Semiconductor Physics, Quantum Electronics & Optoelectronics. 2000. V. 3, N 1. P. 26-30.

PACS: 72.20; 72.40; 73.20; 42.62

Modification of photoelectric and electrical properties of III-V semiconductors by pulsed laser irradiation

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Abstract. The effect of nanosecond ruby laser pulses on the photoelectric and electrical properties of GaAs and InSb single crystals with different pre-treated surfaces was studied. The photoconductivity, surface recombination rate and electrical resistivity of the samples have been analysed before and after irradiation with laser pulses characterized by a wide range of energy densites. An increase in the photoconductivity and decrease in the surface recombination rate of the investigated crystals was attributed to cleaning of the crystal surface and to the laser-stimulated desorption and segregation of electrically active defects at sinks. A considerable reduction in the resistivity of GaAs and a shift of the maximum and of the red edge of the photoconductivity specrtrum of InSb crystals toward shorter wavelengths were observed after irradiation with laser pulses of energy density above the melting threshold. The reasons for the found phenomena have been determined and the mechanism of the action of laser-induced stress and shock waves on the structure and properties of the crystals has been discussed.

Keywords: gallium arsenide, indium antimonide, crystal surface, laser irradiation, photoconductivity, electrical resistivity, desorption.

Paper received 10.11.99; revised manuscript received 20.12.99; accepted for publication 04.01.00.

1. Introduction

One of the most important problems in the manufacture of modern electronic devices lies in a modification of the state and properties of the semiconductor surface, as for instance it is in removal of oxide films, stress relieving, local surface annealing, forming the surface regions enriched or depleted with majority carriers, etc. Based upon advantageous use of laser procedure to attain these ends, as applied to II-VI compounds [1-3], it is of appropriate to study the possibilities of cleaning a surface of III-V semiconductors and modifying their properties by irradiation with nanosecond laser pulses. The application of short laser pulses with light that is strongly absorbed only by thin (of the order of the laser absorption depth) surface layer has excluded the photo- and thermal influence on the bulk of crystals. This has provided means for modification of the physical properties in the surface region without significantly damaging the low-lying layers of semiconductors [4]. Laser technique has some advantages over the traditionally emploied procedures of treatment of semiconductors, as high adaptability, reproducibility, precise spatial control, variable depths and short processing times [4, 5]. In this connection, pulsed laser irradiation of III-V semiconductors could be promising, and it has been studied extensively in recent years [6-8].

The present paper reports the experimental results of irradiation of GaAs and InSb semiconductors with nanosecond ruby laser pulses. Inasmuch as the photosensitivity is the most important property of GaAs and InSb which are used as a working material of photodetectors [9], it is appropriate to study the possibilities to alter the photoelectric parameters of these semiconductors. The photoconductivity spectra, surface recombination rate and electrical resistivity have been studied in GaAs and InSb crystals with different pre-treated surfaces, which were subjected to laser irradiation with energy density below and above the melting threshold of the material. The observed laser-induced photosensitization of investigated GaAs and InSb crystals has opened up fresh potentialities of cleaning the surface, improving the photoelectric characteristics and increasing their stability.

2. Experimental details

The single crystals of GaAs(100) face and InSb(112) face were the subjects of the investigations. All crystals were grown by Czochralski method and exhibited *n*-type conductivity with effective electron density n_{GaAs} ~ 10^{17} cm^{-3} and n_{InSb} ~ 10^{14} cm^{-3}, respectively. Depending on the procedure used for preparation the samples were distinguished by structural perfection of the surface. The crystals with mechanically polished or chemically etched faces as well as with a natural shear of the surface were studied. The linear dimensions of the samples were 3×3 mm^2 and the thickness was about 1–2 mm. Reasonable ohmic electrical contacts were obtained by alloying indium on surface of the crystals. The whole area between contacts was irradiated in air at 300 K using a lens with a frosted surface for more uniform illumination of the samples. A source of single pulses of 20 ns duration was a multimode Q-switched ruby laser (λ = 0.694 µm). The energy density of laser pulses was varied by means of calibrated neutral filters in the ranges E = 0.01-1.0 J/cm^2 and E = 0.1-10 J/cm^2 for the cases of InSb and GaAs, respectively.

