# 1

# Fabrication of Microelectrodes Using Original "Soft Lithography" Processes



## 1.1. Introduction

Nowadays, there is a significant need for low-cost analytical tools that are capable of giving fast and accurate detection for environmental and medical applications. Downsizing devices is the main answer to this issue. It permits a high analysis throughput as well as both a decrease in sample and reactant consumption and a decrease in the instrumentation cost.

The most widely used technology, at the present time, for downsizing devices is photolithography [BRA 94]. A photosensitive resin is spin-coated onto the substrate surface, which is then irradiated through a mask using ultraviolet (UV) light. Whether the resin technology is positive or negative, the irradiated regions or the non-irradiated regions are removed using a developer. Metallic microstructures can be obtained using sputtering and lift-off. This technology makes possible the mass production of micrometric and sub-micrometric structures. However, this technology is not low cost because of the requirement for clean room facilities and high-tech equipment. In addition, this technology is not suitable for non-planar surfaces and it is only applicable on photosensitive materials (e.g. photoresists).

A new type of substrate patterning, known as soft lithography [XIA 98], and more especially microcontact printing, has been developed by Professor Whitesides' team. A soft elastomeric stamp (typically made from

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polydimethylsiloxane (PDMS)) with a relief structure is used to transfer it onto the substrate surface. In the microcontact printing (μCP) technique, the stamp is "inked" with a chemical solution and is then put into close contact with the substrate surface [XIA 98]. The stamp is peeled off and the surface is then patterned with the "ink".

The most popular application of μCP is the transfer of an alkanethiol as "ink" onto a gold surface [KUM 93]. Alkylthiols form a self-assembled monolayer (SAM) at the surface that protects gold from chemical etching. Whitesides' team has demonstrated that using this technology, patterns with characteristic features down to 30 nm can be achieved. Furthermore, this technology is of low cost. Whether the substrate is planar or not [JAC 95], various types of substrates can be used (e.g. silicon [XIA 95], glass [GEI 03] and polymer [HID 96]), and depending on the chemical function at the end of the alkyl chain, various surface chemistries can be obtained.

Our work aims at developing original localized metallization processes for the microfabrication of electrodes to be used in electrochemical biosensors. This technology is applied on polymer [BES 09] or glass substrates (work presented here). Two original processes using alkanethiol μCP are described: the first process consists of a selective peeling of the metal thin-film areas not protected by the SAM, which makes it possible to avoid any chemical etching step in the process; the second process consists of passivating, with the help of a SAM, a gold electroless catalytic coating deposited on the substrate, which makes it possible to trigger localized growth of the metal and to avoid the need for a homogeneous gold thin film deposited using Physical Vapor Deposition (PVD) onto the substrate surface.

## 1.2. Materials and methods

### 1.2.1. *Selective peeling*

For the selective peeling process, glass substrates coated with gold thin films were used. The thin film was deposited using PVD cathode sputtering (EMSCOPE SC 500). To improve the practical adhesion of gold to the glass substrate, a thin layer of silver nanoparticles was first deposited. More precisely, microscope soda-lime glass slides (Roth-Sochiel, Lauterbourg, France) were cleaned in a piranha solution (3:1 mixture of $H_2SO_4$ 96% and $H_2O_2$ 30%) at 130°C for 30 min. Glass slides were then rinsed in ultrapure water (MilliQ, Millipore) and dried under a continuous flow of nitrogen.

The thin layer of silver nanoparticles was prepared directly on the glass slide by successive immersion in a 4% KOH solution, a 0.2 $g.L^{-1}$ $SnCl_2$ solution and, finally, a 10 $g.L^{-1}$ $AgNO_3$ solution. Between each immersion, substrates were rinsed in ultrapure water. After drying under a continuous flow of nitrogen, substrates were metallized using PVD cathode sputtering. The thickness of the thin film was estimated to be about 20 nm following abacus.

