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Terahertz Absorption and Emission upon the Photoionization of Acceptors in Uniaxially Stressed Silicon

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Abstract—Experimental data on the spontaneous emission and absorption modulation in boron-doped silicon under CO_2 laser excitation depending on the uniaxial stress applied along the [001] and [011] crystallographic directions are presented. Room-temperature radiation is used as the probe radiation. Low stress (less than 0.5 kbar) is shown to reduce losses in the terahertz region by 20%. The main contribution to absorption modulation at zero and low stress is made by A^+ centers. Intersubband free hole transitions additionally contribute to terahertz absorption at higher stress. These contributions can be minimized by compensation.

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INTRODUCTION

Searching for different active media for terahertz applications has for a long time been an important area of semiconductor physics. *p*-Ge-based lasers [1], *n*-Si-based lasers [2], and GaAs-based quantum cascade lasers [3] are among the semiconductor sources of terahertz radiation which employ the inversion mechanism. Despite the success of GaAs-based quantum cascade lasers, there is still interest in silicon-based ones due to such reasons as the relative simplicity of manufacturing this type of laser; the stable frequency determined by the energy-level position of the Coulomb center in Si; and the possibility of applying them in promising schemes with impurity atoms, where donors/acceptors are used as the basis of single-atom transistors and other elementary cells of computing machines [4, 5].

Thus far, terahertz stimulated emission has been generated in silicon doped with Group-V donors (phosphorus, arsenic, antimony, and bismuth) under pumping in the mid-infrared spectral range. Si-based lasers operate in the frequency range of ~5–6.5 THz, which is determined by the band gap between the $2p_0$, $2p_\pm$, and $1s$ (E, T_2) levels of donor centers. The position of these levels with respect to the conduction-band valleys well fits the effective mass approximation; i.e., is virtually independent of the chemical nature of the impurity and is not affected by uniaxial stress. Other impurities (e.g., deeper helium-like double donors, such as magnesium) are required for operation in the frequency range above/below 5–6.5 THz. The schemes of using acceptors in silicon remain poorly studied, although they show great promise, since strain in acceptors can substantially change the energy gaps, as opposed to that in donors,. Thus far, stimulated emission has only been recorded for Si:B under intracenter excitation (Fig. 1) (ionization energy of the center being 45 meV). As opposed to Group-V donors, where generation was achieved both for intracenter excitation and ionization, the laser effect for acceptors is only observed under excitation at line *4* (states $1\Gamma_7^-$, $1\Gamma_6^-$, and $4\Gamma_8^-$, and further, $\Sigma4$) [6]. The spectrum of stimulated emission features a single line at 1.7 THz (7.2 meV). Until recently, no unambiguous explanation was provided for this effect because of a lack of understanding of relaxation mechanisms and the spectrum of states in acceptors. In their recent publication [7], Morse et al. partially answered questions regarding the positions of *s*-type states in Si:B, thus making it possible to identify the signal transition ($\Sigma4$–$2\Gamma_8^+$) with confidence. All attempts made so far to generate terahertz radiation by impurity photoionization have failed. The following sources of loss can be mentioned among the reasons responsible for the lack of the stimulated effect under photoionization:

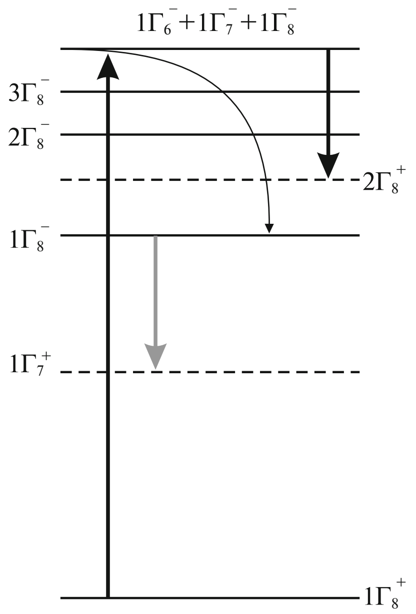

Fig. 1. Diagram of energy levels in Si:B that affect the interpretation of data on the stimulated emission under intracenter excitation. Upward pointing arrow denotes pumping; black downward pointing arrow denotes the presumed laser transition without preliminary energy relaxation; gray downward pointing arrow shows the presumed laser transition in the case of hole relaxation to the longest-lived level. According to [7], the black and gray downward pointing arrows correspond to 58.9 and 61.5 cm^{-1}, respectively.

absorption by acceptors captured at an additional hole (A^+ centers) [8] and absorption caused by transitions between the heavy- and light-hole subbands. In this study, we report the results of investigating the losses in Si:B under photoionization by CO_2 laser radiation, as well as the effect of uniaxial stress on the level of these losses and the intensity of spontaneous emission.

