Force modulation microscopy of multilayered porous silicon samples

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In this paper we report on Force Modulation Microscopy (FMM) study and force-distance curve analysis of porous silicon layers grown on silicon. The characterization has been carried out on the cross section of porous silicon. The FMM images allowed us to investigate the morphological thickness of the layers through local elasticity differences resolving both between porous silicon layers of different porosities and between porous silicon and silicon itself. Force-distance curves showed different adhesion behaviour: porous silicon is more hydrophobic than bulk silicon in cross sectional view.

1 Introduction

In the last years porous silicon (PS) has attracted great interest for its unusual optical properties in the visible range of wavelengths at room temperature. Numerous studies have demonstrated that this material has good perspectives for photonic applications in optoelectronic devices. A multilayer of PS is easily produced by a periodic variation of the etching current density and shows interesting optical properties forming the base for the fabrication of optical devices as dielectric mirrors, Fabry-Pérot interferential filters, resonant cavity light emitting diodes and waveguides [1].

In order to have a more complete characterization of a multilayer sample, it is worth to study also the morphology and the mechanical properties of porous silicon layers at the interface with bulk silicon. We performed such a study by using an extension of the basic Scanning Probe Microscopy topographical mapping capabilities, the Force Modulation Microscopy (FMM) technique. This technique allowed us to investigate the morphology and the thickness of the layers in cross sectional view by studying the local elasticity differences between PS layers of two different porosities and bulk silicon. FMM is especially useful to detect variations in the surface mechanical properties through simultaneous surface topography measurements. In addition, force-distance curve analysis were used to investigate the force interaction between the tip apex of the Atomic Force Microscopy (AFM) probe and the surface of a multilayer of PS of sample. In particular, this technique allowed us to reveal the different adhesion behaviour between PS layers and bulk silicon.

2. Experimental

PS multilayer samples were prepared by electrochemical etching of p-type <100> oriented crystalline silicon substrate with a resistivity of 0.01 Ω cm. The etching process was carried out in a solution of a 30% volumetric fraction of aqueous (48 wt. %) HF in ethanol. Current densities of 50 mA/cm^2 and 7

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mA/cm^2 were applied to grow 4 µm thick high (73%) and low (50%) porosity layers. A single layer sample obtained with a current density of 50 mA/cm^2 was also tested.

The FMM investigation and the force-distance curve analysis were performed using a Solver P-47 AFM, made by NT-MDT Co., equipped with a 90 micron piezoelectric-tube (PZT) scanner. Rectangular Si$_3$N$_4$ contact mode cantilevers, by Mikro Masch®, with spring constant of 1.75 N/m were used. Prior to use, the PZT scanner was calibrated in x,y,z using reference standard grating. Topography and force modulation images were acquired simultaneously. The probe scanned the surface in contact mode and at the same time the amplitude variation of the probe pressure on the surface was detected by applying an alternating voltage to the z-PZT scanner. The FMM characterization and the force-distance curves analysis has been carried out on the cross sectional view of the samples, which was obtained by cutting with a diamond scriber the PS sample.

3. Results and Discussion

The morphology of the cross-sectional surfaces of the studied samples is highly complex due to the crude cutting procedure. Structures, like mountains and valleys, appear which made difficult the interpretation of AFM topographic images. The force modulation technique allows to overcome this problem, since it investigates the local elasticity differences between different materials independently from the morphology [2,3]. The contrast generated and observed in the FMM images reveals the relative local elasticity of a sample that is related to the amplitude variation of the probe deflection: wide cantilever oscillation amplitude and brighter image contrast are observed on hard materials.

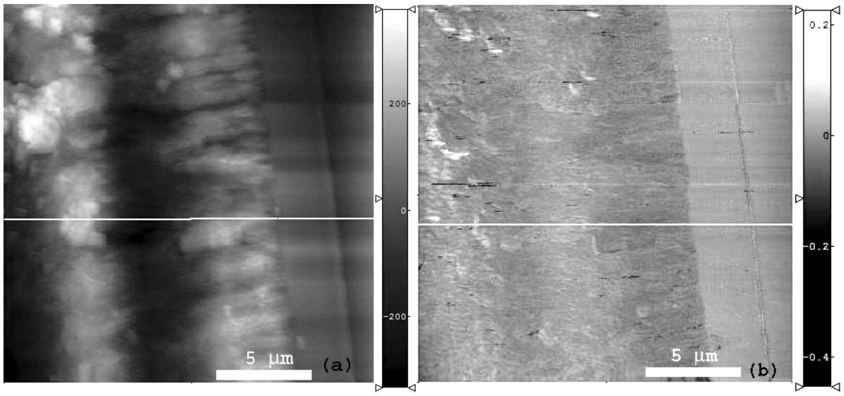

Fig. 1. Room temperature and in air AFM images of a cross sectional view of a single layer of porous silicon on silicon: (a) topography and (b) force modulation images. The porous silicon layer is on the left-hand side of the images. Images sizes are 19.3 µm x 19.3 µm each, 512 x 512 pixel. Z range in topography image is 710 nm; Z range in force modulation image is 0.68 nA.