For the selective peeling process, a monolayer of octadecanethiol was deposited by microcontact printing on the gold-coated substrate surface. To ensure this step, the PDMS stamp was stored in an ethanol solution of octadecanethiol (2 mM). After the octadecanethiol deposition, a glass substrate with adhesive on top (UHU glass adhesive, containing 2-hydroxyethylmathacrylate) was deposited onto the modified substrate. The two substrates were pressed to make possible the spreading of the adhesive along the whole area. The glass slides were then irradiated for 10 min under a UV lamp to ensure polymerization. After cooling, the glass slides were removed. On the gold coating side, areas not protected by the SAM were peeled off but removed gold parts exhibit the original pattern on the slide with the adhesive layer.

### 1.2.2. *Localized passivation*

Cleaned glass substrates (see section 1.2.1) were surface modified with 3- aminopropyltriethoxysilane (APTES) in order to obtain amino groups at the substrate surface. More precisely, substrates were immersed in a 1% APTES solution in methanol for 45 min. Substrates were then rinsed in methanol, ultrapure water and finally dried under a continuous flow of nitrogen.

The gold electroless catalytic coating was obtained by adsorbing gold nanoparticles on the amino groups at the substrate surface. For this matter, substrates were immersed in a gold nanoparticle solution for six hours. This catalytic coating was then passivated by octadecanethiol microcontact printing (2 mM ethanol solution).

For silver electroless metallization, the solution was prepared by mixing 0.5 g of $AgNO_3$, 0.02 g of $SnCl_2$, 31 mL of ultrapure water, 19 mL of ammonium hydroxide (25%) and 40 µL of formaldehyde. The solution was used at ambient temperature and metallization took place for 5 min.

## 1.3. Selective peeling process development and results

In the conventional microcontact printing process applied to gold substrates (Figure 1.1), localized SAM of octadecanethiol protects the substrate from chemical etching. Thus, microstructures are obtained by selective etching of unprotected areas. However, chemical etching necessitates the use of toxic solutions.

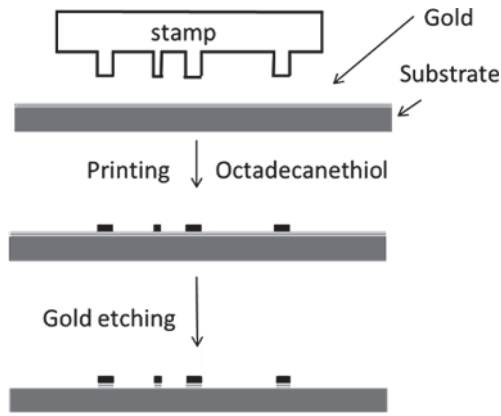


**Figure 1.1.** *Principle of conventional microcontact printing of alkanethiol to protect the gold layer from chemical etching*

In the first original process presented in this chapter (Figure 1.2), microcontact printing is used to obtain a localized monolayer of octadecanethiol. Unlike the conventional process, the gold layer is not etched but peeled off using an adhesive. Indeed, the SAM exhibiting a compact form prevents the adhesive from bonding to the gold layer. For unprotected areas, the adhesive sticks to the metal layer. To remove the adhesive, it is proposed to use a glass substrate that will also strongly stick to the adhesive. During the separation step, the bonding strength between the glass and the gold layer not covered by the octadecanethiol SAM is weaker than the bonding strength between the adhesive and the gold monolayer; thus, the latter will be peeled off.

Figure 1.3 shows an example of microstructures that can be obtained with the selective peeling process. The inset shows a close-up of the photographs and demonstrates the process feasibility for micrometric patterns (estimated smallest width about 60 μm).

