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Formation of Pores in Ge Single Crystal by Laser Radiation

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It was found an increase of a surface recombination velocity (s) on a surface of Ge single crystal under irradiation by YAG:Nd laser. The increase of the s is explained by generation of pores, whose dimensions decrease with the number of laser pulses. This process is explained by uneven light pressure of the running laser modes on the irradiated surface close to a melting temperature.

Keywords: surface recombination velocity, Ge single crystal, YAG:Nd laser, light pressure.

INTRODUCTION

In recent years significant effort has been focused on the formation and characterization of porous silicon nanostructures. An implementation of microelectronics technology is a great perspective for the development of creation of light emitting devices and their integration in microelectronic platform. The main methods of the creation of this structure are anodical etching of a silicon wafer in HF solutions [1], deposition of nanocluster Si-based films by magnetron sputtering [2], laser induced decomposition of silane [3], pulsed laser ablation [4 – 8] etc. The "dry" fabrication methods of porous structure are more convenient for creating optoelectronic devices due to their good compatibility with silicon processing technology. Using laser irradiation to produce local area directly on a silicon based device is important task for microelectronics. For describing of the laser radiation interaction with semiconductors a thermal model is used [9]. According to this model the light energy absorbed by a semiconductor is transformed into thermal energy. The thermal effect of laser radiation may result in different and even controversial phenomena. For example, depending on parameters of laser radiation and semiconductor, the following effects can be encountered: defect annealing after ion implantation [10] or transformation of non-radiation defects into radiation defects on a semiconductor surface in CdS [11] and ZnSe [12] or generation of additional defects on a semiconductor surface of Si [13], InSb [14], CdTe [15]. For direct detection of defect generation threshold in InSb and CdTe the Welker effect is often used. It is the effect of the redistribution and generation of the nonequilibrium charge curriers in a limited homogeneous semiconductor in crossed electric E_x and magnetic B_z fields [16]. This effect has advantages compared to other methods of surface state diagnostics such as AFM and SEM. The Welker effect shows changes in semiconductor surface parameters, such as surface recombination velocity.

Usually *s* decreases under exposure to laser radiation in InSb [13] and CdTe [14] due to generation of potential barrier on the irradiated surface.

In the present study a reverse effect is observed in Ge: irradiation of Ge single crystal by a YAG:Nd laser with above threshold intensities causes increase of *s* from pulse to pulse. The aim of this study is to define mechanism of *s* increase during YAG:Nd laser irradiation.

EXPERIMENTAL

Samples under investigation were *i*-type Ge single crystals with dimensions 0.5×0.5×2.0 cm^3. Preliminary the samples were etched in CP-4A solution [17]. After etching, the samples were stored in air more than 24 hours. Under such treatment a thin layer 2 – 3 nm of GeO_2 hexagonal structure is formed on Ge surface [18]. Later these surfaces with plain {111} and {110} were exposed to laser radiation. The irradiation of the oxidized Ge surface was produced by using the first harmonics of a pulsed YAG:Nd laser (wavelength $\lambda = 1.06$ μm; pulse duration $\tau = 15$ ns).

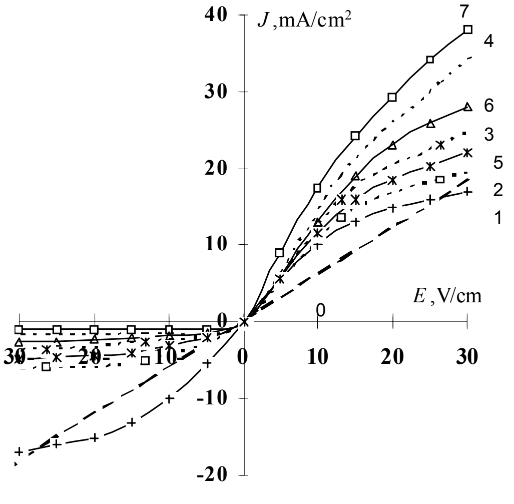

Fig. 1. I – V characteristic for Ge samples in magnetic field $B_z = 0.3$ T. Experimental (curves 1 – 4) and theoretical ($5 – S_+ = 0.5$; $S_- = 20$; $6 – S_+ = 0.5$; $S_- = 30$; $7 – S_+ = 0.5$; $S_- = 50$). The curve (0) is obtained with $B_z = 0$ T. $S_\pm = \frac{s_\pm d}{D}$, where D is the diffusion coefficient, d is the size of a sample in the direction of Lorentz force [12]

