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Even-Parity Excited States in Infrared Emission, Absorption, and Raman Scattering Spectra of Shallow Donor Centers in Silicon

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The Lyman absorption spectra of different shallow dopants in elemental semiconductors at liquid-helium temperature show typically transitions from the even-parity ground state to odd-parity excited states. Such transitions are dipole allowed and observed by absorption spectroscopy. Knowledge on the excited states with other type of symmetry can be derived from absorption and Raman spectra of a heavily doped semiconductor, or at experimental conditions enabling optical dipole-allowed transitions from or into even-parity states. Here, we report on the experimental observation of impurity transitions involving different excited even-parity (*n*s- and *n*d-) states in silicon crystals: 1) doped with group-V hydrogen-like donors in samples with large infrared absorbance, and 2) doped with the magnesium double donor evoking a thermal population of the lowest even-parity excited states.

1. Introduction

The energy structure of the main impurity centers in semiconductors is a key element for design and prediction of the performance of electronic devices. Even in devices for which the operation relies on free charge carriers, impurity centers determine many core parameters such as electron mobility, speed of operation, as well as optical and thermal properties. For silicon-based devices utilizing intracenter processes, ranging from intracenter semiconductor lasers[1] to impurity-based quantum computing technologies,[2] the detailed knowledge of the energy structure of doping centers is a starting point for any reasonable design. Even-parity excited states, which are strongly involved in nonradiative cascade-type intracenter electronic relaxation processes,[3] determine different impurity-phonon resonances.

Odd-parity states of impurities can be directly determined from infrared Lyman absorption spectra of a semiconductor, showing dipole-allowed transitions from a ground impurity state, which is for substitutional centers in silicon a singlet even-parity state. Shallow hydrogen-like impurities as well as multiple charge centers in elemental semiconductors exhibit a hydrogen-like energy spectrum of odd-parity states, which can be accurately modeled in the frame of the effective mass theory (EMT),[4] while their even-parity states differ significantly[5] and are subject of experimental determination. The complex band structure often hampers accurate calculations of binding energies of even-parity excited states. This is why even in well-studied elemental semiconductors research groups revisit and improve the experimental determination of these states by different techniques (see e.g.,[6] for boron doped silicon). In addition, the detailed energy structure of some of the classic dopants, for example, boron in diamond, is still under debate.[7] Most reliable theoretical calculations of the binding energies of excited even-parity states of hydrogen-like centers rely on empiric data of known binding energies of even-parity states, or at least of the impurity ground state.[8,9]

For impurities different from hydrogen-like types, including interstitial centers, only rather coarse estimates of both the energy structure and the values of binding energies are available.

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Several unavoidable defect/impurity atoms, such as oxygen and carbon in silicon, tend to form defect-dopant associations,[10,11] which can affect the concentrations of electrically active impurities, and by this the strength of impurity transitions and the determination of their excited states. Thus, knowledge on binding energies of even-parity states in elemental semiconductors remains an important research topic.

In this work we focus on monoatomic electrically active impurity centers. We summarize the experimental data on binding energies of some excited even-parity states for a set of single substitutional and double interstitial (magnesium) donors in silicon. Also, we compare the accuracy of different experimental techniques, such as various forms of infrared absorption spectroscopy, electronic Raman scattering, photoluminescence as well as emission spectroscopy of optically pumped intracenter terahertz silicon lasers. Beside advantages of multiple equilibrium and nonequilibium spectroscopic techniques used in this work, a remarkable technological progress in production of high quality, research grade samples, especially silicon doped by bismuth and by magnesium, has enabled such investigation.

2. Samples

Monocrystalline float-zone (FZ) grown silicon crystals have been used for the preparation of samples with different dopants, namely substitutional group-V shallow donors (P, As, Sb, Bi) and the interstitial, group-IIa magnesium double donor (Mg). Special attention has been forgiven to the purification of the original silicon crystals and the following growth and doping processes in order to reduce the oxygen and carbon content as well as the formation of related complexes as far as possible. Group-V dopants were introduced during the crystal growth process. A pedestal growth has been used to obtain significant Bi concentrations ($N_{Bi} \geq 10^{15}\,cm^{-3}$) in Si crystals. Some crystals have been prepared with a special axial gradient of the dopant which allows for a targeted impurity concentration. Magnesium doped crystals have been obtained by high temperature diffusion employing a "sandwich" technique, see for details ref. [12].

