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CONDENSED MATTER

Low-Temperature Intracenter Relaxation Times of Shallow Donors in Germanium

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The relaxation times of localized states of antimony donors in unstrained and strained germanium uniaxially compressed along the [111] crystallographic direction are measured at cryogenic temperatures. The measurements are carried out in a single-wavelength pump–probe setup using radiation from the Novosibirsk free electron laser (NovoFEL). The relaxation times in unstrained crystals depend on the temperature and excitation photon energy. Measurements in strained crystals are carried out under stress $S > 300$ bar, in which case the ground-state wavefunction is formed by states belonging to a single valley in the germanium conduction band. It is shown that the application of uniaxial strain leads to an increase in the relaxation time, which is explained by a decrease in the number of relaxation channels.

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INTRODUCTION

In spite of the long history of both theoretical and experimental investigation of shallow impurities in germanium [1], there has recently emerged renewed interest in their properties, in particular, in the studies of excited-state relaxation. This is related to the appearance of new problems, as well as new experimental capabilities that enable direct measurements of ultrafast spectrally resolved dynamics of nonequilibrium charge carriers [2].

The first experimental results on the relaxation times of donors and acceptors in unstrained germanium were obtained in the 1970s using room-temperature background thermal radiation as an excitation source and radiation from a backward wave tube as a probe [3]. Later, using an optical gate to shorten microsecond pulses from a free-electron laser (FEL), it was shown that the photoresponse time in p-Ge with an acceptor concentration of $N_a = 10^{15}$ cm^{-3} and a degree of compensation of ~50% is 1.7 ns [4]. The advent of FEL user stations for pump–probe measurements with pulse durations of 10–100 ps has considerably broadened experimental capabilities. In particular, measurements of capture times in p-Ge were carried out for different doping and compensation levels, which made it possible to determine the parameters required for reducing the response times of germanium detectors and to obtain record-fast photoconductivity response (~150 ps) [2]. The pump–probe technique was used to determine the relaxation times of the lowest excited states in p-Ge (150–250 ps) [5]. It was found using this method that the capture time at liquid-helium temperatures in uncompensated n-Ge crystals moderately doped with antimony donors (Ge:Sb) is 1.7 ns for concentration of $N_d \sim 10^{15}$ cm^{-3} [6].

Here, we use the pump–probe technique to investigate the relaxation times of the excited states of Sb donors in unstrained and strained germanium crystals at cryogenic temperatures.

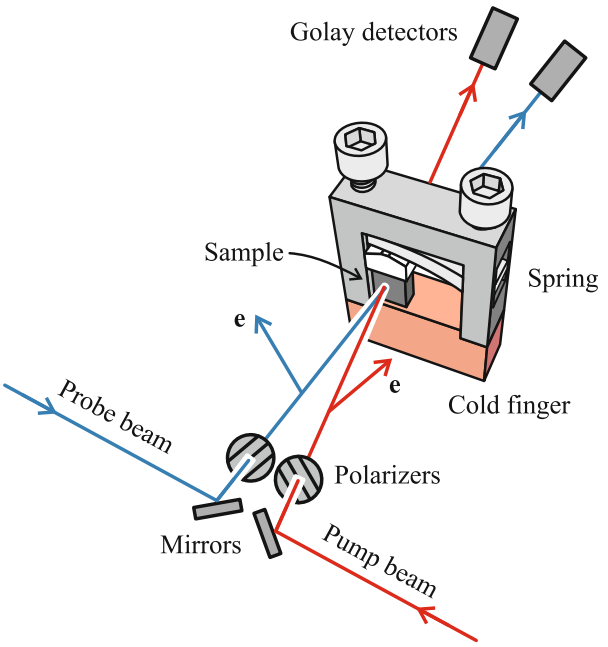

Fig. 1. (Color online) Layout of the experiment.

EXPERIMENT

A single-crystal germanium ingot with a Sb concentration of about 10^{15} cm^{-3} and low compensation (10^{12} cm^{-3}) was grown by the Czochralski method. Sample 1 for measurements under strain had the dimensions of 1.5 × 5 × 7 mm, with the normal to the 1.5 × 5-mm face coinciding with the [111] crystallographic direction. Sample 2 for measurements without strain had a smaller thickness (0.5 mm). The sample faces were polished. The 5 × 7-mm opposite faces, crossed by the laser beams, were tilted by ~1° with respect to each other. The optical layout of the experiment is shown in Fig. 1.