The resistivity of the InSb crystals was equal to 0.5 Ω·cm at 77 K and 0.03 Ω·cm at 300 K. The high-resistivity GaAs crystals were characterized by a low photosensitivity ρ_d/ρ_{ph} ~ 200. Here ρ_d and ρ_{ph} are the resistivities observed at 300 K in darkness and upon illumination with white light from an incandescent lamp (L ~ 100 lx), respectively. The photoelectric and electrical properties of GaAs and InSb crystals were investigated at 300 K and 77 K, respectively. The photoconductivity spectra were measured at a fixed modulation frequency of 400 Hz using a MDR spectrometer or an IKS-21 infrared spectrometer in the cases of GaAs and InSb samples, respectively. The nonequilibrium charge carrier lifetime was estimated from the long-time component of the photocurrent relaxation curves when the excitation was provided with YAG:Nd laser (λ = 1.06 µm) pulses of 20 ns duration in a linear regime of intensities. The surface morphology of the samples was observed using an optical microscope.

3. Experimental results

A study of the surface morphology of the samples revealed that the zone of interaction with laser pulses of the subthreshold energy densities showed no visible surface damage. Irradiation of GaAs and InSb single crystals with laser pulses in the order of increasing energy density allowed one to establish a value of the threshold energy density at which melting of the surface began that showed up in a change of the morphology. This value fell into the range E_{GaAs} = 0.4-0.6 J/cm^2 in the case of GaAs and E_{InSb} = 0.18-0.22 J cm^{-2} for InSb, depending on the state of the crystal surface after pre-treatment. Irradiation of the samples with energy density above the threshold value resulted in melting of a thin (of the order of the depth of laser radiation absorption) surface layer, followed by crystallization.

Fig. 1 shows the photoconductivity spectra of GaAs (a) and InSb (b) crystals with polished surfaces before (curve 1) and after (curves 2, 3) irradiation with laser pulses in ascending order of energy density. The spectra of the original samples (curves 1) have a typical Δ-shape, indicating enhanced surface recombination in the strong absorption region. Irradiation of GaAs samples with the subthreshold energy density did not alter their photoconductivity spectra. Increasing the energy density of the laser pulses (E > E_{GaAs}) resulted in an increase in the photoconductivity and a rise of the short-wavelength wing (Fig. 1a, curve 2). In the case of InSb crystals, it was found that even with laser pulses of an energy density below the melting threshold (up to E ~ E_{InSb}), irradiation resulted in the following changes in the photoconductivity spectra (Fig. 1b, curve 2): the photoconductivity signal increased; the short-wavelength wing rose; the maximum and the long-wavelength edge shifted toward shorter wavelengths.

Taking into account the effective coefficient α of absorption of ruby laser radiation for GaAs and InSb semiconductors [9], the absorption of radiation takes place in a thin ($1/\alpha$ < 0.1 µm) surface layer, but visible surface microdamages are not observed, thus, it is appropriate to imagine that a rise of the short-wavelength wing of the photoconductivity spectra of irradiated samples (Fig. 1a,b, curves 2) is due to a decrease in the surface recombination rate [10]. In addition, an analysis of the photoconductivity spectra of the samples with a surface treated by the various procedures (grinding, polishing, chemical etching or natural shear) allows one to determine the surface recombination rate. This parameter was estimated from the slope of curves 1–3 on the short-wavelength side from the maximum of the photoconductivity spectra by the known method [10], taking into account the wavelength dependence of the light absorption coefficient [9]. As illustrated (Table 1), the surface recombination rate of the irradiated samples was dependent on laser pulses energy density. The nonequilibrium carrier lifetime in the surface layer of the photosensitized samples was greater by 50–80% than the initial value. Storage of the

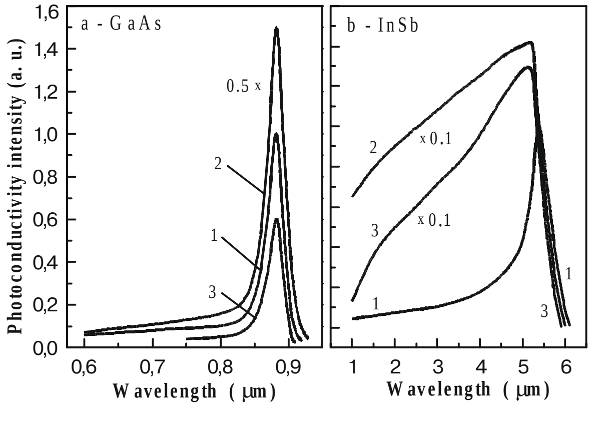

Fig.1. Photoconductivity spectra of GaAs (300 K) (a) and InSb (77 K) (b) crystals before (curves 1) and after (curves 2, 3) irradiation with laser pulses of energy density E (J/cm^2): 5.8 (curve 2), 8.0 (curve 3) (a); 0.20 (curve 2), 0.34 (curve 3) (b).

sensitized samples in natural conditions for one year showed no changes in their photoelectric characteristics: there was no degradation of the irradiated crystals.