In Fig. 1 we show an example of (a) topography and (b) force modulation images acquired simultaneously on PS single layer sample. We can observe two different morphologies: rough structures on the left and a flat surface on the right of each image. Comparing both images and knowing the direction of sample scanning with respect to its position we can recognize, and so attribute, the right part of the topography image (Fig. 1a) to the bulk silicon and the left one to the single layer of PS. One can appreciate better the shape of the rough structures through the cross section line profile (Fig. 2a), taken along the line indicated in the topography image. In effect, as we can see in the topography image, rough structures appear also like mountains and valleys with a variation in height of up to 600 nm. Their presence can be attributed to both the cutting procedure and the intrinsic PS structure.

In order to reveal the mechanical properties and to appreciate better the morphology of this layer the FMM technique outputs has been worth to study. In the FMM image (Fig. 1b) we can observe a clear contrast corresponding to the two materials, which is independent of the shape of the rough structures. Brighter area of the image correspond to harder area of the sample. The cross section line profile (Fig. 2b) taken on the FMM image displays a different oscillation amplitude for the PS layer and the substrate. Thus, these data highlight the different elastic behaviour of PS in the respect to silicon: bulk silicon is harder than PS, as found in literature [4].

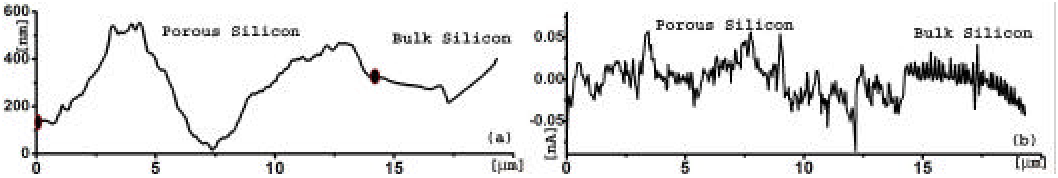

Fig. 2. The cross-section profiles along the lines indicated in Fig.1 on topography (a) and force modulation (b) images. The dots on topography cross section profile define the region of PS.

These encouraging results have directed our efforts towards the study of the cross section morphology of a multilayer sample.

In Fig. 3 we show an example of (a) topography and (b) force modulation images acquired simultaneously on PS double layer sample. The two PS layers differ for their porosity. In topography we can observe a variation in height which does not correspond with the structure shown in the force modulation image. It appears as if there was only one interface: the one between PS and bulk silicon. The variation in height observed in the topography image is due to the cut operation. On the contrary, in the FMM image we can observe clearly three different responses of the probe interaction with the surface, which correspond to the double layer of PS and the silicon substrate. The different contrasts observed in the FMM image suggest that silicon is harder than PS, and that increasing the porosity, PS becomes less hard, as reported in literature [4].

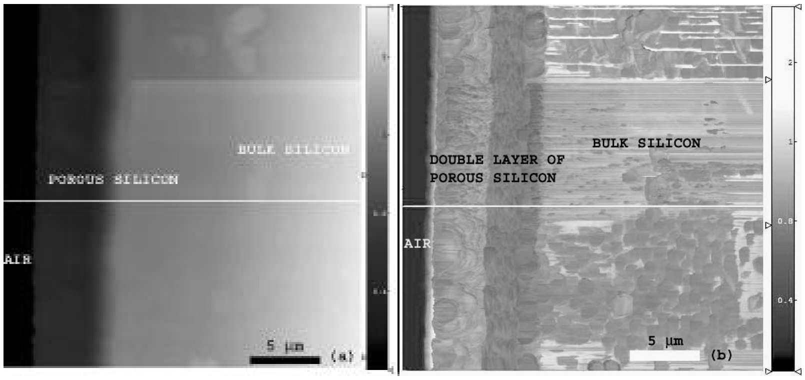

Fig. 3. Room temperature and in air AFM images of a cross sectional view of a double layer of porous silicon: (a) topography and (b) force modulation images. Images sizes are 25.7 µm x 25.7 µm each one, 512 x 512 pixel. Z range in topography image is 1.9 µm; z range in force modulation image is 1.84 nA .

In Fig. 4 we show the cross section line profiles taken along the lines indicated in the topography (Fig. 3a) and FMM (Fig. 3b) images. From the topography cross section we can appreciate and estimate a variation in height between the two porous layers of about 800 nm, while the thickness of the layers is extremely difficult to asses. From the FMM cross section profile we can estimate the thickness of both porous layers due to their different response. Note that this is independent from the complex morphology due to the cut operation. Their thickness is about 4 μm for both, that is in good accordance with the value expected from the etching parameters.

