*Radiation Effects & Defects in Solids*
Vol. 163, Nos. 4–6, April–June 2008, 589–595

# Applications of ions produced by low intensity repetitive laser pulses for implantation into semiconductor materials

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(*Received 11 March 2007; in final form 3 September 2007*)

This work reports experiment concerning specific applications of implantation of laser-produced ions for production of semiconductor nanocrystals. The investigation was carried out in the IPPLM within the EC STREP 'SEMINANO' project. A repetitive pulse laser system of parameters: energy up to 0.8 J in a 3.5 ns-pulse, wavelength of 1.06 μm, repetition rate of up to 10 Hz, has been employed in these investigations. The characterisation of laser-produced ions was performed with the use of 'time-of-flight' ion diagnostics simultaneously with other diagnostic methods in dependence on laser pulse parameters, illumination geometry and target material. The properties of laser-implanted and modified $SiO_2$ layers on sample surface were characterised with the use of different methods (XPS + ASD, Raman spectroscopy, PL spectroscopy) at the Middle East Technological University in Ankara and at the Warsaw University of Technology. The production of the Ge nanocrystallites has been demonstrated for annealed samples prepared in different experimental conditions.

**Keywords:** ion implantation; laser-produced ions; Ge nanocrystallites

## 1. Introduction

Studies of characteristics of plasmas generated with laser beams of low and medium intensity are directed towards determination of physical processes in a laser-produced plasma as well as towards important application, among others: use of laser ion sources for technological applications and for surface modification by laser ablation (*1–4*).

Application of laser ion source for nanocrystal formation may be attractive for direct ultra-low-energy ion beam implantation in thin $SiO_2$ and other semiconductor layers and for production of uniform size and depth-concentration of laser-produced ions of different energies (*5–7*). Although the implantation of laser-produced ions looks as a quite simple technique compared with the traditional ones, there are many technological issues that should be solved before establishing reliable and reproducible nanostructure fabrication procedure. An important advantage of the laser

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ISSN 1042-0150 print/ISSN 1029-4953 online

DOI: 10.1080/10420150701781076
http://www.informaworld.com

ion source is also the great ease of biasing the ion source or implanted sample to a high voltage for additional ion acceleration.

In this paper, attention is devoted to production of ions with the use of low-energy repetitive laser and their application for effective implantation into semiconductor materials for formation of nanostructures, in particular for fabrication of nanocrystals.

## 2. Experimental arrangement

In the Laser Plasmas Division of IPPLM, the interaction chamber with a vacuum pump system, target holder and holders for samples were completed, prepared and tested for measurements of implantation of laser-produced ions into semiconductor substrates. In the deposition/implantation experiment, the new repetitive Nd:glass laser (1.06 $\mu$m, 3.5 ns, $<$0.8 J, $<$10 Hz) focused on the surface of a pure Ge or Si target was applied for production of ions and neutrals destined for implantation. The parameters of ions were estimated with the use of ion time-of-flight diagnostic methods, namely ion collectors and electrostatic ion analyser (*8, 9*). The improved set-up is presented in Figure 1.

The maximum measured ion energy was $\sim$3 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 cm from the laser irradiated Ge target was $>10^{16}$ 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.

## 3. Investigation of properties of $SiO_2$ samples implanted/deposited with laser-produced Ge ions

In this experiment, the laser pulse energy was 550 mJ (laser fluence $\sim$4.5 J/cm$^2$) at laser intensity on the target surface $I_L = \sim 10^{10}$ W/cm$^2$. The Ge ions produced in $\sim$1000 or in $\sim$3000 laser shots were deposited and implanted in $SiO_2$ substrate of thickness of $\sim$20 nm prepared on the Si single crystal. The $SiO_2$ substrates V1B, V3B and V5A were deposited/implanted with Ge ions produced by about 1000, 3000 and 3000 laser shots, respectively. Another set of $SiO_2$ samples were deposited/implanted with Ge ions generated in 100, 200, 400 and 800 laser shots.

