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Si exfoliation by MeV proton implantation

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ABSTRACT

Proton implantation in silicon and subsequent annealing are widely used in the Smart Cut™ technology to transfer thin layers from a substrate to another. The low implantation energy range involved in this process is usually from a few ten to a few hundred of keV, which enables the separation of up to 2 μm thick layers. New applications in the fields of 3D integration and photovoltaic wafer manufacturing raise the demand for extending this technology to higher energy in order to separate thicker layer from a substrate. In this work, we propose to investigate the effect of proton implantation in single crystalline silicon in the 1–3 MeV range which corresponds to a 15–100 μm range for the hydrogen maximum concentration depth. We show that despites a considerably lower hydrogen concentration at R_p, the layer separation is obtained with fluence close to the minimum fluence required for low energy implantation. It appears that the fracture propagation in Si and the resulting surface morphology is affected by the substrate orientation. Defects evolution is investigated with Fourier Transform Infrared Spectroscopy. The two orientations reveal similar type of defects but their evolution under annealing appears to be different.

1. Introduction

Hydrogen implantation has been used for more than 15 years to produce SOI wafers through the Smart Cut™ technology [1]. The usual process consists of three main steps that are the hydrogen implantation of a donor wafer, the subsequent bonding to a receiving wafer and a fracture treatment that enables the material splitting along the implanted layer. So far, the technique has been successfully developed to transfer a variety of materials such as Si [2], Ge [3], GaAs [4], SiC [5], GaN [6], etc. In Si, a damaged zone is created around the projected range R_p during H implantation. A large variety of defects is present; among them are hydrogenated point defects such as vacancy–hydrogen complexes and two-dimensional defects, the so-called "platelets". Under thermal annealing, platelets interchange hydrogen and vacancies through Ostwald ripening mechanism [7], leading to the appearance of microcracks around R_p [8]. Microcracks propagation and interaction induced by hydrogen pressure result in blister formation or entire Si layer delamination in presence of a stiffener [2].

All the studies cited above deal with processes that leads to the separation of layers with thicknesses ranging from a few hundred nanometers to a few micrometers, i.e. using implantation energies in the keV range. Yet, very little has been done with high energy in the MeV range although the extension of ion implantation based separation process to thicker films might meet requirements for various applications in the fields of thick SOI for automotive [9], MEMS [10], power devices [11] and thin wafer fabrication for photovoltaic solar cells [12]. A first study was performed by Assaf et al. [13]. The authors reported the production of free-standing layers in the range of 10–50 μm after implantation of (111) Si at energies up to 2 MeV followed by thermal annealing. The minimum fluence required to achieve separation varied from 5 to 8×10^{16} H/cm^2 depending on implantation energy, which is very close of the fluence usually used at conventional energy (10–100 keV) [14]. Only orientation (111) has been tested but most wafers used in microelectronics and for photovoltaic applications have orientation (100). In this work, we compare the behavior of (100) and (111) Si after hydrogen implantation at high energy as a function of ion fluence and subsequent annealing parameters as well. Preliminary characterizations were performed with optical microscope, SEM, FTIR-MIR spectroscopy and AFM in order to compare with results obtained after low energy implantation.

2. Experimental details

P-type ⟨100⟩ and ⟨111⟩ oriented silicon wafers were implanted with hydrogen by Van de Graaf accelerators at the energy range

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1–3 MeV, with a beam current of a few µA and with fluences from 4×10^{16} to 1×10^{17} H/cm^2.

Implanted substrates were annealed under atmospheric conditions at 350, 450 and 700 °C from 10 to 30 mn.

Sample cross sections were observed with SEM and sample surfaces were observed with SEM and optical microscope. Surface roughnesses were measured with AFM in tapping mode. IR measurements were performed on a Bruker IFS55 Fourier Transform spectrometer coupled with a MIR system and a HgCdTe detector with a 4 cm^{-1} spectral resolution. Spectra were obtained under nitrogen atmosphere. Samples were successively annealed at 450 and 550 °C during 30 min. Spectra were collected after each annealing.

3. Results and discussion

3.1. Influence of thermal annealing

Compilation of studies at lower energies reveals that the minimum hydrogen fluence required to detach a silicon film increases with energy [15]. Extrapolating this minimum fluence evolution to the MeV range suggests that an even higher fluence is required to separate the silicon layer after implantation at high energies. Yet, results obtained in one of the few studies in the MeV range already suggest that the actual minimum fluence is smaller than the value predicted from extrapolation [13]. In order to check whether the extrapolation is correct for (1 0 0) and (1 1 1) orientation, a survey of H-implanted samples behavior under annealing has been performed for implantations at different fluences and energies.