Stress was applied to the sample using a special fixture designed in a way similar to that described in [7]. The samples were placed in a Janis ST-100 helium-flow cryostat with TPX windows. The pump–probe setup [8] at the Siberian Synchrotron and Terahertz Radiation Center employs the NovoFEL free-electron laser [9, 10] as the radiation source.

This experiment made use of the first stage of the FEL tunable between 90 and 220 μm. The input radiation was split by a polarizer into the pump and probe beams, and the probe beam was sent through an automated delay line. The delay τ between the arrivals of the pump and probe pulses at the sample was varied from 0 to 4 ns in ~10-ps steps. The beams were focused so that the diameters of the probe and pump radiation spots at the sample surface were 1 and 2 mm, respectively. The angle between the beams was $\alpha = 15°$. After passing the sample, both pump and probe beams were incident on Golay detectors.

The intensities of both beams could be changed independently using a polarization-maintaining scheme with two polarizers in each channel. The powers of the pump and probe pulses were varied in the ranges of 100–300 W and 1–30 W, respectively. The pulse duration was ~100 ps, which made it possible to attain a time resolution of ~150 ps. To prevent the pump radiation from affecting the signal of the detector in the probe channel, the polarizers in the two beams were set at a right angle, and an additional polarizer was introduced in front of the detector in the probe channel oriented to minimize the transmission of pump radiation. The pump beam was modulated with an optical chopper at a frequency of 15 Hz and the signal from the detector in the probe channel was fed to a lock-in amplifier.

In the simple two-level model, the characteristic decay time of the signal is interpreted as the lifetime of the upper level. If the system has several levels and the excitation photon energy corresponds to transitions above the first excited state, the characteristic decay time of the signal is determined by the time required for the donor to return to the ground state.

RESULTS AND DISCUSSION

We focus on the investigation of the absorption line associated with the transition to the $2p_{\pm}$ states, which is the strongest one in the absorption spectrum of Sb donors in germanium [11]. The experimental setup was tested at a wavelength of 104 μm, which corresponds to the ionization of the Sb donor. Previously, similar experiments with unstrained Ge crystals were performed on a similar setup at the Helmholtz-Zentrum Dresden-Rossendorf [6].

The recorded pump-beam modulation signal is well approximated by an exponential with a characteristic decay time of $t = 1.9$ ns, which is in good agreement with the result of [6]. Figure 2 shows the modulation signal for the case of excitation into $2p_{\pm}$ excited states in unstrained Ge:Sb at lattice temperatures of 4, 20, 30, and 40 K.

Signals recorded at wavelengths of 104 μm (donor ionization), 139 μm ($3p_{\pm}$ states), and 150 μm ($2p_{\pm}$ states) in unstrained sample 2 are compared in Fig. 3. The relaxation times are 1.9, 1.0, and 2.0 ns, respectively. This comparison clearly demonstrates a deviation from the cascade relaxation model, which implies that electrons successively pass neighboring excited energy levels, which should occur under the condition of $qa \gg 1$ (where q is the absolute value of the phonon wave vector and a is the Bohr radius of the impurity state) [12]. This is possibly explained by the influence of intervalley TA phonons with a characteristic energy of ~10 meV, which is close to the excitation energy of the $3p_{\pm}$ level (8.9 meV).

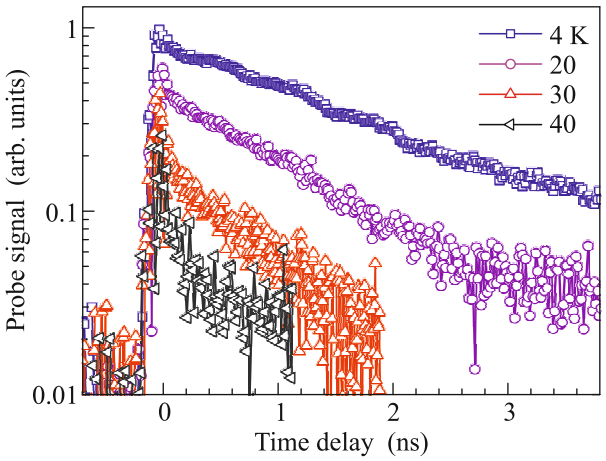

Fig. 2. (Color online) Signal of the transmitted probe pulse modulation in Ge:Sb at different temperatures. The pump and probe pulse powers are $P_{pump} = 110$ W and $P_{probe} = 14$ W, respectively; the wavelength is $\lambda = 150$ μm.

