

Stimulated Terahertz Stokes Emission of Silicon Crystals Doped with Antimony Donors

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Stimulated Stokes emission has been observed from silicon crystals doped by antimony donors when optically excited by radiation from a tunable infrared free electron laser. The photon energy of the emission is equal to the pump photon energy reduced by the energy of the intervalley transverse acoustic (TA) g phonon in silicon (≈ 2.92 THz). The emission frequency covers the range of 4.6–5.8 THz. The laser process occurs due to a resonant coupling of the $1s(E)$ and $1s(A_1)$ donor states (separation ≈ 2.97 THz) via the g -TA phonon, which conserves momentum and energy within a single impurity center.

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In the past few years, significant progress has been made towards silicon based lasers. Silicon is an indirect band gap semiconductor. Therefore, it is difficult to realize an efficient process for light amplification. This fact compels the search for nontraditional approaches for light generation. In the near infrared region, numerous approaches (see Ref. [1] for a review) to overcome this difficulty, such as silicon nanocrystals [2,3], Si/SiO₂ [4] and Si/SiGe [5] superlattices, porous silicon [6], erbium-doped silicon [7], and silicon light-emitting diodes [8], have been attempted. Recently, the first silicon lasers operating at 1.540 and 1.675 μm based on stimulated Raman scattering have been reported [9,10]. The Raman effect in silicon occurs via scattering of photons by optical phonons of the crystal. The strongest Stokes emission is due to the threefold degenerate short-wavelength optical modes at the center of the Brillouin zone of silicon [11].

The first silicon laser was realized by infrared optical excitation of group-V donor centers embedded in a silicon host lattice [12,13]. For this type of laser, the interaction between phonons and electrons is essential. Except zone-centered optical phonons, intervalley acoustic and optical phonons have been found to play a decisive role in energy and momentum relaxation for nonequilibrium charge carriers in silicon [14,15]. Strong resonant intervalley phonon-impurity interaction has been observed in absorption spectra of Bi donors in silicon [16]. When the phonon energy does not exactly coincide with the energy between two impurity states, the contributions from the electronic impurity state and the phonon-related part form a “mixed”

state, as in silicon doped by Ga [17]. These interactions play an important role in the formation of population inversion between excited states, eventually leading to lasing on particular intracenter transitions in Si:Bi [18] as well as in Si:As [19]. A different situation occurs in silicon doped by antimony (Si:Sb). The energy of the transverse acoustic g -TA intervalley phonon and the energy between the $1s(E)$ and $1s(A_1)$ states are almost equal (~ 12 and 12.27 meV, respectively). This enhances the nonradiative electronic relaxation between these states. Terahertz intracenter laser emission in Si:Sb has been observed when the crystal was excited by radiation from a pulsed CO₂ laser [20]. The population inversion is formed due to a cascade-type capture of photoexcited electrons from the conduction band into excited donor states, following their accumulation in the relatively long-living $2p_0$ state. The intracenter Si:Sb laser operates at low lattice temperature ($T < 15$ K). The emission spectrum consists of a single line at 5.15 THz [$2p_0 \rightarrow 1s(T_2)$ transition] [21]. In this Letter, we report on a laser with variable emission frequency in the terahertz spectral region, based on Si:Sb optically excited by a frequency tunable infrared free electron laser.

Silicon crystals doped with antimony at a concentration of $N_D = 4 \times 10^{15} \text{ cm}^{-3}$ were grown by the float zone technique in the [111] direction. The investigated Si:Sb sample is a rectangular parallelepiped of $8 \times 7 \times 5 \text{ mm}^3$. Four facets were polished to form a resonator on total internal reflection modes. The free electron laser (FEL) generates $\sim 6 \mu\text{s}$ long macropulses at a 5 Hz repetition rate in the range 31–43 meV. Each macropulse consists of a

