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Aryl-Diazonium Functionalized Polycrystalline Silicon Nanoribbons Based Device for Lead Detection †

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Abstract: Development of sensors enabling lead traces detection is a burning issue as heavy metals ions are responsible of brain diseases. In this paper, we present a simple electronic resistor based on polycrystalline silicon nanoribbons and functionalized with aryl-diazonium salts in view of using this type of structures for heavy metal detection. The preconcentration of lead at the surface of the functionalized nanostructures has been checked. Finally, electrical characterization of the resistors showed that the sensor sensitivity to these species is improved thanks to functionalization in the range 10^{-7} to 10^{-5} mol·L^{-1}.

Keywords: sensor; nanoribbons; diazonium salts

1. Introduction

The mass production of silicon based components enables to realize low-cost, easy to process and fully embeddable electronic raw material. Polycrystalline silicon (poly-Si) is one of the forms of silicon. It is composed of a combination of silicon crystals and grain boundaries formed during crystallization process. Poly-Si is formed by deposition of the layer and finds a lot of applications such as thin film transistors (TFT) [1], solar cells [2] or strain gauges [3]. It has also proved its efficiency as sensitive material for chemical sensors. The main deposition technique is the Low Pressure Chemical Vapor Deposition (LPCVD) which can provide good homogeneity of the silicon in terms of thickness, doping concentration and stability. It is compatible with relatively low temperature process (<600 °C), allowing to use glass substrates. Few nanometers thick silicon layers can be deposited by this technique. Poly-Si is frequently patterned by conventional UV lithography to form shapes at micrometric scale. Consequently, nanostructures such as nanowires or nanoribbons can be obtained. These nanostructures offer interesting potential for chemical species detection in so far as their high surface/volume ratio enables to have a high exchange surface between analyte and the sensitive material. Furthermore, they can be easily functionalized using miscellaneous materials such as DNA [4], in order to reach selectivity to targeted species.

Aryl-diazonium salts are frequently used to functionalize semiconductors and particularly crystallized silicon-based surfaces and it has been previously demonstrated that it can also be used on poly-Si layers by spontaneous grafting [5]. This efficient and fast grafting process leads to a strong covalent bond, and monolayers or thin films can be obtained in well-controlled conditions. A mechanism has been proposed for the attachment of the aryl radical on hydrogenated Si surfaces.

Nevertheless, the potential of grafting aryl diazonium at the surface has been marginally investigated until now. However, the use of this complexing agent to accumulate heavy metal ions has been previously demonstrated. Indeed, metals such as Li, Cd or Pd [6] can be complexed easily

with these salts. As heavy metals particles are responsible for water pollution and human brain diseases, detection of very low concentration of such species is a major issue to avoid people exposure to them.

The use of this complexing agent to accumulate lead complexes at the surface of a sensor based on Poly-Si nanostructures has not been investigated yet. Otherwise, most of the chemical sensors are based on field effect transistors (FETs) which require several photolithography, plasma etching and deposition steps and can provide reproducibility drawbacks. Consequently, classical passive devices such as Poly-Si nanostructures based resistors following a low-cost is of a main interest for chemical species detection.

In this paper, we present a simple electronic device based on poly-Si nanoribbons and functionalized with aryl diazonium salts in view of using this type of structures for heavy metal detection. The effectiveness of the grafting process was evaluated by NanoSIMS technique. Finally, electrical characterization of the resistors showed that sensitivity to these species is increased by functionalization in the concentration range 10^{-7} to 10^{-5} mol·L^{-1}.

2. Materials and Methods

2.1. Device Fabrication

Silicon nanostructures are formed on silicon wafer (Figure 1). Amorphous silicon is deposited by LPCVD at 550 °C and 90 Pa and then crystallized during an annealing step at 600 °C for 12 h to obtain a 50 nm thick poly-Si layer. This layer undergoes a photolithography step and is etched by reactive ion etching (RIE) to form 500 parallel nanoribbons. The length (L) and width (W) of these nanoribbons are respectively 8 µm and 5 µm. Then, a sacrificial 100 nm SiO_2 layer is deposited following Atmospheric Pressure CVD technique. SiO_2 is then locally etched to open a window at the ends of each side of the nanoribbons. This layer enables deposition of heavily doped N-type poly-Si layer to form contact electrodes. Finally, the sacrificial layer is etched using HF (2%).

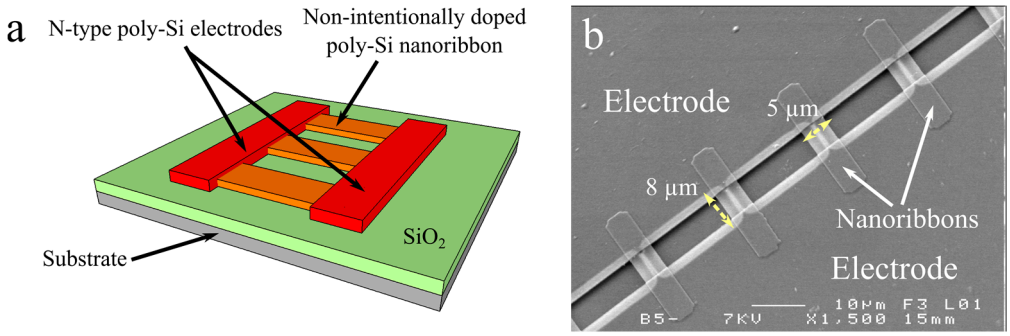

Figure 1. 3-dimensional **s**ketch of the resistor based on 500 parallel 50 nm-thick poly-Si nanoribbons (**a**) and SEM top view of the device (**b**) (geometric parameters: L = 8 µm and W = 5 µm for each nanoribbon).

