Variation of the Reflection Coefficient of Semiconductors in a Wavelength Range from 0.2 to 20 μm under the Action of Ultrasonic Waves

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Abstract—The effect of ultrasonic waves on the spectral coefficient of radiation reflection from the surface of semiconductors used in solar energy converters is considered. A change in the reflectance of semiconductors before and after ultrasonic treatment is determined. It is shown that acoustic stimulation of the semiconductor surface and subsurface layers determines the radiation reflection conditions. © *2002 MAIK "Nauka/Interperiodica".*

Previously [1–3] we experimentally demonstrated for the first time that ultrasonic waves in the megahertz range may change the transport properties and the structure of semiconductors. The results of investigations devoted to the effect of ultrasound on the volume and surface properties of classical semiconductors (Si) and piezosemiconductors (GaAs), including the transport of nonequilibrium charge carriers, were summarized in [4]. Our subsequent studies, as well as the investigations of other researchers, confirmed the proposed concept of acoustically stimulated phenomena in semiconductors, according to which structural changes in semiconductors are related to the diffusion of impurity atoms, decay and formation of complexes, accumulation of impurities, etc., in ultrasonic fields. Further elucidation of the detailed mechanisms of interaction between elastic oscillations and other processes in semiconductors requires investigations in various directions.

One such direction for research is related to the effects of ultrasonic waves on the optical properties of semiconductors. These effects are important since semiconductors are widely employed in photoelectronics and solar power technology, where the optical properties of semiconducting materials determine the main performance characteristics of devices. This investigation is devoted to variation of the optical reflection coefficient R of a semiconductor surface under the action of ultrasonic waves.

We have experimentally studied the effect of ultrasound on the spectral coefficients of reflection $R(\lambda)$ of samples of silicon and gallium arsenide employed in solar energy converters. The experiments were performed at $T = 293$ K with ultrasonic waves in the frequency range $f = 0.8$–25 MHz at a power density varied

within $P = 0$–15 W/cm^2. Waveguides from the ultrasound generator to semiconductor samples represented liquids, viscous media, and solids. The reflectance spectra of the surfaces of samples before and after ultrasonic treatment (UST) for a certain time were measured in a broad wavelength range including ultraviolet (UV), visible (VIS), and infrared (IR) spectral regions.

Silicon. The experiments were performed on silicon plates for solar cells with an area of $S = 2 \times 2$ cm^2 and a thickness of $d = 250$–300 μm. The base p-Si layers possessed a resistivity ρ from 1.8 to 3 Ω cm. An n^+-Si layer with a thickness of 0.5–15 μm was created by diffusion doping with phosphorus. The dopant concentrations were different in the three series of silicon samples studied: $N_1 = 1.75 \times 10^{20}$ cm^{-3}; $N_2 = 4.5 \times 10^{19}$ cm^{-3}; and $N_3 = 7.8 \times 10^{18}$ cm^{-3}. The samples carried neither electric contacts nor antireflection coatings. The ultrasonic wave was incident onto the surface of the n^+-Si layer. The coefficients $R(\lambda)$ were measured before and after UST of the samples.

Upon UST, the n^+-Si layers of certain thickness were removed step by step from the sample surface by chemical etching. At each step, the dopant concentration was determined by four-point-probe resistance measurements and then the $R(\lambda)$ spectrum was measured, after which the procedure was repeated. The reflectance measurements in the IR spectral range were performed on an IKS-14 spectrophotometer; in the UV–VIS range, the measurements were performed with SF-4 and SF-20 instruments.

1. IR reflectance of silicon: low-power UST ($P_m \leq$ 1 W/cm^2). Figure 1 shows the $R(\lambda)$ spectra of silicon samples before (curves *1*, *3*, and *5*) and after (curves *2*, *4*, and *6*) UST at a frequency of $f = 15$ MHz and a power

of $P = P_m \leq 1$ W/cm^2. Here, by low-power (subthreshold) UST we imply treatment at an ultrasonic wave power introducing no changes in the semiconductor defect structure (point defects, formation and decay of complexes, etc.). As can be seen from Fig. 1, all the initial $R(\lambda)$ spectra measured for the samples with various dopant concentrations N exhibit minima. The shapes of the curves are explained by dependence of the absorption index (k) and polarizability (α) of the semiconductor on the radiation wavelength λ [5, 6] (Fig. 1, curves *1*, *3*, and *5*).

