Electroreflectance spectroscopy study of hydrogen plasma immersion ion implanted silicon with ultrathin oxide film

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Abstract. Results are presented from a study of (100)Si substrates, hydrogenated by plasma immersion ion implantation with H⁺ ions with energy of 2 keV and fluence varying from 10¹³ to 10¹⁵ cm⁻². The implanted Si substrates were oxidized at considerably low Si oxidation temperatures of 700 and 750°C. The formed structures are characterized by electroreflectance (ER) spectroscopy. The implanted Si surface was accessed through the ultrathin oxide layer. From the ER spectra the characteristic energetic bands of direct electron transitions in Si and the corresponding broadening parameters are elaborated. The shifts of the direct energy gap are related to the process induced stress in implanted Si that does not exceed 10⁹ N/m². The phenomenological broadening parameters Γ are below 130 meV and H⁺ implanted Si with fluence of 10¹³ cm⁻² has a value of 100 meV. The slight increase of Γ as compared to the unimplanted Si is due to incomplete anneal of ionization induced defects. The oxidation rates of the H⁺ implanted Si increases to values being characteristic for Si wet oxidation.

1. Introduction
The behavior of hydrogen in semiconductors has been extensively studied for the last decades. The efforts of the researchers were provoked not only by a scientific interest, but were motivated by the possibility to improve device performance. Hydrogen is a highly reactive species in semiconductors and can have a profound effect on the electrical and optical properties of a device. It has been found that dangling bonds on the surface and interface, defects in the bulk of the material, as well as at grain boundaries can successfully be passivated by formation of electrically neutral complexes with H species. Therefore hydrogenation can be used as a highly effective technological tool to enhance the performance of electronic and optical devices. Over last two decades, a number of hydrogenation methods have been empirically optimized for device passivation. These include forming gas anneal, ion implantation and dry plasma processing. Despite its success, the fundamental understanding of H passivation is still incomplete, especially when a production scheme of a hydrogenation process for maximum passivation is required.

In an experiment where controllable hydrogenation combined with low defect concentrations has to be investigated, H can be introduced in the surface region of the sample using low energy H⁺ ion
implantation. Ion implantation provides accurate control into Si depth by the choice of acceleration energy and ion fluence. In the present study Si wafers were subjected to hydrogenation of by plasma ion immersion (PIII) technique, which ensures the requirements stated above. On the implanted surface an ultrathin silicon oxide was grown by thermal oxidation at temperatures between 700 and 800°C. The oxidized Si surface was investigated by electroreflectance spectroscopy (ERS), the implanted Si surface being accessed through the oxide layer. This optical technique, as highly sensitive to interface properties [1,2], is very well suited for characterization of the implanted Si surface. From the analysis of the electroreflectance (ER) spectra conclusions can be drawn about the properties of the interfacial region including defect concentrations and stress resulting from the oxidation process. The results enable us to show that hydrogenation through PIII can be effective tool for growing high quality oxide with lowered structural strains at considerably low Si oxidation temperatures.

The oxide growth temperatures are high enough to serve as annealing of implantation-induced defects to a level allowing the record of ERS signals. However, these temperatures lie well below the temperatures needed for relaxation of macroscopic compressive strain in the bulk of the SiO$_2$ film (990°C) and interface relaxation and bond rearrangement process (~ 900°C) [3]. The oxidation temperatures are lower than that used in the present Si-based industry, so that conclusions can be drawn for the possibility to use such low temperatures to obtain structures with smaller defect densities.

2. Experimental details

2.1 Sample preparation
The studied samples were Si/oxide structures, prepared onto (100)p-type Si substrates with a resistivity of 5-8 Ohm.cm. The Si wafers were subjected to H$^+$ ion implantation with energy of 2 keV in a PII installation unit. The hydrogen fluence varied from $10^{13}$ to $10^{15}$ cm$^{-2}$. Further, following standard RCA cleaning, the implanted Si substrates were oxidized at temperatures between 700 and 800°C in dry oxygen atmosphere for 30 min. No further temperature treatments were applied.

