

# Implantation and sputtering of Ge ions into SiO<sub>2</sub> substrates with the use of Ge ions produced by repetitive laser pulses

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## Abstract

Due to the growing demands for high-current ion beams, laser plasma as a potential source of multiple charged ions has been investigated. Selection of proper laser beam characteristics is very important for efficiency of the ion implantation technology.

In this contribution attention is devoted mainly to the characterization and optimization of laser-produced Ge ion streams as well as to analysis of the direct implantation of these ions into SiO<sub>2</sub> substrates. The Ge target was irradiated with the use of repetitive (up to 10 Hz) laser pulses of energy up to 700 mJ at radiation intensities of  $\sim 10^{11}$  W/cm<sup>2</sup>. The implanted samples were placed along the target normal at distances of 6 cm from the target surface. The ion stream parameters were measured using the time-of-flight method. The depth of ion implantation was determined by X-ray photoelectron spectroscopy (XPS) and Microlab 350—the high resolution scanning Auger microprobe. After the implantation the samples were annealed in temperatures in the range of 550–750 °C to create nanocrystal structures and then analyzed by means of Raman spectroscopy and scanning electron microscopy (SEM).

These investigations were carried out for optimization of laser-generated Ge ion streams, suitable for specific implantation technique, namely for fabrication of semiconductor nanostructures within the SRAP “SEMINANO” project.

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## 1. Introduction

Currently available ion sources can produce high average currents only of normally gaseous materials, or lower currents of more desirable, normally

solid materials [1–4]. Recently, laser-driven ion sources (LIS) have been proposed and investigated, which can potentially produce orders of magnitude higher ion currents of normally solid materials, with selectable (up to very high) energy and charge states [5–8]. Lasers can ionize all materials, whether solid, liquid or gaseous. Higher ion current can be traded off against higher ion energy/charge state by adjusting laser power density.

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Reliability, ion species selection, implanting multiple ions in a programmable sequence, and integrated laser micromachining are additional LIS advantages. The combination of adequately high ion flux, flexibility and reliability should finally enable commercial ion implantation applications.

Application of LIS for nanocrystal formation may be attractive for direct ultra-low-energy ion beam implantation in thin  $\text{SiO}_2$  layers [9,10] and for production of uniform size and depth concentration of laser-produced Ge ions of different energies [11]. Although from a nanocrystal production point of view the implantation of laser-produced ions appears as a quite simple technique compared to the traditional ones, there are many technological issues that should be solved before establishing a reliable and reproducible nanostructure fabrication procedure. The literature regarding this technique [5–7,12] concerns application of LIS for the modification of properties of different materials, not fabrication of semiconductor nanostructures.

In this paper attention is devoted to the characterization and optimization of laser-produced Ge ion streams as well as to analysis of the direct implantation of these ions into  $\text{SiO}_2$  substrates.

## 2. Experimental

In the deposition/implantation experiment the new repetitive Nd:glass laser ( $1.06\ \mu\text{m}$ ,  $3.5\ \text{ns}$ ,  $<0.8\ \text{J}$ ,  $<10\ \text{Hz}$ ) focused on the surface of a pure

Ge target was applied for production of Ge ions and neutrals. The cylindrical interaction chamber was evacuated using a new turbo-molecular pump. The parameters of Ge ions were monitored using an ion collector. The improved set-up is presented in Fig. 1.

The ion characteristics were determined with the use of ion diagnostics based on the time-of-flight method (ion collectors and an electrostatic ion energy analyzer). The maximum measured ion energy was  $\sim 3\ \text{keV}$ . The stream of Ge ions emitted along the target normal estimated on the basis of the ion collector signal for the distance of  $6\ \text{cm}$  from the laser irradiated Ge target was  $>10^{16}\ \text{ions/cm}^2$  (for  $\sim 1000$  laser shots). The surface of the sample was deposited also by neutrals (atoms, debris, clusters) not recorded by the ion collector.

The laser pulse energy was  $550\ \text{mJ}$  (laser fluence  $\sim 4.5\ \text{J/cm}^2$ ) at laser intensity on the target surface  $I_L = \sim 10^{10}\ \text{W/cm}^2$ . The Ge ions produced in  $\sim 1000$  or in  $\sim 3000$  laser shots were deposited and implanted in  $\text{SiO}_2$  substrate of thickness of  $\sim 20\ \text{nm}$  prepared on the Si single crystal. The  $\text{SiO}_2$  substrates V1B, V3B and V5A were deposited/implanted with Ge ions produced by 1058, 3000 and 3000 laser shots, respectively. The substrate V5A have been prepared in METU, while the samples V1B, V3B have been received from the Polish semiconductor laboratory. Another set of  $\text{SiO}_2$  samples were deposited/implanted with Ge ions generated in 100, 200, 400 and 800 laser shots.

