

# DYNAMICS OF LASER-INDUCED MELTING AND MODIFICATION OF THE SURFACE OF SEMICONDUCTORS BY NANOSECOND LASER PULSES

Volodymyr Gnatyuk, Toru Aoki, Oleksandr Vlasenko, Olena Gorodnychenko

## Abstract:

*In situ detection and dynamics of laser-induced melting in different semiconductor crystals (CdTe, CdHgTe, GaAs, InSb and SiC) were performed by the time-resolved reflectivity (TRR). The samples were subjected to irradiation with 20 ns pulses of KrF excimer or ruby laser with energy density varied in a wide range. The surface morphology of the crystals was monitored using optical microscopy and time dependences of the temperature of the crystal surface as a function of laser pulse energy density was also calculated. The melting and ablation threshold values were determined and specific features of the laser-induced phase transitions in the surface region of the semiconductors were analyzed.*

**Keywords:** semiconductors, laser irradiation, time-resolved reflectivity, melting threshold.

## 1. Introduction

Laser techniques have been advantageously used to monitor different processes in semiconductors and to modify their properties, including the following procedures: surface cleaning, recrystallization and surface region reconstruction, local annealing and doping, formation of interfaces, etc. [1]-[7]. However, some problems on interaction of short laser pulses with semiconductors are still open. It is particularly concerned with the dynamics of laser-induced melting and determination of the threshold values of energy density at which phase and threshold processes start in the surface region of crystals.

In order to identify the laser-induced melting threshold of different semiconductors and study the dynamics of laser-induced phase transitions in the surface region of crystals subjected to action of nanosecond pulses of KrF excimer or ruby lasers, we used the time-resolved reflectivity (TRR) technique. This method consists in direct detection and in situ observation of the time evolution of optical reflectivity of the surface region of a crystal illuminated with a CW probe laser beam under irradiation with a nanosecond laser pulse [7]-[14]. In addition, the morphology of crystals was monitored and time dependences of the surface temperature of crystals were calculated at different laser pulse energy densities.

The data on the threshold values of energy density of nanosecond laser pulses have principal importance in application of laser procedures in semiconductor surface processing.

## 2. Experiment

### 2.1. Experimental procedures and measurement details

The subjects for investigation were the semiconductors which have been widely used as materials for radiation sensors: CdTe, CdHgTe, InSb, GaAs and SiC. The samples were grown by different methods and were subjected to various preliminary surface treatments [4]-[9].

The pulsed radiation source was KrF excimer ( $\lambda = 248$  nm) or a ruby ( $\lambda = 694$  nm) laser. Single pulses of 20 ns duration (FWHM) were used. The energy density  $J$  of incident laser pulses was varied in a wide range.

The in situ detection and dynamics of phase transitions in the surface region of the semiconductors were monitored by the TRR technique using a CW red ( $\lambda = 633$  nm) or green ( $\lambda = 532$  nm) laser as a probe beam.

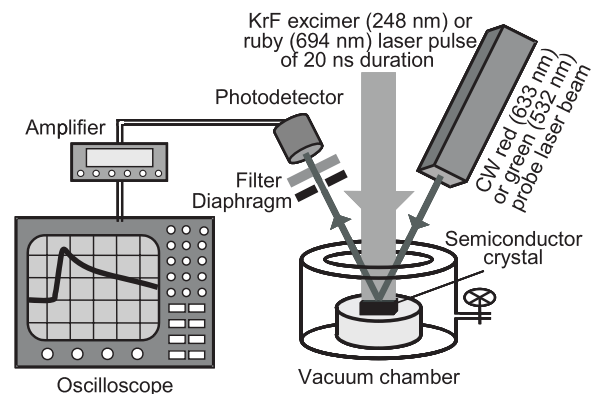


Fig. 1. Diagram of the experimental setup of the time-resolved reflectivity measurements.

The TRR experimental setup is shown in Fig. 1. The reflected probe laser beam was detected by a high-speed photodetector and after amplifying the signal was traced by a storage oscilloscope.

