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Selective organic functionalization of polycrystalline silicon-germanium for bioMEMS applications

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Abstract

We selectively immobilized organofunctional silanes on top of polycrystalline silicon-germanium (poly-SiGe) layers, as a first step towards the fabrication of poly-SiGe-based bioMEMS (biomedical MicroElectroMechanicalSystems) by means of standard UV photolithography. 3-aminopropyl-dimethyl-ethoxysilane (APDMES) and 3-aminopropyl-triethoxysilane (APTES) molecules were immobilized onto resist-patterned poly-SiGe surfaces. The protocols for surface hydroxylation and silane immobilization were designed to be CMOS-compatible and to avoid damage to photoresist. Silanized surfaces were investigated both by means of fluorescence microscopy, and by FEG-SEM observation after labeling with 30 nm-diameter gold nanoparticles (NPs). We report the silanization protocols, together with the results indicating successful organic functionalization of the samples.

Keywords: Poly-SiGe; organofunctional silane; functionalization; bioMEMS.

1. Introduction

Among the several materials used in MEMS fabrication, polycrystalline silicon-germanium (poly-SiGe) opens interesting perspectives, since it can be post-processed on top of CMOS at CMOS-compatible temperatures[1,2]. This allows monolithic integration of MEMS with the driving electronics, while keeping independent optimization of integrated circuits and micromechanical parts. Thus, the investigation of poly-SiGe biocompatibility might lead to the fabrication of novel poly-SiGe bioMEMS with high performance and compactness.

Surface immobilization of organofunctional silanes is an important technology in bioMEMS diagnostic applications, allowing target molecule detection in biological environments[3]. The functional groups of organosilanes can in fact be exploited for adhesion of biomolecules to inorganic surfaces of MEMS devices. Moreover, organosilane patterning allows for spatial arrangement of biomolecules, which is of central importance in biosensing applications. Electron beam lithography, microcontact printing and UV irradiation are widely used as organosilane

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patterning methods[4,5]. Among the various techniques, UV photolithography is the most practical one, both for its wide availability as a standard microelectronic process, and for its property of allowing parallel transfer of many patterns to the substrate in a single step. We achieved patterning of APDMES and APTES layers on poly-SiGe surfaces by making use of standard photoresist lithography. In both cases, the protocols for surface hydroxylation and silane immobilization were designed to be CMOS-compatible and to avoid damage to the resist, and organosilane reactivity was preserved after resist removal.

2. Experimental

A poly-SiGe bilayer (600 nm of PECVD $Si_{0.35}Ge_{0.65}$ on top of 400 nm of CVD $Si_{0.25}Ge_{0.75}$) was deposited on top of a SiO_2-coated, <100>-oriented silicon wafer. Samples of 4 cm^2 area were cut. A rectangular resist pattern was transferred on the samples via standard UV photolithography (see figure 1.a). S1818 resist was spun onto the surfaces, obtaining an average thickness of about 1.6 μm. Postbaking time and temperature were set at 80 seconds and 115° C, respectively, in order to render the resist robust enough to pass through the subsequent process steps intact. The patterned surfaces underwent APDMES or APTES silanization protocols. In both cases, the choice of silane solvents aimed at preserving the quality of the resist film during silanization.

