Investigation of mechanisms of damage to semiconductors by high-power infrared laser radiation

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An experimental investigation was made of the bulk damage to silicon and gallium arsenide single crystals caused by laser radiation pulses of wavelengths $\lambda = 10.6$, 2.94, and 2.76 μ. The threshold intensities for such damage were determined. A correlation was found between the excitation of the nonequilibrium carriers, infrared radiation emitted from the focal region, and appearance of damage. The most probable damage mechanisms were avalanche impact ionization (at $\lambda = 10.6$ μ) and three-photon ionization (at $\lambda = 2.76$ and 2.94 μ). The possible role of microdefects was also noted.

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1. INTRODUCTION

Less work has been done on the laser damage to semiconductors than on the damage to transparent dielectrics. However, semiconductors are convenient for investigating laser damage mechanisms because the electrical and optical properties of many of them are known much better than the corresponding properties of transparent dielectrics. Moreover, experimental methods for the detection of nonequilibrium carriers are highly developed for semiconductors, so that more reliable conclusions can be drawn on the laser damage mechanism if it is associated with electron processes (avalanche and many-photon ionization). Up to now, attention has been mainly concentrated on surface damage to semiconductors. This applies particularly to such widely used infrared laser materials as silicon and gallium arsenide.

The surface damage threshold is known to depend strongly on the quality of the treatment of the surface and its cleanness: for these reasons, it is usually much lower than the bulk damage threshold, which makes it practically impossible to determine the "true" damage mechanism and the ultimate optical strength of a given material from surface damage experiments.

Moreover, laser damage processes in semiconductors may be different from those in transparent dielectrics: the differences may be associated specifically with the narrow forbidden band, long carrier lifetimes, and high carrier mobility.

Our aim was to determine the mechanisms of bulk damage to silicon and gallium arsenide by pulses emitted from a CO_2 ($\lambda = 10.6$ μ) laser and from lasers utilizing fluorite (CaF_2) and yttrium aluminum garnet (YAG) crystals activated with trivalent erbium ions (emitting at $\lambda = 2.76$ and 2.94 μ, respectively).

2. EXPERIMENTAL RESULTS

We used the following lasers emitting the dominant transverse mode:

1) a CO_2 laser with a transverse discharge in an $He:CO_2 = 4:1$ mixture at atmospheric pressure; the resonator consisted of a concave spherical metal mirror and a flat silicon plate, forming nearly semiconcentric configuration; the duration of smooth symmetric bell-shaped laser pulses was 6×10^{-8} sec at midamplitude; the emission wavelength was $\lambda = 10.6$ μ;

2) a $CaF_2:Er^{3+}$ laser which was Q-switched by a rotating mirror; it emitted pulses of $\tau_{0.5} = 10^{-7}$ sec duration and of a smooth symmetric bell shape; the emission wavelength was $\lambda = 2.76$ μ;

3) a $YAG:Er^{3+}$ laser emitting $\tau_{0.5} = 10^{-4}$ sec pulses in the spike-free regime; the emission wavelength was $\lambda = 2.94$ μ.

The shape of the laser pulses was monitored with a time resolution of at least 10^{-9} sec using a pyroelectric detector and an S7-10A fast-response oscillograph. The energy was measured with a calibrated graphite calibrated graphite calorimeter.

The investigated crystals were as follows:

1) a single crystal of undoped high-purity dislocation-free silicon grown in vacuum and characterized by a resistivity $\rho > 10\,000$ $\Omega \cdot$ cm. The oxygen content was $n_O < 10^{15}$ cm^{-3} and the carbon content was $n_C < (1-3) \times 10^{15}$ cm^{-3};

2) a single crystal of partly compensated gallium arsenide with $n_{imp} \sim 10^{16}$ cm^{-3} of electrically active impurities; the dislocation density was $n_D \sim 10^4$ cm^{-2}.