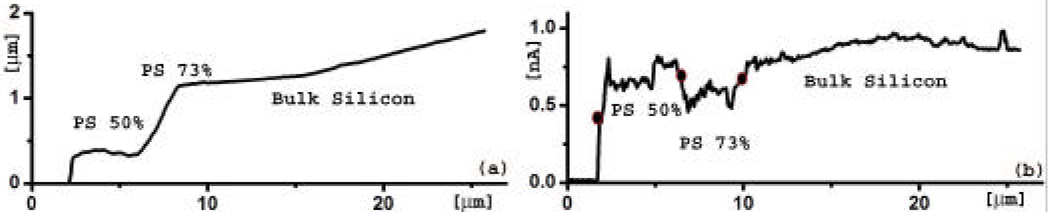

Fig. 4. Cross-section profiles taken along the line indicated in Fig. 3 respectively on the topography image (a) and on the FMM image (b) of the double layer sample. The dots in the FMM cross section profile (b) correspond to the interfaces between different materials.

Force-distance curve analysis were carried out in ambient atmosphere with the same cantilever placed on PS and on silicon identified on the base of the topography images just acquired. A force-distance curve displays the deflection of the cantilever as a function of the vertical extension of the PZT scanner with respect to the surface of the sample. Thus, knowing the spring constant of the cantilever, it is possible to evaluate the vertical force, which the tip applies to the surface [5].

It is worth noting that since the measurements are performed in ambient, humidity affects the measurements: a thin film of water covers both the tip and the surface of the sample. When the tip comes close to the sample surface a capillary force appears between the tip and the sample surface, leading to a strong impact on the force-distance curve. The presence of capillary effects is observed as an enhanced hysteresis between the approaching and retracting branch of the force curve. Water meniscus force exceeds all other adhesion forces masking in particular the Van der Waals force. Due to this fact the study of capillary force allows to distinguish materials with different hydrophobic behaviour [6].

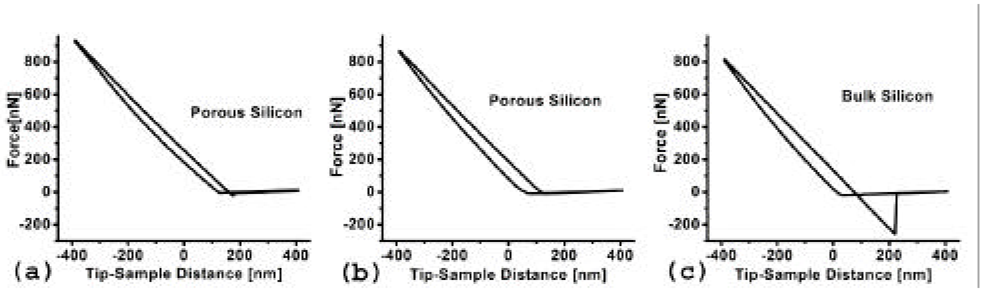

Fig. 5. Force-distance curves acquired locally on various zone of the multilayer sample. In particular on (a) porous silicon layer (50% porosity), (b) porous silicon layer (73% porosity), and (c) bulk silicon.

In Fig. 5 we show, as an example, three force-distance curves acquired locally on the topography image of the multilayer sample, respectively on the double PS layers and on the bulk silicon. We can observe an hysteresis behaviour on the retracting branch of the force-distance curve, typically of capillary interaction. In particular we can observe a small snap–back point on both PS layers, and a big one on the bulk silicon. These data are also confirmed on the single layer sample. In Fig. 6 we show, as an example, two curves acquired locally on the PS single layer and the bulk silicon part on the base of the topography image. No snap-back point on the PS layer and a large one on the silicon bulk are observed. Consequently, these curves allow to suggest that in the cross section view the PS layers have a more hydrophobic behaviour than the bulk silicon.

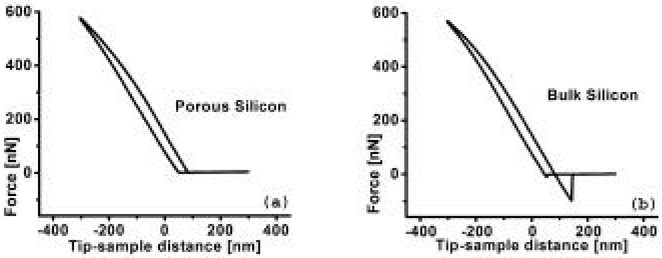

Fig. 6. Force-distance curves acquired locally on the topography image of single layer sample respectively on (a) single porous silicon layer and (b) bulk silicon.

4. Conclusions

The local elasticity differences between PS layers of different porosities and bulk silicon allowed us to evaluate, by the comparison between FMM and topography AFM techniques, the morphology at the porous silicon and bulk silicon interface in cross section view. FMM is insensitive to the details of the topography, while it is sensitive to the different elasticity of the material. This allowed to distinguish between layers of different porosities and, as an example, allowed us to estimate the thickness of the two porous layers. The found values of the thickness are in good agreement with the expected ones. The different contrast observed in FMM images strengthens that the silicon is harder than PS, and also that increasing the porosity the hardness of PS decreases. Through force-distance curves analysis we showed different adhesion behaviour between PS and silicon in cross section view: porous silicon is more hydrophobic than silicon.

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