2.1. APDMES silanization protocol

Patterned samples were hydroxylated for 10 minutes in a 1:1:3 $NH_4OH:H_2O_2:H_2O$ solution at room temperature, allowing the formation of hydroxyl groups on the SiGe surface without damaging the photoresist. The samples were then nitrogen dried and immersed for 90 minutes in a 2.5% v/v APDMES/toluene solution to create amino-terminations on the surface, as shown in figure 1.b. Samples underwent multiple rinsing in toluene, acetone and isopropanol to eliminate the photoresist and any excess of silane. This resulted into patterned areas of APDMES (figure 1.c) where the silane amino-groups could bind fluorescent molecules. The samples were then immersed in a 250 μM, NHS-fluorescein solution in pH 7.2 phosphate-buffered saline (PBS) for 2h and rinsed in H_2O, in order to eliminate any excess of fluorescein (figure 1.d-e).
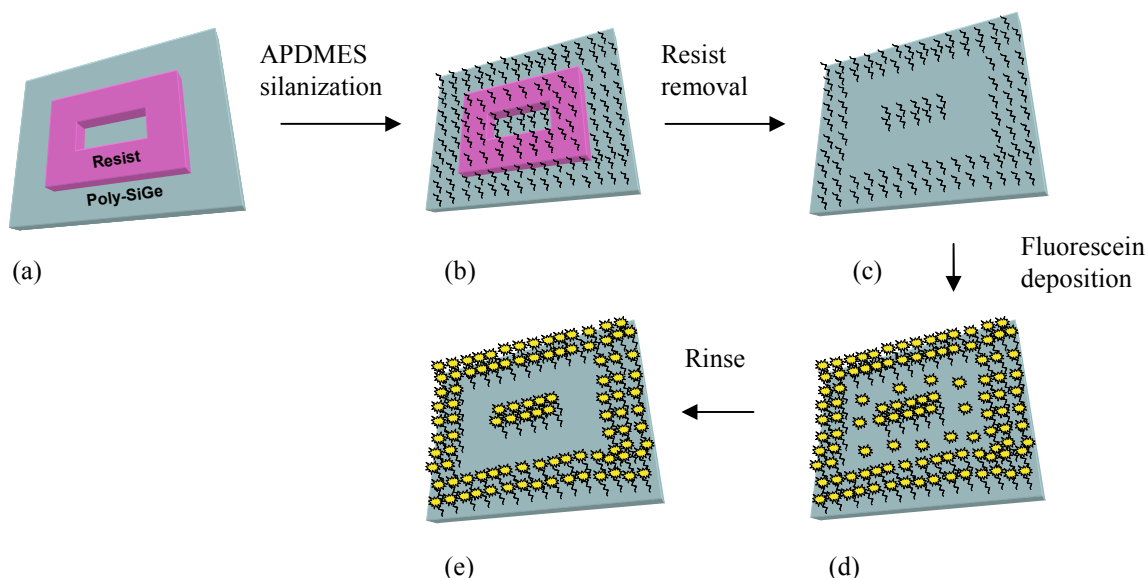

Fig. 1. APDMES silanization process: (a) patterning and resist-compatible hydroxylation, (b) deposition of APDMES, (c) resist removal and silane lift off, (d) fluorescent molecule deposition and (e) rinse of the excess of fluorescein.

Amino-modified poly-SiGe surfaces were also investigated by means of gold NP grafting. Unpatterned (i.e. without resist) samples were prepared. The samples were hydroxylated for 40 minutes in a 3:1 $NH_4OH:H_2O_2$ solution at room temperature and immersed for 24 hours in a 2.5% v/v APDMES/toluene solution. After rinsing in toluene and ethanol, a drop of gold nanoparticle colloid (British Biocell EMGC30, 30 nm diameter) was placed onto each surface and, after 1 hour, the samples were rinsed in H_2O. For comparison, the same protocol was used on a sample without silane.

2.2. APTES silanization protocol

The reaction of a trialkoxysilane (i.e., APTES) with poly-SiGe surfaces was also explored, by means of gold NPs grafting. Resist-patterned poly-SiGe samples (see figure 1.a) underwent hydroxylation for 10 minutes in a 1:1:4 $NH_4OH:H_2O_2:H_2O$ solution. The samples were then nitrogen dried and immersed for 5 minutes in a 0.05% v/v APTES/H_2O solution. A first rinse in H_2O allowed the removal of loosely-bound silanes and a subsequent curing in acetone for 1 hour removed resist residues. A thorough rinse and a curing step are crucial to the adhesion of the gold NPs. In fact, in aqueous phase silanization trialkoxysilanes undergo hydrolysis and polymerization in the bulk solution, before depositing on the surface[6]. This might result in physisorbed silane aggregates at the poly-SiGe surface, which cause gold NPs aggregation during dipping in the gold colloid. The phenomenon was confirmed by APTES silanization experiments without curing. After curing, the samples were rinsed in ethanol and underwent gold NPs grafting, by means of the same procedure which was used for the APDMES protocol (30 nm-diameter gold NPs colloid, 1 hour dipping).

3. Results and discussion

Fluorescence microscopy observation was performed on the patterned surfaces which were silanized by fluorescein-labeled APDMES. Figure 2 shows a boundary between a silanized and an unsilanized area. The contrast in the image indicates that fluorescent molecules grafted onto amino-termination (left brighter area), while excess of fluorescein was rinsed away in the unsilanized area.
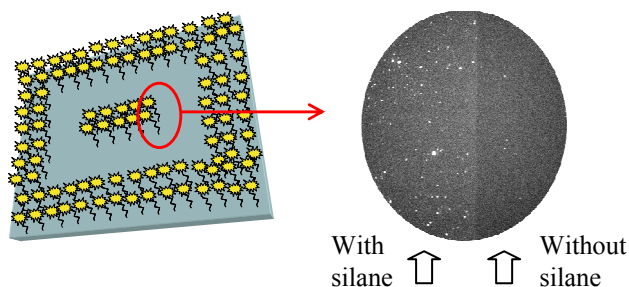