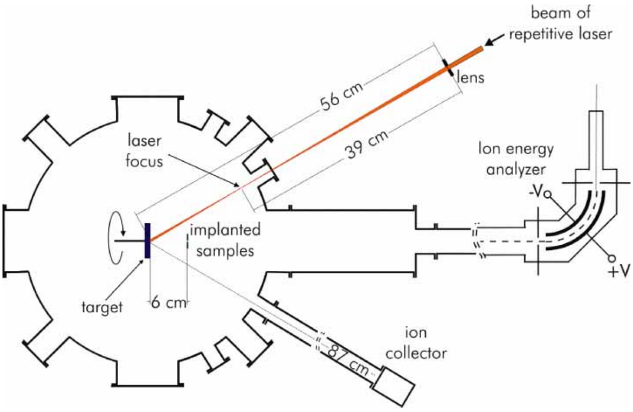

Figure 1. Experimental arrangement used for investigation of implantation of laser-produced ions into semiconductor materials.

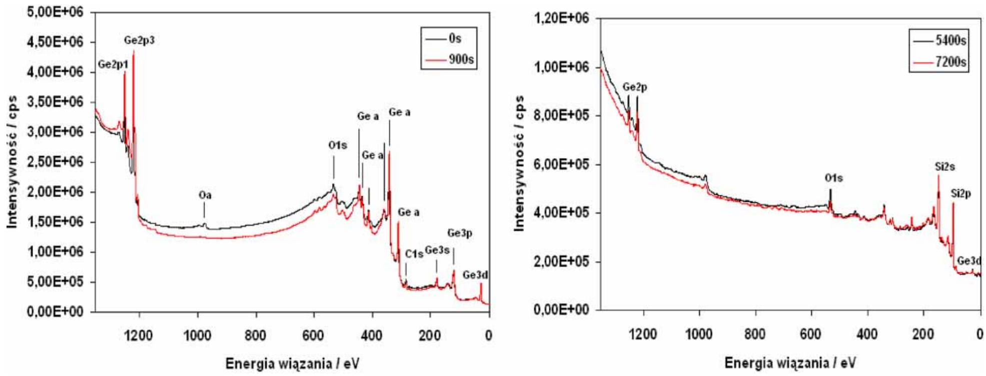

Figure 2. The examples of the XPS + AES spectra recorded at different etching times (0, 5400 and 7200 seconds) for $SiO_2$ sample implanted with Ge ions produced by 400 laser shots. The Auger lines are marked with letter ‘a’.

The analysis of the samples was performed with the use of the XPS + AES method and ion etching (using 1-$\mu$A current of Ar + ions having energy of 3 keV) in the Warsaw University of Technology (Faculty of Material Engineering). The etching speed was 0.0025 nm/s on a sample surface of $8 \times 8$ mm$^2$. The examples of the XPS + AES spectra recorded after different etching times for $SiO_2$ sample implanted with Ge ions produced by 400 laser shots are shown in Figure 2.

On the basis of the XPS + AES spectra the depth profiles of different elements in the $SiO_2$ layer were estimated (Figure 3). In the layer of $<4$ nm, the amount of deposited laser-produced Ge atoms is very high, in depth of $\sim$2.5 nm more than 50% Ge atoms was estimated. In this layer, there are also oxygen and carbon atoms (probably contaminants). In the $SiO_2$ layer, the number of implanted Ge ions decreases up to several percent in depth of $\sim$10 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 Raman spectroscopy measurements of the surface of substrates deposited/implanted with the use of repetitive laser were performed in Middle East Technical University (METU) in Ankara within IPPLM-METU cooperation. The Raman scattering spectra were obtained using the experimental arrangement mentioned above. Figure 4a presents the exemplary Raman spectra of Ge structures for samples as-deposited/implanted (before annealing) at different numbers of laser shots.

The shape of Raman spectrum shown in Figure 4a essentially indicates an amorphous Ge deposited on the surface of a sample, but the sharp peak at $\sim$300 cm$^{-1}$ is due to the Ge crystallite formed probably be 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

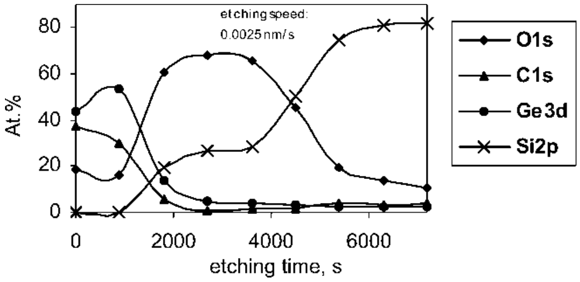

Figure 3. The dept profiles of different elements in the layer of $SiO_2$ estimated on the basis of XPS + AES spectra.