train of micropulses with duration between 3 and 10 ps separated by 1 ns. The spectrum of the emission pulse has a Lorentzian shape with a full width at half maximum (FWHM) of 0.1–0.2 meV. The silicon crystals were cooled to ~ 5 K in a continuous flow liquid helium (lHe) cryostat and optically excited by the FEL radiation. The power on the sample was controlled by a step attenuator. The largest facet of the sample ($\langle 111 \rangle$) was irradiated (inset in Fig. 1). The emission was detected by a lHe cooled Ge:Ga detector with a rise time of ~ 50 ns. FEL radiation was blocked by a room-temperature crystalline quartz filter in front of the detector (cutoff energy > 31 meV). The emission was spectrally analyzed by a Fourier transform spectrometer with a resolution of ~ 0.5 cm $^{-1}$ (0.06 meV).

At a certain pump power, a pronounced threshold is observable above which the output power of the Si:Sb laser increases by several orders of magnitude (Fig. 1). This is an indication of a laser process. The higher the impurity state, which is optically populated, the higher the laser threshold. It is important to note that laser emission appears not only when the pump transition ends in one of the excited donor states but also when the pump frequency does *not* correspond to any transition frequency between the $1s(A_1)$ ground state and an excited state of an impurity atom (33.45 meV curve in Fig. 1). In this case, the laser threshold is the highest, but the signal does not exhibit any pronounced saturation with increasing pump power as observed when pumping into the odd-parity excited donor states.

The spectra measured for pump photon energies in the range 31–40 meV show two types of lines with different properties (Fig. 2). The frequency of one line does not depend on the pump frequency, and its frequency corresponds to the $2p_0 \rightarrow 1s(E)$ intracenter transition of Si:Sb as determined by spectroscopy [22]. The other line changes its frequency proportional to the pump photon energy from 19.2 to 24.1 meV (4.6–5.8 THz). Its linewidth is significantly broader (FWHM $_S = 0.18$ –0.76 meV) than that of

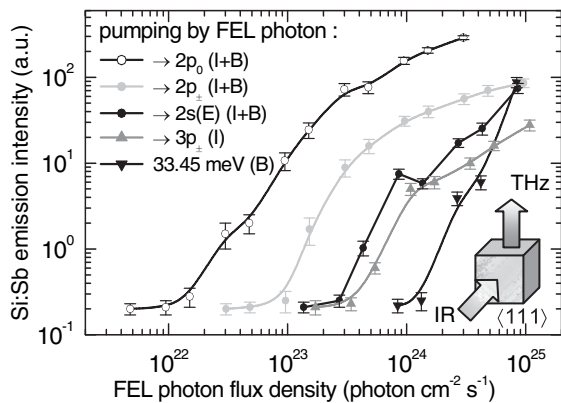


FIG. 1. Typical Si laser thresholds. The pumped Sb states and pump photon energy are shown in the left corner (inset: sketch of the experiment).

the intracenter line (FWHM $_I = 0.12$ –0.20 meV). For direct pumping into one of the excited donor states such as $2p_0$, $2s$, $2p_{\pm}$, both lines appear simultaneously. When pumped into the $2p_0$ state, their energies differ by 0.37 meV. This is another indication that the lines are of different origin. The relation between the energies of the pump and the emitted light is

$$\hbar\omega_S = \hbar\omega_P - (12.10 \pm 0.02) \text{ meV}. \quad (1)$$

The energy of the emitted photon $\hbar\omega_S$ differs from the pump photon energy $\hbar\omega_P$ by a constant value of 12.10 ± 0.02 meV, which is close to the energy of the intervalley g -TA phonon in silicon $h\nu_{g\text{-TA}}$. Magnetophonon resonance technique gives $h\nu_{g\text{-TA}}$ values of 11.3 meV (for magnetic field direction $\langle 111 \rangle$), 12 meV ($\langle 110 \rangle$), and 12.2 meV ($\langle 100 \rangle$) for pure silicon at a lattice temperature of 65 K [11]. Intervalley scattering in n -silicon involving the transfer of an electron in a $[100]$ -type direction to the equivalent valley (g scattering) is an umklapp process, in which the sum of the wave vector \mathbf{q}_g of the g phonon and the change of the wave vector of the electron $\Delta\mathbf{k}$ is equal to a principal vector of the reciprocal lattice \mathbf{K}_{001} . Momentum conservation for this process can be written as

$$\Delta\mathbf{k} = \mathbf{K}_{001} \pm \mathbf{q}_g. \quad (2)$$

Intervalley phonons can accelerate the intracenter relaxation of an electron if the energy of the phonon coincides