Table 1. Surface recombination rate of nonequilibrium charge carriers (cm/s).

Type of sample	Energy density of laser pulses E, J/cm^2				
	initial	0.20	0.34	5.8	8.0
GaAs (300 K)	2.0·10^5	-	-	1.6·10^5	1.8·10^5
InSb (77 K)	8.0·10^3	4.7·10^2	7.2·10^2	-	-

The following increase in energy density of laser radiation pulses interacting with samples resulted in a decrease in the photoconductivity signal (Fig. 1a,b, curves 3) as well as an increase in the surface recombination rate (Table 1) because of very appreciable alterations in the crystals (the occurrence of microcracks) and erosion of the surface region. Fig. 1 demonstrates the results of the photoconductivity investigation of the samples with mechanically polished surfaces. The revealed laser-stimulated effects (photosensitization and a decrease in the surface recombination) were most conspicuous for such samples which were characterized by an increase in the total photosensitivity by a factor of 5–8 in the case of GaAs and 30–50 for InSb crystals. Similar changes in the profile of the photoconductivity spectra after irradiation were observed also in the cases of the samples with a surface polished by chemical-dynamic etching and for the samples with a natural shear of the surface after storage in air for one month or more. However, the initial spectra for those samples were distinguished by their short-wavelength drops, and the laser photosensitization of them was to a lesser degree than in the case of the samples with a mechanically polished surface.

It was found that the photoresistivity ρ_{ph} of GaAs crystals was not affected by irradiation with nanosecond ruby laser pulses, while the dark resistivity ρ_d began to decrease at energy density $E \geq E_{GaAs}$ (Fig. 2, curve 1). The resistivity of irradiated InSb peaked at $E \sim E_{InSb}$ then it was reduced with increasing energy density of laser pulses (Fig. 2, curve 2).

4. Discussion of results

Studies of the photoelectric properties of GaAs and InSb crystals irradiated with different numbers of nanosecond laser pulses corresponding to the fundamental absorption region, carried out in a wide range of energy densities, revealed a number of features associated with the dependence of the mechanism of the interaction with radiation on the structural perfection of the crystal surface and on the radiation energy density. The laser-stimulated photosensitization of either crystals with a disturbed surface layer or samples after storage in air was manifested in a greater extent than in the case of the crystals after chemical-dynamic polishing or etching. Thus, the following changes discussed above in the properties of GaAs and InSb crystals subjected to laser irradiation: a rise of the photosensitivity mainly in the strong absorption region of the spectrum (Fig. 1a,b curves 2), a decrease in the surface recombination rate (Table 1) and increase in the nonequilibrium carrier lifetime are in agreement with the hypothesis of the laser-stimulated cleaning of the crystal surface. The surface layer of semiconductors usually has an enhanced density of point and extended defects as well as surface oxide film [9, 11]. These defects are effective sinks for nonequilibrium charge carriers and, so, are responsible for increased recombination in the surface region of a crystal. A decrease in the surface recombination rate (Table 1) as a result of laser irradiation of the crystals could be due to the annealing of residual structural imperfections and cleaning of the surface. In the case of irradiation of the samples with a mechanically polished surface, and for etched crystals after storage in air, the removal of foreign impurities from the surface layer as well as oxide film removal took place as a result of laser desorption. A rise of the dark resistivity, which was observed in the InSb samples after irradiation with laser pulses of energy density $E \leq E_{InSb}$ (Fig. 2, curve 2) was an additional evidence of a decrease in the total concentration of electrically active point defects which had formed shallow donor levels in a bandgap of the semiconductor [9]. The second reason for an increase in the electrical resistivity of the irradiated InSb crystals can be associated with the laser-induced formation of point defects acting as acceptors, which are able to compensate the donor centres. But in this case the photoconductivity should fall, in contrast, one observes an increase in the photosensitivity (Fig. 1b, curve 2). Therefore, the first reason (a reduction in the concentration of point defects) is more suitable to explain the peak in the laser energy density dependence of the electrical resistivity (Fig. 2,