Samples with typical flat areas $10 \times 10\,mm^2$ have been cut from the grown crystals. The sample thickness d (ranging from 350 to 2000 μm) has been chosen in order to maximize the "optical thickness" σNd, that is, the absorbance of weak optical transitions with low cross-section σ. Finally the samples have been wedged to 1.5°–2° and the large facets were optically polished.

3. Results

3.1. Low-Temperature Absorption Spectroscopy

Even-parity excited states with relatively small binding energies become observable in low-temperature impurity absorption spectra at moderate concentrations from above $10^{16}\,cm^{-3}$. The appropriate choice of optical thickness for the investigated sample allows observing transitions from the ground state to a few even-parity states, while infrared light with frequencies of dipole-allowed transitions becomes fully absorbed. In **Figure 1** infrared

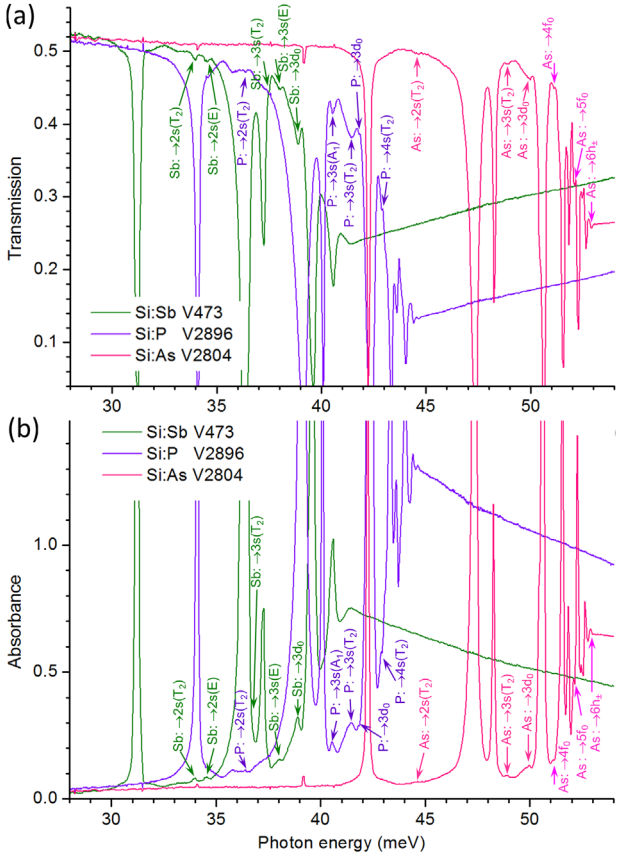

Figure 1. Low-temperature (4.2 K) impurity absorption spectra for silicon samples doped by group-V donor centers, concentrations of the donors are: $N_{Sb} \approx 7.0 \times 10^{15}\,cm^{-3}$, $N_P \approx 1.0 \times 10^{16}\,cm^{-3}$, $N_{As} \approx 6.9 \times 10^{15}\,cm^{-3}$. Transitions to even-parity states are marked. Transitions to high odd-parity As states which are not reported before are marked in magenta color. Note that some transitions well resolved in the transmission spectra (a) lose their easy identification in the derived absorption spectra (b).

absorption spectra of silicon crystals with three different dopants are shown. The spectra were taken with a Bruker Vertex 80v spectrometer equipped with a liquid helium cooled silicon bolometer. The samples were kept in a Janis ST100 liquid-helium flow cryostat at a fixed temperature of 4.2 K. The spectral resolution was 16 μeV and the number of the averaged scans was 64.

Note that beside the well-known strong absorption lines corresponding to dipole-allowed intracenter transitions from the ground donor state, $1s(A_1)$, into the odd-parity excited states (marked in different colors corresponding to the color label of the particular dopant), there are also weak lines at photon energies, which fit well to the transitions from the $1s(A_1)$ state into the even-parity states considering the calculated values of binding energies in ref. [8]. As it was shown earlier[13] such transitions which are not infrared-active become observable in samples with moderate doping due to perturbations caused by large concentration of substitutional impurity centers in the silicon lattice. Additionally, optical transitions to a few highly excited nf-, nh-type states have been observed for the first time. A comparison of the derived binding energies for even-parity states is shown in **Table 1**.