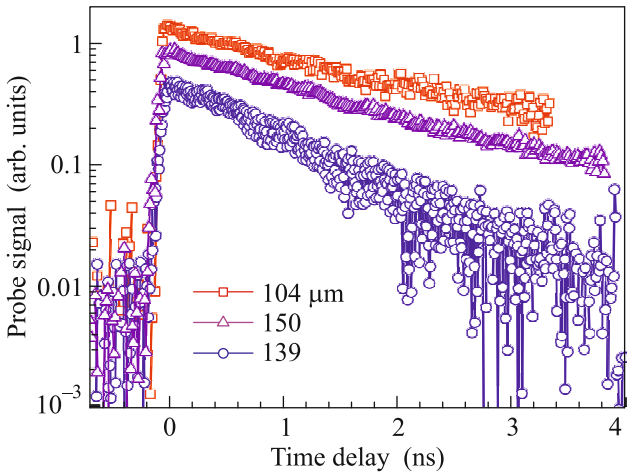

Fig. 3. (Color online) Signal of the transmitted probe pulse modulation for pump wavelengths of $\lambda = 104$, 139, and 150 μm. The pump and probe pulse powers are $P_{pump} = 190$ W, $P_{probe} = 19$ W; $P_{pump} = 160$ W, $P_{probe} = 2$ W; and $P_{pump} = 270$ W, $P_{probe} = 27$ W, respectively. The temperature is $T = 4$ K.

The response obtained for the $2p_{\pm}$ state in a sample compressed along the [111] direction is compared to that in an unstrained sample at a temperature of 4 K in Fig. 4. One can see both qualitative and quantitative differences in the pump–probe signal: the application of stress leads to the appearance of a short (~100 ps) peak near zero delay and to the general increase in the relaxation time to 3.2 ns. Figure 5 shows the arrangement of the donor levels in the absence of stress ($S = 0$) and for a [111] uniaxial stress $S > S_0$ corresponding to the situation where the valley splitting exceeds the "chemical" shift (about 0.4 meV for antimony) and it is safe to consider the ground state of impurity as formed by only one valley of the Ge conduction band [13]. The donor ground state is singlet and, for the case $S = 0$, is separated from the first excited level (triplet) by a small "chemical-shift" energy. For this reason, the contribution from the upper valleys to the ground-state wavefunction can be neglected for stresses $S > 300$ bar, and optical transitions from the ground state take place within a single valley.

For $S = 0$, the crystal possesses cubic symmetry and the choice of two mutually perpendicular polarizations for the pump and probe is arbitrary. Under a uniaxial stress $S > S_0$, $1s \to 2p_{\pm}$ transitions are allowed by the selection rules only if the electric field of the wave has a component perpendicular to the stress direction [111]. Thus, for $S > S_0$, we set the pump and probe polarizations at an angle of 45° to the [111] axis (see Fig. 6). This fact may lead to a difference in the behavior of the experimentally detected response for $S = 0$ and $S > S_0$ at delays about the pulse duration $\tau \sim \Delta t$.

Indeed, the polarization **P** induced in an unstrained crystal is parallel to the polarization of pump radiation and does not couple to the probe signal, and the recorded change in the absorption is proportional to the occupancy of the lowest state $\Delta\alpha \sim N_{1s}$. Under uniaxial strain, the polarization induced in the crystal by pump radiation is determined by the orientation of the valley along which the [111]

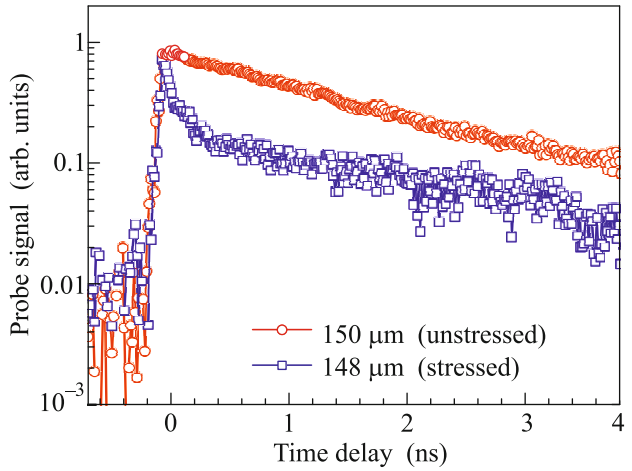

Fig. 4. (Color online) Signal of the transmitted probe pulse modulation in an unstrained Ge:Sb crystal and a Ge:Sb crystal uniaxially strained along the [111] crystallographic direction. The pump and probe pulse powers are $P_{pump} = 270$ W and $P_{probe} = 27$ W for $\lambda = 150$ μm and $P_{pump} = 180$ W and $P_{probe} = 18$ W for $\lambda = 148$ μm. The temperature is $T = 4$ K.

