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Ellipsometric study of crystalline silicon hydrogenated by plasma immersion ion implantation

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ABSTRACT

The structure and the optical properties of thin Si layer hydrogenated by shallow plasma ion implantation with different fluences up to 10^{15} cm^{-2} are studied using spectroscopic ellipsometry and simulation of the distributions of the ions and implantation induced defects. The implantation was regarded to proceed into Si through the native SiO_2. Two-layer optical models are applied for examination of the composition and dielectric function behavior of the formed structures. The native oxide is found to be 3 nm thick. The thickness of the Si modified layer decreased 23 to 14 nm with ion fluence due to increased formation of highly hydrogenated surface region that hinder further H-penetration into the Si bulk, especially at the highest fluence. Shifts of the features in the obtained dielectric functions related with Si interband transitions at about 3.4 and 4.2 eV are found caused by process-induced tensile stress. The modified Si region is related rather to defects created by the ion implantation process than the projected range of hydrogen ions. The overall layer modification can be characterized by a low degree of amorphization (up to 5.8%), creation of structural defects and internal tensile stress.

1. Introduction

Hydrogen is ubiquitous component in solids and strongly affects the properties of semiconductor materials and the behavior of electronic devices. The implications of such effects for the fabrication of solid-state devices are now widely recognized and careful control of hydrogen during semiconductor processing is attempted to tailor the electrical properties. New developments, for example improvements in hydrogen storage systems and fuel cells, layer exfoliation for smart-cut processing, require detailed studies of hydrogen behavior in semiconductors. Of special interest is the behavior of hydrogen on the silicon surface and its role in the growth process. Hydrogen can easily be introduced into semiconductors through proper hydrogen containing environments. In Si technology hydrogenation is usually achieved by implantation process, either beam [1–3] or plasma ion implantation (PIII) [4,5]. In spite of the advantages (shallow implants and large implanted area) PIII technique still is related with formation of lattice defects induced by collisions of implanted ions with the surface and atoms of substrate material in addition to plasma radiation.

Hydrogen as impurity can play important roles, both detrimental and beneficial. Hydrogen plasma (H-plasma) treatments applied on standard Czochralski (Cz) silicon wafers are known to cause a structuring of the surface regions in the sub-100 nm scale. Several hydrogen related defects, i.e. Si—H bonds, hydrogen induced platelets (HIPs), monatomic hydrogen, hydrogen molecules, and hydrogen-related complexes have been discussed in the literature [1,6]. The mechanisms that govern interactions of hydrogen-related species with silicon defects and their role in growth process are still under debate.

The present study is devoted to the mechanism of influence of hydrogen introduction in Si through ion implantation on the structure and optical properties of the nanoscaled surface layer. Hydrogenation of the surface region of c-Si substrates is achieved by shallow low energy plasma-beam H^+ ion immersion implantation with different fluences up to 10^{15} cm^{-2}. The study is performed using ellipsometry, as a highly sensitive optical method even to a monolayer on Si surface, combined with modeling the distributions of the ions and implantation induced defects. The process-induced changes in the structure and optical properties of the thin hydrogenated Si layer are studied. Different optical models are applied for examination of the composition and dielectric function behavior of the formed structures in terms of H^+ ion fluence.

2. Experimental details

The object of this study is monocrystalline Si (c-Si), Cz-grown Wacker wafers with orientation Si(100) and Si(111) and

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resistivity ranging from 4 to 10 Ohm cm. The c-Si surface was modified by plasma immersion ion (PII) implantation accomplished in a planar plasma reactor. No external heating was applied to the substrates. The energy of H^+ implant was chosen as low as 2 keV, so that the projected H^+ implantation depth in Si substrate to be approximately within 20–30 nm inwards the Si surface. The H^+ fluence varied from 10^{13} to 10^{15} H^+/cm^2. Before implantation the samples underwent a standard RCA cleaning procedure, while after implantation, possible surface contaminations were removed by a short dip in diluted HF.

The ellipsometric measurements were carried out on a Wollam M-2000DI rotating compensator spectroscopic ellipsometer working in the spectral range of λ = 193–1690 nm at angles of incidence ranging from 45° to 90°. The ellipsometric angles Ψ and Δ were measured at incident angles of 65° and 70° and then analyzed applying different optical models to the Si surface layer modified by the H^+ implantation.

It was expected that the implantation-induced damage of the Si surface region together with presence of hydrogen ions changed the optical properties of this layer and, hence its optical constants differed from those of c-Si. In order to determine the layer structure and composition as well as the optical constants of the implantation modified Si region, two-layer optical models were used as one layer was the native oxide and the second was the modified Si layer. The former, that is always present on air exposed Si, was assumed as stoichiometric SiO_2. The latter was taken into account using an effective medium composition [7,8] of single-crystalline Si (c-Si) [9], ion implantation amorphized Si (data taken from [10]) and voids (for density correction). As a first approximation, we assumed that below the top native oxide the implantation induced damaged layer was homogeneous. With this assumption good fit of the experimental data was achieved which infer that this optical model was suitable for further study of basic structural properties as a function of the implantation parameters.