2.2. Chemicals

The resistor is then functionalized using following description of spontaneous grafting of aryl diazonium salts. 4-carboxymethyl-benzenediazonium salts were prepared according to literature and stored under argon in a freezer. After 15 s of immersion in HF (2%), a solution containing 5 mg of 4-carboxymethyl-benzenediazonium salts in 50 mL of anhydrous deoxygenated acetonitrile was cannulated into the reactor cell. After 15 min, the surface salts are grafted at the surface of the device that is finally washed in three successive baths of acetonitrile of 5 min each.

3. Results and Discussions

3.1. NanoSIMS Analysis

NanoSIMS analysis was performed in order to ensure that carboxylate is able to trap lead ions via complexation mechanism. To validate this trapping process, we exposed the samples to Pb^{2+} solution (10^{-3} mol·L^{-1}) during 15 min. After this exposure, samples were simply dried using N_2 flow. Analysis of the device was then done targeting isotope 128 of lead (^{128}Pb) using NanoSIMS measurement. We compared grafted and non-grafted devices. The obtained results are presented on Figure 2. One can see that on non-grafted device (Figure 2a), signal is globally low, highlighting that the Pb quantity is negligible at its surface. Conversely, signal intensity is relatively high on grafted structures (Figure 2b). It means that the lead quantity is drastically higher on functionalized nanoribbons than on non-grafted structures.

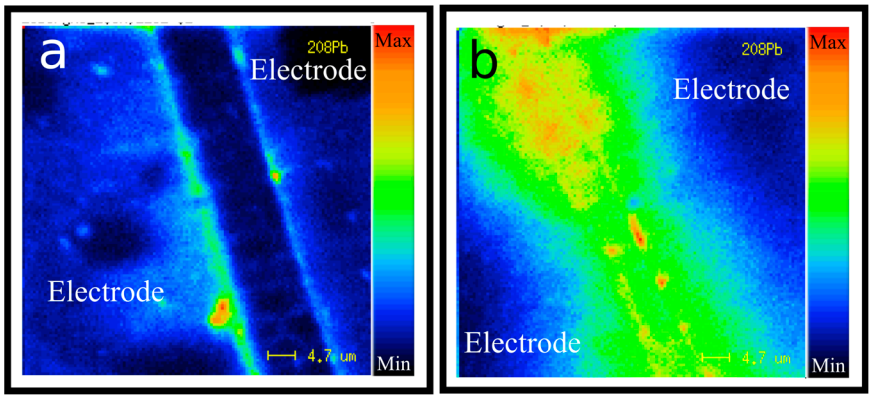

Figure 2. NanoSIMS imaging of the nanoribbons based device. ^{208}Pb tracking after 15 min exposure to lead solution before (**a**) and after (**b**) grafting process. Functionnalization enables preconcentration of Pb ions at the surface of nanoribbons.

3.2. Electrical Characterization

Finally, we performed electrical behavior analysis of the nanoribbons-based resistors in order to highlight interesting grafting effects on lead detection. This detection is based on charge measurement principle (at 1 V). Charge quantity flowing through the resistor is real-time calculated by integrating current as a function of time (i(t) = dq(t)/dt)). Figure 3 presents the obtained measurements for different concentrations of lead solutions. For convenience, measured charges were normalized by first charge values in order to compare easily different devices performances.

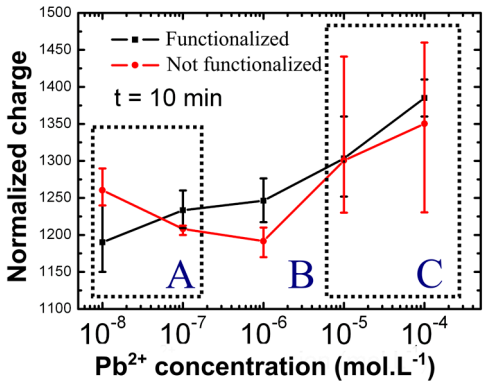

Figure 3. Normalized charge measurement for different Pb^{2+} concentration after 10 min exposure. Normalized charge comparison between grafted and non-grafted poly-Si nanoribbons.

Errors bars represent the dispersion of values for 5 different devices, tested in the same conditions. After 10 min exposure, one can consider that functionalized surfaces enable higher signal

value compared with non-grafted structures in the zone demarked as "B" (10^{-7} to 10^{-5} mol·L^{-1}). In the A and C zones, no conclusion can be done as ions concentration is too low (A-zone) or too high (C-zone), leading to saturated surfaces.

4. Conclusions

Grafting aryl-diazonium on silicon nanostructures has been investigated to accumulate lead complexes. Then, electrical behavior analysis of the nanoribbons-based resistors has been performed in order to highlight grafting effect on lead detection. First results of electrical characterization prove that lead ions can be detected in the concentration range 10^{-7} to 10^{-5} mol·L^{-1} thanks to classically processed resistors based on functionalized polycrystalline silicon nanoribbons. Moreover, this study shows that electronic devices based on silicon nanoribbons are promising for low-cost and portable chemical sensors for the direct detection of heavy metal species.

Conflicts of Interest: The authors declare no conflicts of interest.

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