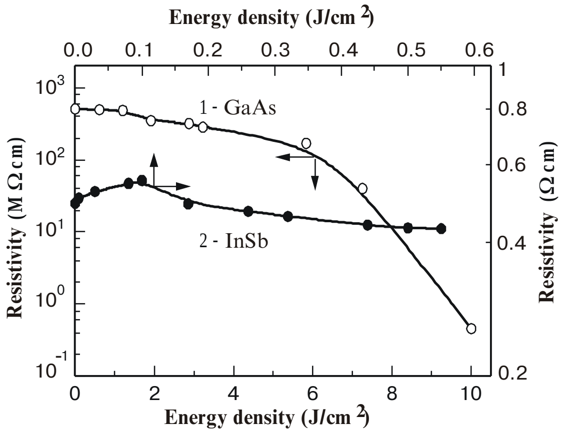

Fig. 2. Dependences of the dark resistivity of GaAs (300 K) (curve 1) and InSb (77 K) (curve 2) crystals on energy density of laser pulses.

cuve 2) at E when the highest photosensitivity of the samples by laser irradiation was achieved.

In the case of GaAs, irradiation of the crystals with laser pulses of energy densities $E \geq E_{\mathrm{GaAs}}$ resulted in melting the damaged surface layer and improved the stoichiometric homogeneity of the surface region during following crystallization. The laser-induced recrystalization of the surface layer of GaAs crystal followed the epitaxial mechanism [12] that improved the structural perfection of this layer, increased the photoconductivity (Fig. 1a, curve 2) and decreased the surface recombination rate (Table 1). The fact that the photoresistivity of the GaAs did not depend from laser irradiation was evidence of conservation in the occupancy of the recombination centers [9]. A considerable reduction in the dark resistivity of GaAs crystals after laser irradiation with $E >> E_{\mathrm{GaAs}}$ (Fig. 2, curve 1) could be caused by the formation of a thin surface film of a component of the compound (probably Ga film) [13].

A considerable rise of the total photoconductivity signal in particular at the maximum of the photoconductivity spectrum (Fig. 1a,b, curves 2) as well as the observed short-wavelength shift of the red edge of the spectrum (Fig. 1b, curves 2, 3) were evidence of a laser-stimulated modification of the defect structure in the bulk of the irradiated samples [1-3]. Because the maximum and the long-wavelength edge of the photoconductivity spectrum were formed in a relatively thick (~ 1-2 μm), layer and the absorption of laser radiation took place in a thin (< 0.1 μm) surface layer [9], therefore one could hardly expect the photo- or thermal influence on low-lying layers of the crystals during laser action, in particular, taking into account the short duration (20 ns) of laser pulses [3]. The most probable mechanism of laser activation of a material in layers of thickness considerably greater than the depth of laser radiation absorption and the thermal diffusion length [4, 9] can be attributed to the generation and propagation of the laser-induced stress and shock waves and their influence on the photoelectric properties [3, 4]. It was stress or shock waves, which appeared as a result of strong absorption of high-power laser pulses, that were capable of modifying the defect structure and altering the properties in the bulk of semiconductors. It should be mentioned that one deals with laser pulses of the energy densities which satisfy the criterion for shock wave formation [3]. It is known that the damaged regions in a crystal such as extended growth defects (dislocations, vacancy clusters, precipitates, small-angle boundaries, etc.) can act as sinks [2]. An increase in the photosensitivity of the irradiated GaAs and InSb crystals as a result of the action of the laser-induced stress and shock waves can be attributed to the gettering of electrically active point defects (acting as recombination centres) by extended macrodefects (acting as sinks) followed by recombination of these defects [2].

The short-wavelength shift of the maximum and the long-wavelength edge of the photoconductivity spectra, which was observed in InSb crystals subjected to irradiation with laser pulses of energy density $E \geq E_{\mathrm{InSb}}$ (Fig. 1b, curve 3), was due to the formation of an elastically deformed surface region with a wider bandgap [1, 14]. This was an additional evidence of the important role of the stress and shock waves generated by nanosecond laser pulses in the photosensitization of the samples that was associated with the gettering properties of extended defects, particularly dislocations, which were responsible for the laser-stimulated segregation of impurities and intrinsic point defects at these macrodefects.

Conclusion

Irradiation of GaAs and InSb crystals with nanosecond ruby laser pulses modifies the defect structure in the surface region and changes the photoelectric and electrical properties. Using laser techniques for treatment of III-V semiconductors one can choose the range of energy densities of nanosecond pulses to modify the structure of the surface region and to improve the photoelectric characteristics of the samples. The laser-stimulated photosensitization of the irradiated GaAs and InSb samples take place owing to a decrease in the surface recombination rate as well as desorption and segregation of electrically active point defects at sinks (macrodefects). Pulsed laser treatment of GaAs and InSb crystals shows promise as an effective procedure for cleaning and well-ordering the crystal surface along with increasing stability of the electrophysical parameters of device structures.

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