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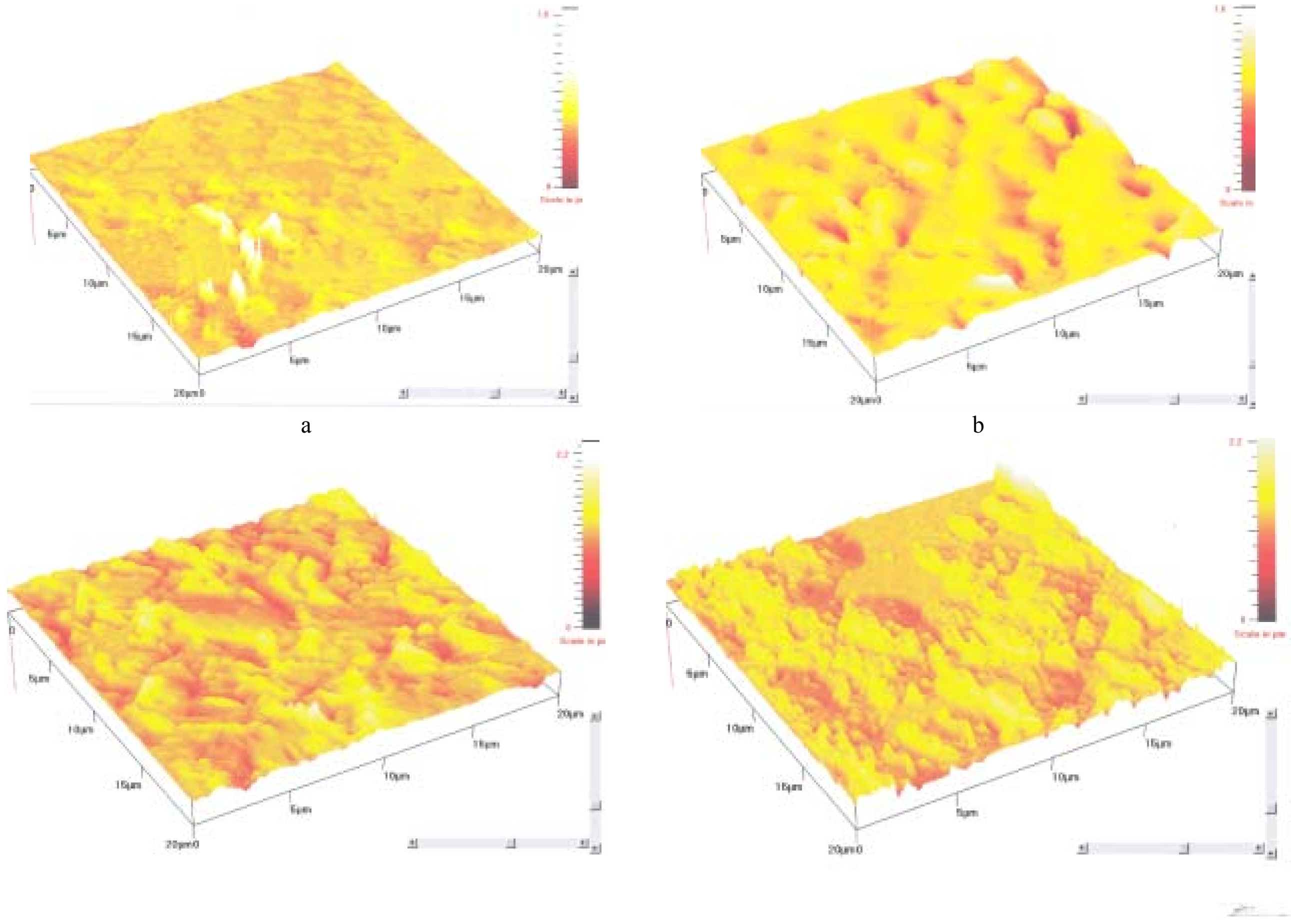