After implantation at 1.5 MeV with fluences ranging from 5×10^{16} to 1×10^{17}, we found that annealing at 700 °C – 10 min is sufficient to induce blistering or delamination. This thermal budget was used as our standard thermal treatment. It must be pointed out that a lower thermal budget might be enough to reach same results. By performing implantation on both (1 1 1) and (1 0 0) Si, the following main results can be extracted:

- (1 1 1) Si: Implantations at 1.5 MeV lead to delamination of the entire surface after annealing for (1 1 1) samples with all tested fluences. An example of the remaining substrate surface obtained after delamination is shown in Fig. 1a. This is in good agreement with the minimum fluence to detach a silicon layer found by Assaf et al. [13] for energies up to 1.5 MeV.

- (1 0 0) Si: Implantation at 1.5 MeV with fluence of 5×10^{16} H/cm^2 did not display any observable modification before and after thermal annealing. Implantation with fluence of 7×10^{16} H/cm^2 resulted in sample blistering (Fig. 1b). It appears that a 30 µm thick silicon layer above the implanted area is not stiff enough to prevent blistering in this case. Dark areas correspond to blisters that burst with a total detachment of the cap layer from the implanted substrate. Small lines that can be seen in area with no blisters are traces of blisters that burst and deflated after breaking at an edge. Blister diameters range from 100 to 400 µm. These values are much larger than the average blister diameter observed for implantation in the keV range but they conform to the trend of average blister diameters increasing with the implantation depth [16].

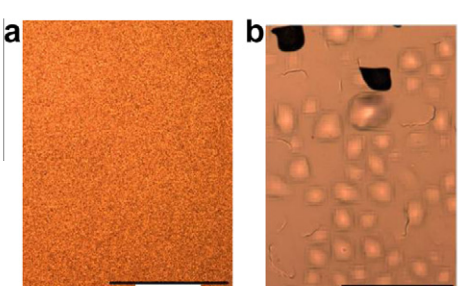

Fig. 1. Sample surfaces after implantations at 1.5 MeV – 7×10^{16} H/cm^2 and subsequent annealing (700 °C – 10 mn). (a) Fully delaminated (1 1 1) Si surface; (b) blistered (1 0 0) Si surface.

These results obtained with the two silicon orientations are summarized in Table 1.

Delamination has been achieved with implantation fluence of 1×10^{17} H/cm^2 for all energies tested in the range of 1–3 MeV. The thinnest films that we obtained have thickness of a few tens of micrometers and are therefore highly breakable. However, films obtained after delamination of substrate implanted with 3 MeV are thick enough to be easily handled. An example of delamination obtained after implantation at 3 MeV in (1 0 0) Si and subsequent annealing can be seen on Fig. 2. It appears that the entire implanted surface delaminated as a whole and the 100 µm thick detached layer can be handled.

These results show that the minimum fluence required for blistering or delamination after implantation in the MeV range is about 7×10^{16} H/cm^2. This value is slightly higher but still in the same order of magnitude as the minimum fluence required to obtain the same results after implantation at 100 keV, that was found to be about 3.9×10^{16} H/cm^2 [17]. As straggling increases with energy, high energy implantation result in a lower H concentration at R_p and a broader H implanted profile compared to standard energy implantation. It is known that platelet nucleation occurs preferentially at R_p and platelets then grow through Ostwald ripening [7], using H implanted in the surroundings of R_p. Our results underline that key factor for blistering or delamination is not only the maximal local concentration at R_p but also the total amount of hydrogen available for microcracks growth. This implies that defects located at R_p are able to soak up hydrogen on several hundreds nanometers on either side of R_p to enable platelets and microcracks growth.

A second conclusion resulting from the comparison between orientations (1 0 0) and (1 1 1) is that the implantation process is more efficient in (1 1 1) Si, i.e. that layer separation can be obtained at lower fluence compared to (1 0 0) Si case. That seems in contradiction with previous study at lower implantation energy from Zheng [18] who found that H implanted (1 0 0) Si shows a faster blistering rate than (1 1 1) Si. Fracture of H implanted Si is a complex balance between multiples physical and chemical parameters that drive platelets formation and their evolution up to the separation. Our results indicate that predominant factors that drive the fracture mechanism may be different at high and low energy.

In order to highlight differences between (1 0 0) and (1 1 1) Si orientations, IR spectroscopy has been used to investigate Si–H bonds evolution under annealing after high energy implantation. Assignment of Si–H stretch modes can be found elsewhere [19–22]. Still, precise attribution is complicated due to peaks overlapping and broadening.

(1 0 0) and (1 1 1) Si have been implanted at 1 MeV, with 1×10^{17} H/cm^2, that leads to delamination for both orientations. In addition, (1 0 0) Si has been implanted at 1 MeV with 8×10^{16} H/cm^2 which results in Si blistering under sufficient annealing.

Table 1
Behavior of 1.5 MeV hydrogen implanted samples after annealing at 700 °C – 10 mn under atmospheric conditions for (1 0 0) and (1 1 1) orientations.

Fluence(H/cm^2)	5×10^{16}	7×10^{16}	1×10^{17}
(1 0 0)	No change	Blistering	Splitting
(1 1 1)	Splitting	Splitting	Splitting