High Resolution X-Ray Diffractometric, Topographic and Reflectometric Studies of Epitaxial Layers on Porous Silicon Destined for Exfoliation

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Abstract

The presently studied porous layered structure predicted for obtaining freestanding silicon epitaxial layer contained two porous layers with different porosity. The upper layers were of significantly lower porosity and after annealing enabled obtaining possibly smooth surfaces for deposition of epitaxial layers. Contrary to that, the deeper layers were of greater porosity enabling easier destruction necessary for obtaining the freestanding epitaxial foil. The layered structures have been studied by means of synchrotron diffraction topography and recording of rocking curves from small local area. The samples have been additionally examined by means of conventional high resolution diffractometry and reflectometry.

The porous layers without epitaxial deposition provided strong narrow maximum at low angle side of the substrate maximum common for the both porous layers. The most probable effect of the deposition of epitaxial layer is the decrease of lattice parameter in the upper layer with lower porosity which provided the maxima in the diffraction curves located on low angle side of the substrate maximum.

The topographic investigations revealed some defects in deposited epitaxial layers, which might be connected with some irregularities of the annealed porous layer. Very characteristic common defects were large caverns, overgrown in the epitaxial process with the diameters of several tenths of micrometers. The other category were tiny defects (possibly the overgrown submicron caverns, or other irregularities), which often were associated with some bundles of dislocations resolved in the topographs. In layers of large thickness the characteristic long black and white stripes along <110> have also been observed, which most probably were stacking faults with dislocation loops.

The most effective method of revealing defects in free standing exfoliated layers were Bragg-case projection topographs and “zebra” pattern monochromatic beam topographs providing a map of sample curvature.

1. Introduction

The first paper concerning the porous silicon formed in silicon substrates had been published more than 50 years ago [1]. The main application of porous silicon formerly was "silicon on insulator" technology (SOI) [2-4]. The present improved technology of manufacturing of porous layer enabled variety of new applications in technology of sensors and optoelectronic elements thanks to the possibilities of using the porous silicon as a host materials for introducing various nanoparticles [5-8]. The other application of porous layer is obtaining of the freestanding epitaxial layers, which can be used in the technology of photovoltaic elements and the process can be successfully repeated several times in the same silicon substrate wafer [9-12].

Obtaining of good quality epitaxial layer and the effective exfoliation had been realized thanks to introducing two porous layers with different porosity. After annealing the upper less porous layers provided smooth and homogenous surface suitable for growth of epitaxial layers. The lower more porous layer enabled easy destruction leading to the exfoliation of the epitaxial layer. The moderate roughness of the silicon with partly destroyed porous layer after the exfoliation allow further multiple processes of deposition and exfoliation of epitaxial layers. The main reason of developing the exfoliation technology is economic manufacturing of highly efficient photovoltaic cells which should be made of crystalline silicon [9,10] while the use of multicrystalline and amorphous silicon provide cells with lower efficiency.

Manufacturing of highly efficient photovoltaic cells requires crystalline silicon with low concentration of structural defects. The important methods of characterization of porous layers and epitaxial layers grown on porous layers are X-ray diffraction methods accompanied by scanning and the transmission electron microscopy [13-19]. The characteristic effect observed by means of X-ray diffraction is significant increase of interplanar distances in the porous layer, as well as the small width of the diffraction maxima coming from the porous layer comparable with those of ideal crystals [12,13]. The formation of interference maxima connected with the porous layer had also been reported [13]. The influence of wetting of the porous layer introducing the changes of interplanar distances was reported by Dolino and Bellet [18]. The present authors [20-22] reported the diffraction topographic investigation of various porous layers and epitaxial layers deposited on porous layer for SOI technology.

The presently studied porous layers and epitaxial layers grown on the porous layers were destined for final obtaining of the freestanding exfoliated layers. The purpose of the investigations was wide and complete characterization of structural properties and the crystallographic defects occurring in the porous layer and the epitaxial layer. The recording of high-resolution diffraction curve and X-ray diffraction topography have been used. The investigation included studying of separated final exfoliated epitaxial layers.

2. Experimental

2.1. Manufacturing of the freestanding silicon epitaxial layers grown on the porous layers

Obtaining of freestanding exfoliated silicon layers for the photovoltaic cells can be successfully realized by preparation of the substrate with two porous layers of different porosity. The first of them is the surface layer of low porosity and the second one is buried layer with much higher porosity. The upper layer is necessary for growth of smooth and perfect epitaxial layer while the lower more porous layer should be easy destructible enabling the separation of the epitaxial layer from the substrate.

The porous layers were introduced in the silicon plates of (111) and (100) orientation and the diameters close to 3". The plates had been highly boron doped of p^+ type and their resistivity of the plates was between 0.004 – 0.005 Ωcm. The sequence of studied layers is schematically shown in Fig. 1.