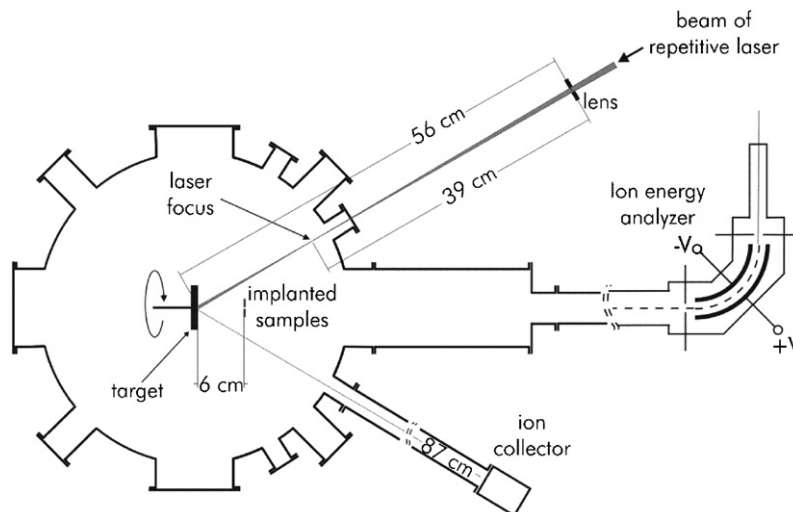


Fig. 1. Experimental arrangement used for investigation of implantation of laser-produced ions into semiconductor materials.

### 3. Results and discussion

The analysis of the samples was performed with the use of the XPS + AES method and ion etching (using  $1\ \mu\text{A}$  current of  $\text{Ar}^+$  ions having energy of 3 keV) in the Warsaw University of Technology (Faculty of Material Engineering). The etching speed was  $0.0025\ \text{nm/s}$  on a sample surface of  $8 \times 8\ \text{mm}^2$ . On the basis of the XPS + AES spectra the depth profiles of different elements in the  $\text{SiO}_2$  layer were estimated (Fig. 2). In the layer of  $<4\ \text{nm}$  the amount of deposited laser-produced Ge atoms is very high; in depth of  $\sim 2.5\ \text{nm}$  more than 50% Ge atoms was estimated. In this layer there are also oxygen and carbon atoms (probably contaminants). In the  $\text{SiO}_2$  layer the number of implanted Ge ions decreases up to several percent in depth of  $\sim 10\ \text{nm}$ . It was shown that laser-produced Ge ions were implanted even at the depth of 18 nm—a maximum depth investigated in this test. The spatial distributions of Ge atoms implanted into the  $\text{SiO}_2$  substrate were calculated using the TRIM simulation code [13] by Prof L. Torrisi and his co-workers in the Messina University. Fig. 3 shows an example of calculated depth profile of Ge atoms in the  $\text{SiO}_2$  layer assuming the Maxwell–Boltzmann distribution of velocity of implanted laser-produced Ge ions have maximum energy of 3 keV and dose of  $10^{16}\ \text{ions/cm}^2$ .

The Raman spectroscopy measurements of the surface of substrates deposited/implanted with the use of repetitive laser were performed in METU in Ankara within IPPLM–METU cooperation. Fig. 4 presents the exemplary Raman spectra of Ge

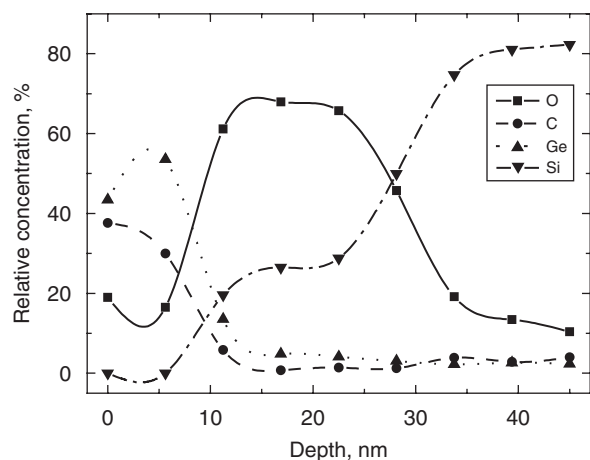


Fig. 2. The depth profiles of different elements in the layer of  $\text{SiO}_2$  estimated on the basis of XPS + AES spectra.