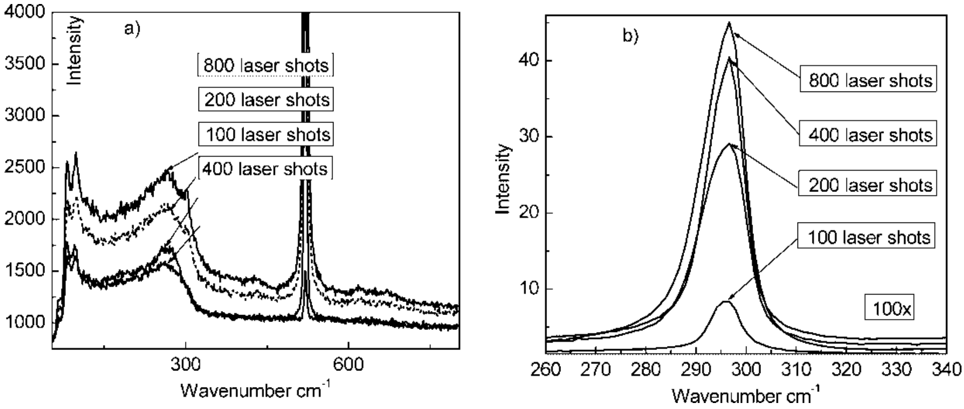

Figure 4. The Raman spectra of $SiO_2$ samples with Ge ions generated at different numbers of laser shots; 4a) – spectra for samples as-deposited/implanted (before annealing); 4b) – spectra for annealed (at temperature 600°) samples.

cooperation (Figure 4b). The obtained Raman spectra clearly display the band at 300 cm$^{-1}$ that come from scattering of Ge nanocrystallites on the $SiO_2$ sample formed in the process of ion deposition/implantation and subsequent annealing. The full width at half maximum (FWHM) of Raman lines estimated for Ge crystalline structures of investigated samples were 7.1–10.6 cm$^{-1}$.

## 4. Investigation of laser-induced deposition of layers of semiconductor materials using complex targets

The set-up described in the Section 2 has been used for investigation of laser-induced deposition of thin layer of semiconductor materials. The experiment has been carried out in collaboration with METU. The experimental conditions ware as follows: laser energy – 550 mJ, laser spot diameter – 4 mm, laser intensity – up to $\sim 10^{10}$ $1.5 \times 10^9$ W/cm$^2$, (laser fluence – 4.5 J/cm$^2$) laser irradiated targets – Ge and complex targets Si (70%) + $Al_2O_3$ (30%) or Si(50%) + $Al_2O_3$ (50%), deposited substrates – 20-nm $SiO_2$ layers (mostly ‘n’) located at distance of 6 cm at angles of 0°, 30° and 40°. In the case of complex targets, the laser spots covers 70% (or 50%) of Si slab and 30% (or 50%) of $Al_2O_3$ slab mounted closely. The laser beam irradiated the target at an angle of 30° with

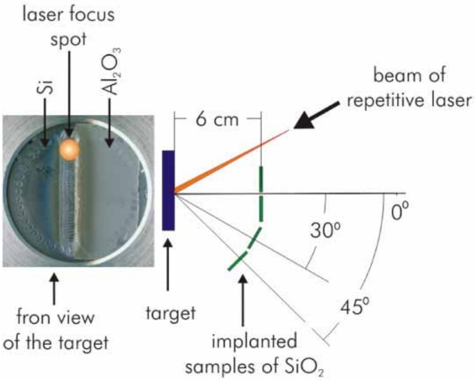

Figure 5. The geometry of laser-induced deposition of semiconductor materials.

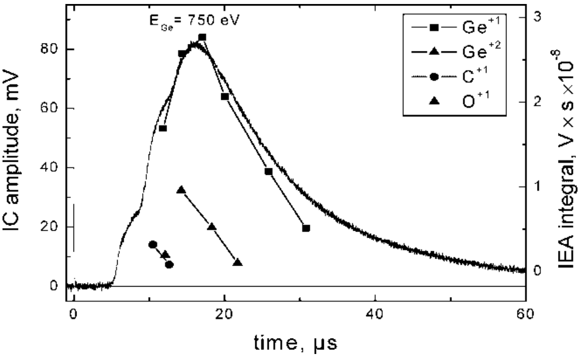

Figure 6. An example of the IC signal of slow Ge ions emitted from laser-produced plasma. The distributions of particular ions calculated on the basis of the IEA spectra. $E_L = 540\,\mathrm{mJ}$, $d = 3\,\mathrm{mm}$, $I = 2.5 \times 10^9\,\mathrm{W/cm^2}$.

respect to the target normal. The target material was evaporated with the use of different number of shots. The geometry of the experiment is shown in Figure 5.