In the anode oxidation, etching the hydrofluoric acid diluted in isopropyl alcohol has been used with the concentration of HF on the level of 30%. The parameters of the process have been selected in course of systematic numerous experiments but generally the deeper more porous layer had been obtained by increasing of the etching current in the final stages of the process. The current density between 10 and 200 mA/cm^2 had been used depending on the resistivity of the silicon plate.

Before deposition of the epitaxial layer, the wafers with double porous layers had been annealed at least 30 minutes in hydrogen at 1100ºC. A certain problem of this process was the formation of several caverns caused by coagulation of several pores [9]. The epitaxial layers had been deposited at 1100ºC in the Gemini 1 epitaxial reactor with induction heating. The deposition rates were close to 1 μm/min. The thickness of the layers was in the range 30 - 50 μm and the resistivity of epitaxial layers was close to 0.5 Ωcm. The exfoliation had been realized with the use of ultrasounds in a liquid bath.

2.2. X-ray diffraction and reflectometric investigation

The X-ray synchrotron diffraction experiments had been performed at E2 and F1 experimental stations of DORIS III in HASYLAB. In the present case a very important method was the Bragg-case section topography realized using 5 mm narrow slit, which allowed to indicate the presence of small lattice defects and to evaluate the perfection of the sample better than other X-ray methods. Together with section topographs the white beam projection topographs had been taken. In both cases a small glancing angle of 4º was used. The samples had also been studied by taking monochromatic beam topographs and measurements of rocking curve from small local area using 0.115 nm synchrotron radiation with small 50 μm probe beam diameter and a counter with large window.

Many of the investigated samples, especially the exfoliated freestanding epitaxial layers had been significantly bent with radii of curvature in the range 30 – 20 m. In this case it was convenient to expose so called "zebra pattern" monochromatic beam topographs [23]. These topographs had been obtained by recording on one film a series of exposures for step-wise altered angle of incidence with a step of 0.002º. The important point of the investigation was studying of the exfoliated epitaxial layers.

Apart from synchrotron measurements, the samples had been examined with conventional high resolution diffractometer using $CuK_{\alpha1}$ radiation. It was equipped with two bounce channel-cut Ge monochromator with 004 reflections, which provided high intensity of the X-ray beam. The diffractometer had been used for obtaining diffraction curves with widely opened window as well as for reflectometric investigations. In the last case, the roughness of the investigated samples had been determined by fitting the theoretical curve calculated using Siemens REFSIM program.

3. Results and discussion

Similarly, as it was reported by several authors [13-17], the porous layers without epitaxial deposition exhibited strong and usually narrow maximum at low angle side of the maximum due to the substrate. The representative rocking curve of the sample with porous layer is shown in Fig. 2 together with white beam topographs. The width of the peak coming from porous layer was practically of similar width as those of the substrate peak - both close to 11 arc sec in case of 400 symmetrical reflection. Some broadening of the porous layer peak has been observed in the case of very thin porous layers as it is illustrated in Fig. 3. In this case the broadening seem to be the diffraction effect analogous to that observed in the case of thin crystalline or polycrystalline layer, as it was also discussed by Buttard *et al.* [15].

The topographs of the single porous layer shown in Fig. 2 confirmed a good perfection and uniformity of the layer manifesting in particular in lack of interference effects connected with the variation of layer thickness and other imperfections, which have been observed by us in the previously studied layers [20-22]. The Bragg-case section pattern exhibited two separated stripes corresponding respectively to the porous layer and to the substrate. The uniformity of this pattern in horizontal direction was also an important proof of the uniformity of the porous layer.

The projection and section topographs of another porous layer with thickness of 1.2 μm shown in Fig. 4 revealed numerous caverns providing distinct contrasts – marked representatively by *"V"*. In case of section topography, we observed some fringes characteristic for the bent crystals appearing on the relatively large distance behind the stripe coming from incident beam, marked representatively by *"I"* . These fringes have been modulated by the segregation pattern connected with the distribution of boron in the substrate, marked by *"S"*. Only a week line coming from the porous layer was present in the upper part of the topography, but the caverns provided distinct images with numerous interference fringes also in lower part of the picture (marked again by *"V'*).