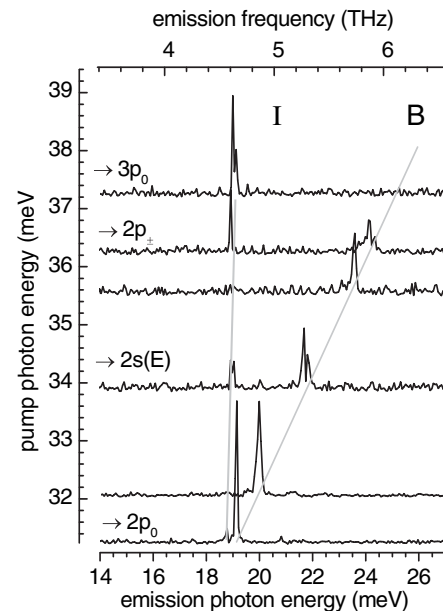


FIG. 2. Emission spectra from Si:Sb taken at different pump frequencies (same symbols as in Fig. 1). The accuracy of the central wavelength of the FEL pump pulse is < 0.01 meV and the FWHM is ~ 0.1 –0.2 meV. The instrumental resolution for the emission spectra is ~ 0.06 meV. The dip in the emission spectrum (when pumped in the $2s$ state) is due to atmospheric absorption at ~ 21.8 meV.

with the energy gap between a pair of particular impurity states. In the resonant intracenter interaction, the $\Delta\mathbf{k}$ wave vector is reduced to the wave vector connecting the extrema of two opposite valleys in the conduction band, so that, in the reduced Brillouin zone, the intracenter relaxation due to scattering on a g phonon occurs as a “vertical” transition (no change of the momentum of an electron is required). Equations (1) and (2) describe the energy and momentum conservation for the observed emission (Fig. 3). We call this emission process Brillouin-type (B) lasing since it involves acoustic g -TA phonons in contrast to Raman silicon lasers [9,10] where an optical phonon is employed. The specific feature of this emission is that the photon scattering occurs at the antimony donor center. The laser transition corresponds to Stokes scattering component and originates always from the pumped state (virtual or excited donor) and terminates about 0.3 meV below the $1s(E)$ level. We assume that this is an indication for a mixed $1s(E)$ state with an electronic part $1s^{\text{EL}}(E)$ and a phonon-related part $1s^{\text{PH}}(E)$, which is induced by strong interaction with the g -TA phonon, similar as in Si:Ga [17]. Momentum conservation is obtained because the umklapp scattering process of Eq. (2) cancels the large momentum of the emitted g -TA phonon [$q_{g\text{-TA}} \approx 3.4 \times 10^7 \text{ cm}^{-1} \gg \omega_p(n/c), \omega_s(n/c)$; here n is the refractive index of silicon and c is the velocity of light (see Fig. 3)]. No emission was observed when pure (residual doping $\sim 10^{13} \text{ cm}^{-3}$) silicon crystals were optically pumped.