2.2 Measurements
The method used to characterize the samples was the electroreflection spectroscopy. Analysis of the ER spectra in a specific region in the $k$-space of the Brillouin zone makes it possible to determine the transition energy $E_g$ the phenomenological Lorentz broadening parameter $\Gamma$, which allows for dissipation processes in the electron transition, and the energy relaxation time of the light excited charge carriers. The energy of transition and the value of the phenomenological broadening parameter are used to make conclusion about the implanted Si surface region and as indicators of Si/oxide interface perfection.

The ERS consists in recording the modulation of the reflectivity of the sample that appears when an external modulating electric field is applied to the sample. The measured quantity is the relative reflectivity modulation, $\Delta R/R$. The ER spectra were measured through the oxide layer in the photon energy region of 3.0 - 3.8 eV, over the spectral range of the Si direct bandgap energy. The ER response of the structures was measured by a standard technique using 0.1 N KCl solution in an electrolytic cell to apply modulating voltage of 1 V. DMR-4 monochromator was used with automatic recording of the spectra with a 0.003-eV resolution. The sensitivity of the device in measuring $\Delta R/R$ was one part in a million, and the accuracy of measuring the signal strength was 2%. The measurements were performed at room temperature in the low-field mode condition of $\hbar \Omega < \Gamma/3$, where $\hbar \Omega$ is the electro-optical energy and $\Gamma$ is the phenomenological parameter of broadening [4,5]. The values of the direct transition $E_g$ and $\Gamma$, were calculated from the analysis of the ER spectra line shape using the Aspnes three-point technique [4,6].
The thickness of the oxides was determined by ellipsometry at $\lambda = 632.8$ nm with an accuracy of $\pm 0.2$ nm. The oxide thickness at 750°C was below 9 nm, varying depending on hydrogen ion fluence. By applying SRIM code (Stopping and Range of Ions in Matter) simulations [7] the distributions of the implanted ions, the ionization effects and vacancy formation were modelled.

3. Results and discussion

Figure 1 presents the ER spectra from hydrogen implanted Si surface oxidized at 700 and 750°C. According to electron band structure of silicon, the spectra correspond to the direct transition, which occurs between the valence and the conduction band at the center of the Brillouin zone. In this range the Si known to exhibit two neighbouring direct electron transitions around the center of Brillouin zone: $E_0^v (\Gamma_{25} - \Gamma_{15})$ at 3.3 eV and $E_0^c (\Gamma_{25} - \Gamma_2^c)$ at 3.37 eV. In view of broadening, the signals from the two transitions overlap and usually are not resolved at room temperature [8,9] and are viewed as a single transition at $E_g = 3.4$ eV. As reported, silicon surface in unstressed conditions is characterized by 3.37 eV of the direct transition [10,11]. The record of the near 3.4 eV structure in the ER signal in our spectra is evidence that the ER signal originates from the Si substrate and the observed shifts and shape changes with ion fluence are connected to the condition at the interface region.

![Figure 1](image1.png)

**Figure 1.** Electroreflectance spectra of the oxidized Si surface for different H$^+$ implantation fluences. Oxidation was performed at 700°C (a) and at 750°C (b).

The transition energies and phenomenological broadening parameters for Si wafer with different implantation fluences are given in figure 2.

![Figure 2](image2.png)

**Figure 2.** Transition energies (a) and phenomenological broadening parameters (b) for Si wafer with different implantation fluences. The values for unimplanted Si are given at zero fluence. The lines are given to show the tendency behaviour.
The transition energies are shifted relative to the unstressed position and are indicative for the stress revealed in the Si during oxidation. On the left axis of figure 2a the energy shifts are transferred to the stress scale. For that purpose, the correlation of the energy shift with the stress level is needed. Photoreflectance study of Si oxidized at 850°C [12] showed a correlation coefficient of $2.09 \times 10^7$ N/m²/meV. Applying Raman spectroscopy for light-emitting anisotropically etched Si yielded a value of $1 \times 10^7$ N/m²/meV [13]. Here we used the data from the photoreflectance because the resemblance to the experimental technique used in the present study. Moreover, in that case the Si was also subjected to a high temperature, although higher (850°C) than in our experiments ($\geq 700^\circ$C). It can be seen that the stress in implanted Si does not exceed $10^9$ N/m².