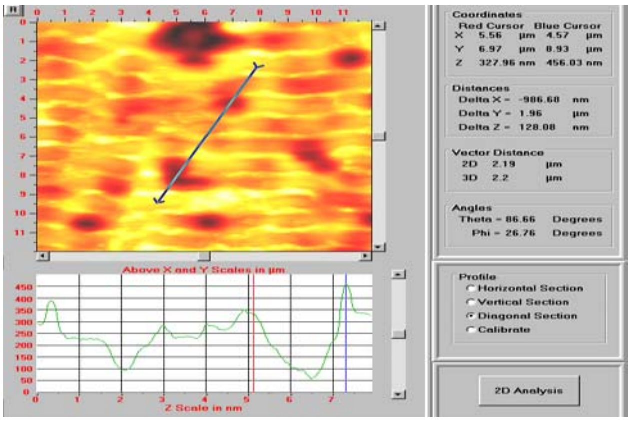
a

b

c

d

Fig. 2. The surface topography image of an oxidized Ge surface: a – virgin, and irradiated by YAG:Nd laser with $I = 30$ MW/cm^2: b – 1 pulse; c – 5 pulses; d – 10 pulses



Coordinates
Red Cursor Blue Cursor
X 5.56 µm 4.57 µm
Y 6.97 µm 8.93 µm
Z 327.96 nm 456.03 nm

Distances
Delta X = -986.68 nm
Delta Y = 1.96 µm
Delta Z = 128.08 nm

Vector Distance
2D 2.19 µm
3D 2.2 µm

Angles
Theta = 86.66 Degrees
Phi = 26.76 Degrees

Profile
○ Horizontal Section
○ Vertical Section
● Diagonal Section
○ Calibrate

Fig. 3. Cross section of Ge sample irradiated by 10 pulses of YAG:Nd laser at 25 MW/cm^2

Samples' surfaces were irradiated by different number of pulses with an threshold intensity $I_{th} = 30$ MW/cm^2 reaching increase of s.

Irradiation was carried out pulse by pulse. The first sample was irradiated with one pulse, the second – with 5 pulses and the third with 10 pulses. The fourth sample was not irradiated at all.

Measurement of the surface topography was carried out with an Atomic Force Microscope (AFM) (QScope-250, Quesant Instrument Corp.) in the contact mode in air. The levers used had elasticity constants varying between 0.01 and 0.2 N/m and provided a non-destructive mode of investigation of Ge surface.