The reflectance spectra measured after UST for a time of $t > 1$ h clearly reveal a shift of the $R(\lambda)$ minima toward longer wavelengths and a general decrease in the reflectance of each sample (Fig. 1, curves *2*, *4*, and *6*). We believe that the shift of $R(\lambda)$ is unambiguous evidence of the acoustically stimulated diffusion [3, 4, 7, 8] of impurity (phosphorus) inward the p-Si base layer, which results in a decrease of the dopant concentration N in a subsurface layer of the semiconductor.

In order to confirm this statement, we performed layer-by-layer etching of the silicon samples. The dopant concentration N and the reflectance $R(\lambda)$ were measured after the removal of each layer with a thickness of $d = 0.1$ µm. It was found that all silicon samples after UST exhibited a decrease in N at the surface and an increase in the dopant concentration in depth of the p-Si base layer. For example, Figs. 2a and 2b show the $N(d)$ and $R(d)$ depth profiles obtained in the course of sequential removal of layers down to a depth of $d_1 = 0.5$ µm, $d_2 = 1.5$ µm, and $d_3 = 2.5$ µm. As noted above, features of the $R(\lambda, N)$ functions were considered in detail elsewhere [5, 6].

2. UV–VIS–IR reflectance of silicon: UST at threshold powers (1.0 W < P_L < 5.0 W/cm^2). As was demonstrated above, the reflectance of silicon $R(\lambda)$ in the IR spectral range can be changed by UST at a low power of $P_m \leq 1.0$ W/cm^2 for a relatively long time $t > 60$ min. UST at a threshold (medium) power in an interval of 1.0 W < P_L < 5.0 W/cm^2 leads to the production of various defects in the bulk and subsurface layers of the semiconductor, an acoustically stimulated diffusion of impurities [3, 7–11], and the emergence of some defects at the semiconductor surface [12]. It should be noted that changes in the $R(\lambda)$ curves measured in the IR range upon UST at $P = P_L$ were generally analogous to those observed after the treatment