Fig. 2. Scheme of a APDMES-terminated surface (left) and fluorescence image (right) of a boundary between a silanized and an unsilanized area. The left brighter area was coated with APDMES. The image contrast indicates that fluorescent molecules were immobilized onto amino-terminations, while excess of fluorescein was rinsed away in the unsilanized area.
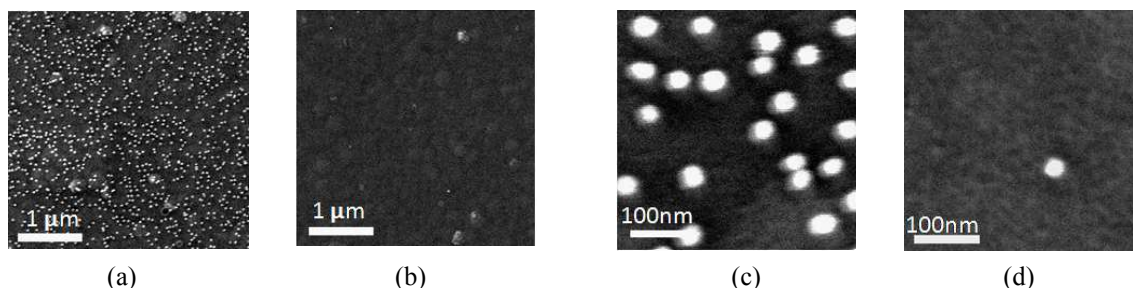

Fig. 3. SEM image of two poly-SiGe samples after dipping in a suspension of gold NPs for 1 hour. Images (a) and (c) refer to a APDMES-modified surface, while images (b) and (d) refer to an unmodified (i.e., not exposed to APDMES) surface.
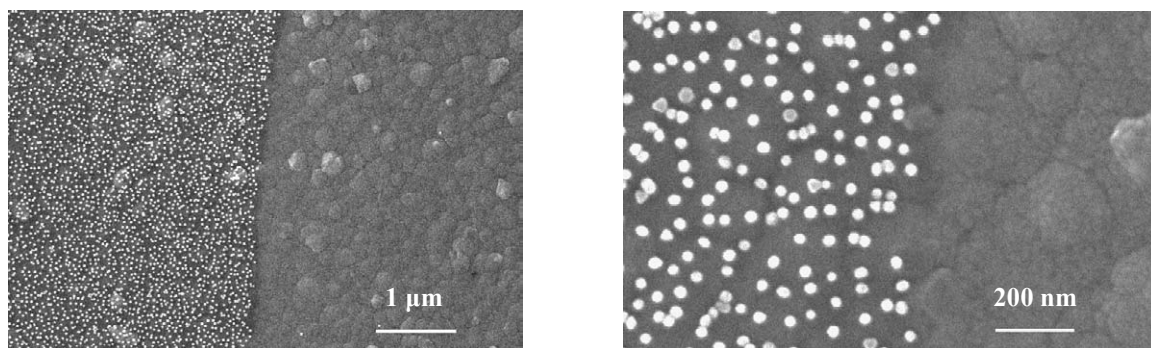
Fig. 4. SEM images of a poly-SiGe sample after patterned APTES silanization and gold NPs colloid dipping for 1 hour. Both images show a boundary between a silanized (left side, where a dense NP coverage is evident) and an unsilanized area (right side, with almost no trace of gold).

Figure 3 shows the results of SEM observation on APDMES-modified and unsilanized poly-SiGe surfaces after dipping in a gold NPs suspension for 1 hour. It is evident that NPs could be immobilized only onto silanized samples. In this case, the NP density was evaluated to be about $100/\mu m^2$.

Figure 4 illustrates SEM images of a sample with patterned APTES, after dipping in the same suspension for 1 hour. The two pictures, belonging to the same surface at different magnification, show the presence of gold NPs only on the silanized area. In the presence of APTES modification, the NP density is about $200/\mu m^2$. As compared with APDMES-modified surfaces, the APTES silanization protocol provides a higher density of NPs, which might be associated with a higher quantity of the silane layer.

4. Conclusions and future work

Interaction of APDMES and APTES with poly-SiGe surfaces was explored, yielding successful organic functionalization of the samples. The APTES silanization protocol seems to provide a higher surface coverage of gold NPs, even if the silane film quality still needs to be investigated. The obtained results demonstrated compatibility of poly-SiGe with organosilanes and the possibility of silane patterning via standard photoresist lithography. Immobilization of biomolecules on poly-SiGe surfaces is planned as well. This might lead to future research and development of poly-SiGe bioMEMS.

Acknowledgements

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