Study of silicon surface layers modified by hydrogen plasma immersion ion implantation and oxidation

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Abstract. We report a study of p-Si(100) surface layers modified by plasma immersion ion implantation (PIII) and dry oxidation. This is expected to allow one to engineer near-surface layers with different thicknesses and levels of amorphization. Hydrogen ions were introduced into a shallow near-surface Si region through PIII with energy of 2 keV and doses ranging from $10^{13}$ ion/cm$^2$ to $10^{15}$ ion/cm$^2$. The implanted Si surface was subjected to oxidation in dry oxygen atmosphere at temperatures ranging from 700 °C to 800 °C. The optical and structural properties of the modified Si layers were studied in detail by spectroscopic ellipsometry (SE) in the IR spectral range of 300 – 4000 cm$^{-1}$. The surface morphology was examined by atomic force microscopy (AFM) imaging at different scales and by fractal analysis. Through decomposition of the main Si-O bands into Gaussian peaks, different Si oxidation states were identified, suggesting non-stoichiometric oxide layer composition.

1. Introduction

Surface modification is becoming increasingly important for the next generation of devices where the active areas are located in shallow surface layers. Surface engineering is particularly useful in obtaining new materials with different properties or in tailoring the properties of existing materials for specific applications.

For long years, the Si technology involved introducing hydrogen at various stages of device fabrication using different techniques. Early on, annealing of interface traps in MOS devices was performed \cite{1}; further, such processes found uses in many industries, e.g., from neutralization of defects in bulk materials producing solar cells \cite{2}, hydrogenated nano-crystalline silicon (nc-Si:H) thin films \cite{3}, formation of materials like SiC$_x$N$_y$(H) for applications in medicine \cite{4}, to ion-cut technology for Si-film transfer onto an oxidized substrate \cite{5,6}. Different techniques are being used for the purpose of introducing hydrogen, with plasma immersion ion implantation (PIII) having the advantage of being a low-cost flexible technique. The main advantage of introducing hydrogen is that non-thermal processes of charge neutralization and annealing take place, especially processes of hydrogen passivation of defects and impurities. However, hydrogen introduced in near-surface Si

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regions is known to lead to the formation of different defects in the surface texture, as platelets, Oswald ripening etc. [6].

The main purpose of the present study is to engineer near-surface Si layers with different thicknesses and levels of amorphization through hydrogen PIII implantation followed by thermal oxidation at moderate temperatures. It would allow fine-tuning of the amorphous structure and charge balance in a shallow subsurface oxide layer that could serve as a protective coating. To assess the properties of the grown oxide layers, ellipsometric measurements were implemented in a vast spectral wavelength range. Ellipsometry is a non-destructive surface technique allowing one to determine a variety of film parameters that are of prime importance for application purposes, such as film thickness, optical constants \((n, k)\), and chemical and structural composition of the layers. In the IR spectral range, it can provide information on film characteristics such as: anisotropy, roughness, non-uniformity, LO and TO phonon modes. Combined with AFM studies of the layers’ surface topology, it can yield useful information on the processes involved in the formation of the layers.

2. Experimental details

The layers studied were formed in Cz-grown p-type Si Wacker wafers oriented along \((100)\) with a resistivity of 5 – 8 ohm cm that is standard for the Si technology. The wafers were subjected to a standard RCA clean before any technological steps. Part of the samples was exposed to PIII in a planar plasma reactor operating at variable number of pulses and exposure time. The hydrogen ions were implanted with an energy of 2 keV and three doses, namely, \(10^{13} \text{ cm}^{-2}\), \(10^{14} \text{ cm}^{-2}\) and \(10^{15} \text{ cm}^{-2}\). No external heating was applied. Because of the low energy, the \(\text{H}^+\) ions could be implanted in a shallow depth of approximately 20 – 30 nm in the surface of the Si substrate. After implantation, possible surface contaminations and native oxide were removed by a short dip of the samples in diluted HF.

Next, the hydrogen-implanted Si wafers were oxidized in a dry \(\text{O}_2\) ambient at temperatures of 700 °C, 750 °C and 800 °C. Unimplanted Si wafers were oxidized simultaneously. This allowed us to compare the oxidation rates and to elucidate the role of the hydrogen in the oxidation process. An important point is that no further thermal treatment was applied to the samples studied.

