Surface disorder production during plasma immersion implantation and high energy ion implantation

M.A. El-Sherbiny, N.Q. Khánh, H. Woxmeester, M. Fried, T. Lohner, I. Pintér, J. Gyulai

Abstract

High-depth-resolution Rutherford Backscattering Spectrometry (RBS) combined with channeling technique was used to analyze the surface layer formed during plasma immersion ion implantation (PIII) of single crystal silicon substrates. Single wavelength multiple angle of incidence ellipsometry (MAIE) was applied to estimate the thickness of the surface layer. The thickness of the disordered layer is much higher than the projected range of P ions and it is comparable with that of protons.

Another example of surface damage investigation is the analysis of anomalous surface disorder created by 900 keV and 1.4 MeV Xe implantation in (100) silicon. For the 900 keV implants the surface damage was also characterized with spectroellipsometry (SE). Evaluation of ellipsometric data yields thickness values for surface damage that are in reasonable agreement with those obtained by RBS.

1. Introduction

Plasma immersion implantation (PIII) is a promising method to fabricate very shallow junctions and this can be a significant contribution to the development of solar cell fabrication processes. In conventional photovoltaic devices the junction is formed by diffusion followed by a partial etch back step in order to achieve the required junction depth. For process optimization it is necessary to characterize the near surface region of the silicon after the PIII process. In this study, the phosphorous depth profile and the thickness of damaged surface layer were determined by Rutherford Backscattering Spectrometry (RBS) and the surface layer was probed using single wavelength multiple angle of incidence ellipsometry (MAIE).

The details of disorder formation in ion irradiated silicon have been the subject of extensive investigations motivated by fundamental and technological reasons. The properties of defects generated by ion irradiation determine the basic features of implantation-related processes such as ion beam induced layer-by-layer recrystallization and amorphization.

Ion irradiation induced anomalous surface disordering was observed in several cases [1-3]. In this case, anomalous means that this disorder is far from that in the depth of the projected range. Earlier we saw this phenomenon in boron implanted silicon using a combination of single-wave ellipsometry and high-depth-resolution RBS [4,5].

Ion bombardment induced surface damage can be observed in sapphire too. Considerably larger surface peaks from Al and O were found after implanting sapphire with 300 keV Cr ions than in the virgin crystal [6], and recently, an increased surface peak was detected due to 150 keV Co ion bombardment in sapphire [7].

The applicability of spectroellipsometry (SE) for the nondestructive determination of ion-implantation induced damage profiles was demonstrated in detail by several research groups [1,2,8-11]. It was found that the thickness of the surface-damaged silicon layer (beneath the native oxide layer) increased monotonically with increasing implantation dose [12]. The amorphization rate at the surface was found to be proportional to the nuclear stopping power for N, Si and Ar implantations [13].

In the present paper we report on an RBS and SE study of Xe implantation induced anomalous surface amorphization.

2. Experimental

For PIII experiments, a single wafer, parallel plate Reactive Ion Etching chamber was used, with an excitation...
frequency of 13.56 MHz and a maximum power density of 3 W/cm². For PII a gas mixture of 0.5% PH₃ in Ar at a flow rate of 33 sccm and a pressure of 0.8 mbar was applied. The bias voltage was 900 V.

To investigate the surface amorphization process, 900 keV Xe²⁺ and 1.4 MeV Xe³⁺ ions were implanted at room temperature into (100) silicon. The implantation was performed into as delivered Wacker single-crystal silicon at the Central Research Institute for Physics, Budapest. The implantation was done at room temperature with a current density of about 20–25 nA/cm².

RBS and channeling techniques with 1.5 or 2.95 MeV He⁺ ions were used in the experiments. Two detectors were placed to detect ions scattered through 165° and 97° (i.e. with a glancing exit angle of 7° to the surface). In the latter geometry, the depth resolution was better than 5 nm [14]. To evaluate the spectra we used the RBX code written by Kőta [15], which can also handle channelled spectra.