The properties of the ion stream generated by laser were estimated with the use of ion collector. An example of the ion collector signal of ions emitted from the Ge target is presented in Figure 6. The distributions of different ion species were estimated on the basis of spectra recorded by an ion energy analyzer obtained at different deflecting voltages.

The deposited samples as-grown and annealed were characterised in METU. For instance, the sample B10 produced by deposition of laser ablated Si (30%) and $Al_2O_3$ (70%) onto Si substrate was analysed using XPS method both before and after heat treatment (annealed at 1000 °C for 1 h under $N_2$ atmosphere), as shown, in Figure 7.

Spectra were measured after successive $Ar^+$ sputtering to clean the surface contamination. However, C contamination was calculated as high as 50% in atomic concentration. For exact analysis of the characteristics the total areas will be normalised.

The Si has five ionisation states $Si^0$, $Si^{1+}$, $Si^{2+}$, $Si^{3+}$ and $Si^{4+}$, which are representing, Si-Si, Si-$Si_2O$, Si-SiO, Si-$Si_2O_3$ and Si-$SiO_2$, respectively. While, as-grown sample has peaks resulted from both $SiO_x$, where $x < 2$ and $SiO_2$, annealed sample has $SiO_x$ and Si-Si peaks. The existence of Si-Si peaks indicates the formation of Si nanocrystals (Figure 8).

The PL analysis of B10 sample (and similar B13 and B14 samples) has been also performed in METU. The weak PL peak seen at 570 nm is probably related to F centres (see Figure 9).

The S70, S73 and S74 samples produced by deposition of laser-ablated Ge and $SiO_2$ on 22 nm $SiO_2$ placed onto Si substrate are currently investigated in METU with the use of the Raman

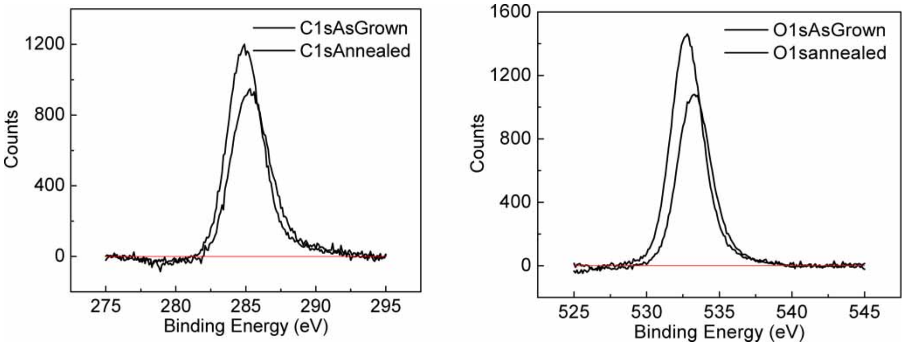

Figure 7. The XPS not normalised characteristics of the sample B10 annealed at 1000 °C for 1 h under $N_2$ atmosphere. Both as-grown and annealed samples were analysed.

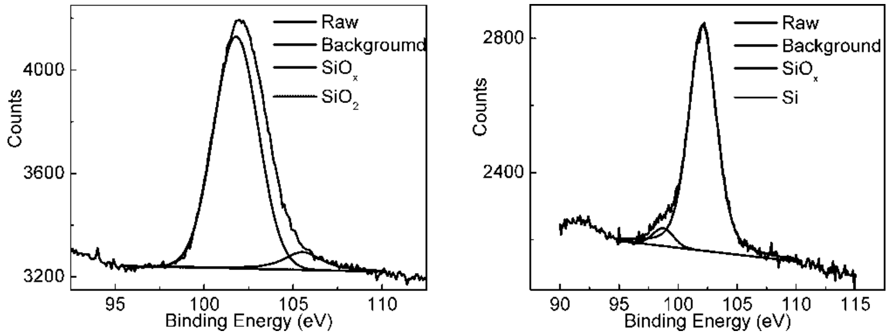

Figure 8. The XPS signals of Si 2p for both as-grown (left) and annealed (right) samples.