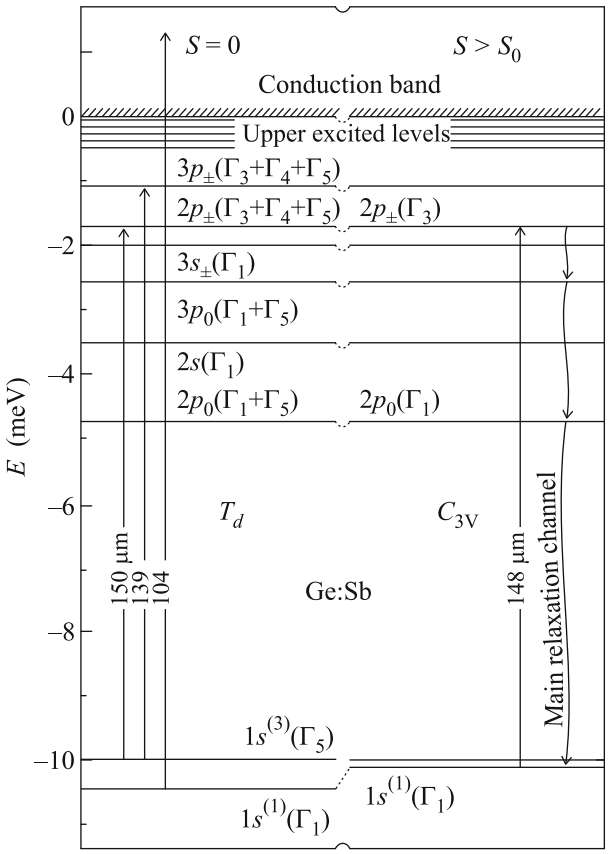

Fig. 5. Scheme of the energy levels in the Sb donor in unstrained and strained Ge crystals (left and right panels, respectively). Stress is applied along the [111] crystallographic direction. Upward arrows show the excitation lines. Wavy downward arrows show the most probable relaxation channel for $2p_{\pm}$ states.

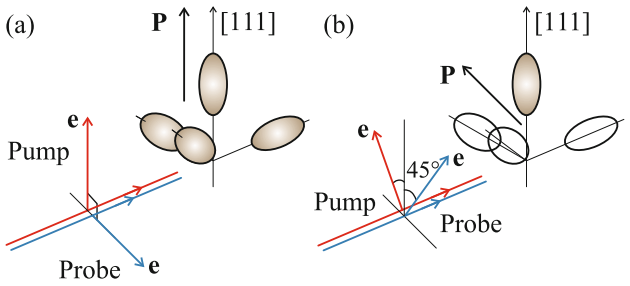

Fig. 6. (Color online) Relative orientations of the Ge conduction-band valleys and electric-field polarizations in the pump and probe pulses (a) for $S = 0$ and (b) under stress $S > S_0$.

compressive stress is applied and, in general, may be misaligned with respect to the polarization of the field in the pump wave. In the case of transitions into the $2p_{\pm}$ states for $S > S_0$, the vector **P** is perpendicular to the [111] direction and couples to the probe signal. Then, the change in absorption is proportional to the population difference $\Delta\alpha \sim N_{1s} - N_{2p\pm}$, a situation that can be avoided in a medium possessing cubic symmetry (unstrained crystal).

It is known that, in a two-level system in the field of a light wave, the electron undergoes oscillations at the generalized Rabi frequency $\Omega = (\mu^2 E^2/\hbar + \delta^2)^{1/2}$ (where μ is the matrix element of the transition induced by the field, E is the electric-field strength, $\hbar$ is the Planck constant, and δ is the detuning between the frequencies of the wave and the transition). According to our estimate, under the conditions of this experiment, $\Omega\Delta t \sim 1$ (where Δt is the duration of the excitation pulse).