Table 1. Comparison of the binding energies (meV) of some even-parity donor states in silicon derived from different spectroscopic techniques with the theoretical calculations. The temperature for the experiments is ≈5 K, unless something else is shown.

State	Donor	Infrared absorption	Infrared absorption at elevated T	Si lasing spectra	e-Raman or PL spectra	Theory[8]
1s(E)	P		32.55[25] (45 K) 32.58[26] (30 K)	32.61 ± 0.06	32.56[15]	32.7
	As		31.26[25] (59.9 K) 31.26[22] (59 K)	31.34 ± 0.02	31.44[15]	31.2
	Sb		30.55[25] (30.1 K) 30.47[26] (30 K)	30.50 ± 0.02	30.59[15]	30.5
	Bi	30.15[23]	29.9[25] (89.4 K) 30.1[20] (89.4 K)	30.17 ± 0.02	30.56	31.26[5]
	Mg°		47.4 ± 0.1 (110 K)			
1s(T_2)	P		33.88[25] (45 K) 33.89[26] (30 K)	33.91 ± 0.03		34.2
	As		32.69[25] (59.9 K) 32.67[26] (59 K)	32.70 ± 0.02		32.6
	Mg°		49.9 ± 0.2 (110 K)			
1s(T_2:Γ_7)	Sb		33.16[25] (30.1 K) 32.91[26] (30 K)			
	Bi	32.89[25]		32.63 ± 0.01		
1s(T_2:Γ_8)	Sb		32.86[25] (30.1 K) 32.89[26] (30 K)	32.83 ± 0.02		32.9
	Bi	31.89[25]	32.08[20] (89.4 K)	31.88 ± 0.03		
2s(A_1)	P				10.61[18]	10.3
	As				11.28[18]	10.9
2s(T_2)	P	9.19 ± 0.01			9.07[19]	9.19
	As	9.14 ± 0.02 9.11[25]				9.01
	Sb	8.80 ± 0.01				9.04
2s(E)	Sb	8.24 ± 0.01				8.76
2s	Bi	8.78[25]		8.83 ± 0.02		8.86[5]
3s(A_1)	P	5.15 ± 0.01			5.32[18]	5.22
	Sb	5.25 ± 0.03				5.15
3s(T_2)	P	4.11 ± 0.01				4.88
	As	4.85 ± 0.01				4.82
	Sb	4.74 ± 0.01				4.83
3d_0	P	3.76 ± 0.01 3.82[25] 3.73[26]				3.75
	As	3.78 ± 0.01 3.8[25]				3.75
	Sb	3.86 ± 0.01				3.75
4s(T_2)	P	2.7 ± 0.1				2.92

3.2. Low-Temperature Electronic Raman Scattering Spectroscopy

There are a few Raman-active intracenter transitions for donors and acceptors in silicon.[6,14–16] For group-V donors this is the 1s(A_1) ↔ 1s(E) transition. This transition has been observed in the electronic Raman spectra taken under excitation with an infrared 1064 nm laser at low lattice temperatures for the P, Sb, As dopants at concentrations almost at the metal-insulator phase transition in silicon.[15] We have used a Labram HR800 Horiba multi-wavelength Raman spectrometer equipped with a liquid helium flow cryostat for observation of electronic Raman spectra from Bi doped silicon crystals. Raman spectra obtained with visible lasers (514 and 633 nm) do not exhibit electronic Raman features apparently due to a small number of scattering centers within the volume limited by the light absorption. At infrared wavelengths (785 nm, 31 mW, 1 min acquisition time) such transition appears at the Stokes shift of ≈326 cm^{-1} (**Figure 2**) that corresponds to the binding energy of the 1s(E) Bi state of 30.56 meV.