EXPERIMENTAL

The experimental samples were prepared using silicon grown by the Czochralski method doped with boron (concentration of 10^{15} cm^{-3} or 4×10^{15} cm^{-3} and a compensation level of less than 1%). The samples were shaped like a rectangular parallelepiped; 3 × 5 × 7 mm in size. The samples were cut out so that the crystallographic direction [100] (10^{15} cm^{-3}) or [110] (4×10^{15} cm^{-3}) coincided with that of the longer side of the parallelepiped. The sample sides were subjected to mechanical polishing. The samples were then placed into a special module that allows the application of uniaxial stress. The module was placed into a specially designed cryogenic insert for a modified STG-40 portable Dewar vessel with a neck diameter of 50 mm. The design of the insert makes it possible to let in pump radiation and room-temperature background radiation through separate channels. Terahertz radiation was recorded using a detector based on impurity-induced photoconductivity in *n*-GaAs (donor ionization energy of ~6 meV). Mid-infrared radiation (scattered pump radiation and background radiation at 8–30 μm) was cut off from the detector using a filter made of a sapphire wafer (thickness 1 mm). An additional detector based on Ge:Ga photoresistance was used for alignment in the pump-radiation channel. A Q-switched CO_2 laser (wavelength of 10.6 μm, pulse-repetition period of ~3 ms; pulse duration of ~300 ns; average intensity of ~400 mW) was used as the pump-radiation source. Figure 2 shows the experimental scheme.

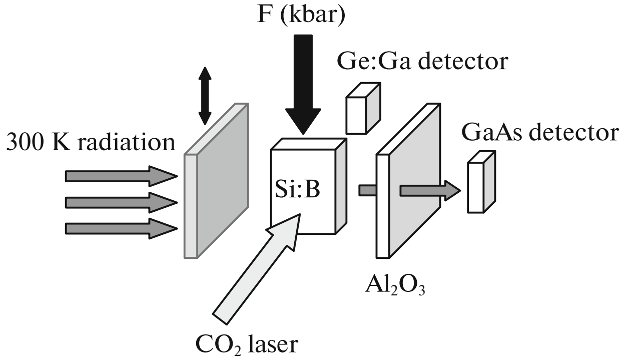

Fig. 2. Experimental scheme for observing spontaneous emission and induced losses during CO_2-laser photoionization of the Si:B sample under applied uniaxial stress.

The existence of a "cold" shutter allows one to single out the component responsible for absorption modulation in the medium caused by CO_2 laser radiation. The spontaneous-emission curve is plotted using data recorded for a closed shutter, while the total signal is recorded for an open shutter. The behavior of the total signal, as well as that of the spontaneous signal for a closed shutter, can change depending on the configuration of the measurement system and frequency characteristics of the detector. Nevertheless, the dependence of the modulation signal of background radiation and the spontaneous emission will qualitatively remain the same in spite of variations as it is a parameter of the sample. It should be mentioned that the procedure for isolating the modulation signal from the total signal can be modified by placing a filter that would cut off spontaneous emission from the detector. However, preferably a sufficiently narrow-band filter should be used in this case to prevent a significant decrease in the sensitivity of the measurement system.

Figure 3 shows the dependence of absorption modulation under the photoionization of boron acceptors in silicon under uniaxial stress applied along the crystallographic direction [001]. This dependence is nonmonotonic: a decrease in the background absorption

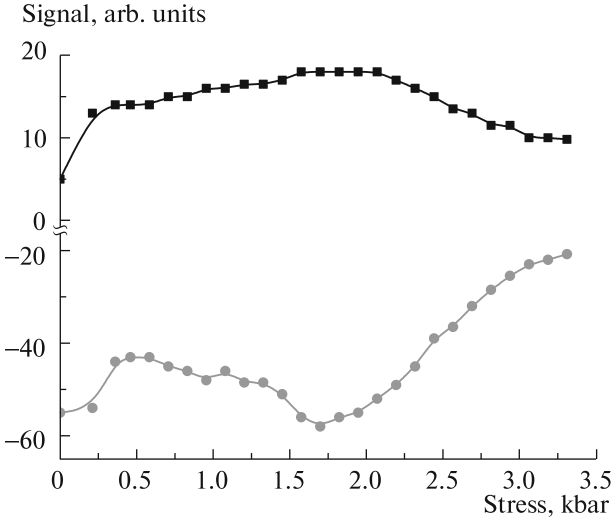

Fig. 3. Intensity of spontaneous emission (the upper curve) and pump-induced losses (the lower curve) during photoionization as a function of uniaxial stress applied along the crystallographic direction [001]. The experimental data are denoted by dots; the interpolation is shown with curves.