at low powers of $P = P_m$. However, UST at threshold powers leads to the appearance of additional maxima and minima in the $R(\lambda)$ curves (Fig. 3a). These $R(\lambda)$ features in the IR range are probably related to the production of defects of the type described in [12] in the subsurface region at $P = P_L$ (Fig. 3a). Such defects can be decorated by diffusing impurity atoms, which leads to the formation of impurity "atmospheres" influencing the shape of the $R(\lambda)$ curve.
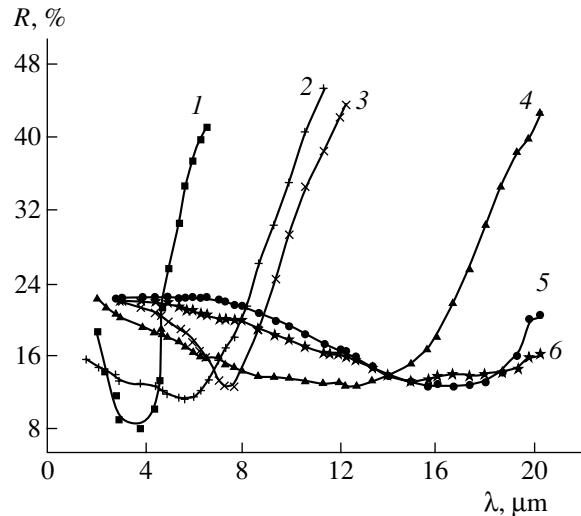
Fig. 1. Spectral dependences of the reflection coefficient R of silicon measured (*1–3*) before and (*4–6*) after UST ($P_m \leq$ 1 W/cm^2; $f = 15$ MHz; $t > 60$ min) for three samples with different degrees of doping of the n^+-Si layer: (*1, 4*) sample 1, $N_1 = 1.75 \times 10^{20}$ cm^{-3}; (*2, 5*) sample 2, $N_2 = 4.5 \times 10^{19}$ cm^{-3}; (*3, 6*) sample 3, $N_3 = 7.8 \times 10^{18}$ cm^{-3}.
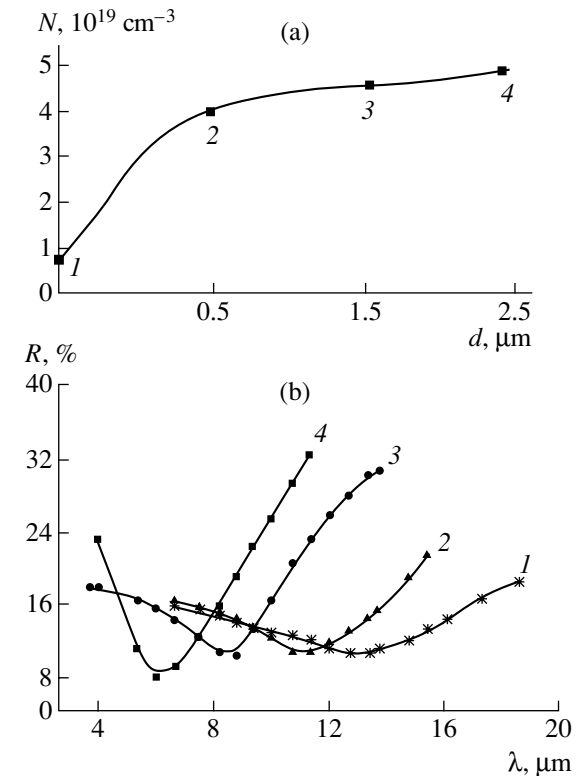
Fig. 2. The results of depth profiling of silicon (sample 4) after UST ($P_m \leq 1$ W/cm^2; $f = 15$ MHz; $t = 8$ h): (a) phosphorus concentration N profile in an n^+-Si layer etched to a depth of $d = 0$ (*1*), 0.5 (*2*), 1.5 (*3*), and 2.5 µm; (b) variation of the reflection coefficient spectrum in the course of profiling; curves *1–4* correspond to points *1–4* of the dopant depth–concentration profile, where $N \approx 8.8 \times 10^{18}$ (*1*), 3.2×10^{19} (*2*), 4.3×10^{19} (*3*), and 4.8×10^{19} cm^{-3}.
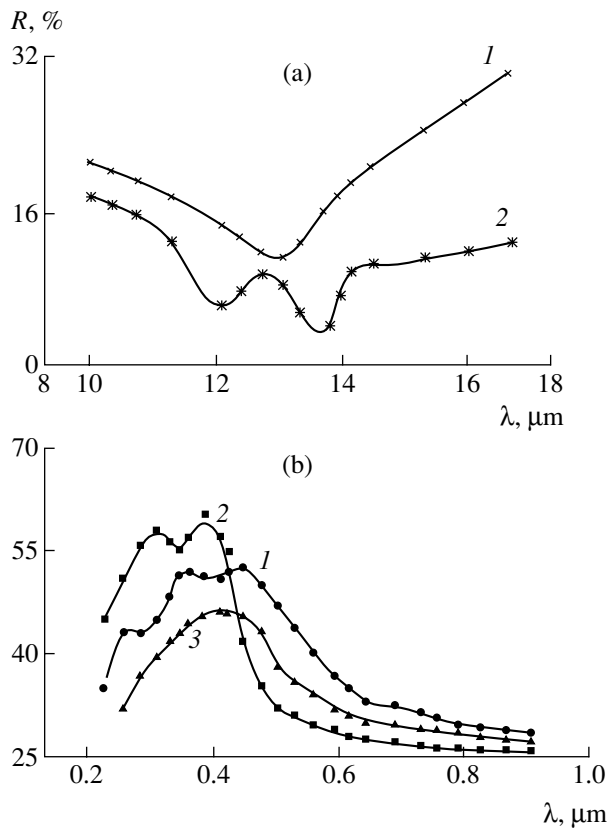
Fig. 3. Spectral dependences of the reflection coefficient R of silicon: (a) sample 03 with the initial dopant concentration in the n^+-Si layer $N = 2 \times 10^{19}$ cm^{-3}, measured (*1*) before and (*2*) after UST at $P = 5$ W/cm^2, $f = 15$ MHz, $t = 30$ min; (b) sample 05 ($N \approx 8 \times 10^{18}$ cm^{-3}) measured (*1*) before and (*2*, *3*) after UST at $P_c \geq 15$ W/cm^2, $f = 15$ MHz, $t = 15$ (*2*) and 30 min (*3*).