The broadening parameter $\Gamma$ is inversely proportional to the relaxation time and mobility of the electrons $\mu \sim e \hbar / m^* \Gamma$ [14], where $m^*$ is the reduced effective mass and $\hbar$ and $e$ have their usual meaning of the Plank constant and elementary charge, and therefore characterizes the scattering process at the Si interface region. In figure 2b the mobility is given at the right axis, normalized to the unstressed mobility $\mu_0$.

The referent Si without implantation oxidized at both 700 and 750°C show a shift of $E_g$ to 3.37 eV for unstressed Si. This indicates a low level of tensile stress at the Si surface, compressive stress at the oxide, respectively, which is a result of the oxidation. It is known that the relaxation of oxide stress is observed at temperatures about 900°C and above. For comparison, mechanical stress of the order of $10^9$ N/m² is typical for oxides grown thermally at 850°C as obtained from spectroscopic ellipsometry analysis [15]. The broadening parameter $\Gamma$ of 95 meV is relatively small. Being inversely proportional to the carrier relaxation time, this value characterizes the scattering process at the unimplanted Si interface region and its small value is an indication of a high quality region.

The spectra for the H⁺ implanted Si with fluences of $10^{13}$ and $10^{14}$ cm⁻² reveal a shape and polarity typical for oxidized Si surface [10]. The implantation at these fluences causes no measurable changes of $E_g$, while changes are observed for the broadening parameter $\Gamma$ (Figure 2). This is reasonable since implantation with the light H⁺ ions is not expected to cause severe damage in the Si lattice. However, the ionization effects can be substantial. Simulation using SRIM code shows the development of ionization events inside the Si substrate due to H⁺ PIII as evident from Figure 3a.

![Figure 3.](attachment:figure3.png)

**Figure 3.** Hydrogen ion distributions into Si substrate after implantation (a) and ionization defects due the implantation process (b).

Ionization leads to defect generation in the Si space charge region and at the interface. These defects have contribution to scattering processes and result in larger $\Gamma$. As a consequence, the mobility decreases (figure 2b). The annealing process during oxidation is not sufficient to anneal out
completely the defects. A high hydrogen concentration in the Si subsurface region is evident from SRIM results in figure 3b, which however, seems not to result in complete hydrogen saturation of the dangling bonds at the interface.

For ion fluence 10^{15} \text{ cm}^{-2} the observed red shift of \( E_g \) approaching 3.39, which is very close to 3.37 eV, can be attributed to relaxation of the substrate stress due to annealing effects. The decrease of the broadening \( \Gamma \) also indicates development of the interface region with higher structural perfection and less scattering centers. Hydrogen RF plasma has been shown to cause stress relaxation in our earlier study using spectral ellipsometry [16]. Also, passivation of the surface with hydrogen has lead to strain relaxation upon treatment of a porous Si surface in hydrogen plasma [17].

The inversion of the polarity of the ER spectra, found only for 10^{15} \text{ cm}^{-2} ion fluence, for both oxidation temperatures should be noted. The opposite ER signal is usually attributed to formation of a thin defective Si layer near the surface [10,11]. However, even if such a layer is present, the defect concentration cannot be high, since otherwise it would not be possible to record ER signal. The \( E_g \) and \( \Gamma \) also indicate high quality interface as discussed above. Most probably, at this fluence the ER shape has to be considered as a unipolar signal typical for intrinsic Si surface. This could be due to formation of hydrogen complexes with the substrate doping atoms in the space charge region. Similar effect has been found in RF hydrogen plasma treated oxides [18].

An interesting point is the influence of the oxidation temperature. It can be seen from figure 2 that the transition energies for all fluences are higher for the higher oxidation temperature. At higher oxidation temperature larger Si region is consummated during oxidation moving the interface deeper into the implanted region. From figure 3 it can be inferred that this region contains higher net concentrations of hydrogen ions and ionized defects causing the bigger \( E_g \) shift.

The oxidation of the implanted region of the Si is expected to exhibit increased oxidation rates. Due to the implantation defects the diffusion of the oxidizing species is facilitated. The presence of H-atoms in the Si surface layer can promote the surface reaction rate of the oxidation process. An illustration of the increased rate is shown in figure 4. For the oxides, grown on implanted Si at a certain oxidation temperature, the experimental points refer to the different ion implantation fluences.