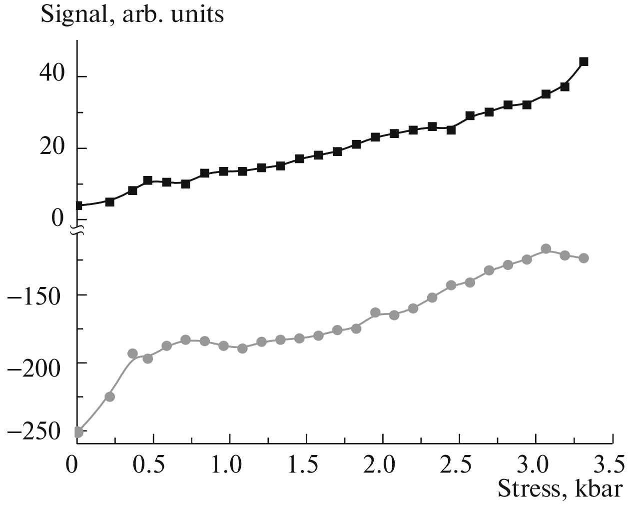

Fig. 4. Intensity of spontaneous emission (the upper curve) and pump-induced losses (the lower curve) during photoionization as a function of uniaxial stress applied along the crystallographic direction [011]. The experimental data are denoted by dots; the interpolation is shown with curves.

signal within the stress range of 0–0.5 kbar with a small extremum (maximum) at ~1 kbar; an increase at pressures up to ~1.7 kbar, followed by a drop in the region up to the maximum allowable stress (3.25 kbar). The dependence of spontaneous emission in the same pressure range is characterized by an increase at stress up to 0.5 kbar, a virtually unchanged level at 0.5–2 kbar, and a smooth decline at 2–3.25 kbar. The opposite sign of signals of spontaneous emission and background modulation at the same bias polarity at the photodetector is shown by the fact that spontaneous emission increases the conductivity of the photodetector, while absorption modulation in the sample (in this case) prevents penetration of the background signal onto the detector.

Figure 4 shows the dependence of absorption modulation of the background radiation on stress applied along the crystallographic direction [011]. The pump-induced absorption decreases at stress below 0.5 kbar. Similar to the previous case, there is a weakly pronounced extremum at 1 kbar, the maximum at 2 kbar is lacking, and the signal decreases at stress up to the maximum allowable value. The signal from the spontaneous emission (Fig. 4) increases more slowly up to 0.5 kbar and then continues to rise, although with a smaller derivative on stress.