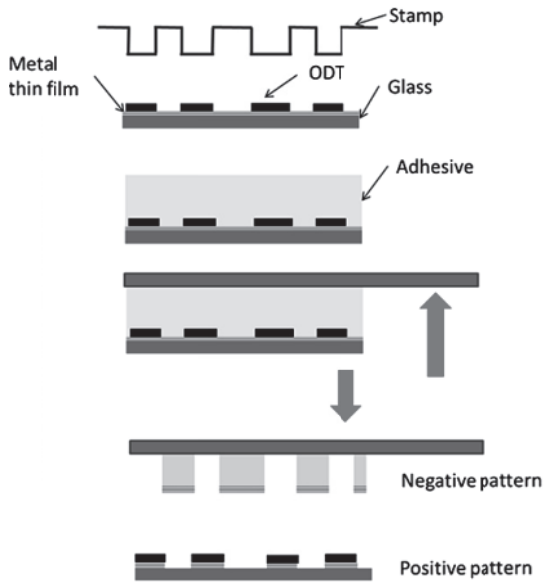


**Figure 1.2.** *Principle of the selective peel-off process*

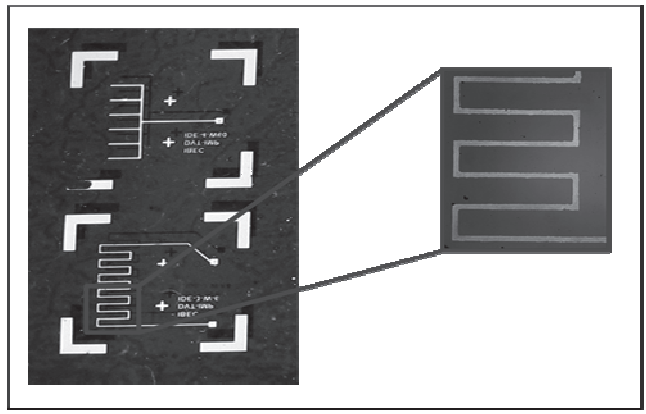

**Figure 1.3.** *Picture of an interdigitated electrode system obtained using the selective peel-off process applied with a gold thin layer and an alkanethiol self-assembled monolayer*

## 1.4. Localized passivation process development and results

In the localized passivation process, the aim is to grow a localized layer of electroless silver. Electroless metallization (Figure 1.4) is based on a

reaction between ions from the metal to be deposited and a chemical reducer, both being mixed in the same bath. The bath must be stabilized by the use of a complexing agent to limit spontaneous reduction of metal ions. Upon contact with a catalytic substrate surface (e.g. gold nanoparticles), reaction takes place and hence there is metal deposition specifically on this surface.

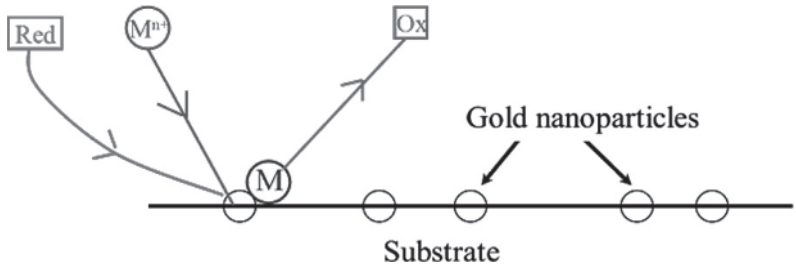


**Figure 1.4.** *Electroless metallization principle at the interface of a substrate coated with gold nanoparticles that are catalytic to silver electroless metallization*

The principle of the original process described in this chapter (Figure 1.5) consists of coating the whole surface of a glass substrate with a layer of gold nanoparticles that are catalytic to silver electroless metallization. In order to grow a localized silver electroless layer, octadecanethiol microcontact printing is used to passivate the catalytic layer. The octadecanethiol monolayer at the nanoparticle surface makes it possible to avoid any chemical etching at the surface. Thus, a silver deposit is obtained only in areas not protected by the SAM of octadecanethiol.

