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Facile preparation of catalytically active, microstructured gold patterns on quartz and silicon substrates

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ABSTRACT

Here we report that “liquid bright gold” (LBG), a precursor for the thermal gilding of ceramics, can be structured using photolithography. No expensive and complicated equipment (such as high vacuum) is needed making the method favorable over electron beam evaporation and sputtering processes. Additionally, the method stands out by its simplicity needing only a few steps to create gold structures within a size range of 50 μm to 1 μm, which in turn consist of either an irregular network or isolated nanoparticles, depending on the treatment. Such hierarchically structured gold patterns could find a variety of applications, as exemplified for the patterned growth of silicon nanowires.

1. Introduction

Miniaturization of patterned structures is an important step in the fabrication of new micro-sized devices, e.g. for microelectronics [1], for biosensing [2], or for cell patterning [3]. Well-established ways to create micro- and nano-structures are often based on micro-contact printing [4] or lithographic techniques [5]. For the so-called subtractive processes, first a complete film of the desired material is deposited, e.g. by physical vapor deposition (PVD), on which then certain regions are protected either by a self-assembled monolayer or some polymer, followed by removal of the unprotected parts of the film by etching. In the additive manner, typical for most photolithographic processes, the patterned polymer is first deposited on the substrate, followed by the deposition of the respective material. Dissolution of the polymer then also removes all the unwanted parts of the film (“lift-off”). While for the subtractive methods very smooth films, such as those obtained by electron-beam evaporation, are required to attain a high spatial resolution, the additive method partly can also deal with rougher and more uneven films, which might even be nanostructured within themselves. If somewhat rougher or less even surfaces are desired, other surface patterning approaches have to be used [6].

Very different surface morphologies can be attained by using a group of methods summarized under the term chemical vapor deposition (CVD) [7]. For these, some molecular precursor becomes decomposed on or near the surface by supplying energy, e.g. in the form of heat, light, or plasma. Typically, the deposition efficacy and the nature of the deposited material, such as its crystallinity [8], composition [9], and appearance [10], is strongly influenced by the character of the substrate. These properties can often be controlled by catalytically active materials present at the surface, the patterning of which then also results in a patterned deposition of the CVD product [11]. Controlling the constitution of the patterned surface is therefore a key step in the creation process of new materials [12].

Here, we wish to present a new approach for patterning catalytically active gold nanoparticles onto surfaces such as quartz or silicon, which in turn can be used for the CVD of silicon wires. The method stands out by its simplicity and its ability to produce hierarchical patterns of gold nanostructures with a lateral resolution down to the size of 5 μm (for quartz) and 1 μm (for silicon), respectively. Our method does not require a preformed gold surface (thus eliminating the need for PVD equipment, such as an electron-beam evaporator) and does not involve a commercial photoresist, permitting to work under ambient light. Furthermore, no acids or other corrosive chemicals are required, so that the work can be performed under standard laboratory conditions. As gold precursor, we employ so-called “liquid bright gold” (LBG), a mixture obtained by heating gold, sulfur, and terpenes [13], which is used in the porcelain manufacturing industry to paint gold rims

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onto tableware. When the tar-like material is heated to 650 °C in the presence of air, the sulfurized organic components of the LBG burn away leaving a layer of pure gold on the surface [14]. As we found, the resulting gold films are typically a more or less connected network of gold nanoparticles, the catalytic properties of which should be exploited for the deposition of further materials. Due to the current interest in nano-structured silicon e.g. for photovoltaics [15] or as energy storage materials [16], we wanted to use these gold patterns for the gold-catalyzed, patterned growth of silicon nanowires [17].

2. Materials and methods

LBG (Screen Printing Bright Gold 14603, gold content 7–15%) was obtained from Surcotech, UK. According to the manufacturer's information, this material consists mainly of terpineol (10–30%) and low amounts of eugenol as well as aromatic and aliphatic hydrocarbons (1–5% each) [18]. These mixtures are typically reacted with gold chloride and sulfur or with sulfurized organic compounds to yield the LBG [19]. For the deposition, a chloroform solution containing 6 wt% of LBG and 10 wt% of toluene was produced and filtered through a 0.2 μm PTFE syringe filter (VWR). The dark solution was found to be stable over several months when stored at 7 °C under exclusion of light.

The silicon and quartz substrates were cleaned with freshly prepared piranha solution (3 parts of H_2SO_4 (96%) + 1 part H_2O_2 (30%). Caution! This mixture reacts violently with organic materials, in particular solvents!), washed with copious amounts of demineralized water, and dried in a stream of nitrogen prior to use.

A custom made chromium mask on quartz (ML&C, Jena, Germany) was used as a photomask. This mask provided several line patterns with line widths varying between 50 μm and 1 μm.