3) single crystals of compensated "optical-grade" gallium arsenide with $n_{imp} \sim 10^{16}$ cm^{-3} and $n_D \sim 10^4$ cm^{-2}.

The dimensions of the samples were $10 \times 20 \times 35$ mm.

The laser radiation was focused inside a sample by a planoconvex silicon lens, whose plane surface was separated by 0.1 mm from the entry face of a sample. The lens was placed in the far-field zone of the laser radiation. The diameter of the laser beam entering the lens was measured by the knife method[1] and it was 4 mm for all the lasers (at $1/e$ of the maximum intensity). The lens focus was located 10 mm from the entry face.

The distribution of the intensity in the focal region inside the sample was determined by numerical calculations, employing the diffraction theory of aberrations.[2] The results of the calculations are presented

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in Fig. 1. We can see that allowance for the aberrations altered considerably the intensity distribution pattern: additional maxima appeared on the beam axis and the maximum intensity decreased by a factor of 2 at $\lambda = 10.6\ \mu$ and by a factor of 4 at $\lambda = 2.76\ \mu$.

The damage was investigated by infrared microscopy, by detecting infrared radiation emitted from the focal region, and by detecting emission of nonequilibrium carriers (by a microwave diagnostic method).[3] Our infrared microscope had a magnetically focused image converter with a resolution of at least 30 lines/mm; an optical microscope was placed in front of its photocathode. The magnification of the system was 40×. Infrared radiation was detected with an FÉU-62 photomultiplier and an optical microscope was again placed in front of the photocathode. This made it possible to detect infrared radiation solely from the damage zone. The emission of nonequilibrium carriers was detected during the infrared-microscope examination of the damage.

All three lasers produced bulk damage in the investigated Si and GaAs samples. The threshold intensities of the laser radiation and corresponding intensities of the optical wave field are listed in Table I.

An investigation of the damage morphology indicated that, in all cases, the "threshold" damage caused by laser pulses of duration $\tau \sim 10^{-7}$ sec was concentrated in very small regions (5–10 μ) and these regions appeared at random at various points in the caustic region within the range of 5–10 μ along the beam axis. Fluctuations of the damage threshold from point to point did not exceed 30%. Typical damage patterns observed above the threshold were of the type shown in Fig. 2. The usual shadow method in transmitted light was unsuitable for the detection of these very small

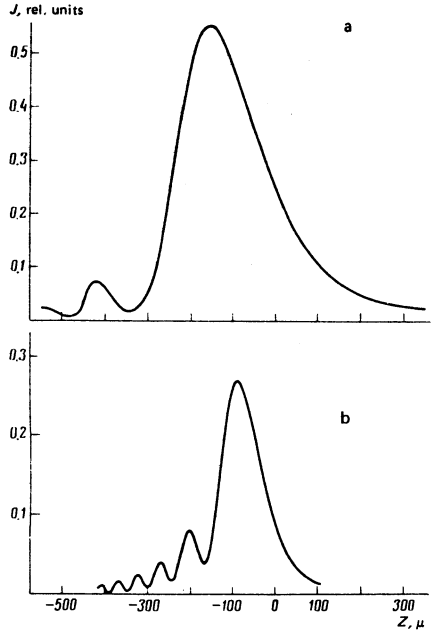

FIG. 1. Distribution of the intensity J of laser radiation on the beam axis z near the focus for $\lambda = 10.6\mu$ (a) and $\lambda = 2.76\mu$ (b). The value of J is normalized relative to the maximum intensity in the absence of other aberrations.

TABLE I. Threshold intensities of laser radiation J_{th}(GW/cm^2) and effective field intensities E_{eff}(MV/cm) in bulk laser damage to Si and GaAs.