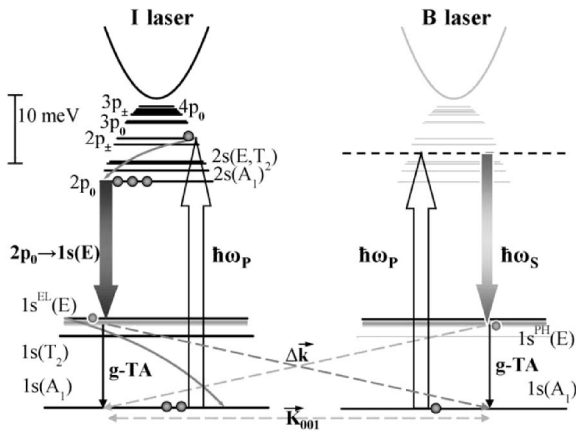


FIG. 3. Schematic energy diagram of the intracenter (I laser) and the Brillouin-type (B laser) mechanisms in Si:Sb. The two parts of the graph represent two opposite equivalent valleys of the silicon conduction band. Gray bold arrows are for stimulated emission; hollow up arrows indicate optical pump transitions. Diagonal arrows indicate intervalley phonons. Curved arrows are for cascade relaxation of electrons due to intravalley acoustic phonon-assisted transitions. Donor states are labeled as in Ref. [24]; $1s^{\text{EL}}(E)$ and $1s^{\text{PH}}(E)$ represent the electronic (black thin line) and phonon-related (graded gray rectangle) contributions, respectively, in the mixed $1s(E)$ donor state [separation of the $1s^{\text{EL}}(E)$ and $1s^{\text{PH}}(E)$ states is not to scale].

Therefore, the presence of antimony impurity centers is mandatory for the Brillouin-type lasing. Since no absorption of FEL radiation was registered at photon frequencies corresponding to pumping in between the $2p_0$ and $2p_{\pm}$ states, only a pair of principle electronic states taking part in the g -TA phonon-assisted electron relaxation, i.e., $1s^{\text{PH}}(E)$ and $1s(A_1)$ states, can be involved in this laser mechanism, while pumping and emission occur via a virtual state (dashed line in Fig. 3, on the right). On the contrary, for intracenter lasing, pumping occurs exclusively in the dipole-allowed optical transitions terminating in the odd-parity donor excited states. At least three donor levels, always including the long-living $2p_0$ state and the short-living $1s^{\text{EL}}(E)$ state, are involved in the I -laser mechanism (Fig. 3, on the left).

One may systemize the observed laser emission as follows. There are three different cases: pure intracenter emission (I), pure Brillouin-type emission (B), and simultaneous emission of both ($I + B$). I lasing is similar to what was observed for Si:P under intracenter pumping. Photoexcited electrons accumulate in the long-living $2p_0$ state, which is the upper laser level for all pump photon energies. In contrast to the Si:P laser, the lower laser level is the $1s(E)$ state independent of the pump transition [23].

Brillouin-type lasing has a different nature. Pure B emission occurs when the Si:Sb crystal is pumped with a photon energy out of resonance with an excited impurity state. It occurs for pump photon energies between 31 meV, the smallest available energy in the experiment, and 36 meV. Above 36 meV, the pump process is apparently not efficient enough to maintain laser emission. B lasing has a lower efficiency than I lasing and requires peak pump intensities of $\sim 5\text{--}50 \text{ kW cm}^{-2}$ for pure Brillouin-type lasing compared to $\sim 0.1\text{--}10 \text{ kW cm}^{-2}$ for I lasing. With respect to I emission, the pure B emission is relatively unstable and delayed by about $1.5 \mu\text{sec}$ (Fig. 4). Above the laser threshold, B emission grows rapidly with the pump intensity and does not saturate (Fig. 1). For direct pumping into an excited state, the absorption length of the pump radiation is $\sim 0.5 \text{ mm}$ due to the large optical cross section for intracenter donor transitions ($\sim 10^{14} \text{ cm}^2$ [24]). Therefore, the gain volume of the I laser is much smaller than the Si:Sb crystal. In contrast, the Brillouin-type emission uses the entire volume due to the smaller cross section at frequencies out of resonance with donor transitions. The g -TA phonon dispersion is determined mainly by momentum-space localization of the $1s(E)$ state, which is much larger than the free-spectral range of the Si:Sb laser ($\sim 0.04\text{--}0.09 \text{ cm}^{-1}$). Hence, the Brillouin-type gain always overlaps with a number of eigenmodes of the Si:Sb laser resonator. One can estimate the gain of the Brillouin-type laser using the method described in Ref. [25] and scaling the magnitude of the scattering susceptibility from the infrared to the terahertz frequency range. Taking the measured Brillouin linewidth of 0.2 meV at