In reflection ellipsometry the experimental result is given by:

\[ \rho = R_p/R_s = \tan \Psi \exp(i \Delta), \]

where \( \rho \) is the complex reflectance ratio, \( R_p \) and \( R_s \) are the complex amplitude reflection coefficients for the parallel (p) and perpendicular (senkrecht, s) to the plane of incidence polarizations respectively, \( \tan \Psi \) is the intensity ratio and \( \Delta \) is the relative phase difference. With a rotating element ellipsometer one can determine directly \( \tan \Psi \) and \( \cos \Delta \). Using manual ellipsometry one can measure \( \Psi \) and \( \Delta \). The SE spectra were obtained at Twente University in the range of 300–650 nm with a rotating polarizer ellipsometer. A manual ellipsometer was used for MAIE to estimate the thickness and the refractive index of the surface layer of PII samples. The wavelength was 632.8 nm (He–Ne laser).

3. Results and discussion

3.1. Plasma immersion implantation

Figs. 1a and 1b present the high-depth resolution RBS spectra of α’s scattered through 97° and 165° respectively, for a PII sample. The depth of phosphorus atoms is shallow enough to be analyzed by RBS. The surface region of the sample consists of an oxide layer and a disordered layer. The evaluation yields a thickness of 19 nm for the oxide layer (assumed to be SiO₂) and a thickness of 15 nm for the disordered Si layer. The thickness of the disordered layer is much greater than the projected range of P⁺ ions (3.5 nm) and is comparable with that of protons (14 nm). The amount of P atoms was found to be 8.5 × 10¹⁵ atoms/cm². However, the majority of P atoms are located in the oxide layer.

3.2. Anomalous surface amorphization

Figs. 3a and 3b present the high-depth resolution RBS spectra recorded with a detector placed at a scattering angle of 97° and also a spectra recorded with a detector placed at a scattering angle of 165°, respectively. They include spectra for the series of 900 keV xenon implanted samples and for the virgin sample. In accordance with projected range calculations, significant buried disorder is observable around a depth of 280 nm (Fig. 3b). The energetic xenon ions are shown to have created a disorder at the silicon surface. The thicknesses of the surface oxide and disordered layers in units of atoms/cm² were deduced.
Fig. 2. Measured single wavelength MAIE data for the PIII sample together with the result of evaluation; \( n \) is the refractive index, \( k \) is the extinction coefficient. \( \sigma_w \) characterizes the quality of the fit.

Fig. 3. (a) Random and (100)-aligned high-depth-resolution RBS spectra for 900 keV xenon implanted samples recorded with the detector placed at 97° scattering angle. (b) Random and (100)-aligned normal resolution spectra for 900 keV xenon implanted samples recorded with the detector placed at 165° scattering angle.

crystalline silicon and fine-grain polycrystalline silicon [17], i.e. the complex refractive index of the slightly disordered layer was calculated by Bruggeman effective

### Table 1

<table>
<thead>
<tr>
<th>Ion (Energy)</th>
<th>Dose ( 10^{15} \text{ cm}^{-2} )</th>
<th>( D_{\text{Si}} ) [nm] ( D_{\text{oxide}} ) [nm]</th>
<th>( \sigma ) ( 10^{-3} )</th>
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<tbody>
<tr>
<td></td>
<td>SE</td>
<td>RBS</td>
<td>SE</td>
</tr>
<tr>
<td>Virgin</td>
<td>2.2 ± 0.05</td>
<td>1.4 ± 0.2</td>
<td>4.2</td>
</tr>
<tr>
<td>Xe (900 keV)</td>
<td>5.4 ± 0.05</td>
<td>1.09 ± 0.25</td>
<td>2.3 ± 0.05</td>
</tr>
<tr>
<td>Xe (1.4 MeV)</td>
<td>9.3 ± 0.05</td>
<td>1.46 ± 0.36</td>
<td>2.0 ± 0.05</td>
</tr>
<tr>
<td>Virgin</td>
<td>4.2 ± 0.1</td>
<td>1.3 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>Xe (900 keV)</td>
<td>5.0 ± 0.1</td>
<td>0.7 ± 0.1</td>
<td>1.5 ± 0.2</td>
</tr>
<tr>
<td>Xe (1.4 MeV)</td>
<td>6.7 ± 0.1</td>
<td>1.1 ± 0.1</td>
<td>1.5 ± 0.2</td>
</tr>
<tr>
<td>Xe (1.4 MeV)</td>
<td>7.5 ± 0.1</td>
<td>1.0 ± 0.1</td>
<td>1.4 ± 0.2</td>
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medium approximation using crystalline and fine-grain polycrystalline silicon as end-points.

