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Covalent functionalization of polycrystalline silicon nanoribbons applied to Pb(II) electrical detection

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ABSTRACT

Although recent studies in the field of nanomaterials have allowed the realization of highly sensitive sensors, research regarding new types of functionalization of nanostructures to reach high selectivity are still missing. Here, a simple electronic device based on polycrystalline silicon (poly-Si) nanoribbons used for lead detection is presented. This device is functionalized by reduction of aryl diazonium salts in order to detect heavy metals. The effectiveness of the grafting process and thickness homogeneity of the coating layer were evaluated by XPS and NanoSIMS techniques. The preconcentration of lead (Pb^{2+}) at the surface of the functionalized nanostructures was substantially verified. Finally, electrical characterization of the resistors based on the functionalized nanoribbons, showed that the sensitivity to these species is increased in the concentration ranging from 10^{-7} to 10^{-5} mol L^{-1}. This technique could pave the way for use of complexing agents to enhance heavy metal detection.

1. Introduction

Lead is one of the heavy metals, of which its presence in water at high concentrations has become a growing concern. Heavy metals form an important class of pollutants [1]. They can be found in water naturally but also due to mining, agriculture and industry. Detecting and eliminating heavy metals is of concern because they are highly persistent and not generally degraded by bacteria. They are toxic and their accumulation in living cells leads to serious pathologies [2]. Some heavy metals have been subject to severe regulations due to high levels of toxicity even in trace amounts. Thus, exposure to heavy metals may result in cancer, damage to the kidneys and even death in some cases where concentration levels are very high [3].

The mass production of silicon based components allows the realization of low-cost, easy to process and fully embeddable electronic raw material. Polycrystalline silicon (poly-Si) is one of the many forms of silicon, which is composed of a combination of silicon crystals and grain boundaries that are formed during crystallization process. Poly-Si is prepared by layer deposition and is used in a variety of applications, such as thin film transistors (TFTs) [4,5], solar cells [6,7], strain gauges [8,9] or diodes [10]. One of its deposition technique is Low-Pressure Chemical Vapor Deposition (LPCVD) which can provide good homogeneity of the silicon in terms of thickness, doping concentration and stability.

Most electronic sensors are based on field effect transistors (FETs) which have proven high sensitivity and electrical performances [11–13]. However, they require several photolithography processes, plasma etching and deposition steps that can provide reproducibility drawbacks. In contrast, new passive devices such as resistors have recently shown that they enable chemical species detection, exhibiting low detection limits (e.g. for gases [14] or biological materials [15]). More specifically, poly-Si is very sensitive to charged species although its fabrication process is less demanding and cheaper.

Nanostructures such as nanowires [16–18] or nanoribbons [19,20] can be obtained from few nanometers thick poly-Si layers by LPCVD at low temperature (<600 °C) [21,22]. These nanostructures offer interesting potential for chemical species detection so

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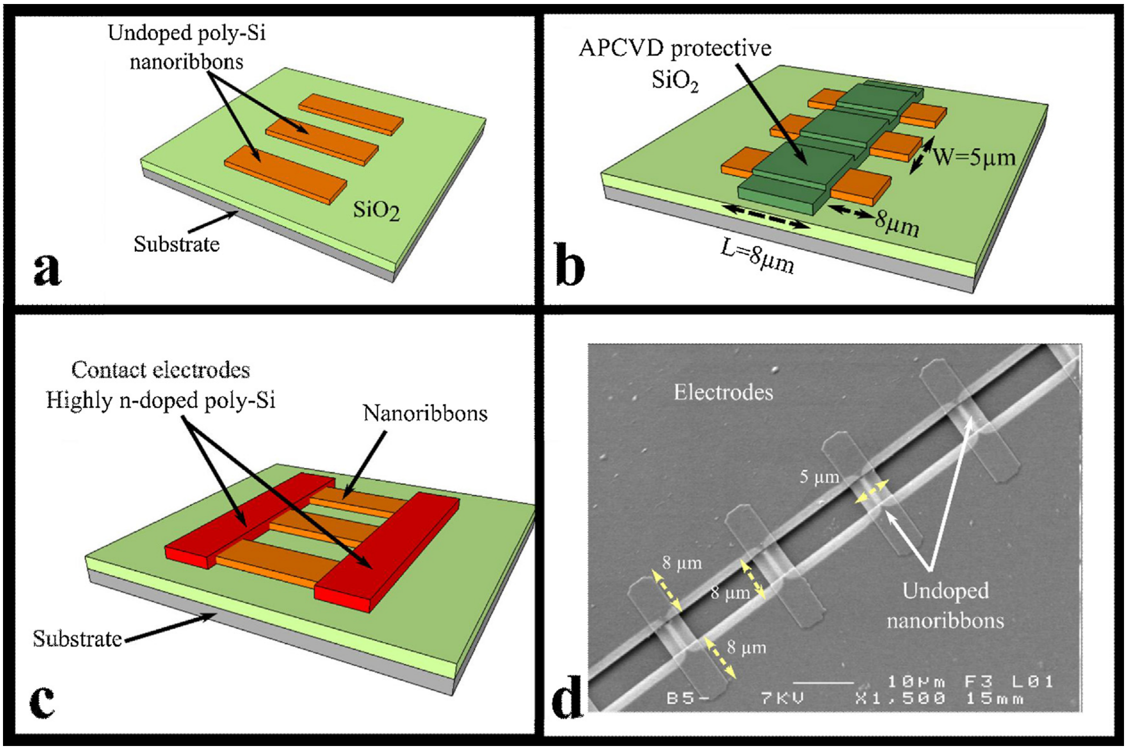