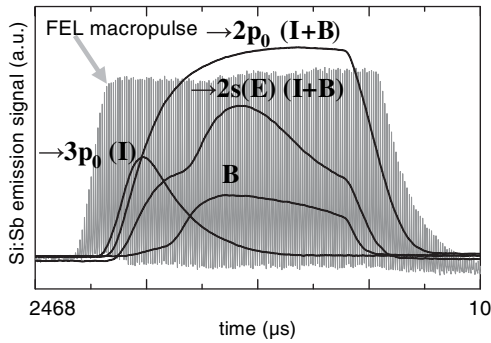


FIG. 4. Typical silicon laser emission pulses (black lines) with the corresponding pump Sb states. The flat top of the emission pulse when pumped in the $2p_0$ impurity state is due to saturation of the Ge:Ga detector. The FEL macropulse (gray) is recorded using a fast infrared photodetector.

$\omega_S = 3.32 \times 10^{13} \text{ sec}^{-1}$, one calculates a gain per unit pump intensity of $\gamma_S \approx 1.7 \times 10^{-3} \text{ cm MW}^{-1}$ at a lattice temperature of 77 K. Another way to estimate the gain is from the exponential intensity increase at the very start of the B emission. For a pump energy of $\hbar\omega_p = 33.45 \text{ meV}$, this yields $7.4 \times 10^{-3} \text{ cm MW}^{-1}$, somewhat larger than the previous value. The difference might be caused by an enhanced scattering of pump photons due to the resonance of the g -TA phonon with the interstate energy gap $1s(E) - 1s(A_1)$, also known as resonant Brillouin scattering [26].

Simultaneous intracenter and Brillouin-type emission ($I + B$) appears for excitation into the $2p_0$ state, the $2s(E)$ state, and the $2p_{\pm}$ state. In these cases, scattering of pump photons is enhanced by both incoming [$\omega_p: 1s(A_1) \rightarrow \text{ex.st.}$] and outgoing [$\omega_p: \text{ex.st.} \rightarrow 1s(E)$] resonance with impurity states. Excitation into higher states yields only I emission. In the case of resonant pumping into the $2p_0$ state, I - as well as B -laser emission have the lowest pump threshold (Fig. 1), with B emission much stronger than I emission and without any delay (Fig. 4). Pumping into donor states higher than $2p_0$ involves intracenter relaxation of electrons into the $2p_0$ state and, thus, is less efficient. In this case, B emission appears always with a significant delay after I emission. The time delay of B lasing with respect to I lasing is caused by the comparatively low gain of the Brillouin-type process. I lasing is dominating due to its larger optical cross section [$\sim(1-7) \times 10^{-15} \text{ cm}^2$ [24]], which results in a gain of $\sim 1 \text{ cm}^{-1}$ at moderate pump intensities. The power of Brillouin-type emission decreases with increasing pump photon energy, where the intracenter transitions contribute more (or solely) to the laser emission. This is apparently due to high density of the impurity states above $3p_0$ and the dominating role of intracenter relaxation over scattering processes.

In summary, we have shown that Brillouin-type stimulated Stokes emission based on resonant scattering by

intervalley transverse acoustic g phonons is realized in silicon doped by antimony donors. The emission frequency can be varied over a wide range between 4.6 and 5.8 THz by changing the pump laser frequency. The low gain of this laser mechanism, $\sim 10^{-3} \text{ cm}^{-1}$ at a pump intensity of 100 kW cm^{-2} , results in a few microsecond delay for the buildup of the laser signal. The multivalley structure of excited donor states in silicon allows for the compensation of the large phonon momentum needed for the laser emission within a single Coulomb center.

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