Template-Fabricated Gold Nanowires from Gas-Phase Transport Reactions

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Aluminium oxide membranes are partially filled with solid nanowires of gold by chemical vapour transport (1000 to 650 °C) using iodine as the transport agent. The transport is due to the formation of gas-phase AuI.

Introduction

The fabrication of solid-state nanostructures has mainly been motivated by their expected quantum-size physical phenomena. In particular, nanowires are interesting entities in which carriers are confined in the radial dimension although transport is possible along their axial dimension. Various fabrication techniques have been developed for the synthesis of the nanowires, including template synthesis[1] and the vapour–liquid–solid growth mechanism.[2]

Porous anodic alumina has frequently been used for the templated synthesis of nanowires since this porous template material consists of a self-assembled honeycomb array of uniformly sized parallel channels. Because of the transparent, thin, sheet-like character of the porous material it is often called "alumina membrane". Thus, arrays of aligned nanowires that are uniform in diameter can be obtained reproducibly by filling the pores of these membranes. Moreover, these membranes are thermally inert up to about 1000 °C.

Two successful strategies to fill these alumina nanotubes have been investigated so far, namely electrochemical deposition processes[3] and chemical processes involving degradation of precursors (inorganic or organometallic[1,4]) after immersing the template material in solution.

In this work we will report on our investigations to fill aluminium oxide membranes by means of chemical transport reactions in the gas phase in a chemical equilibrium. This type of reaction[5] can be characterised in a way where a solid or a liquid substance A reacts with a gas B to form only gaseous products [e.g. C, Equation (1)].

$$i\,A_{s,l} + k\,B_g + \ldots \rightleftharpoons j\,C_g \quad (1)$$

In a temperature gradient, i.e. areas of different temperature in a closed system (e.g. a sealed ampoule), a reversible decomposition of this gaseous product results in the formation of the solid/liquid A and the gas B again. From the outside the situation appears to be a sublimation or distillation of A, although the vapour pressure of the transported species A is negligibly small. In fact, the solid/liquid A is chemically transported.

In order to start with this new technique and to gain experience for the planned incorporation of semiconductor materials (see below), we decided to perform the synthesis of gold colloids inside aluminium oxide nanotubes, which has been thoroughly investigated by several research group before.[4] The chemical transport of gold by means of iodine has only been reported in a qualitative way;[6] the transport effect by chlorine was first described by Biltz.[7,8]

In this work we report on the chemical transport of gold by gaseous iodine in a temperature gradient between 1000 and 650 °C by means of AuI. Gaseous AuI is supposed to be the essential species of the transport mechanism according to Equation (2).

$$(650\,^{\circ}C)\ Au_{(s)} + \tfrac{1}{2}\,I_{2(g)} \rightleftharpoons AuI_{(g)}\ (1000\,^{\circ}C) \quad (2)$$

This mechanism is substantiated by calculations of the partial pressures of the gaseous species. These calculations are based on the thermodynamic data of some halides of gold which were experimentally not accessible until now, but which were recently provided by quantum-chemical investigations.[9,10]

Results

Chemical Vapour Transport

In a typical experiment, both 100 mg of gold and 50 mg of iodine were sealed in an evacuated quartz tube (outer diameter: 10 mm; wall thickness: 1 mm) of about 8 cm^3 vol-

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ume. The ampoule was placed in an oven with two independently heated zones at 1000 and 650 °C (at 650 °C the total pressure in the ampoule is estimated to be 2 bar). After two days, irregular shaped crystallites consisting of gold were formed at the low-temperature side of the quartz ampoule. When placing aluminium oxide membranes at the low-temperature side, the colour of the template material changed from colourless before the transport reaction to purplish red after the experiment (Figure 1). This change of colour is an indication of the successful filling of the membrane with gold.[1] Within 48 h about 5 mg of gold are chemically transported. Performing the experiment under identical conditions but without iodine did not lead to any gas-phase transport of gold.