Investigation of the behavior of $R(\lambda)$ in the UV–VIS range showed that UST at $P = P_L$ for $t < 30$ min does not lead to significant changes in shape of the $R(\lambda)$ curves due to variation of the dopant concentration or the appearance of new defects in the subsurface region of the semiconductor, because optical reflectance in this spectral range is determined predominantly by the interband transitions of charge carriers [13, 14].

The results of experiments devoted to the study of changes in $R(\lambda)$ upon UST at $P = P_m$ or $P = P_L$ did not depend on the type of waveguide material (liquids, viscous media, solids).

3. UV–VIS–IR reflectance of silicon: UST at critical powers ($P = P_c > 5$ W/cm^2). UST at a power $P = P_c$ in this range leads to the production of various structural defects in the bulk and subsurface layers of the semiconductor and to the acoustically stimulated diffusion of impurities, these phenomena taking place irrespective of the waveguide material.[1]

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[1] Identification of defects produced by UST at $P = P_L$ and P_c falls outside the framework of this study.

In the experiments with viscous and solid waveguides, we did not observe any significant changes in $R(\lambda)$ in the UV–VIS spectral range for $P = P_c$ (similar to the case of $P = P_L$ considered above): the shapes of the curves measured before and after UST were generally similar (Fig. 3b, curve *1*). Physical mechanisms responsible for this behavior of $R(\lambda)$ are considered in [13, 14].

However, the pattern dramatically changed in the experiments with liquid waveguides: for $t < 30$ min, the $R(\lambda)$ significantly increased in the wavelength region of 0.2 μm $< \lambda <$ 0.42 μm and sharply dropped at $\lambda >$ 0.42 μm (Fig. 3b, curve *2*). A comparison of the $R(\lambda)$ curves measured after UST for $t = 30$ min to that observed for $t = 15$ min (Fig. 3b, curves *3* and *2*, respectively) reveals a decrease in the region of 0.2 μm $< \lambda <$ 0.45 μm and an increase at $\lambda > 0.45$ μm. It was of interest to determine the reasons of these effects observed for the liquid waveguide. An analysis of the experimental conditions and results showed that the liquid medium exhibited cavitation [15], which resulted in the formation of depressions of various shapes on the surface of silicon. The parameters of these depressions (shape, depth) varied depending on the UST regime (power and time). As a result, the semiconductor surface acquired a kind of roughness (or texture), which is known to determine the reflectance of a semiconductor. Previously [10], we reported on the destruction of oxides on a semiconductor surface under the action of ultrasonic waves.[2]

The UST effects upon the silicon reflectance observed in different spectral intervals can be explained taking into account the presence of cavitation-induced depressions, their mean dimensions (L_m), and their surface density (N_s).

(a) 0.2 μm $< \lambda <$ 0.45 μm; $t < 15$ min. As soon as the cavitation leads to the formation of depressions on the sample surfaces with a mean size of $L_m \approx 0.15$–0.45 μm (comparable to the UV radiation wavelength $\lambda = 0.2$–0.4 μm), the reflection coefficient $R(\lambda)$ in this spectral region increases (Fig. 3b, curve *2*). This is explained by increased absorption of radiation with $\lambda = 0.2$–0.4 μm on these surface defects; as is known, an increase in the absorption leads to a corresponding increase in reflectance [14].

(b) 0.2 μm $< \lambda <$ 0.75 μm; $t > 15$ min. As the duration of UST grows, the number of depressions on the semiconductor surface increases and their dimensions exceed the radiation wavelength: $L_m \approx 1.5$–2.5 μm $> \lambda$. The sample surface in the cavitation zone becomes rougher and the reflection coefficient $R(\lambda)$ for 0.2 μm $< \lambda <$ 0.45 μm decreases in comparison to the preceding case (Fig. 3b, curve *3*). A comparison of curves *2* and *3* in Fig. 3 shows that additional 15-min treatment (to a

