Determination of porous silicon growth profiles in the presence of non-uniform doping by means of a switching current method

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Porous silicon is an interesting material with technological applications in optoelectronics, micromachining, biomedicine, and others. In this work an original switching current method is proposed for the determination, with one only experiment, of the temporal evolution profiles of porous silicon layers during the anodization process. This technique has proved to be a valuable tool for testing and improving a two-dimensional macroscopic simulator implemented for the prediction of porous silicon formation in samples with arbitrary doping profiles. Experimental results are presented and discussed, along with the principle of the simulator and the simulation results.

1 Introduction

In the last few years porous silicon (PoSi) with pore size of the order of nanometers (microporous silicon) has been recognized as an interesting material for different technological applications. It has been used as an active layer for optoelectronic devices such as LEDs [1]; as a sensitive layer for gas sensors [2]; as a sacrificial and a mechanical layer for silicon micromachining applications for hot-plate fabrication [3]; and in the fabrication of optical filters [4].

It is well known that PoSi formation requires the presence of holes at the silicon/electrolyte interface. For this reason this process can be controlled by exploiting the dependence of the PoSi growth rate on the material doping: when anodized in the dark, PoSi grows preferentially in p-type material, while n-type silicon is not affected. Moreover, PoSi growth proceeds at a faster rate through p⁺ areas with respect to adjacent areas with lighter doping [5].

So far this property has not been investigated in detail, although it can be of fundamental importance for the fabrication of the structures mentioned above. In fact, the comprehension of the effect of arbitrary doping profiles on PoSi growth could be exploited to design properly and optimize devices based on porous silicon.

In this work we propose an original switching current method for the determination, with one only experiment, of the temporal evolution of PoSi growth during the anodization process, independently from the doping (uniform or not) of the substrate. This technique has proved to be a valuable tool for testing and improving a two-dimensional macroscopic simulator implemented for the prediction of PoSi formation in samples with arbitrary doping profiles. The principle of the simulator is detailed below.

The switching method is successfully used for determining the PoSi profiles in an n⁺–p⁺–p silicon structure. The experimental results are compared with the simulation results in order to check the validity of the model used by the program to represent the PoSi growth mechanism.

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2 Fabrication details The anodized samples consisted of a double-diffused n"–p"–p silicon structure, previously used by our group for LED and gas sensor fabrication [6, 7]. The starting material is a p-type (100) wafer with a series of lines consisting of a 4 μm wide p" boron implantation, followed by an 8 μm wide n" arsenic shallow implantation. On top of each line an n" polysilicon strip is deposited. The polysilicon strip has no effect on the anodization process performed in the dark and it is only used to provide an electrical contact for fabricated devices. A schematic cross-section of a single line is shown in Fig. 1. The structure described above was repeated on the silicon substrate with a pitch of 20 μm in order to make a device of appropriate dimensions. The wafers were produced by ST Microelectronics, Italy. From the process data we estimated the following parameters for the doping profiles (assumed as Gaussian): for the p" implant we estimated a projected range of 70 nm, a peak value of 10<sup>18</sup>/cm<sup>3</sup> and a standard deviation of 200 nm; for the n" a projected range of 70 nm, a peak value of 3 × 10<sup>19</sup>/cm<sup>3</sup> and a standard deviation of 40 nm. The anodization experiments were performed in the dark in order to avoid radiation-induced hole generation, which would also cause anodization of the n" implant and polysilicon layer. The anodization solution was a 1 : 1 (v/v) mixture of HF (48% in water) and pure ethanol. After the anodization, the samples were rinsed in ethanol and pentane and slowly dried in nitrogen ambient to avoid cracks in the porous layer. All the fabricated samples were finally cleaved in order to allow observation of the cross-sections using scanning electron microscopy (SEM).

3 Experimental and simulation results In order to study the doping effects on the PoSi growth as a function of the anodization current and etching time and allow a straightforward comparison with the simulated profiles, we successfully used an original method based on continuous switching of the anodization current between low and high values, a well-known technique for the formation of multilayers with different porosity [8]. In practice, the anodization current of interest was periodically switched for a few seconds to a completely different value (e.g. 100 mA/cm<sup>2</sup> when the current density of interest was as low as 5 mA/cm<sup>2</sup>) in order to fabricate a PoSi layer with different porosity and thus with different visual contrast, as thin as necessary not to perturb the PoSi growth profiles.

A SEM cross-section of a PoSi sample fabricated using the switching current method is shown in Fig. 2 for an anodization current of 5 mA/cm<sup>2</sup>. In this case, the current density was switched every 100 s to a
value of 100 mA/cm², maintained for 2 s, resulting in the thin darker layers (i.e. of higher porosity) visible in the figure. This method allows the determination of the temporal evolution of PoSi profiles using only one sample, once the anodization current of interest is fixed. By choosing appropriately the parameters for the current step (value and time duration) used to highlight PoSi layers at different etching time, it is possible in principle to apply the method to a large variety of experimental conditions. As matter of fact, we made PoSi samples with a current density ranging from 5 mA/cm² up to 100 mA/cm² in order to study the effect of the current density on the growth of PoSi layer. In Fig. 3 a SEM cross-section of a PoSi layer fabricated using an anodization current density of 100 mA/cm² is shown. In this case, the current density was switched every 10 s to a value of 5 mA/cm² for 10 s, in order to have a layer with a lighter appearance on the SEM images (lower porosity).