## 3. Results and discussion

### 3.1. TRR measurements

As seen from the oscillograms showing the dynamics of the reflection coefficient  $R$  of a red probe laser beam from the CdTe crystal surface under irradiation with KrF excimer laser pulses of different energy densities (Fig. 2, curves 1-3), irradiation with  $J \geq J_m \sim 50$  mJ/cm<sup>2</sup> results in an increase in  $R$  with following decaying with time. The maximum of  $R(t)$  is independent of energy density that is evidence of formation of a laser-melted surface layer with higher reflectivity. The contribution of the long-time component to the total relaxation of  $R(t)$  increases with

rising  $J$  (Fig. 2, curves 1-3). This can be attributed to melting and following crystallization of a deeper surface layer when laser pulse energy density increases.

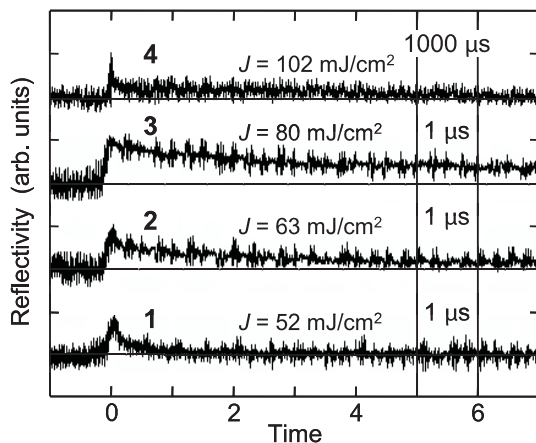


Fig. 2. Dynamics of the reflectivity of the CdTe crystal surface illuminated with a red probe laser beam under irradiation with KrF excimer laser pulses of different energy densities  $J$ .

The relaxation of  $R(t)$  occurs during the time much longer than laser pulse action time (Fig. 2, curves 2-4). This is associated to deterioration of the crystallinity, amorphization and following crystallization of the surface layer [14]. The irradiation of CdTe surface causes an increase in the steady-state reflection coefficient and this is a reason that  $R(t)$  does not decay to the initial value  $R_0$  (Fig. 2, curve 4).

One of difficulties in the TRR measurements was that the absorption depth of a red probe beam was  $\sim 1.6 \mu\text{m}$  however the absorption depth of KrF excimer laser radiation was very shallow ( $\sim 10 \text{ nm}$ ) and hence the melted surface layer was very thin. It was reasonable to use a probe laser with a shorter wavelength.

Fig. 3 shows the dynamics of TRR of CdTe crystals under irradiation with a KrF laser pulse using a CW green probe laser. The changes in  $R$  were about 6-7% in comparison with 3-4% as in the case of a red probe laser. There was no any change in the reflectivity at  $J < J_m$  (curve 1) and a sharp increase in  $R(t)$  under pulsed laser irradiation with  $J > J_m$  indicated melting of a thin surface layer (curves 2-4).

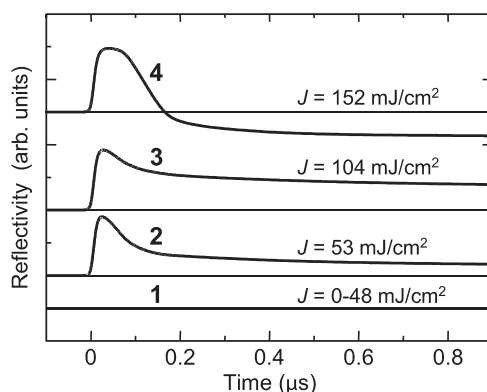


Fig. 3. Dynamics of the reflectivity of the CdTe crystal surface illuminated with a green probe laser beam under irradiation with KrF excimer laser pulses of different energy densities  $J$ .

Pulsed laser processing of CdTe crystals with  $J = J_m$  resulted in improvement of surface smoothness [8]. Irradiation of CdTe crystals with KrF laser pulses  $J > J_a \sim 150 \text{ mJ/cm}^2$  modified the dynamics of TRR. The reflection coefficient  $R(t)$  increases and falls to a value lower than initial one (Fig. 3, curve 4). This is due to an increase in roughness of the surface because of boiling, evaporation and ablation of an overheated surface layer and following solidification. Thus, the value  $J_m \approx 50 \text{ mJ/cm}^2$  and  $J_a \approx 150 \text{ mJ/cm}^2$  can be considered as the melting and ablation thresholds, respectively.