In the reflectance SE study, the spectra were collected on two different ellipsometers (J.A. Woollam Co. Inc.) to cover the range from UV to mid-IR wavelengths. In the UV to near-IR spectral range, complementary SE measurements were performed in the 193 – 1700 nm wavelength region at angles of incidence of 60°, 70° and 75°. The SE measurements in the mid-IR (IR-SE) were performed in the 300 – 4000 cm\(^{-1}\) wavenumber range at angles of incidence of 70° with a resolution of 16 cm\(^{-1}\) and 20 scans.

The topography measurements were performed before and after oxidation of the Si wafers under ambient conditions on a XE-100 (Park Systems, 2011) apparatus in a non-constant force mode. The surface roughness was assessed with an accuracy of less than 1 nm. Ultra-sharp tips from NanosensorsTM with a spring constant of 48 N/m were used. The sample surfaces were scanned over an area of 1×1 \(\mu\text{m}^2\) and the XEI software was used for statistical data analysis. The 2D and 3D AFM images were used to determine the amplitude parameters, namely the peak-to-peak height, \(S_h\), the root-mean-square (RMS) roughness, \(S_q\), the surface skewness, \(S_{sk}\) and the surface kurtosis, \(S_{ku}\). In addition, fractal analysis was conducted by examining the Fourier spectra registered at angles ranging from 0° to 180° to obtain the amplitude plots for each sample, from which the spatial parameters mean fractal dimension (MFD) and texture direction index \(S_{tdi}\) were calculated. The \(S_{tdi}\) value is a measure of the weight of the dominant direction and is defined as the sum of the average amplitudes divided by the sum of amplitudes of the dominating direction.

3. Results and discussion

After implantation, the thickness of the implanted Si region as estimated from the SE measurements decreased as the \(\text{H}^+\) dose was raised. We assume that the higher dose of \(\text{H}^+\) implant causes a stronger lattice disordering and a larger amount of defects in the Si surface region, hindering the penetration of the next incident ions. This was substantiated by the increased degree of amorphization as the
implantation dose was increased. The thickness of the modified layers and their degree of amorphization are presented in table 1.

It is reasonable to suggest that the modified Si region is related to defects created by the ion implantation process. In an earlier modeling of the implantation profiles using SRIM code simulation bearing in mind that the implantation proceeds through an inevitable native oxide, we concluded that a highly hydrogenated region can be formed in the early stages of implantation that hinders the further penetration of hydrogen into the Si bulk. The modified Si region would then extend to about 20 nm depending on the ion dose [7], which correlates well with the thicknesses of the modified Si surface layer ranging within 23 – 14 nm.

The evolution of the optical properties of the grown layers can be indicative of their stoichiometry. The SE spectra can be split in two spectral areas.

Our previous results from studies in the UV-Vis – near-IR wavelength range (200 – 1000 nm) have indicated the appearance of under-oxidized oxide layers [8]. For example, at a wavelength of 632.8 nm, although depending on the implantation dose and the oxidation temperature, the refractive index value was systematically below 1.54, which is typical for SiO₂, as found in the literature [9].

In the entire studied IR range from 300 cm⁻¹ to 4000 cm⁻¹, no evidence was found of bands related to SiHₓ (x = 1, 2, 3) stretching vibration at ~2200 cm⁻¹ [10]. Moreover, no bands related to (O)SiH or (O)SiH₂ [11], or due to the Si-O(H) bond stretching vibration at approximately 950 cm⁻¹ [12], were observed. Further, we focused our attention on the 400 – 1600 cm⁻¹ part of the spectrum. The ellipsometric measurements were interpreted in terms of the imaginary dielectric function ε₂ and the dielectric loss function Im(-1/ε). Figure 1 a and b presents as an example the respective spectral results for oxides grown at 700 °C on Si implanted with different H⁺ doses. The main oscillation zones observed are related to TO and LO oscillations of the bridging oxygen in the Si-O bonds, the vibration frequencies of which are distributed in the spectral ranges of 1010 – 1150 cm⁻¹ and 1180 – 1300 cm⁻¹, respectively, with corresponding Si-O-Si bond angles in the range of 120° < Θ < 180°. The shape and position of the characteristic bands of the Si-O chemical bonds depend on the H⁺ ion dose.