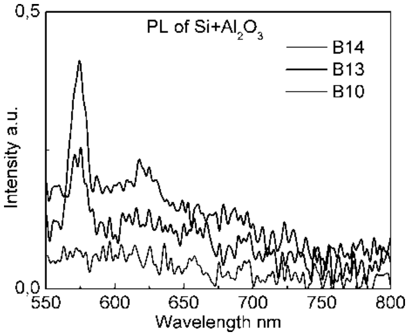

Figure 9. The PL spectra of samples B10, B13 and B14 produced by deposition of laser ablated Si and $Al_2O_3$ onto Si substrates.

analysis. The Raman spectrum of as-grown S73 sample shows the amorphous Ge peak. The Raman spectra for annealed samples, which could show the nanocrystallinity will be analysed.

## 5. Summary

The experimental arrangement with a new repetitive Nd:glass laser system has been used in IPPLM for investigations of implantation of laser-produced Ge and Si into the semiconductor materials. The measurements were performed mostly at laser intensity of $2.5 \times 10^9\,W/cm^2$. The Ge ion stream attained maximum energy of ~3 keV and maximum total intensity (ion fluence) of $\sim 5 \times 10^{16}\,ions/cm^2$ on the $SiO_2$ substrate.

The depth profiles of different elements in the $SiO_2$ layer of samples deposited/implanted in the IPPLM experiment were estimated on the basis of XPS + AES spectra. In the layer of <4 nm the amount of deposited laser-produced Ge atoms is very high, in depth of ~2.5 nm more than 50% Ge atoms was estimated. Taking into consideration the dependence of the FWHM of the Raman peak on the nanocrystalite size the dimensions of investigated Ge nanocrystals was roughly estimated as 5–10 nm.

The experimental arrangement used for laser-induced ion implantation has been applied for formation of thin semiconductor layers by laser-induced material deposition. The Ge and $Si + Al_2O_3$ targets were irradiated by laser pulses and etched material has been deposited on the surface of 20-nm layer of $SiO_2$. The modified substrates were investigated in with the use of XPS and PL methons. The existence of Si-Si in the XPS signals of Si 2p peaks indicates the formation of Si nanocrystals. These properties of implanted substrates will studied with other diagnostic methods.

## Acknowledgements

This work has been supported by the European Commission within the 6FP STRAP project 'SEMINANO' under the contract NMP4-CT-2004-505285.

## References

(1) Townsend, D.; Kelly, J.C.; Hartley, N.E.W. *Ion Implantation, Sputtering and their Applications;* Academic Press: London, New York, San Francisco, 1996; p. 289.

(2) Boody, F.P. et al. *Laser Part. Beams* **1996,** *14,* 443.

(3) Láska, L.; Juha, L.; Krása, J.; Mašek, K.; Pfeifer, M.; Rohlena, K.; Králiková, B.; Skála, B.; Peřina, V.; Hnatowicz, V. et al. *Czech. J. Phys*. **2000,** *50,* 81–90.

(4) Wołowski, J.; Badziak, J; Boody, F.P.; Gammino, S.; Hora, H.; Jungwirth, K.; Krása, J.; Láska, L.; Parys, P.; Pfeifer, M. et al. *Plasma Phys. Control. Fusion* **2003,** *45,* 1087–1093.

(5) Wu, X.L.; Gao, T.; Bao, X.M.; Yan, F.; Jiang, S.S.; Feng, D. *J. Appl. Phys.* **1997,** *82,* 2704.

(6) Masuda, K.; Yamamoto, M.; Kanaya, M.; Kanemitsu, Y. *J. Non-Cryst. Solids* **2002,** *299–300,* 1079–1083.

(7) Rosiński, M.; Badziak, J.; Boody, F.P.; Gammino, S.; Hora, H.; Krása, J.; Láska, L.; Mezzasalma, A.M.; Parys, P.; Rohlena, R. et al. *Vacuum* **2005,** *78,* 435–438.

(8) Woryna, E.; Parys, P.; Wołowski, J.; Mróz, W. *Laser Part. Beams* **1996,** *14,* 293–321.

(9) Wołowski, J.; Badziak, J.; Boody, F.P.; Gammino, S.; Hora, H.; Jungwirth, K.; Krása, J.; Láska, L. Parys, P.; Pfeifer, M. et al. *Plasma Phys. Control. Fusion* **2003,** *45,* 1087–1093.