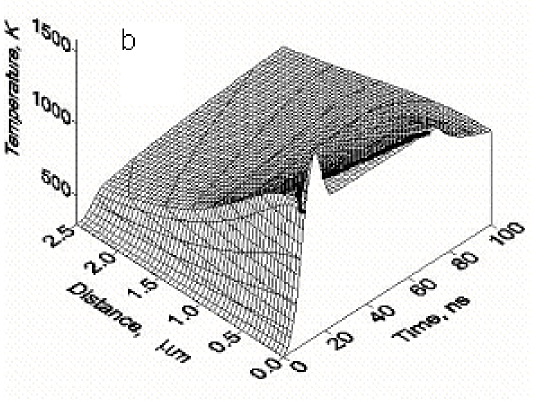
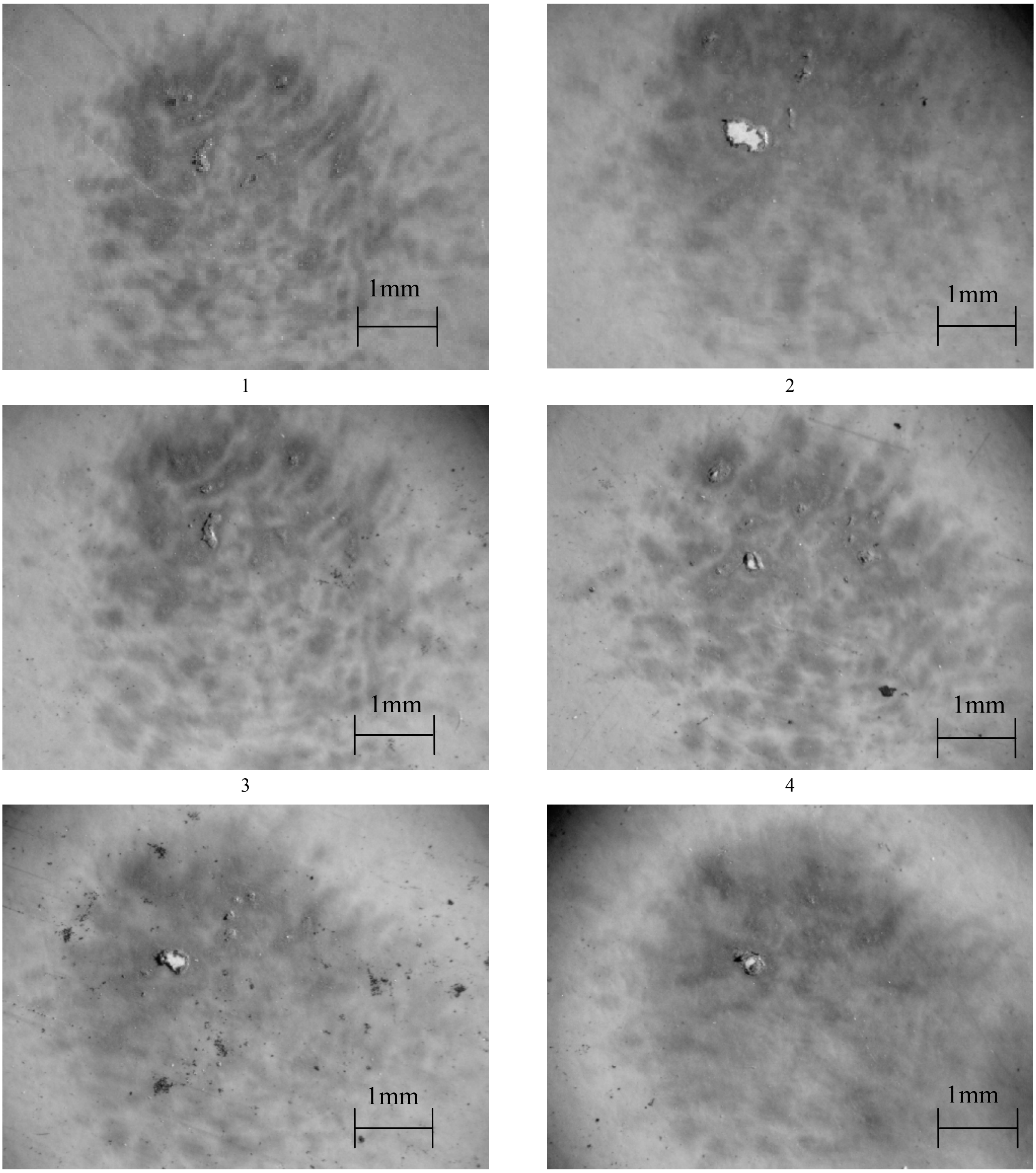


Fig. 4. Calculated time dependent distribution of temperature in the bulk of Ge single crystal at intensity of YAG:Nd laser 30 MW/cm^2

For in-situ measurement of s the current density-electric field intensity (J-E) characteristics were recorded in magnetic field $B_z = 0.3$ T perpendicular to the electric field E_x.