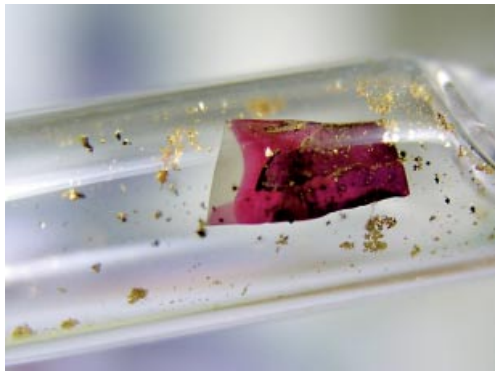

Figure 1. Low-temperature side of a quartz ampoule after chemical transport of gold with iodine.

Transmission Electron Microscopy (TEM)

The membranes were analysed by transmission electron microscopy (TEM). The samples were prepared by milling in a mortar and by suspending the material together with ethanol onto the copper grid by means of an ultrasonic bath. This preparation provides a qualitative view of the dimensions of the membrane and its filling. Figure 2 shows images of the partially filled alumina membrane, including a transverse and a top view of a channel filled with a solid gold nanowire of the exact diameter given by the membrane. As expected from the anodisation voltage of 40 V, channels with a diameter of 50 nm are observed.[1] The aspect ratio of the gold nanorods is about 8. Spherical colloids or flakes, as reported by the groups of Schmid[1] and Martin,[11] are not found.

Further investigations, for example the dissolution of the template material and the analysis of the free gold nanowires by TEM, are underway because, in contrast to the solubility of "as prepared" membranes, the heated template is not soluble in aqueous solutions of acids and bases and therefore this common technique cannot be applied.

Spectroscopic Characterisation

UV/Visible absorption spectra were recorded with an LOT Oriel SPEC II diode array and spectrograph with the

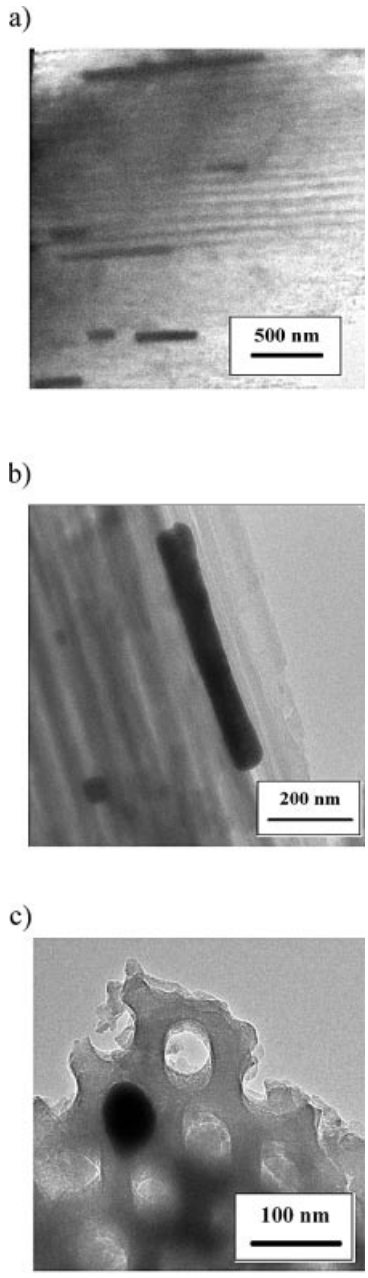

Figure 2. TEM images of the aluminium oxide membrane (channels of 50 nm diameter): a) several solid gold wires, b) transverse view and c) top view of a single wire.

template membranes oriented perpendicular to the incident beam. The absorption spectrum of a filled membrane, with λ_{max} at 550 nm, is shown in Figure 3. This observation is in line with earlier reports on aluminium oxide filled with gold wires and colloids by different methods. Martin et al. have analysed the effects of particle size and aspect ratio on the optical spectra of gold nanowires prepared by electrodeposition.[12] For an aspect ratio of gold nanowires (diameter 60 nm) of between 1.6 and 7.4, an absorbance maximum of 520 nm is reported. Furthermore, Schmid and Sawitowski have reported a bathochromic (red) shift of 20 nm when comparing tempered with untempered alumina (diameter 50 nm) filled with gold colloids. This shift is caused by an

increase of the dielectric constant after phase transformation leading to crystalline Al_2O_3 upon heating the samples to about 800 °C.[11,13] The extinction maximum (550 nm) found by us is in line with these reports.