Contrary to the synchrotron diffraction curve the presently obtained conventional diffraction curves exhibited significant apparatus broadening. That can be seen in Fig. 5 a, presenting the conventional diffraction curve of the same sample as in Fig. 2. The width of the conventional rocking curve was equal to 16" for layer and 13" for the substrate respectively. The reflectometric curve of this sample shown in Fig. 5 b revealed interference fringes indicating the presence of additional thin layer on the surface most probably formed from some oxide. The thickness of the layer T may be evaluated from the simple formula [24]:

$$T = {}^{\lambda}/_{2\Delta\omega cos\theta}$$

where λ is the wavelength, $\Delta\omega$ is the fringe period and the cosine of a very low angle may by very accurately approximated by 1. The evaluated thickness of the layer was 40 nm. The reflectometric curve of another sample with double porous layer – 1 μm top layer with the porosity 15% and deeper 10 μm with 27% porosity – indicated the considerably low value of roughness close to 0.51 nm.

Similarly as it had been concluded in [4,9], the annealing of the porous layer performed for improving of the top layer surface roughness was connected with introduction of some imperfection manifesting both in the obtained topographs and recorded rocking curve. That may be observed in Fig. 6 and 7 reporting the rocking curve and topographs for the samples with double porous layers annealed respectively during 60 and 30 min. in hydrogen at 1100ºC. The rocking curves of both annealed samples with double porous layers still contained two peaks attributed respectively to the porous layer and the substrate. The topograph reported in fig. 7 a revealed some characteristic extended defects, marked by *"V"*, which are interpreted by us as caverns, formed at the surface of the annealed substrate. The exposed zebra pattern monochromatic beam topograph indicated some irregular bandings of the sample.

In case of the sample annealed during 60 min. (fig. 6) we observed very narrow peak due to the porous layers, which was even higher that the substrate peak. That may suggest that there is no significant spread of the lattice parameter on the surface. In addition, one could observe some additional maxima, most probably of interference character between these two very high peaks, similarly as it had been reported in [15]. The image of defects revealed by white beam and monochromatic beam topographs were not as much different as in the case of the sample annealed during 30 min. The exception concerned some more extended oval defects around some craters marked by *"V"*.

It was indicated that the diffraction maximum coming from both porous layers has been significantly changed after the annealing and deposition of the epitaxial layer. That may be followed in the representative rocking curve of the sample with 50 μm layer shown in Fig. 8. The epitaxial deposit provided a very high maximum on low angle side of the maximum due to the substrate. On the low angle side of the maximum due to epitaxial layer we observed lower maximum, which we attributed to the deeper more porous layer. In addition the upper less porous layer located directly below the epitaxial deposit seem to be responsible for broaden peak located mostly on the right side of the substrate maximum. This effect may be caused both by the annealing and the nucleation of epitaxial deposit inside the pores.

It should be noted that a good visibility of the signal coming from the layers situated below thick 40-50 μm layer is still possible in view of using relatively short wavelength close to 11 nm. That is caused by relatively low linear absorption coefficient close to 58.5 cm-1 which gives the attenuation of the substrate peak only about two times in case of symmetrical 400 reflection by 50 μm epitaxial layer.

The diffraction topographs of the samples with deposited epitaxial layer (Fig. 9) revealed some characteristic defects. In the most often case, we observed relatively dense irregular contrasts, which could be probably attributed to overgrown tiny caverns or some irregularities of the surface of annealed porous substrate, accompanied by some dislocations generated at these irregularities, marked by *"D"*. These defects provided much stronger contrasts in case of section topographs, which confirmed their location in epitaxial layer. The characteristic common defects were connected with the formation of some large caverns on the top of the annealed porous layer, which were overgrown and filled in the epitaxial layers – marked again by *"V"*. Both types of defects can be seen in Fig. 9.

The another characteristic type of defects had been observed in some epitaxial layers of large thickness (marked *"ld"* in Fig. 10). These defects are in the form of elongated narrow black and white stripes extended along <110> directions. The important result was provided by section topographs (Fig. 10 b, c, e) indicating the location of these defects in the whole thickness of the layer. The possible interpretation was that they were stacking faults bounded by imperfect dislocation loops with long segments parallel to the interface.

The exfoliated epitaxial layers often exhibited the significant curvature, which affected the contrast in the Bragg-case section topographs as it may be seen in Fig. 11. In the case of most thick, 50 μm, freestanding layer the section topograph was more transparent as it may be seen in Fig. 12. The most effective method of revealing the defects in such layers was white beam Bragg-case projection topography. The white beam Bragg-case projection shown in Fig 12 d) and section (e) topographs of another 50 μm epitaxial layer grown on double porous layer revealing similar stripe formed defects, as those in Fig. 10.

The useful possibility offered the "zebra" pattern topographs exposed with the use of monochromatic beam, which provided a map of crystal curvature as it is shown in Fig. 13. The characteristic increase of the curvature was observed around the overgrown caverns..