![Figure 4](image_url)

**Figure 4.** Comparative data for Si oxidation rates. The oxidation time is 30 min.

In the figure the data (open asterisks) for oxidation of implanted Si is compared with oxidation rates of Si according to Deal-Grove model (full lines) [19] in wet and dry oxygen atmosphere. The substantial increase of the oxidation rate of the H^+ PII implanted Si up to values characteristic for wet oxidation is evident, the increase being even more pronounced at 700°C. No strong dependence of the oxidation rates has been found on the implantation fluence as evident from the close experimental points for a given oxidation temperature. Increase of oxidation rates was also found in our earlier experiments on oxidation of Si hydrogenated in RF plasma [19], as is demonstrated in figure 4 (diamonds).
4. Conclusions
The direct energy gap \( E_g \) of Si wafer hydrogenated through hydrogen plasma immersion ion implantation and oxidized in dry \( O_2 \) at 700° and 750°C was examined by means of electroreflectance spectroscopy. The Si surface is under small tensile stress up to \( H^+ \) fluence of \( 10^{14} \) cm\(^{-2}\), while at \( 10^{15} \) cm\(^{-2}\) stress relief is observed. The increased broadening parameter is due to incomplete anneal of ion induces interface defects.

Hydrogenation through plasma immersion ion implantation allows for a substantial increase of the oxidation rate at temperatures as low as 700°C up to the values typical for wet oxidation. The values of the direct energy gap and the broadening parameter indicate the possibility to obtain small structural strains and low concentration of defects in the interface region being of importance for the Si technology.

The results show that hydrogenation through PIII shows a potential for growing high quality oxide with lowered structural strains at considerably low Si oxidation temperatures suitable for practical use.

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References
[1] Kapil Dev, Jung M Y L, Gunawan R, Braatz R D and Seebauer E G 2003 Phys. Rev. B 68 195311
[2] Vlasenko A I, Gentsar P A and L.A. Demchyna 2005 Ukr. J. Phys. 50 9 997
[3] Lucovsky G and Phillips J C 2004 Appl. Phys. A 78 453
[4] Aspnes D E and Rowe J E 1972 Phys. Rev. B 5 4022
[5] Misiewicz J, Sitapek P and Sek G 2000 Opto-Electron. Rev. 8 1
[6] Aspnes D E 1972 Phys. Rev. Lett. 28 913
[7] http://www.srim.org/
[8] Venger E F, Gorbach T Ya, Matveeva L A and Svechnikov S V 1999 J. Exper. Theor. Phys. 89 948
[9] Grower J W and Handler P 1974 Phys. Rev. B 9 2600
[10] Matveeva L A, Venger E F and Holiney R Yu 1999 Semicond. Phys. Quantum Electron. & Optoelectron. 2 10
[11] Gorbach T Ya, Holiney R Yu, Matiyuk I M, Matveeva L A, Svechnikov S V and Venger E F 1998 Semicond. Phys. Quantum Electron. & Optoelectron. 1 66
[12] Gorbach T Ya, Rudko G Yu, Smertenko P S, Svechnikov S V and Valakh M Ya 1994 Applied Physics A: Materials Sci. & Processing 58 183
[13] Fitch J T, Bjorhmann C H, Lucovsky G, Pollak F H and Yin X 1989 J. Vac. Sci. Technol. B 7 775
[14] Begishev A P, Galiev G B, Kapaev VV and Mokerov V G 1982 Phys. Tech. Polup. 16 426
[15] Szekeres A 1998 in Fundamental Aspects of Ultrathin Dielectrics on Si-based Devices Eds Garfuncel E., Gusev E and Vul’ A (Kluwer Academic Publishers) NATO Science Series 3 High Technology vol 47 p 65
[16] Szekeres A, Paneva A, Alexandrova S, Lisovskyy I and Litovchenko V 2003 Vacuum 69 355
[17] Venger E F, Holiney R Yu, Matveeva L A and Vasin A V 2003 Semiconductors 37 103
[18] Szekeres A 1991 Radiat. Eff. and Defects in Solids 116 145
[19] Deal B E and Grove A S 1965 J. Appl. Phys. 36 3770
[20] Szekeres A, Alexandrova S, Lytvyn P and Komptsas M 2005 J. Phys: Conf. Ser 10 246