DISCUSSION

The observed drop in the absorption modulation signal under the photoionization of acceptors within the range of 0–0.5 kbar under stress applied along the crystallographic direction [001] can be attributed to a decrease in absorption by A^+ centers. Haug and Sigmund [9] reported that uniaxial stress results in splitting and a shift of the energy levels of positively charged centers. In the absence of stress, the ionization energy of a single A^+ center is ~2–2.5 meV. At relatively small stress values, the ionization energy of the A^+ centers decreases approximately twofold due to the reduced effective mass upon splitting of the subzones of light and heavy holes in the valence band of silicon. This reduces the lifetime of the centers at finite temperatures due to interaction with long-wavelength acoustic phonons. It should be additionally mentioned that the maximum of the absorption coefficient shifts to lower frequencies [9]. The maximum of the photoionization-induced absorption observed at 1.7 kbar is related to the maximum coincidence between the sensitivity band of the detector and splitting of the valence band (~ 3.3 meV/kbar) [10], which is indicative of intersubband hole transitions. When stress is applied to the crystal along the crystallographic direction [110], absorption is reduced at pressure values up to 0.5 kbar, which is also caused by a decrease in the energy of A^+ centers. There is no well-pronounced maximum at higher stress, which is probably because of a different (higher) mass ratio in the subbands along the direction of the applied stress [011]. Spontaneous emission in both cases demonstrates that the intensity increases in the range of 0–0.5 kbar, which correlates with the decrease in absorption. However, the further behavior of the intensity of spontaneous emission with increasing stress is different for different directions. Unfortunately, we could not perform spectral measurements of the emission because of its low intensity. As mentioned above, the experiment [6] demonstrated that the stimulated effect emerges only for resonant pumping at line *4* of the Lyman series of the acceptor (combined state $1\Gamma_7^-$, $1\Gamma_6^-$, and $4\Gamma_8^-$). The excitation of deeper-lying odd-parity states $1\Gamma_7^-$, $2\Gamma_8^-$, and $3\Gamma_8^-$ did not result in generation. We can suggest the following technical explanation of the results: there was no vacuum channel from the radiation source to the optical cryostat with the sample in this experiment, which could have significantly reduced the supplied pump intensity in lines *1* and *2* as a result of absorption by water vapor. In turn, the intensity of line *3* could be insufficient to ensure efficient excitation; although there were no lines of water vapor lying close to it. This assumption was qualitatively confirmed by Fig. 2 in [6]—a study reporting the positions of absorption lines of water vapor. On the other hand, pump-probe measurements revealed a tendency towards a shorter relaxation time for the excitation of odd-parity states in a boron atom at lower binding energies [11]. Thus, the relaxation time for excitation in lines *1* ($1\Gamma_8^-$) and *4* ($1\Gamma_7^-$, $1\Gamma_6^-$, and $4\Gamma_8^-$) is 100 and 30 ps, respectively. Hence, the lowest-lying *p*-type state $1\Gamma_8^-$ is expected to be the longest-lived one. This result also shows significant deviation from the cascade relaxation model for the Coulomb center, since the relaxation time for the cascade-relaxation mechanism is supposed to become longer because the energy gaps between states increase and the total relaxation time should increase when approaching the band bottom (superposition of the relaxation times in the cascade). Vinh et al. [11] attributed this result to an increased density of phonon modes at higher transition energies. The electroluminescence of Si:B under impurity-breakdown conditions at low temperatures was demonstrated in [12, 13]. The electroluminescence spectrum contained three lines corresponding to the transitions from $1\Gamma_8^-$, $2\Gamma_8^-$, and $3\Gamma_8^-$ to the ground state of the acceptor $1\Gamma_8^+$ and no long-wavelength transitions, which probably indicates that the matrix element of the transition $n\Gamma_8^-{-}1\Gamma_7^+$ is relatively small. Until recently, there has been uncertainty because it was difficult to determine the positions of the *s*-type levels. In spite of theoretical predictions, the position of the level $1\Gamma_7^+$ at 23 meV has been confirmed only in a few experimental studies via Raman scattering [14] or high impurity concentrations for Fourier-transform spectroscopy to observe the forbidden transition $1\Gamma_8^+{-}1\Gamma_7^+$ [15]. Meanwhile, knowledge of the transition energy from [6], with allowance for the non-cascade mechanism, allowed the authors to suggest an alternative for the transition $1\Gamma_8^-{-}1\Gamma_7^+$: transition $\Sigma4{-}2\Gamma_8^+$. The position of the $2\Gamma_8^+$ level (13.44 meV) calculated using this hypothesis correlated rather well with the known theoretical [16] and experimental [17] data and was confirmed by the findings reported in [7] due to which the difference between the energies of transitions $1\Gamma_8^- - 1\Gamma_7^+$ and $\Sigma4{-}2\Gamma_8^-$ was measured (61.5 cm^{-1} and 58.9 cm^{-1}, respectively). Hence, despite the existence of a relatively long-lived level $1\Gamma_8^-$, $\Sigma4$ is the upper laser level. This circumstance allows one to put forward an additional hypothesis about the resonance Raman effect (electron scattering) under excitation of the $\Sigma4$ level (in other words, the transition from the $1\Gamma_8^+$ state to $2\Gamma_8^+$ state accompanied by the emission of a photon). In the case of the inversion mechanism under short-pulse excitation, the lasing rise time is approximately equal to the lifetime of the upper laser level. In the case of Raman effect, the rise time is equal to the excitation-pulse length. Since the excitation time was ~10 ps, which is close to the lifetime of state $\Sigma4$, the contribution of stimulated resonance Raman scattering can be high. However, it is impossible to differentiate between the inversion and Raman mechanisms in the case of resonance. As opposed to this case, Raman radiation in donors was identified based on the linear dependence between the output quantum energy and the excitation quantum energy; the signal was observed not only under resonance pumping [18].

In terms of finding for ways to generate stimulated radiation in Si:B upon photoionization, we can suggest using low stress (<500 bar) which would reduce the level of absorption by A^+ centers (when the laser transition energy does not change so much) and employing a TEA CO_2 laser as the pump source. As opposed to the Q-switched laser used in our study (which is preferable when measuring low-intensity signals because of the constant discharge in the laser tube which reduces interference in the recording circuit), the TEA CO_2 laser is characterized by a higher output intensity. The possible drawbacks of this approach include a reduced gain because of finite broadening of the laser transition levels due to the non-uniformly applied stress and changes in the energy gaps, which will inevitably affect the relaxation times and, therefore, the population inversion. The question about the inversion mechanism in strained *p*-Si should be discussed separately [19]. The use of a compensating impurity (donors) is an alternative method to reduce the population of A^+ centers. Compensation should significantly accelerate free hole capture [20], which will reduce the effect of both A^+ centers and free-hole absorption. A similar approach was demonstrated for silicon lasers based on donor centers [21].

We have studied the effect of uniaxial stress on terahertz losses and spontaneous emission in Si:B under CO_2-laser photoionization. Low stresses were shown to reduce the absorption caused by A^+ centers by approximately 20%. The use of compensation to suppress the absorption effect in the absence of pressure to avoid non-uniform broadening was suggested.

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