As clearly shown by the two extreme cases shown in Figs. 2 and 3, the PoSi growth profiles strongly depend on the anodization current density: at the lowest current densities the p⁺ layer causes a concentration of the anodization current lines, so that the porous layer grows preferentially under the n⁺ implant, where the p⁺ is located, until a continuous buried layer is formed (see Fig. 2). On the contrary, when the current density is as high as 100 mA/cm² a quasi-isotropic PoSi formation occurs, and a continuous layer can be obtained only at the cost of a much greater PoSi thickness (see Fig. 3).

This interesting and useful property of the PoSi growth can be ascribed to two antagonistic phenomena: (i) the effect of doping on the voltage barrier at the forward-biased Si/electrolyte interface [9, 10] and (ii) the ohmic voltage drop along the current paths due to the resistivity of silicon, of the electrolyte and of the PoSi layer. The first phenomenon tends to enhance the anisotropy of the etching, while the second, which can be expected to be more relevant at the highest current densities applied, tends to reduce the anisotropy by hindering the current crowding along preferential etching directions. The simulator has been developed to check if this mechanism can satisfactorily explain these aspects of PoSi growth. The simulator operates on representations of two-dimensional cross-sections of the samples, including the silicon substrate, the porous layer, the solution and the cathode; the simulated area is modelled by means of an equivalent electrical network. Numerical solution of this network yields the current density throughout the cross-section and, in particular, at the solution/silicon interface (or PoSi/silicon interface). The current density is used to calculate the local porosity and PoSi growth rate, using interpolation of empirical data [11] including the effect of silicon doping and HF concentration. The electrical network is created by dividing the sample into cells according to a non-uniform rectangular mesh and connecting adjacent cells by branches. The latter are linear (conductances) except for those connecting cells separated by one of the following interfaces: (i) n-silicon/p-silicon, (ii) n-silicon/solution, (iii) p-silicon/solution. In this schematization the PoSi cells are treated as solution cells with the only difference being that the conductivity of PoSi cells is reduced by a constant factor $f_n$ with respect to the
solution cells, due to the percolating nature of conduction inside the porous medium. An average value of 50 has been determined for $f_\sigma$ by monitoring the voltage increase during anodization experiments performed on uniformly doped samples at various constant current values. In all the three cases of non-linear branches, conduction across the interfaces can be modelled by means of equivalent diodes. In particular, for the p-silicon/solution interfaces, where most of the PoSi formation occurs, the following equation is used to calculate the saturation current density:

$$J_s = K_0 [\text{HF}]^{1.16} \exp \left( \frac{qC_0 \sqrt{N_A}}{k_B T} \right),$$

where $N_A$ is the doping, $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, $q$ is the electron charge and $C_0$ and $K_0$ are parameters adapted to obtain an acceptable fit of the experimental data [9, 10]. Note that by this model, the observed doping-selective PoSi formation can be the result of the effect of doping on either $J_S$ or silicon conductivity. In practice, we have proved that eliminating the doping effect on $J_S$ (i.e. setting $C_0 = 0$) the anisotropy disappears, demonstrating that the sole effect of non-uniform conductivity cannot explain the preferential etching of the p' structures [12].

As far as the n-silicon/electrolyte interface is concerned, the breakdown behaviour of the equivalent diodes has been carefully modelled, since, due to the current direction (from silicon to the electrolyte), they are always reverse biased. Finally, the p/n interfaces are modelled as classical abrupt p/n junctions. The complete network is solved using the Newton–Raphson algorithm, with some modification aimed at exploiting the particular structures of the samples in order to optimize convergence and memory requirements.

The results of simulated PoSi growth profiles are shown in Fig. 4. In particular, the profiles of Fig. 4a have been obtained using the same parameter choice as the experiment shown in Fig. 2, i.e. the anodization current was set to a low value (5 mA/cm$^2$) and periodically switched to a higher value (100 mA/cm$^2$). Figure 4b shows simulated growth profiles obtained with the same parameter choice as Fig. 3. The duration of the two phases (working and marker) was also the same with respect to the experiments. It can be observed that at low current densities the simulator actually predicts the anisotropy caused by the p' implant (see Fig. 4a). Increasing the current density (see Fig. 4b) causes the anisotropy to reduce, in agreement with the experiments. An accurate comparison between simulated and real profiles reveals that the current density effects are less pronounced in the simulations. This is possibly due to overestimation of the ionic conductivity in the PoSi layer and/or to a discrepancy between the real and simulated n' and p' implant.

Fig. 4  Simulated growth profiles obtained with different anodization parameter choices: a) same parameter as in Fig. 2; b) same parameter as in Fig. 3.
4 Conclusions  The switching current method has been demonstrated to be a valid procedure for highlighting PoSi growth profiles. With a proper choice of the duration of the two phases (working and marker phase) it is possible to minimize the perturbation introduced by the marker phase while maintaining continuous thin layers of material with different porosity. The procedure has been successfully applied to study the strong dependence of the growth profiles on the level of anodization current density.

Comparison between the real PoSi profiles and the results of simulations, performed with identical anodization parameters, reveals that the model used to describe the phenomenon qualitatively explains the effects of non-uniform doping and the anisotropy reduction observable at high current density levels.

References