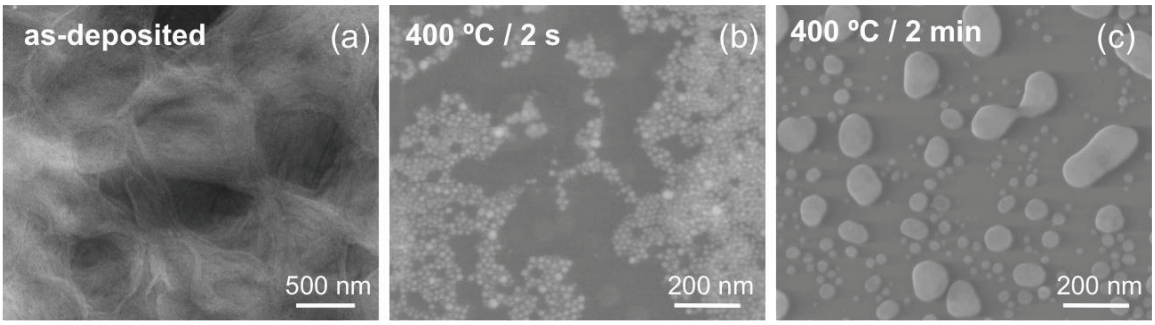

Fig. 3. SEM images of the as-deposited AuNW layer (a), after 2 s (b) and after 2 min (c) at 400 ºC.

We also investigated thermal treatment at 200 °C. The results were comparable: the evolution of the nanostructure was as above, but it took longer to reach large particles. The fragmentation of AuNWs is dominated by the Rayleigh instability that occurs (slowly) even at room temperature,[10,11] while the large particles probably form by Ostwald ripening. Both processes are accelerated by increased temperatures.

Plasma treatment was investigated as alternative method to remove the OAm. As-deposited layers were exposed to pure O_2 plasma or to a mixture of 5% H_2 in Ar (denoted as H_2-plasma) for different times. All layers were conductive after treatment and the same trend was found in both cases: sheet resistances decreased with treatment times. Table 1 collects the sheet resistance averages for all studied samples. Moreover, the transparency of the layers remained unchanged as can be seen in the photographs and in the UV-vis spectra included in Fig. 4(a).

Table 1. Conductivity values obtained for layers treated, oxygen- and hydrogen-plasma during the indicated time.[7]

Sintering\Time	1 min	5 min	15 min
O_2-plasma	$7 \cdot 10^5$ Ohm/sq	200 Ohm/sq	100 Ohm/sq
H_2-plasma	$2 \cdot 10^5$ Ohm/sq	80 Ohm/sq	50 Ohm/sq

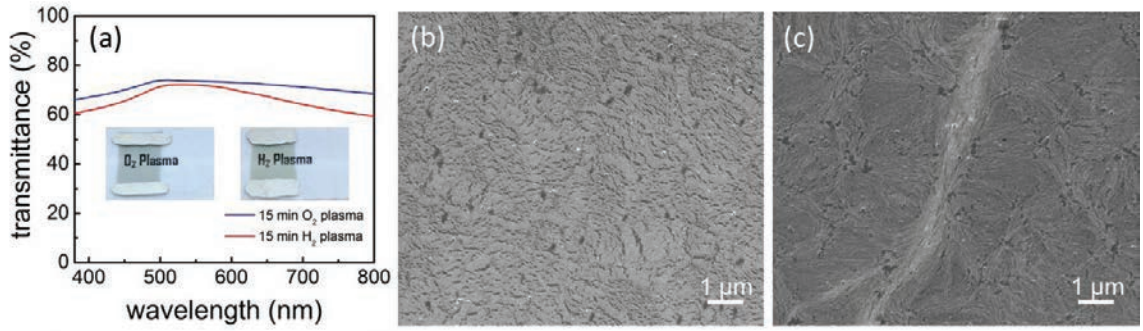

Fig. 4. (a) UV-vis spectra of the layers treated by O_2- and H_2-plasma. Photograph of the layers are included as insets. SEM images of the layers after 15 min (b) O_2- and (c) H_2-plasma.

Fig. 4(b) and 4(c) show the morphology of the resulting layer after O_2-plasma and H_2-plasma treatments respectively. While the H_2-plasma sinters of AuNWs and coarse the structures formed by them, O_2-plasma alters the morphology of the layer due to the partial oxidation of gold. The absence of spheres was confirmed using higher magnifications.

During thermal annealing, the fragmentation caused by the Rayleigh instability is accelerated and occurs faster than the OAm removal. As result, the AuNWs decomposed into spheres faster than they sinter together. Plasma

treatments remove the organic ligands and sinter the wires at the same time, which lead to bigger structures more stable toward Rayleigh instability. To clarify the mechanisms involved in the sintering processes further experiments should be performed.

Thermal treatments destroyed the original nanostructure entirely and caused large gaps between metal islands. We find that plasma treatments are preferable for the creation of TCMs from AuNW.[7]

4. Conclusions

Ultrathin gold nanowires were studied for transparent conductive materials. The conductivity of layers deposited directly from AuNWs dispersion was limited by insulating barriers formed by the capping ligand, oleylamine. We demonstrated that thermal annealing cannot remove the ligands and causes the AuNWs to decompose into unconnected spheres. Plasma treatments were more efficient in removing the ligand shells while retaining structures suitable for TCMs. The best results were obtained using reducing hydrogen plasma that yielded films with 50 Ohm/sq while retaining transparency.

We believe that the combination of ultrathin AuNWs with plasma treatment is a promising route to transparent electronics.

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