Material	Laser radiation wavelength λ, μ: 10.6 J_{th}	10.6 E_{eff}	2.76 J_{th}	2.76 E_{eff}	2.94 J_{th}	2.94 E_{eff}
Si	5.0	0.75	2.3	0.51	0.15	0.13
GaAs, partly compensated	16.5	1.4	0.82	0.32	0.083	0.1
GaAs, optical grade						
sample No. 1	1.27	0.39	–	–	–	–
sample No. 2	14.5	1.3	–	–	–	–
sample No. 3	10.3	1.1	–	–	–	–
sample No. 4	12.4	1.2	–	–	–	–

damage zones and this was clearly why the damage was not observed in Si crystals earlier.[4]

The "multifocus" structure of the laser radiation associated with aberrations was manifested most clearly by the morphology of the damage zones observed in silicon at a wavelength of 2.76 μ.

In all the investigated cases, the infrared radiation emitted from the focal region could only be recorded when damage appeared. The time resolution of the apparatus was insufficient for measuring the duration of the pulses of this radiation: all one could say was that they were shorter than 10^{-6} sec.

Nonequilibrium carriers were emitted from silicon only when the damage appeared. These carriers were not observed for gallium arsenide even when the laser power exceeded the threshold value by three or four orders of magnitude and the damage zones become large (1 mm). This could be due to insufficient time resolution and sensitivity of our microwave apparatus and the short (compared with Si) nonequilibrium carrier lifetime.

3. DISCUSSION OF RESULTS

We shall now consider possible damage mechanisms in the case of silicon and gallium arsenide. Since these materials are very pure, only the electron avalanche ionization is relevant.

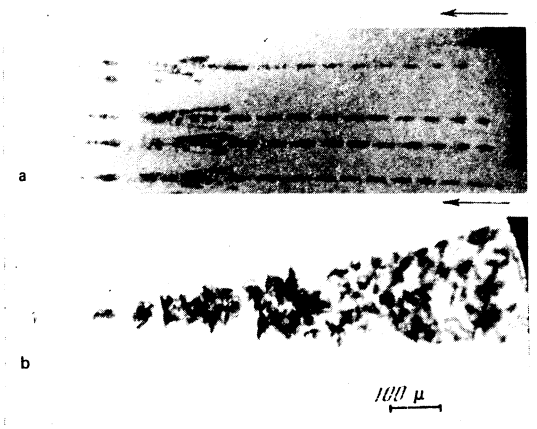

FIG. 2. Damage to silicon (a) and gallium arsenide (b) photographed by means of an infrared microscope. The wavelength of the laser radiation causing the damage was 2.76μ and its power was $P \sim 100 P_{cr}$. The arrows indicate the direction of propagation of the laser radiation.

According to the theory of avalanche ionization (diffusion approximation), the breakdown field is[5]

$$E^2_{\text{eff}} = \Lambda \frac{m^2_{\text{eff}} v_s^2 I}{4kTe^2} \left(\Omega^2 + \frac{I}{m_{\text{eff}} L^2} \right), \quad (1)$$

where Λ is the quantity which depends weakly on the laser pulse duration and is of the order of unity; Ω is the field frequency; v_s is the velocity of sound; I is the ionization potential; T is the absolute temperature; m_{eff} and L are, respectively, the effective mass and mean free path of an electron of energy near the ionization potential.

Since important parameters in Eq. (1), such as m_{eff}, I, and L are not known sufficiently reliably, it is difficult to estimate directly E_{eff}. Therefore, we shall compare the experimental values of E_{eff} obtained under laser breakdown conditions with the known critical fields E_{cr} needed for breakdown in static fields in which electrons participating in avalanche ionization acquire energy by the diffusion mechanism: $E_{\text{cr}}(\text{Si}) = 5 \times 10^5$ V/cm and $E_{\text{cr}}(\text{GaAs}) = 3.7 \times 10^5$ V/cm.[6,7] Such a comparison for $\Omega = 1.78 \times 10^{14}$ sec^{-1} ($\lambda = 10.6$ μ) gives the effective collision frequency $\nu_{\text{eff}} = I/m_{\text{eff}} L^2$ of 1.6×10^{14} sec^{-1} for Si and 5×10^{13} sec^{-1} for GaAs. These values seem to be reasonable if we bear in mind the possible role of the impact ionization mechanism of the damage caused to these materials by CO_2 laser radiation.