Fig. 1. 3-dimensional sketches of the fabrication process. (a) Deposition and formation of 500 parallel undoped poly-Si nanoribbons (50 nm thick) on an APCVD deposited SiO_2 layer. (b) Deposition and formation of an SiO_2 protective layer. (c) Deposition and formation of the highly doped poly-Si contact electrodes and removal of the protective layer. (d) SEM top view of the device with geometric parameters: L=8 μm and W=5 μm.

far as their high surface/volume ratio enables them to have a high exchange surface between analyte and sensitive material. Furthermore, they can be easily functionalized using miscellaneous materials such as antibodies [23] or DNA [24] in order to reach selectivity to targeted species. Aryl-diazonium salts are frequently used to functionalize semiconductors [25], particularly crystallized silicon-based surfaces [26] and their spontaneous grafting on poly-Si layers has been previously demonstrated [27]. This efficient and fast grafting process leads to a strong covalent bond and monolayers or thin films, can be obtained in well-controlled conditions [28,29]. Nevertheless, the potential of aryl diazonium grafting at the nanostructures surface has been marginally investigated to date [30,31].

The interest of a complexing agent to accumulate heavy metal ions at the surface of sensors has been previously demonstrated. Indeed, some complexing agents for Cd [32], Pd [33] and Pb [32] ions have been already immobilized on surfaces by reduction of their diazonium salts. The use of complexing agents to accumulate ions (i.e. in aqueous solution) at the surface of a resistor based on poly-Si nanostructures has not been investigated and requires exploration. The coating layer would be expected to give a higher sensitivity to the sensors.

In this work, we present a simple resistor based on poly-Si nanoribbons for heavy metal detection. The presented device is formed by a row of nanoribbons which is fully compatible with CMOS technology and enables direct *in-situ* measurement. These nanoribbons were functionalized with aryl diazonium salts containing complexing groups in view of using this type of structure for heavy metal detection. The effectiveness of the grafting process is evaluated. After which, the preconcentration of lead ions (Pb^{2+}), chosen as an example of heavy metal ion, at the surface of the functionalized nanostructures is checked. Finally, an electrical characterization of the sensor shows that the coating layer increases the detection capabilities.

2. Materials and methods

2.1. Devices fabrication

Silicon nanostructures were formed on a cleaned silicon wafer and native oxide was removed by chemical etching using a diluted HF solution (2%). A 1.2 μm thick SiO_2 insulating layer was deposited by Atmospheric Pressure Chemical Vapor Deposition (APCVD) technique at 420 °C using silane (SiH_4) and dioxygen (O_2) gas sources. Amorphous silicon was deposited by LPCVD at 550 °C at 90 Pa using SiH_4 source and crystallized during an annealing step at 600 °C for 12 h in order to obtain a 50 nm thick poly-Si layer. The layer underwent photolithography and was etched using SF_6 plasma reactive ion etching (RIE). Thus, 500 parallel nanoribbons (Fig. 1a) were formed. The length (L) and width (W) of these nanoribbons were 8 μm and 5 μm, respectively. A protective 100 nm thick SiO_2 layer was deposited following APCVD. SiO_2 was etched in order to open a window on each side of the nanoribbons (Fig. 1b). This layer enabled the deposition of heavily *in-situ* doped N-type poly-Si layer using SiH_4 and phosphine (PH_3) sources for the formation of contact electrodes. This last layer was etched by SF_6 plasma RIE. Finally, the protective layer was etched using HF (2%) (Fig. 1c). Fig. 1d presents a SEM image of the obtained device.

2.2. Chemical

The resistor was functionalized by spontaneous grafting of aryl diazonium salts (Fig. 2) according to the following protocol, described in previous studies [34]. All manipulations were carried out under argon using a Schlenk line with standard airless techniques. A 2% hydrofluoric acid solution was cannulated into a reactor cell, which contained the samples under argon, in order to remove the native Si oxide. After 15 s of immersion, the HF solution was eliminated. A solution of 4-carboxymethyl-benzenediazonium