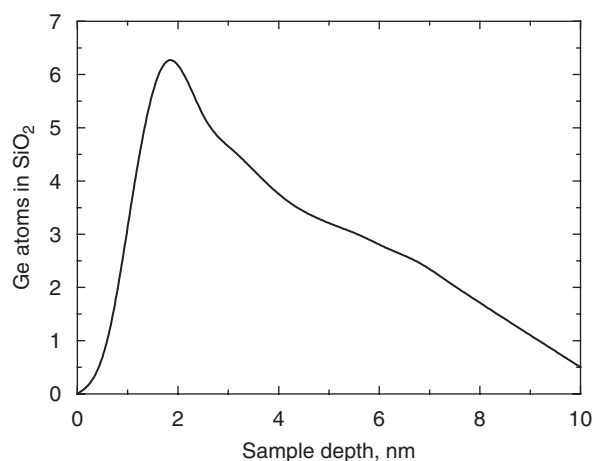


Fig. 3. Calculated TRIM depth-concentration profile of laser-generated Ge implanted into  $\text{SiO}_2$  layer.

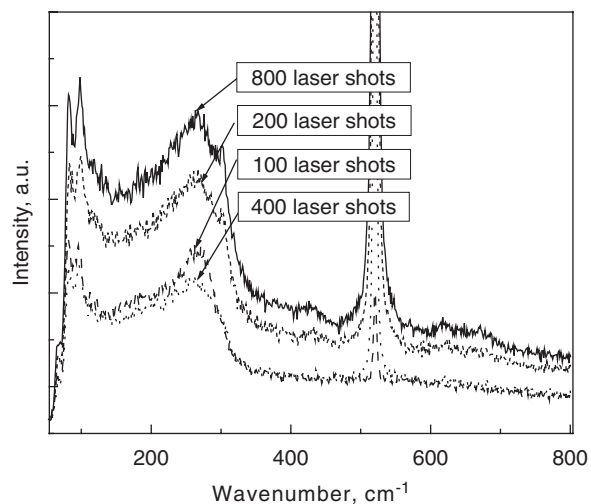


Fig. 4. The Raman spectra of  $\text{SiO}_2$  samples as-deposited/implanted (before annealing) with Ge ions generated at different numbers of laser shots.

structures for samples as-deposited/implanted (before annealing) at different numbers of laser shots. The shape of Raman spectrum shown in Fig. 4 essentially indicates an amorphous Ge deposited on the surface of a sample, but the sharp peak at  $\sim 300\ \text{cm}^{-1}$  is due to the Ge crystallite formed probably by fast laser-produced debris or clusters striking the sample surface. The Raman spectroscopy measurements of the surface of annealed substrates previously deposited/implanted with the use of repetitive laser were also performed in METU in Ankara within IPPLM–METU cooperation. Fig. 5 presents the exemplary Raman spectra of Ge structures for samples deposited/implanted at

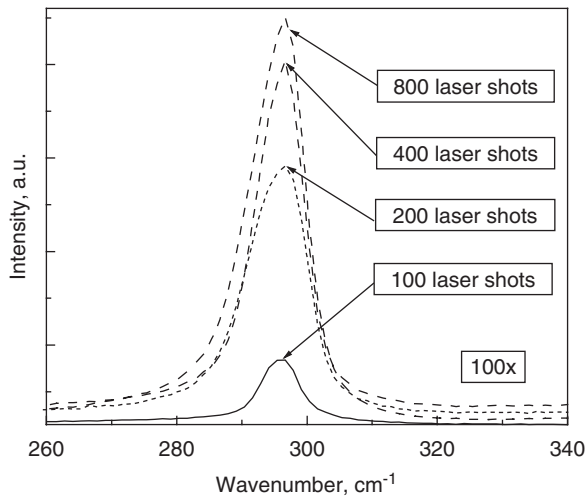


Fig. 5. The Raman spectra of  $\text{SiO}_2$  samples deposited/implanted with Ge ions generated at different numbers of laser shots. The annealing temperature was  $600^\circ\text{C}$  in this case.

different numbers of laser shots. The obtained Raman spectra clearly display the band at  $300\text{cm}^{-1}$  that come from scattering of Ge nanocrystallites on the  $\text{SiO}_2$  sample formed in the process of ion deposition/implantation and subsequent annealing. The linewidth (FWHM) of the Raman lines estimated for Ge crystalline structures of investigated samples was  $7.1\text{--}10.6\text{cm}^{-1}$ . Taking into consideration the dependence of the FWHM of the Raman peak on the nanocrystal size presented in [14] the size of investigated Ge nanocrystals was roughly estimated as  $5\text{--}10\text{nm}$ .

#### 4. Conclusions

The experimental arrangement with a new repetitive Nd:glass laser system has been used in IPPLM for investigations of implantation of laser-produced Ge into the  $\text{SiO}_2$  substrate. The depth profiles of different elements in the  $\text{SiO}_2$  layer of samples deposited/implanted in the IPPLM experiment were

estimated in WUT on the basis of XPS + AES spectra measured. In layer of  $\sim 2.5\text{nm}$  depth more than 50% Ge atoms was estimated. The approximated dimensions of  $5\text{--}10\text{nm}$  of the Ge nanocrystallites in the surface layer of the annealed  $\text{SiO}_2$  samples have been estimated on the basis of a shape of Raman spectra measured in METU.

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