Note that to date only shallow group-V and group-III centers have been shown to exhibit the electronic Raman features for

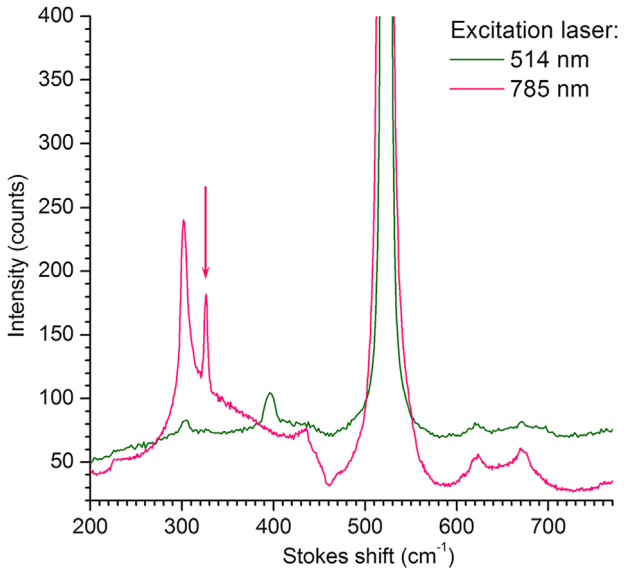

Figure 2. Low-temperature (5 K) Raman spectrum of the Si:Bi V443 sample ($N_{Bi} \approx 3.0 \times 10^{15}$ cm^{-3}) under different laser excitation. The arrow indicates the electronic Raman resonance corresponding to the 1s (A_1) → 1s(E) bismuth donor transition. One spectral bin is ≈0.6 cm^{-1} at 785 nm and better than 2.4 cm^{-1} in the visible wavelength range.

their Raman-active transitions. Despite the optimum choice of the excitation laser (below the band gap photon energy) no electronic Raman scattering has been observed in Si:Mg.[17] Some even-parity excited states for P, As, Li donors in silicon were observed in the photoluminescence spectra.[18,19]

3.3. Variable-Temperature Absorption Spectroscopy

Split-off-ground states with large binding energies can be accessed by either their thermal population or by analysis with non-equilibrium spectroscopy. Thermal population of the lowest excited states enables dipole-allowed absorption transitions from the lowest even-parity excited state.[20] In general, the strongest transitions into the $2p_0$ and $2p_\pm$ donor states are observed at elevated temperatures. The temperature range for optimal observation of such transitions depends on the valley-orbit split (VOS) energy, Δ, which varies from less than 10 meV for the most shallow Sb center in silicon to almost 40 meV for the deepest group-V Bi donor, see **Figure 3**. This figure also contains data for interstitial Mg° centers. The experiments with variable temperature of the samples have been carried out using the same equipment as for low-temperature absorption spectroscopy (section 3.1) using a temperature controller for the liquid helium flow cryostat.

The 1s(T_2), 1s(E) → $2p_\pm$ transitions of the neutral Mg donor center (line positions are at 351.4 cm^{-1} [43.57 meV] and at 330.87 cm^{-1} [41.02 meV]) have been observed (**Figure 4**) at relatively high lattice temperature (peak intensity at about 105–110 K) and only for the heavily doped Si:Mg samples ($N_{Mg} \approx 6.0 \times 10^{15}$ cm^{-3}). Considering the binding energy of the odd-parity state $2p_\pm$ as 6.38 meV,[21] we conclude that the binding energies for the VOS ground states of the neutral double Mg° donor are 47.4 ± 0.1 meV (1s(E)) and 49.9 ± 0.1 meV (1s(T_2)). We were also able to derive the binding energy of the 1s(T_2) Mg°-state from the absorption spectrum of an uniaxially stressed Si:Mg sample. The transitions 1s(B_2) → $2p_0{}^{2\Delta}$, $2p_\pm{}^{2\Delta}$ within the valleys along the applied deformation ($^{2\Delta}$) have been observed at 307.36 cm^{-1} (38.11 meV) and at 350.09 cm^{-1} (43.41 meV) at a lattice temperature of 90–110 K. These data yield the binding energy of the unstressed 1s(T_2) state as 49.8 ± 0.1 meV.