4. **Conclusions**

The characterization and structural quality evaluation of the epitaxial layers deposited on porous silicon can be very effectively realized by means of X-ray diffraction methods. The present investigation included white beam Bragg-case projection and section topography and the monochromatic beam topography connected with recording rocking curves from small local area. The experiments were performed at F1 and E2 stations of DORIS III. It was also possible to study the exfoliated epitaxial layers with all of these methods.

The porous layers without epitaxial deposition provided strong and narrow diffraction maximum at low angle side of the substrate maximum. The rocking curves recorded after the deposition of the epitaxial layers, indicated the decrease of lattice parameter in the top layer with lower porosity while the layer with higher porosity still contained the material with larger lattice parameter. The topographic investigation in practically all samples revealed irregular contrasts, which can be the dislocations, generated at the annealed porous substrate. Other common defects were craters in the annealed porous layer overgrown and filled in the epitaxy. In layers of large thickness, we also observed narrow black and white stripes along <110>, most probably stacking faults with imperfect dislocation loops.

Acknowledgments

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Figure captions

Fig. 1 Schematic structure of the sample with epitaxial layer grown on porous layers destined for exfoliation

Fig. 2. a) - the representative rocking curve of the sample with 20 μm porous layer with the porosity 50% in 400 reflection of 0.1115 nm radiation, b) - the white beam reflection superimposed projection and section topographs and c) – white beam projection topograph. Here and in other topographs the $\vec{X}$ denotes the direction of incident beam.

Fig. 3. The rocking curve of the sample with 1.2 μm porous layer with the porosity 20% in 400 reflection of 0.1115 nm radiation.

Fig. 4. Reflection topographs: a – projection and b – section of the silicon wafer with the 1,2 μm porous layer. *V*, *I* and *S* denote respectively overgrown voids, interference fringes characteristic for bent crystal and segregation fringes caused by differences in boron concentration.

Fig. 5. a – Conventional diffraction curve in 004 reflection of $CuK\alpha_1$ recorded with widely opened counter, b - reflectometric curve in $CuK\alpha_1$ radiation of the silicon sample with single 20 μm porous layers of 50% porosity indicating the presence of 40 nm oxide layer and c – the experimental reflectometric curve of the double porous layer consisting of the 1 μm layer with 15% porosity and 10 μm layer with 27% porosity with fitted theoretical curve. The evaluated roughness of the second sample (denoted by ρ) was equal to 0.51 nm.

Fig. 6. a) – The rocking curve in 004 reflection of 0.115 nm radiation b) – monochromatic beam „zebra“ pattern topograph exposed with angular step 0.002º and c) - white beam projection topograph of the sample with two porous layers respectively of 1 μm with 15% porosity and 15 μm with 50% porosity annealed 60 min in hydrogen atmosphere at 1100ºC.

Fig. 7. a) – monochromatic beam „zebra“ pattern topograph exposed with angular step 0.002º in 004 reflection of 0.115 nm radiation and b) - white beam projection topograph of the

sample with two porous layers respectively of 1 μm with 15% porosity and 15 μm with 50% porosity, annealed 30 min in hydrogen atmosphere at 1100ºC.

Fig. 8. Rocking curve of the 50 μm epitaxial layer grown on two porous layers with different porosity. It should be noted that the substrate peak is visible in case of 50 μm epitaxial layer due to relatively low linear absorption coefficient being on the level of 58.5 cm^{-1} which gives the attenuation of the substrate peak about two times in case of symmetrical 400 reflection by 50 μm epitaxial layer.

Fig. 9. Large defects formed by overgrowth filling of the caverns formed in the annealed porous substrate layer revealed by the white beam projection reflection topograph in 50 μm epitaxial layer. *D* denotes probably the dislocation bundles.

Fig. 10. White beam Bragg-case projection (a), superimposed section and projection (b) and (c) section topographs of a 50 μm epitaxial layer grown on double porous layer revealing characteristic stripe formed defects being most probably dislocations with stacking faults. *Ld* and *p* denote respectively dislocation loops accompanied by stacking faults and small precipitates.

Fig. 11. Large defects formed by overgrowth filling of the caverns formed in the annealed porous substrate layer revealed by the white beam projection reflection topograph in 50 μm epitaxial layer. The superimposed section topograph is strongly black due to the curvature of the sample.

Fig. 12. White beam reflection topographs of the exfoliated (111) oriented 47 μm epitaxial layer. a – superimposed projection and section topographs, b – projection topograph and c – section topograph.

Fig. 13. Monochromatic beam "zebra" patterns of two exfoliated epitaxial layers, a - 45 μm and b - 30 μm, exhibiting the curvature changes around overgrown caverns initially formed in the annealed top porous layer at the substrate and c - pattern taken from the back side of 45 μm exfoliated epitaxial layers. *Z* denote single stripe of zebra pattern.