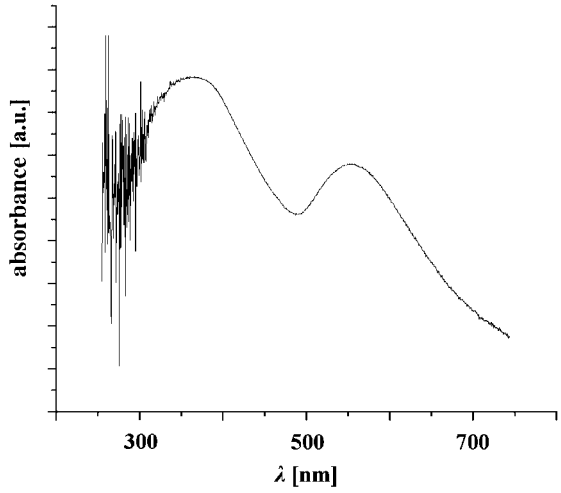

Figure 3. UV/Vis transmission spectrum of an aluminium oxide membrane filled with gold.

Thermodynamic Considerations

In order to obtain information on the gas-phase species responsible for the observed transport of gold, we performed thermodynamic calculations on the partial pressures of the possible gaseous iodides of gold: AuI, AuI_3 and their dimers Au_2I_2 and Au_2I_6.

The reactions inside the quartz ampoule can be described by the following gas phase equilibrium involving Equations (3), (4), (5), (6), (7) and (8):

$$2\,AuI_{(g)} \rightleftharpoons Au_2I_{2(g)} \quad (3)$$

$$2\,AuI_{(g)} + 2\,I_{2(g)} \rightleftharpoons 2\,AuI_{3(g)} \quad (4)$$

$$2\,AuI_{3(g)} \rightleftharpoons Au_2I_{6(g)} \quad (5)$$

$$Au_{(s)} \rightleftharpoons Au_{(g)} \quad (6)$$

$$I_{2(g)} \rightleftharpoons 2\,I_{(g)} \quad (7)$$

$$Au_{(g)} + I_{(g)} \rightleftharpoons AuI_{(g)} \quad (8)$$

The values for the entropy and heat of formation of gaseous I atoms, I_2 and solid and gaseous gold were taken from the collection of thermochemical data of Binnewies.[14] However, experimentally deduced thermodynamic data of the gold iodides are not yet available. Fortunately, these species have been investigated by means of quantum-chemical methods taking into account electron correlation and relativistic effects.[9,10] Thermochemical data on the reactions that may be relevant for the transport experiment in the system gold/iodine are given in Table 1. In addition to the thorough work of Schultz and Hargittai,[10] Schwerdtfeger[9] has reported highly correlated calculations, especially on the AuI molecule. The data obtained − geometric structure, bond dissociation energy and vibrational frequency − are necessary to obtain the heat of formation and entropy of $AuI_{(g)}$, and therefore we mainly use these data for the following discussion. Solid AuI is not relevant for these calculations for the following reason: from thermogravimetric analysis we found that solid AuI is completely decomposed at 140 °C. This observation was confirmed by the calculation of the dissociation pressure by means of the reverse reaction (2′).

$$AuI_{(s)} \rightleftharpoons Au_{(s)} + 1/2\,I_{2\,(g)} \quad (2')$$

According to this calculation the vapour pressure of I_2 over solid AuI at about 200 °C should already be 3 bar, and at 650 °C, as in our experiments, no solid AuI should be present at all because the dissociation pressure should be more than 3 kbar.[14]