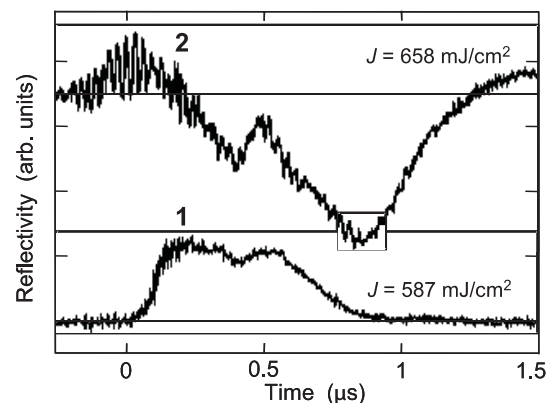


Fig. 4. Dynamics of the reflectivity of the SiC crystal surface illuminated with a green probe laser beam under irradiation with KrF excimer laser pulses of energy densities  $J$  higher than the melting (curve 1) and ablation (curve 2) threshold.

The dynamics of the reflectivity of SiC crystals irradiated with KrF laser pulses of energy densities  $J > J_m$  and  $J > J_a$  is shown in Fig. 4. A jump in  $R(t)$  is due to the beginning of melting of the surface, however the decrease and following increase in  $R$  up to the second maximum (curve 1) is associated with the interference of the probe beam reflected from the surface and from the moving solid-liquid interface [14]. Curve 2 in Fig. 4 has the similar shape as curve 4 in Fig. 3. Decrease in  $R(t)$  with time is associated with ablation of the SiC surface under laser irradiation with  $J > J_a$ .

The TRR measurements were performed for CdTe, CdHgTe, GaAs, InSb and SiC semiconductors and a ruby laser as a pulsed laser source was also used. The following values of the melting  $J_m$  and ablation  $J_a$  thresholds have been obtained:

- for CdTe and  $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$  with  $x = 0.3-1$ ,  $J_m \approx 50 \text{ mJ/cm}^2$ ,  $J_a \approx 150 \text{ mJ/cm}^2$  (KrF excimer laser pulse) and  $J_m \approx 100 \text{ mJ/cm}^2$  (ruby laser pulse). In the case of the solid solutions the melting thresholds vary by 10-20% depending on  $x$ ;
- for SiC  $J_m \approx 580 \text{ mJ/cm}^2$ ,  $J_a \approx 650 \text{ mJ/cm}^2$  (KrF excimer laser pulse);
- for InSb  $J_m \approx 100 \text{ mJ/cm}^2$  (KrF excimer laser pulse),  $J_m \approx 140 \text{ mJ/cm}^2$  (ruby laser pulse);
- for GaAs  $J_m \approx 400 \text{ mJ/cm}^2$  (ruby laser pulse).

### 3.2. Surface morphology study

The surface morphology of semiconductor crystals was monitored by optical and atomic force microscopy [5, 8, 14]. Figs. 5 and 6 show the micrographs of the surface of

$\text{Cd}_x\text{Hg}_{1-x}\text{Te}$  ( $x \sim 0.3$ ) and InSb crystals respectively, irradiated with ruby laser pulses of different energy densities. Irradiation of samples with  $J > J_m$  resulted in melting of a thin surface layer, followed by crystallization. The recrystallized material was in the form of local islands filling the whole area of the laser interaction zone when the energy density was increased Figs. 5(b, c) and 6(b, c).

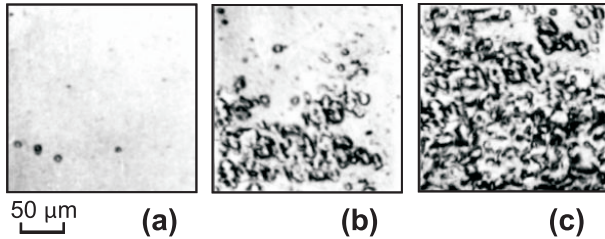


Fig. 5. Micrographs of the surface of  $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$  ( $x \sim 0.3$ ) crystals before (a) and after irradiation with ruby laser pulses of energy density  $J = 160 \text{ mJ/cm}^2$  (b) and  $J = 180 \text{ mJ/cm}^2$  (c).

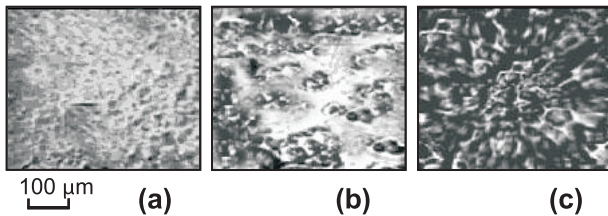


Fig. 6. Micrographs of the surface of InSb crystals before (a) and after irradiation with ruby laser pulses of energy density  $J = 150 \text{ mJ/cm}^2$  (b) and  $J = 160 \text{ mJ/cm}^2$  (c).