It is interesting to note that, in such strong laser breakdown fields as those in the case of Si and GaAs, the energy acquired by an electron even during half the field period is comparable with the ionization energy. This is evidence of a considerable contribution of the drift process of energy acquisition to the impact ionization mechanism.

The damage threshold decreases at the wavelength of 2.76 μ and this cannot be explained by the avalanche ionization theory. One of the possible reasons for the reduction in the threshold is an increase in the importance of the three-photon ionization mechanism. We shall estimate the three-photon ionization coefficient β needed for damage to silicon at the threshold intensities observed in our experiments.

The following equation describes the change in the electron density as a result of the three-photon ionization mechanism when electrons are lost by diffusion from the caustic and recombination:

$$\frac{\partial N}{\partial t} = D \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial N}{\partial r} \right) + \gamma J^3(t) \delta(r) - \frac{N}{\tau_r}, \quad (2)$$

where $\gamma = a^2 \beta / D$; a is the caustic radius; D is the electron diffusion coefficient; β is the three-photon ionization coefficient; τ_r is the recombination time;

$$\delta(r) = \begin{cases} 1, & r \leqslant a \\ 0, & r > a \end{cases}.$$

The solution for $r = 0$ has the form

$$N(0,t) = \gamma \int_0^t J^3(t-\tau) e^{-\tau/\tau_r} [1 - e^{-1/4\tau}] d\tau.$$

In the case of rectangular pulses of duration $t_p \sim 10^{-7}$ sec interacting with silicon, we find, bearing in mind that the characteristic time for the diffusion of electrons from the caustic is $t_d = a^2/D \ll t_p$ and the recombination time is $\tau_r \gg t_p$, we obtain

$$N(t) = \frac{\beta a^2 J_0^3}{D} \ln \left(t \frac{D}{a^2} \right).$$

The temperature in the region of the caustic can be estimated from

$$c\rho \frac{\partial T}{\partial t} = \sigma N J_0 = \frac{\sigma \beta a^2 J_0^4}{D} \ln \left(t \frac{D}{a^2} \right),$$

where σ is the cross section for the absorption of radiation by an electron. Hence,

$$T \approx \frac{\sigma \beta a^2 J_0^4 t}{Dc\rho} \ln \left(t \frac{D}{a^2} \right).$$

If we assume that the threshold damage intensity J_{th} corresponds to a temperature close to the melting point of the investigated crystal T_{mp}, the three-photon ionization coefficient needed for the damage to occur is

$$\beta \approx \frac{T_{mp} D c \rho}{\sigma a^2 J^4_{\text{th}} t \ln (tD/a^2)}.$$

An estimate based on this expression gives $\beta \approx 10^{-1}$ cm$^3 \cdot$ W$^{-3} \cdot$ sec^{-1}. An estimate of the coefficient β from the Keldysh theory[8] gives 0.3×10^{-1} cm$^3 \cdot$ W$^{-3} \cdot$ sec^{-1}, which is quite close to our value.

Our samples of partly compensated GaAs and Si are characterized by fairly strong absorption at the wavelength of 10.6 μ ($\alpha = 0.935$ cm^{-1} for GaAs and $\alpha = 1.44$ cm^{-1} for Si). However, estimates indicate that such linear absorption is insufficient for thermal damage. This is also supported by the observation that samples of optical-grade gallium arsenide ($\alpha \sim 10^{-2}$ cm^{-1}) have approximately the same damage threshold as that of the sample exhibiting the stronger absorption given above.

It should be noted that the nonlinear absorption associated with the thermal generation of carriers is negligible for such short laser radiation pulses.