Figure 7 shows the results of calculations of Rabi oscillations in an ensemble of impurity atoms under pulsed pumping for a set of parameters corresponding to the conditions of our experiment. One can see that the occupancy of the upper level experiences oscillations during the time of the pump pulse Δt, after which its value remains nearly constant and lower than the maximum.

Thus, the short peak in Fig. 4 can be attributed to the occurrence of Rabi oscillations in donor atoms, which cannot be directly measured in these experiments because of the limited time resolution, determined by the FEL pulse duration. The second, longer, part of the signal is associated with the relaxation of the donors to the ground state with the emission of acoustic phonons.

An increase in the relaxation time upon the application of uniaxial strain to the germanium crystal can be explained by both a reduction in the degree of degeneracy of the lower levels (since the wavefunctions of impurity states cease to include components associated with the upper conduction-band valleys) and by the "disabling" of the previously mentioned interaction with intervalley acoustic phonons.

Theoretical estimates indicate that the main relaxation channels for $2p_{\pm}$ states in unstrained and strained crystals are $2p_{\pm} \to 3p_0 \to 2p_0 \to 1s^{(3)}(\Gamma_5)$ and $2p_{\pm} \to 3p_0 \to 2p_0 \to 1s^{(1)}(\Gamma_1)$, respectively (see Fig. 5). The main difference between the relaxation times of $2p_{\pm}$ through these two channels is due to the difference between the relaxation rates of the intermediate $2p_0$ state: owing to the higher degeneracy of the $1s^{(3)}(\Gamma_5)$ state, the rate of $2p_0 \to 1s^{(3)}(\Gamma_5)$ transitions, relevant for an unstrained crystal, is higher than the rate of $2p_0 \to 1s^{(1)}(\Gamma_1)$ transitions in a crystal compressively strained in the [111] direction.

It should be mentioned that measurements of the relaxation time of shallow donors by nonequilibrium submillimeter spectroscopy in unstrained crystals [3] are in good agreement with the results obtained here for $2p_{\pm}$ states. We also note that the relaxation times

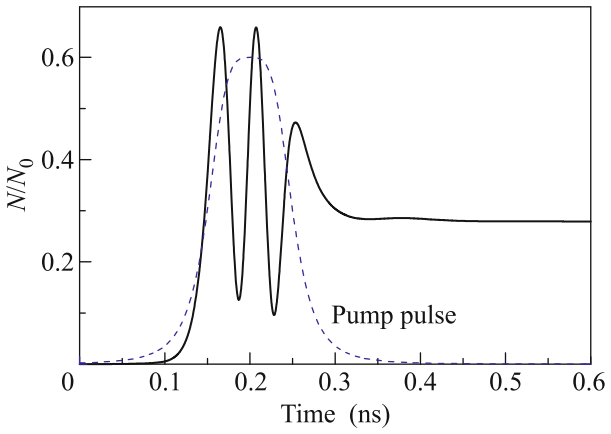

Fig. 7. (Color online) Average occupancy of $2p_{\pm}$ states induced by a pump pulse with an intensity of 3 kW/cm^2 and detuning $\delta = 0$ in an ensemble of impurity atoms characterized by inhomogeneous broadening of 0.1 ($2\pi \times 10^{12}$ s^{-1}).

obtained in our experiments are in the nanosecond range, while the relaxation times of the excited states of acceptors (gallium) measured using the same technique are an order of magnitude shorter [6]. As a test of the NovoFEL setup, we measured the relaxation time of one of the transitions obtained previously [5] and found that this time is indeed much shorter (200–250 ps).

CONCLUSIONS

We have measured the relaxation times of excited states of Sb shallow donors in germanium at cryogenic temperatures. Upon the excitation of $2p_{\pm}$ states, the electron relaxation time is about 1.8 ns at a temperature of 4 K and decreases to 0.8 ns with an increase in the temperature to $T = 30$ K. Upon the excitation of $3p_{\pm}$ states, the electron relaxation time is about 0.9 ns. This decrease in the relaxation time can possibly result from the proximity of the intervalley phonon band. Upon the application of uniaxial stress along the [111] crystallographic direction, the relaxation time of electrons from the $2p_{\pm}$ level becomes about 3.2 ns. We attribute this to an increase in the relaxation time from the $2p_0$ level to the $1s(A_1)$ ground level.

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