The melting thresholds determined from the surface morphology investigations were a little higher than the values obtained from the TRR measurements. However, laser-induced changes in the dynamics of TRR of semiconductors irradiated with nanosecond laser pulses with  $J > J_m$  corresponded to the modifications of the morphology and structure of the surface region of the irradiated crystals [4], [5], [8].

### 3.3. Calculations of temperature

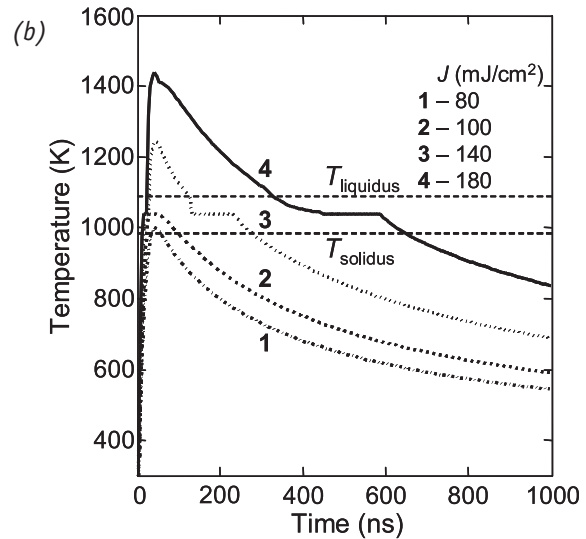
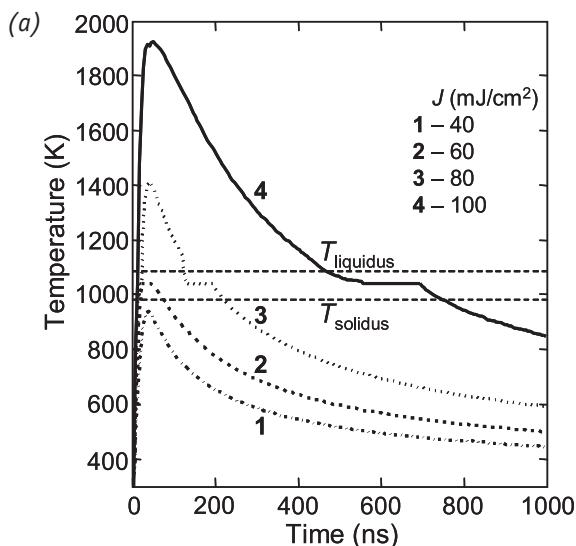


Fig. 7. Time dependences of the temperature of the surface of the  $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$  ( $x \sim 0.3$ ) crystal under irradiation with KrF excimer (a) and ruby (b) laser pulses with different energy densities.

The TRR experimental data were in good agreement with the calculations of the temperature of the semiconductors subjected to pulsed laser irradiation. The simulation was made by solving the time-dependent heat flow equation [9]. As an example, the time distributions of the surface temperature in  $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$  crystals under irradiation with KrF excimer (a) and ruby (b) laser pulses are shown in Fig. 7. Curves 2 correspond to the energy densities of KrF excimer (a) and ruby (b) laser pulses when the melting of a surface layer of is attained.

## 4. Conclusion

The TRR is an effective technique to determine the threshold energy densities during laser processing of semiconductors and for in situ study of the dynamics of phase transitions in the surface region of semiconductors subjected to nanosecond laser irradiation.

## AUTHORS

**Volodymyr Gnatyuk\*** - V.E. Lashkaryov Institute of Semiconductor Physics of National Academy of Sciences of Ukraine, Prosekt Nauky 41, Kyiv 03028, Ukraine, and Research Institute of Electronics, Shizuoka University, 3-5-1 Johoku, Naka-ku, Hamamatsu 432-8011, Japan. E-mail: gnatyuk@lycos.com.

**Toru Aoki** - Research Institute of Electronics, Shizuoka University, 3-5-1 Johoku, Naka-ku, Hamamatsu 432-8011, Japan. E-mail: rtaoki@ipc.shizuoka.ac.jp.