1 2 3 4 5 6

Fig. 5. Tracks of 6 pulses on the photo-sensitive paper

RESULTS AND DISCUSSION

J-E characteristic of the sample 4 in the crossed magnetic and electric fields is shown in Fig. 1, curve 1. The symmetrical shape of this *J-E* characteristic means that s is minimum. Comparing the experimental *J-E* characteristics with the theoretical ones from [12], the minimum value of s is estimated to be equal to $s \approx 100$ cm/s.

The irradiation of the Ge semiconductor surface with pulses of intensity equal to $I \approx 30\ \mathrm{MW/cm^2}$ changes the previous *J-E* characteristic measured in the crossed magnetic and electric fields, into a diode type (Fig. 1, curves 2 – 4). Usually, these changes indicate the increase of $\boldsymbol{s}$ on irradiated surfaces of semiconductor.

From *J-E* characteristics it is seen that rectification coefficient increases with the increase in number of pulses ($K_1 = 1 < K_2 < K_3 < K_4$), where K_1, K_2, K_3, K_4 are the *J-E* rectification factor of the curves 1 – 4 for $E_x = \pm 20$ V/cm. 3D images of a sample surfaces obtained by AFM are shown on Fig. 2 (a – d). From figures 2 b, 2 c and 2 d it is seen that an increase of the pulse number causes a decrease of the surface grain dimensions. It means the increasing of ***s*** is determined by increasing of geometrical area of a surface.

If we assume that laser radiation doesn't induce chemical processes on the irradiated surfaces and laser generated defects are not charged (e.g. S_{min} is not changed) then increase of rectification coefficient of the *J-E* characteristics (Fig. 1) and decrease of pores size (Fig. 2 b, c, d) with the growth of number of laser pulses may be explained by increase of geometrical area of the irradiated surfaces.

The evaluation of changes in geometrical area of the irradiated surface (under 10 pulses, curve 4) using *J-E* characteristics according to [12] formula $S_{eff} = GS_{min}$, (where G is the geometrical factor, which shows how many times geometrical surface has increased compared to a flat surface, S_{eff} is an effective surface recombination velocity obtained from the experiment (Fig. 1), and S_{min} is a velocity of recombination on the non-irradiated surface) gives an enhancement coefficient equal 100.

The study of the irradiated surface shows that in our conditions an accumulation effect takes place: e.g. with the increase of pulse number, ***s*** increases (Fig. 2 b, c, d) but typical grain dimension decreases from 5 μm (at 1 pulse) to 1 μm (at 10 pulses).

Investigation of a surface profile (Fig. 3) shows presence of a middle line of an initial flat surface, e.g. a volume of the light-extruded material is equal to a volume of the material bumps. It indicates that, close to the melting temperature, the surface geometry is changed by uneven light pressure of the laser beam modes on the irradiated surface (Fig. 4). An evidence of this effect, i.e. the running laser modes can be found on Fig. 5, where arrow of pulse by pulse tracks of a laser beam on a light sensitive paper is shown. It is seen that the intensity distribution of the laser beam is not homogeneous and is not repeated. It means that the laser modes are distributed chaotically and change the position pulse by pulse.

CONCLUSIONS

1. Possibility of creation of a porous structure on the surface of Ge single crystal is shown.
2. Increase of a surface recombination velocity in crystalline Ge under irradiation with YAG: Nd laser is explained by an increase of the geometric area of the crystal surface due to formation of pores.
3. Evaluation shows a hundredfold enhancement of the geometric area of the surface of a sample irradiated with YAG: Nd laser with intensity 30 MW/cm^2.
4. Pores formation on the surface of Ge single crystal is explained by running laser modes on the irradiated surface close to a melting temperature.

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