In order to describe the complex equilibrium situation in which seven gaseous species are involved (Au, I, I_2, AuI, Au_2I_2, AuI_3, Au_2I_6) quantitatively, one needs the six expressions [Equations (3–8)] of law of mass action given above and, additionally, the equation for the total pressure of iodine describing the mass balance of iodine:

$$p_{total}(I_2) = [p(I) + 2p(I_2) + p(AuI) + 2p(Au_2I_2) + 3p(AuI_3) + 6p(Au_2I_6)]/2$$

where $p_{total}(I_2)$ represents the pressure of I_2 before realisation of the chemical equilibrium. The calculated partial pressures are given in Figure 4 for a typical experiment. The gaseous Au-containing species with the largest partial pressure is monomeric AuI (1300 K: 9×10^{-3} mbar; 1000 K: 1×10^{-5} mbar). All data presented so far are mainly based on the theoretical calculations of Schwerdtfeger[9] (see above). However, the thermodynamic data from the quantum-chemical calculations of Schultz and Hargittai lead to an essentially similar situation.[10] The temperature dependence of $\Delta_R H^0$ and $\Delta_R S^0$ was not taken into account in the calculations due to several other uncertainties (see below).

Discussion

The reaction of gold with iodine in a sealed quartz ampoule in a temperature gradient leads to a chemical transport of gold from the high- to the low-temperature side. From thermochemical calculations we found that, in principle, the reaction given in Equation (2) is responsible for this transport. Gaseous gold is not the transport-relevant species as its vapour pressure in the temperature range under discussion is about three orders of magnitude lower than the partial pressure of AuI.[14] From a rough quantitative estimation of the transport rate based on diffusion processes as the main transport mechanism, only about 0.1 mg of Au should be transported within 24 h. Therefore, the observed higher transportation rate leads to the conclusion that both diffusion and convection contribute to the transport effect. This mechanism seems plausible as the total pressure in the ampoule can reach up to 4 bar in a typical

Table 1. Thermodynamic data for the formation of gaseous Au_2I_6, AuI_3, Au_2I_2 and AuI from solid Au and gaseous I_2.

Reaction	$\Delta_R H^0$ [kJ mol^{-1}]	$\Delta_R S^0$ [J mol^{-1} K^{-1}]	References
$2\,AuI_{(g)} \rightleftharpoons Au_2I_{2(g)}$	–112.1	–129.6	[9]
$2\,AuI_{(g)} + 2\,I_{2\,(g)} \rightleftharpoons 2\,AuI_{3(g)}$	–117.3	–224.1	[9]
$2\,AuI_{3(g)} \rightleftharpoons Au_2I_{6(g)}$	–135.3	–194.5	[9]
$Au_{(g)} + I_{(g)} \rightleftharpoons AuI_{(g)}$	–200.9	–96.8	$\Delta_f H^0(Au_g)$, $\Delta_f H^0(I_g)$: ref.[14] D_0(AuI): ref.[9] ΔS^0 (AuI) derived from ν(AuI) [9]
$Au_{(s)} \rightleftharpoons Au_{(g)}$	368.4	132.9	[14]
$I_{2(g)} \rightleftharpoons 2\,I_{(g)}$	151.4	101.4	[14]

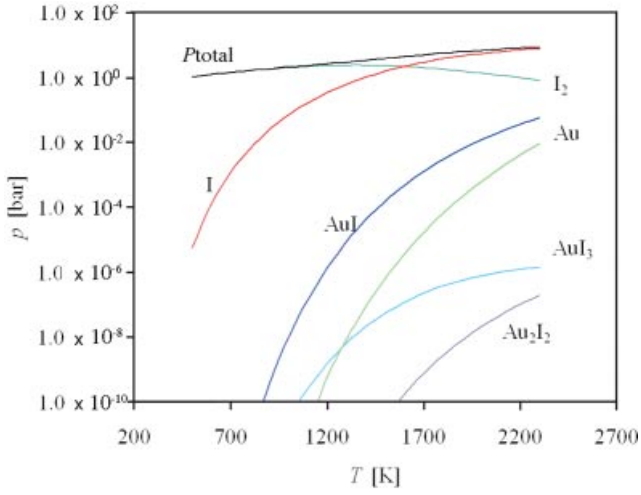

Figure 4. Partial pressures in a typical transport experiment [volume 8 cm^3, $m(I_2)$ = 50 mg].