**Oleksandr Vlasenko** - V.E. Lashkaryov Institute of Semiconductor Physics of National Academy of Sciences of Ukraine, Prosekt Nauky 41, Kyiv 03028, Ukraine. E-mail: o\_vlas@isp.kiev.ua.

**Olena Gorodnychenko** - Taras Shevchenko Kyiv National University, 64 Volodymyrska Str., Kyiv 01033, Ukraine. E-mail: semicondalf2002@rambler.ru.

\* Corresponding author

## References

- [1] Perriere J., Millon E., Fogarassy E., *Recent advantages in laser processing of materials*, Elsevier: Amsterdam, 2006, p. 472.
- [2] Berchenko N.N., Yakovyna V.S., Nikiforov Y.N., Izhnin I.I., Kurbanov K.R., "Laser-induced shock waves processing of IIVI solid solutions interface", *J. Alloys Compd.*, vol. 371, no. 1-2, 2004, pp. 86-88.
- [3] Medvid' A., Fedorenko L., Korbutjak B., Kryluk S., Yusupov M., Mychko A., "Formation of graded band-gap in CdZnTe by YAG:Nd laser radiation", *Radiat. Meas.*, vol. 42, no. 4-5, 2007, pp. 701-703.
- [4] Gnatyuk V.A., Aoki T., Hatanaka Y., Vlasenko O.I., Mozol' P.O., "Application of pulsed laser irradiation in the semiconductor sensor fabrication", *Proceed. 4th Inter. Conf. on Global Research and Education: Inter-Academia 2005*, vol. 2, 2005, pp. 543-552.
- [5] Gnatyuk V.A., Gorodnychenko O.S., "Influence of pulsed laser radiation on the morphology and photoelectric properties of InSb crystals", *Semicond.*, vol. 37, no 4, 2003, pp. 396-398.
- [6] Gnatyuk V.A., Aoki T., Hatanaka Y., "Laser-induced shock wave stimulated doping of CdTe crystals", *Appl. Phys. Lett.*, vol. 88, 2006, pp. 242111-3.
- [7] Aoki T., Gnatyuk V.A., Nakamura A., Tomita Y., Hatanaka Y., Temmyo J., "Study of a CdTe high-energy radiation imaging device fabrication by excimer laser processing", *Phys. Stat. Sol. C*, vol. 1, no 4, 2004, pp. 1050-1053.
- [8] Gnatyuk V.A., Aoki T., Nakanishi Y., Hatanaka Y., "Surface state of CdTe crystals irradiated by KrF excimer laser pulses near the melting threshold", *Surf. Sci.*, vol. 542, 2003, pp. 142-149.
- [9] Gnatyuk V.A., Aoki T., Gorodnychenko O.S., Hatanaka Y., "Solid-liquid phase transitions in CdTe crystals under pulsed laser irradiation", *Appl. Phys. Lett.*, vol. 83, no 18, 2003, pp. 3704-3706.
- [10] Timoshenko V.Yu., Dittrich Th., Sieber I., Rappich J., Kamenev B.V., P.K. Kashkarov, "Laser-induced melting of porous silicon", *Phys. Stat. Sol. A*, vol. 182, no 1, 2000, pp. 325-330.
- [11] Ivlev G., Gatskevich E., Chab V., Stuchlik J., Vorticek V., Kocka J., "Dynamics of the excimer laser annealing of hydrogenated amorphous silicon thin films", *Appl. Phys. Lett.*, vol. 75, no 4, 1999, pp. 498-450.
- [12] Gatskevich E., Ivlev G., Prikryl P., Cerny R., Chab V., Cibulka O., "Pulsed laser-induced phase transformations in CdTe single crystals", *Appl. Surf. Sci.*, vol. 248, no 1-4, 2005, pp. 259-263.
- [13] Kovalev A.A., Zhvavyi S.P., Zykov G.L., "Dynamics of laser-induced phase transitions in cadmium telluride", *Semicond.*, vol. 39, no 11, 2005, pp. 1299-1303.
- [14] Baidullaeva A., Vlasenko A.I., Gatskevich E.I., Gnatyuk V.A., Ivlev G.D., Mozol' P.E. *Nanosystems, Nanomaterials, Nanotechnologies*, vol. 6, no 4, 2008, pp. 1167-1174. (in Russian)