3.4. Even-Parity State Energies Derived From Emission Spectra of Intracenter Si Lasers

The energies of a few particular even parity states can be derived from the frequencies of THz stimulated emission caused by infrared optical pumping of donors in silicon at low lattice temperature (**Figure 5**).[22] Such transitions belong to a four-level

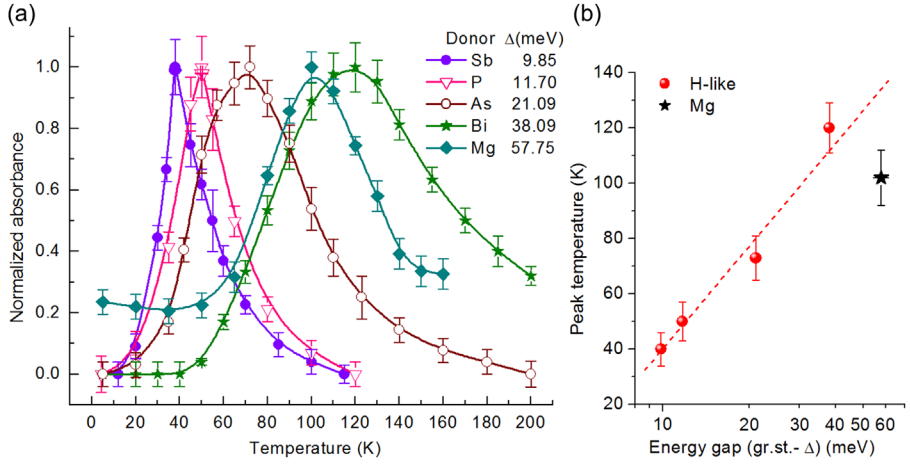

Figure 3. a) Temperature ranges for observation of dipole-allowed optical intracenter transitions from valley-orbit-split energy Δ ground states for a set of shallow donors in silicon; b) semi-log plot showing the temperature where the largest magnitude of the intensity of the transitions from the VOS states of different donors into the higher excited odd-parity states occurs.

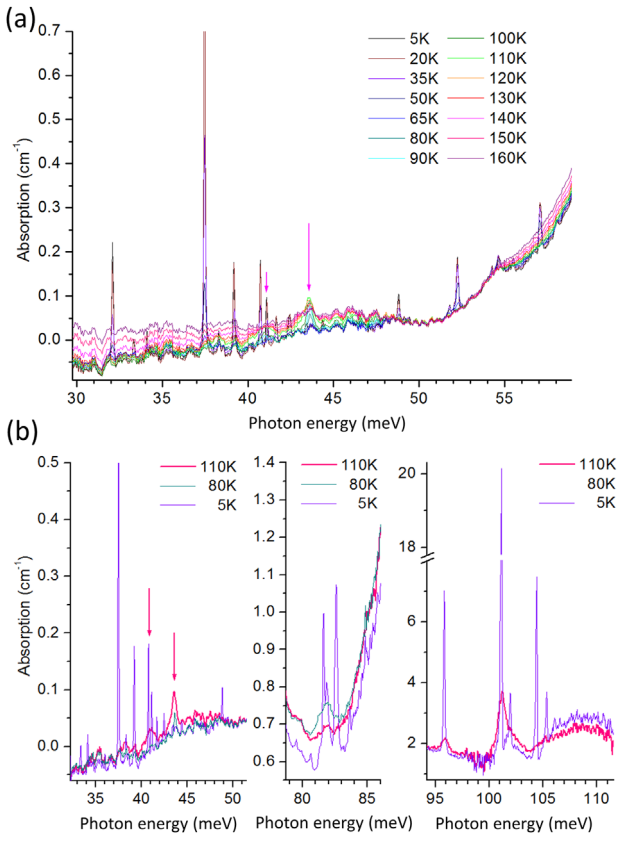

Figure 4. a) Infrared absorption spectra of the Si:Mg 138-2 sample ($N_{Mg} \approx 6.0 \times 10^{15}$ cm^{-3}) at different lattice temperatures. The arrows indicate absorption lines whose magnitude grows between 90 and 110 K. Note that all other Mg° absorption lines, seen at low temperature, have monotonously decreasing intensity with increasing temperature. b) The same, zoomed in specific spectral ranges for clarity.

laser scheme and terminate in different even parity excited donor states, which are usually the VOS ground states. Due to the spectrally narrow lasing line, an accurate determination of the binding energy of the even-parity state becomes possible. Such experiments have been performed under optical pumping by either a pulsed CO_2 laser (Edinburgh Instruments) with pumping wavelengths between 9.2 and 10.8 μm or by radiation of an infrared free electron laser (FEL) at the FELIX Laboratory (Radboud University, Nijmegen, The Netherlands) with wavelengths in the range from 17 to 41 μm. Si lasing spectra were acquired with a step-scan Fourier transform spectrometer with a spectral resolution down to 0.1 cm^{-1} and a Ge:Ga far-infrared liquid helium cooled detector.