Although the above arguments support the possible role of the "pure" damage mechanisms associated with the impact and many-photon ionization, we cannot exclude the possible influence of various types of defect on the damage to our crystals. This is supported by the morphology of the damage zones: isolated random microdamage zones are exhibited both by Si and GaAs in the region of the caustic when the intensity is close to the threshold; when the excess over the threshold is large, these microzones occupy a considerable part of the region near the caustic. In silicon, the concentration of such microdamage zones is ~10^9 cm^{-3}.

The observed influence of defects on the damage process may be associated with the thermal explosion of these defects as a result of strong absorption[9] or with easier conditions for the development of avalanche and many-photon ionization at defects. Unfortunately,

the available information on the optical and other properties of defects in Si and GaAs are insufficient for drawing reliable conclusions on the avalanche mechanism; the many-photon ionization has not yet been considered in the literature at all but the sensitivity of the avalanche and many-photon ionization processes to the structure of a crystal is highly likely.

Thus, our experimental results and theoretical estimates suggest that the most probable laser damage mechanism in the case of pure Si and GaAs crystals subjected to CO_2 laser radiation is the avalanche impact ionization. In the case of the damage caused by the radiation of the Er^{3+} lasers, it is more likely to be due to the three-photon ionization process. However, final conclusions on the dominant damage mechanism cannot be drawn without further experiments, especially on the kinetics of excitation of nonequilibrium carriers, and without detailed development of the theory for specific materials.

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Optical characteristics of bound polaron and phonon states

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The change of the phonon spectrum in the presence of a polaron is investigated and the frequencies of the lowest bound states are calculated. The oscillator strengths are estimated for absorption and Raman scattering of light with excitation of bound states of phonons.

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The author and Rashba[1] were the first to consider the restructuring of the phonon spectrum in the presence of a continual tight-binding polaron. It was proved that the change of the polarizability of the crystal near the polaron gives rise to an infinite number of phonon states whose frequencies lie lower than the frequency of the free phonon and differ from it by universal numerical factors. To our knowledge, this was the first example of formation of a bound state of an electron and phonon. It turned out subsequently that such states arise in a large class of cases (see the review[2]).

In all the investigated situations it is possible to explain only the qualitative features of the energy spectrum. The only exception is the autolocalized electron state produced in a contact interaction with phonons in a one-dimensional system,[3] when the problem of the spectrum and wave functions of the bound state has an exact analytic solution.[4] In all other cases it is necessary to resort to numerical methods to obtain quantitative results.

The present paper is a continuation of the earlier[1] investigation of the phonon spectrum in the presence of a polaron, describes the method and results of a numerical calculation of the lowest bound states, and presents an estimate of the oscillator strengths for optical transitions with excitation of these states.

The Hamiltonian of an electron interacting with dispersionless polarization phonons and with an electric field E is of the form

$$H=\frac{p^2}{2}+H_{\mathrm{ph}}^0+(2^{3/2}\pi\alpha)^{1/2}\sum_{\mathbf{k}}\frac{e^{i\mathbf{kr}}}{k}q_{\mathbf{k}}+\frac{e}{m^{1/2}\omega^{3/2}}\mathbf{Er}, \tag{1}$$

where α is the electron-phonon interaction constant, $\mathbf{p}$ is the electron momentum, $q_{\mathbf{k}}$ is the coordinate of a phonon with momentum $\mathbf{k}$, H_{ph}^0 is the Hamiltonian of the free phonons, the energy is measured in units of ω_0, and the length is measured in units of $(m\omega_0)^{-1/2}$ (ω_0 is the phonon energy and m is the electron mass).

In the strong-interaction limit we can obtain from (1) the Hamiltonian of a polaron interacting with phonons.[5] We repeat here briefly this derivation, with an aim of finding the connection between the electric field and the coordinates of the bound states. A shift of the origin of

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