In the multi-parameter fitting program an iterative least-squares method was used for minimizing the difference (mean square error denoted as MSE) between the experimental Ψ and Δ data and the theoretical ones. For each optical layer, from the ellipsometric data analysis the film thickness, the refractive index, n, and extinction coefficient, k, were obtained with an accuracy of ±0.2 nm and ±0.005, respectively, and the dielectric function $\varepsilon = \varepsilon_1 - i\varepsilon_2$ ($\varepsilon_1 = n^2 - k^2$, $\varepsilon_2 = 2nk$) was revealed.

3. Results and discussion

Once present, H modifies the properties of the material and, thus influences its optical constants. Therefore, performing the optical modeling we searched for the thickness of the layer being modified by the hydrogen implant and the alteration of its optical constants from those of c-Si material. The quality of the data fit with proper optical models is demonstrated in Fig. 1, where the experimental angles Ψ and Δ (symbols) and the generated theoretical ones (lines) are presented for Si sample, PII implanted with H^+ fluence of 10^{15} cm^{-2}.

The optical modeling of the ellipsometric data established a thin native oxide on the Si substrates, the average thickness of which was 3 nm (Fig. 2). Therefore, the H^+ ions passed through this oxide and implanted into Si surface layer modifying it. The thickness of the modified Si layer, given also in Fig. 2, was dependent on H^+ fluence, as it was shrinking with increasing the fluence. Most probably, higher fluence of H^+ implant caused stronger lattice disordering and larger amount of defects in the Si surface region, being an impediment to the H motion inwards. The other reason for that could be the H solubility-related saturation of the Si surface, which additionally hinders the H implants motion [11,12].

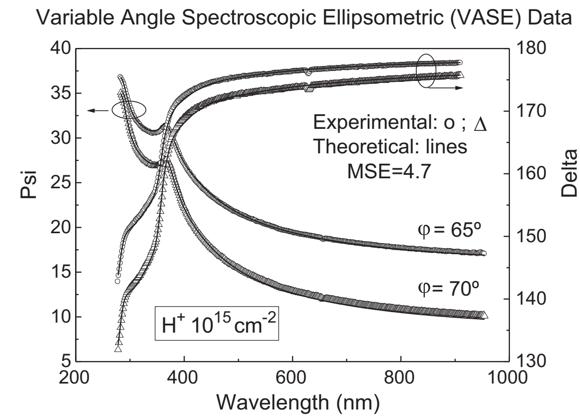

Fig. 1. Experimental (○, Δ) and generated (lines) ψ and Δ data as a function of wavelength measured at 65° (○) and 70° (Δ) of Si substrate PII implanted with H^+ fluence of 10^{15} cm^{-2}.

Indirect evidence for the process induced damage was the presence of an amorphized Si fraction in the Si surface layer. Depending on H^+ fluence this volume fraction amounted to 2.4%, 2.7% and 5.8% (with an error of ± 0.2%) for 10^{13}, 10^{14} and 10^{15} cm^{-2} H^+ fluence, respectively (see the insert in Fig. 2). Including voids fraction in the modeling of the effective medium composition gave poor fitting results pointing out that no voids introduced by the implantation process.

Fig. 3 shows the depth profiles of the implanted H^+ obtained by performing SRIM simulation for the implantation energy of 2 keV used. The implantation was taken to proceed into Si through the native SiO_2, the thickness of which was 3 nm as found from the SE data modeling evident in Fig. 2. From that figure it can be inferred that the thickness of the H-modified Si region depends on the ion fluence. The question is whether this dependence can be related to the profile of the implanted hydrogen since it is known that different fluences change only the intensity of peaks and not their position [13].

As seen in Fig. 3, the deconvolution of the ion concentration spectrum resulted in two components, one of which is the high energy one extending into the Si bulk. It could be expected that the low energy peak lies in the native oxide. However, this peak has its maximum at a much deeper position than the SiO_2 thickness. Then

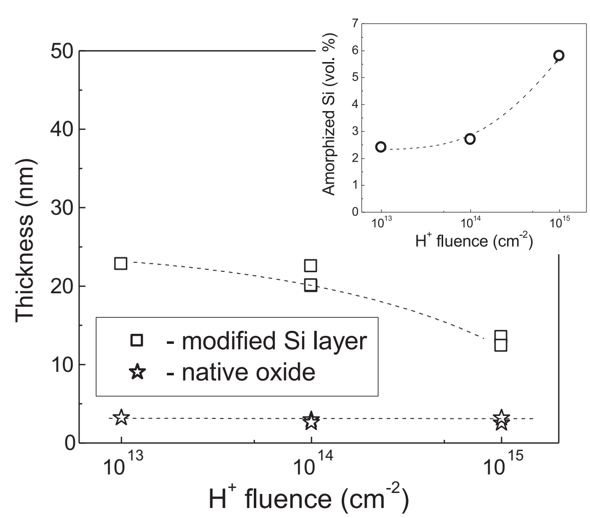

Fig. 2. Thickness vs. H^+ fluence of the native oxide (stars) grown on c-Si substrate and of the Si surface layer (squares) modified by PII H^+ implantation. Insert: volume fraction of amorphized Si in the modified Si layer.