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[2] Presenting detailed description of the behavior of $R(\lambda)$ depending on the depth, size, and density of depressions on the sample surface is beyond the scope of this paper.
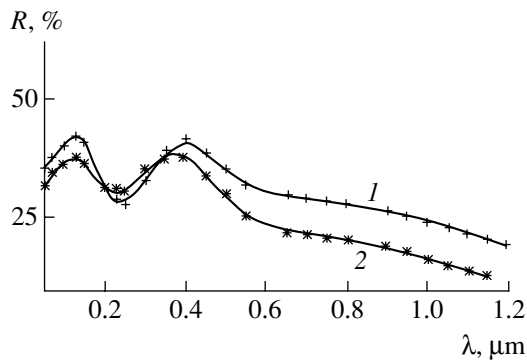
Fig. 4. Spectral dependences of the reflection coefficient R of gallium arsenide (sample 3) measured (*1*) before and (*2*) after UST.

total of $t = 30$ min) leads to an increase in $R(\lambda)$ in the range of $\lambda > 0.45$ μm.

Further increase in the UST duration t leads to the growth of $R(\lambda)$ in the entire region 0.2 μm $< \lambda < 0.75$ μm as a result of increasing cavitation damage of the semiconductor surface. Destruction of the surface is accompanied by increasing absorption and, hence, reflection of radiation in the UV–VIS range [14].

We believe that the above features in the UST-induced changes of $R(\lambda)$ in the UV–VIS and IR ranges are related not only to the cavitation erosion of the semiconductor surface. Since the behavior of $R(\lambda)$ in the UV range is determined by the energy band structure of semiconductors [13, 14], it can be suggested that a prolonged exposure to high-power ultrasound ($P = P_c$) not only generates the aforementioned surface defects, but produces irreversible deformation of the crystal as well. The effects of straining on semiconductors are considered in detail in [16].

The conclusion about semiconductor crystals being strained by ultrasound at $P = P_c$ is confirmed by the results of mechanical tests determining the effect of cavitation of the strength of metals [17]. It was found that cavitation significantly changed the mechanical properties of samples as a result of modification of the metal structure. Similar cavitation effects leading to changes in the crystal structure probably take place in semiconductors and determine the behavior of $R(\lambda)$ in the UV spectral range.

Gallium arsenide. The experiments with this semiconductor were performed using model solar cell elements representing GaAs single crystal photodetectors prepared as described in [18]. The samples were made of semi-insulating GaAs crystals ($\rho \approx 10^7 – 10^8$ Ω cm) with a thickness of 100–500 μm and a working area S of up to 3 cm^2. The GaAs samples treated with ultrasound exhibited changes in $R(\lambda)$ analogous to those observed for silicon. It should be emphasized that behavior of the $R(\lambda)$ spectra in both GaAs and Si samples is determined by the same mechanisms (Fig. 4).

Conclusions. Based on the above results, we can draw the following conclusions:

(i) Irradiation of a semiconductor with low-power ($P = P_m$) ultrasonic waves in the megahertz frequency range leads to a decrease in the reflection coefficient $R(\lambda)$ in the IR spectral range. This drop is caused by a decrease in the concentration N of a doping impurity in the subsurface layer of the semiconductor as a result of acoustically stimulated diffusion of the dopant inward the sample bulk.

(ii) UST at a medium (threshold) power $P = P_L$ leads to the appearance of additional maxima and minima in the $R(\lambda)$ curves in the IR range, which is related to the production of defects of various types in the bulk and subsurface layers of a semiconductor. The trapping of diffusing impurity atoms on these defects leads to the formation of impurity "atmospheres" contributing to the changes in $R(\lambda)$ in the IR range.

(iii) The acoustically stimulated effects observed in $R(\lambda)$ of semiconductors upon UST at $P = P_m$ and $P = P_L$ are independent of the type of a waveguide material.

(iv) UST in a liquid waveguide at a critical power of $P = P_c$ is accompanied by cavitation in the liquid medium, which leads to straining of the semiconductor bulk and degradation of the surface. These effects account for changes in $R(\lambda)$ in the spectral region of 0.2 μm $< \lambda < 1.0$ μm. The degree of variation of the $R(\lambda)$ spectrum depends on the ultrasonic wave power, frequency, and duration of action.

In concluding, it should be noted that the question as to which types of defects influencing the optical properties are formed in semiconductors under the action of ultrasound requires additional investigations.

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