experiment as the temperature gradient is large. Furthermore, the bond-dissociation energy of AuI is difficult to determine by quantum-chemical means. The calculated value (200.9 kJ mol^{-1}) is lower than the value determined by mass spectrometry [217.7 kJ mol^{-1} > D_0(Au–I) > 267.9 kJ mol^{-1}] [15] and microwave spectroscopy (276.3 kJ mol^{-1}).[16] Consequently, its vapour pressure and the transport rate can only be calculated within this uncertainty. [Estimations of the transport rate using these data lead to values of 0.4 (D_0 = 217.7 kJ mol^{-1}), 42.2 (267.9 kJ mol^{-1}) and 91.7 mg Au/24 h (276.3 kJ mol^{-1}), respectively].

In this work we have presented a novel method to fill aluminium oxide membranes by a gas-phase transport reaction. In order to be useful for this process, these reactions must fulfil the following prerequisites: a) the reaction must transport a bulk material in a temperature gradient and the reaction should work in a temperature range in which the vapour pressure of the relevant gaseous species exhibits significant changes; b) the reaction should take place in a temperature range below 1000 °C where aluminium oxide membranes are known to be thermally stable. Furthermore, the transport gas (here I_2) must be chemically inert with respect to the template material; c) to obtain long solid wires the supersaturation of AuI in the gas phase should be low. A low number of growing crystal seeds inside the template leads to a rather low degree of filling and the aspect ratio of these solid wires is high. In contrast, a high supersaturation, which is a consequence of a high transport rate, leads to a preferential crystallisation of gold outside the channels. Therefore, under these conditions perfect gold crystals are observed on the surface of the membrane.

We believe that this introduction of chemical-transport reactions to nanoscience is only the first step in a strongly developing field. This progress was made possible, and may be expanded in the future, because thermochemical calculations can now be supported by quantum-chemical investigations of unknown thermodynamical data also for hypothetical gaseous species.

Using this method it should be possible to fill almost any metal into alumina membranes, even those with a very low vapour pressure. Furthermore, alloys, mixed crystals with tunable composition[17] and semiconductor materials may be suitable. Therefore, based on the results presented here, we have started experiments for the transport of gold at lower temperatures in order to fill thermally less-stable nanoporous materials (e.g. zeolites). Furthermore, we intend to fill nanoporous aluminium oxide with the semiconductors GaP[18] or GaAs.[19] For this purpose, we first investigated an unexpected chemical-transport reaction [Equation (9)[20]] where only the elements gallium and phosphorus or arsenic are involved such that very pure semiconducting materials can be expected.[18,19]

$$GaX_{(s)} + X_{4(g)} \rightleftharpoons GaX_{5(g)}\ (X = P, As) \quad (9)$$

Experimental Section

Preparation of Aluminium Oxide Membranes: The mesoporous alumina membranes were produced by anodising electropolished, high purity aluminium plates in oxalic acid, using a lead plate cathode. Full details are given elsewhere.[1] The pore diameters are monodisperse and linearly related to the anodising voltage (40 V, 50 nm). The pores are perpendicular to the membrane surface and are packed in an ordered hexagonal array with a wall thickness comparable to the pore diameter. The membrane thickness, ranging up to several hundred microns, can be controlled by the time of the anodising process.

Acknowledgments

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[20] Although the transport of bulk GaP or GaAs takes place in a temperature gradient (1000 to 900 °C) in which the ordered alumina pores are still thermally stable, we were unable to produce nanotubes or nanowires consisting of GaX with a Ga:X ratio of exactly 1:1, probably due to the reaction of X_4 with the membrane material.

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