For patterning, the substrates were spin-coated with the LBG solution for 30 s at 7000 rpm. To reduce the stickiness of the LBG layers, they can be treated with a O_2 plasma prior to illumination. However, since the stickiness did not turn out to be a major problem, this step did not become part of the general procedure. The substrates were then placed directly behind the photomask and illuminated with a 150 W medium-pressure mercury vapor lamp (TQ 150, Peschl Ultraviolet) for 3 h. To develop the structures, the substrates were immersed in chloroform for about 15 s to remove the unexposed LBG. The patterns, which are typically visible to the bare eye, were then dried in a stream of nitrogen and analyzed by atomic-force microscopy (AFM, Bruker DI 3100,) and scanning-electron microscopy (SEM, Atomica/Amray 1920 ECO and FEI Nova Nanolab 600) measurements. Additionally, optical micrographs (Reichert, Univar) of the larger structures were recorded.

To transform the LBG patterns into gold patterns, the substrates were annealed at 650 °C in the presence of air. Alternatively, a 3 h treatment with an O_2 plasma (Harrick Plasma Cleaner/Sterilizer PDG-32G) can be used to the same effect. The full patterning process is schematically shown in Fig. 1. The resulting gold patterns again were analyzed with SEM and AFM measurements.

On the patterned gold surfaces, silicon nanowires could be grown in the published manner [20]. In this case, neopentasilane [21] was used as silicon precursor and was carried by a stream of argon over the patterned substrates, which were heated to 650 °C. Within an hour, a deposit of nanowires clearly visible to the bare eye could be found on the substrate. Since those nanowires were typically longer than 20 μm, smaller patterns only became visible after sonicating the substrate in ethanol for 1 min to shorten the nanowires.

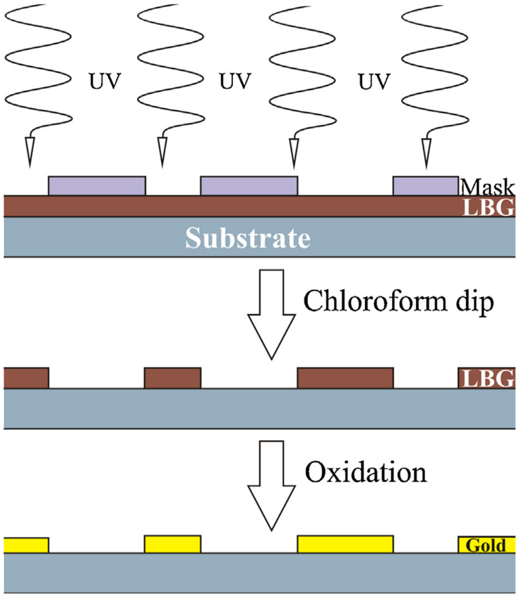

Fig. 1. Scheme of the lithographic process used to create gold patterns on a surface.

3. Results and discussion

Based on the assumption that the gold compounds in LBG would behave similar to the silver compounds in the classic photographic process, we tested the photochemical properties of LBG. Surprisingly, irradiation of the material did not result in the direct formation of gold, but rather in the formation of an insoluble resin, presumably by photochemical crosslinking of the organic matrix. This matrix consists of oligomerized terpenes, a class of substances rich in double bonds. The photo-induced copolymerization of the main compound, terpineol, has already been reported [22]. Since this behavior is similar to the one of 'negative' photoresists, it was obvious to apply LBG in a photolithographic process. For this, solutions of the LBG were spin-coated onto inert substrates, such as silicon or quartz. Of the different solvent systems tested, a 9:1 mixture of chloroform and toluene turned out to be most advantageous: The LBG is almost completely soluble in this mixture, it remains stable over months if stored in a refrigerator, and the evaporation properties of the mixture permit the spin coating of smooth, thin films. These films were irradiated with a medium-pressure mercury vapor lamp in a water-cooled quartz housing to achieve the photoreaction. This step requires prolonged exposure times (3 h) because the LBG is a black material with a low penetration depth for UV photons. Thinner films which were obtained by using lower concentrated LBG solutions permitted a reduction of the exposure times, but also lead to lower gold concentrations on the substrate surfaces. For thicker LBG films, the dark color of the material leads to much longer exposure times and even then the films could not be completely converted, what resulted in a lift-off and loss of the patterns in the development step.

To generate patterns within the LBG films, a chromium mask supported on a quartz substrate was employed. In this case, the mask consisted of an array of line patterns with line width (and distances in between lines) of 1 to 50 μm. After exposure through this mask, the non-irradiated parts of the LBG films remain soluble in chlorinated solvents, so a short treatment with chloroform resulted in the development of the patterns. The larger LBG patterns (down to 10 μm) could be imaged by optical microscopy, while the smaller structures were analyzed by AFM measurements (Fig. 2).

The optical as well as the AFM micrographs of the patterned substrates show well separated line patterns in all size ranges,