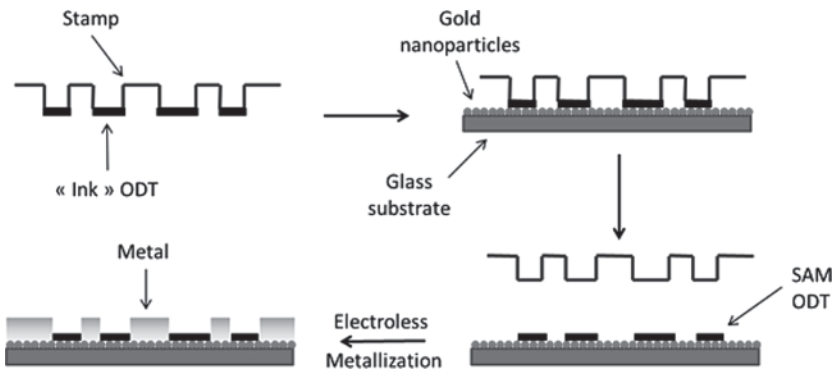


**Figure 1.5.** *Principle of the localized passivation process developed in this work*

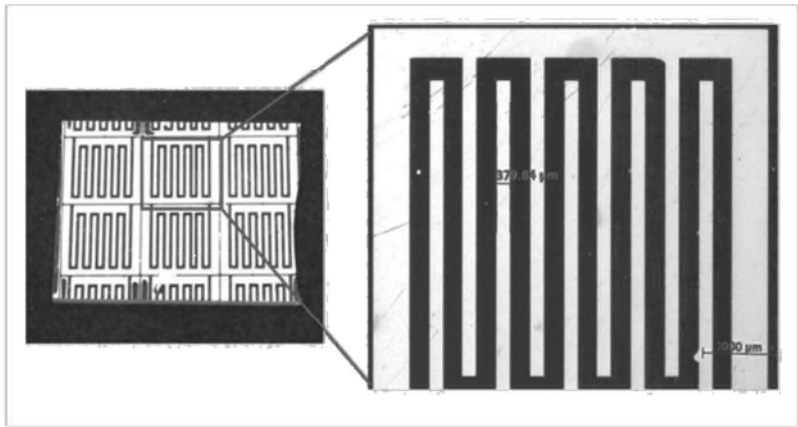

**Figure 1.6.** *Picture of a set of interdigitated electrodes obtained using the localized passivation process described in Figure 1.5*

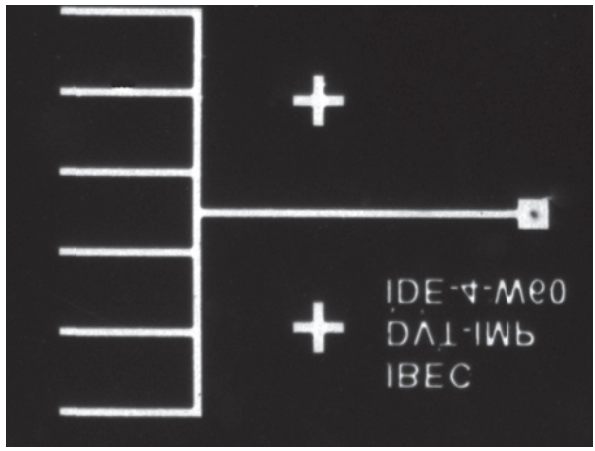


**Figure 1.7.** *Picture of a microelectrode obtained using the localized passivation process described in Figure 1.5. The smallest width is 60 µm*

Figure 1.6 shows an example of a set of interdigitated electrodes obtained using the localized passivation process based on a layer of gold nanoparticles, SAM localized deposition followed by silver electroless metallization. The pattern exhibits the smallest width dimension of about

300 μm. The same process was used to obtain electrodes exhibiting the smallest width of about 60 μm, as can be seen in Figure 1.7. It demonstrates the ability of this process to reproduce micrometric scale patterns.

## 1.5. Conclusions

Due to soft lithography and especially due to microcontact printing, two original processes making it possible to replicate microelectrodes were successfully developed.

In the first process (selective peeling process), an adhesive was used to reveal the patterns obtained using microcontact printing, which makes it possible to avoid any chemical etching step.

In the second process (localized passivation process), microcontact printing was used to obtain a localized passivation of a catalytic layer (gold nanoparticles), which makes it possible to obtain a localized silver electroless layer.

## 1.6. Bibliography

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