The data for the implanted samples was analyzed using a FORTRAN program developed at the Pennsylvania State University. We used grid search before fitting. The goodness of the fit is estimated by the unbiased estimator:

$$\sigma = \frac{1}{2N - p - 1} \times \sqrt{\sum_{j=1}^{N} \left( \cos \Delta_j^{exp} - \cos \Delta_j^{calc} \right)^2 + \left( \tan \Psi_j^{exp} - \tan \Psi_j^{calc} \right)^2},$$

where $N$ is the number of wavelengths and $p$ is the number of fitted parameters.

To study anomalous surface disorder (assuming a thin amorphous layer) SE is extremely useful because of its sensitivity.

Measured ellipsometric spectra of silicon samples implanted with xenon ions together with the results of multi-parameter fitting are shown in Fig. 4. For comparison, a reference spectrum of virgin (unimplanted) silicon was also presented.

Table 1 summarizes the layer thickness values resulting from the evaluation of RBS and SE measurements. For

<table>
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<tr>
<th>Ion</th>
<th>Energy [keV]</th>
<th>Nuclear stopping power [eV/Å]</th>
<th>Surface amorphization rate (normalized amorphous layer thickness) [nm/10^14 atom/cm^2]</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>200</td>
<td>4.1</td>
<td>0.035 ± 0.0028</td>
</tr>
<tr>
<td>Ar</td>
<td>800</td>
<td>18.1</td>
<td>0.19 ± 0.0086</td>
</tr>
<tr>
<td>Si</td>
<td>200</td>
<td>20.5</td>
<td>0.22 ± 0.018</td>
</tr>
<tr>
<td>Xe</td>
<td>1400</td>
<td>1.39</td>
<td>1.39 ± 0.12</td>
</tr>
<tr>
<td>Xe</td>
<td>900</td>
<td>1.68</td>
<td>1.68 ± 0.19</td>
</tr>
</tbody>
</table>

RBS analysis we used the density of silicon (5 × 10^{22} atoms/cm^2) to calculate the thickness of the surface disordered layer. Evaluation of ellipsometric data yields thickness values for surface damage that are in reasonable agreement with those obtained by RBS. However, some differences can be observed in thickness values. This reveals that SE is sensitive to surface damage induced by heavy ion implantation, but for precise evaluation a more adequate optical model is needed.

The difference in the thickness of the surface (native) oxide can be explained on the basis of morphological and compositional properties of this layer. We use the refractive index of the SiO, but this surface is possibly a roughened and unstoichiometric one. SE determines an effective thickness but RBS gives atoms/cm^2.

To relate the surface amorphization rate to the amount of nuclear energy deposited, the increase in the amorphized surface layer thickness with respect to ion dose was calculated by fitting a straight line to the points belonging to a given implantation energy. The dependence of the surface amorphization rate (normalized amorphous layer thickness) on the nuclear energy deposited at the surface is shown in Table 2. The nuclear stopping power at the implantation energy was calculated using TRIM code [12].

For comparison, the values for N, Ar and Si ions were taken from Ref. [13]. The surface amorphization rate was found to be proportional to the nuclear stopping power for N, Si and Ar implantations [13].

4. Conclusion

It was demonstrated that RBS combined with channeling has the potential to yield the concentration of phosphorous atoms, the thickness of the surface oxide, and the thickness of the disordered layer in silicon samples which were processed by PHI. We determined the surface amorphization rate for the case of high energy Xe ion implantation into Si. We think the surface amorphization is an analogous process to Ion Beam Induced Epitaxial Crystallization and Ion Beam Induced Amorphization [19–23].
The most probable explanation for the surface disordering is the diffusion of point defects to the surface. Spectroscopic ellipsometry, high-depth-resolution Rutherford backscattering and channeling have been used to examine the surface damage formed by room temperature Xe implantation into silicon. A multiparameter fitting procedure of ellipsometric data was applied to evaluate the surface damage. The results demonstrate the applicability of spectroscopic ellipsometry together with a proper optical model construction for probing surface damage.

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References