| H⁺ dose (ion/cm²) | Thickness (nm) | Degree of amorphization (%) |
|-------------------|----------------|-----------------------------|
| 10¹³              | 22.8           | 2.7                         |
| 10¹⁴              | 20             | 2.4                         |
| 10¹⁵              | 13.5           | 5.8                         |

Table 1. Thickness and degree of amorphization of the modified Si surface layer.

The main absorption features are evident within the range between 1300 cm⁻¹ and 900 cm⁻¹. In order to obtain detailed information on the bonds configurations, we deconvoluted the spectra into Gaussian components. As an example, figure 2 presents the Gaussian peaks fitted to the spectra of Si implanted with H⁺ dose of 10¹⁵ ion/cm² and oxidized at a temperature of 750 °C.

![Figure 1](image1.png)

**Figure 1.** IR-SE spectra of the imaginary part ε₂ (a) and the dielectric loss function Im(-1/ε) (b) of the dielectric function for oxides grown at 700 °C.
The deconvolution of the main Si-O bands reveals multiple Gaussian peaks with positions that allow us to assume that the Si-O chemical bonds are in different configurations, thus indicating the non-stoichiometric nature SiOₓ (1 < x < 4) of the grown oxide. The under-oxidized Si-O bond configurations are as follows: Si-O₂-Si₂ units manifested by the peaks appearing at ~1045 cm⁻¹ (TO) and ~1190 cm⁻¹ (LO); Si-O₃-Si units at ~1070 cm⁻¹ (TO) and Si-O-Si₃ at ~1130 cm⁻¹ (LO). The peaks around ~1090 cm⁻¹ (TO) and ~1250 cm⁻¹ (LO) that are characteristic of stoichiometric SiO₄ tetrahedral units are not observed.

Figure 2. Deconvolution of the Si-O band in the 900 – 1300 cm⁻¹ spectral region in the IR-SE spectra of the imaginary dielectric function ℇ₂ (a) and the dielectric loss function Im(-1/ℇ) (b).

Figure 3 shows scanned 1 µm×1 µm AFM images of oxides grown at different temperatures on Si implanted with a dose of 10¹³ cm⁻², together with the results of the fractal analysis conducted. It is clear that the morphology changes occur at different temperatures.

The values of the texture direction index Stdi are close and larger than 0.7, which indicates that the surface texture is isotropic for all samples studied. The MFD values are within 2.3 – 2.8, which is
evidence that, independently of the technological processes, the sample surfaces exhibit a self-similar behavior (fractal behavior). The RMS roughness values are in the range of 0.33 – 0.6 nm, with a tendency to increase as the H⁺ dose is increased and to decrease when the oxidation temperature is raised.

4. Conclusions
In the present study, the structural composition of oxides grown on hydrogenated Si wafers was assessed at different temperatures. The hydrogenation was achieved by plasma immersion ion implantation of H ions. The post-implantation oxidation in dry O₂ ambient led to the formation of non-stoichiometric oxide containing Si species at different oxidation levels. The detailed analysis of the IR-SE spectra within the 300 – 4000 cm⁻¹ spectral region showed the presence of bands associated with vibration modes of the Si-O bonds. No H-related bands could be observed proving the “dry” nature of the formed oxide layers. Deconvolution of the Si-O bands in the 900 – 1300 cm⁻¹ spectral region revealed different configurations of Si-O bonding in a mixture of SiO₂ and SiOₓ constituents, the non-stoichiometric ones being predominant. The intensity and position of the corresponding Gaussian peaks were found to depend on the implantation dose. The AFM imaging of the H⁺-implanted Si substrates’ surface registered relatively flat tops and deep valleys, the number and size of which decreased by the subsequent thermal oxidation. It can be concluded that the overall modification of the Si surface layer could be characterized by a low degree of amorphization (up to 5.8%), creation of structural defects and internal layer stress.

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