When pumped by an infrared tunable free electron laser (FEL) source, some even-parity states cause spectral signatures in the dependences of the integrated stimulated Raman signal intensity on the pump wavelength.[22] This method, however, does not give sufficiently precise values of the state energies because of the relatively broad FEL radiation spectrum (the linewidth is typically larger than 0.3% of the central wavelength).

4. Discussion

The derived binding energies for high excited *n*s- and *n*d-states of the group-V donors in silicon fit well to the theoretical values, as predicted by the effective-mass theory (EMT) with a model Hamiltonian, adjusting the energy of states expressed by the elliptical trial wave functions to the experimentally known energies of the ground and odd-parity excited states.[8]

Although the $1s \rightarrow ns$ dipole transitions are not allowed in the frame of the EMT, the accurate calculations using realistic wave functions of the impurity states in cubic semiconductors yields the non-vanishing probability of the $1s(A_1) \rightarrow ns(T_2)$ transitions due to the "p-like" contribution in the wave function of T_2 triplet state.[23] The probability of such optical transition strongly depends on valley-orbit coupling of a particular state, and the

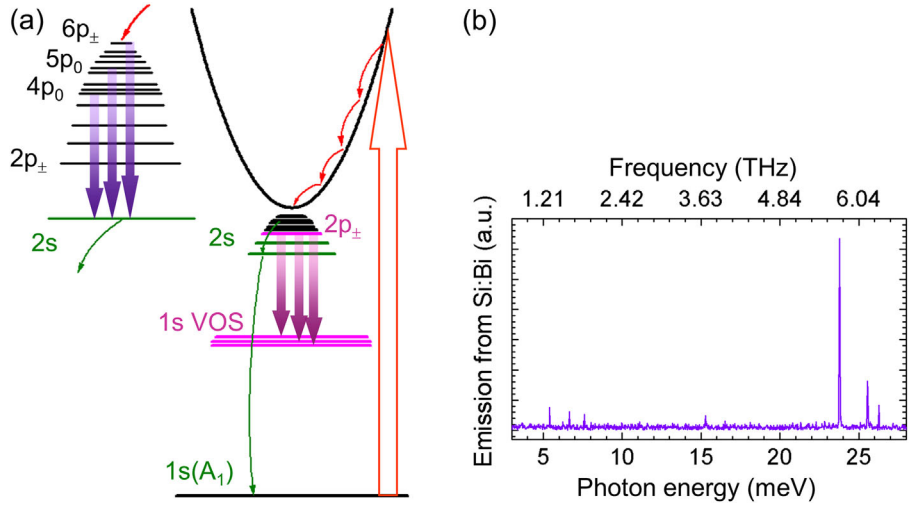

Figure 5. Different lasing transitions observed under photoionization pumping of Si:Bi #0.35 ($N_{Bi} \approx 3.0 \times 10^{15}$ cm^{-3}) by CO_2 laser emission (9.6–10.6 μm) at low temperature (5 K). a) The lasing transitions terminate in particular even-parity states, depending on the pump wavelength. b) Laser emission spectrum under photoionization pumping.

larger the deeper is the excited state. Obviously, heavy doping increases optical absorption, and by this, observability of these transitions.

Observation of the $1s(A_1) \rightarrow ns(E)$, $ns(A_1)$ transitions is feasible by electronic Raman scattering, however, only the $1s(A_1) \rightarrow 1s(E)$ Raman active transition is usually observed due to its larger matrix element.[14] Moreover, optimum wavelength of an excitation laser, such as just below the band gap of the semiconductor,[6,17] is desired for observation of electronic Raman scattering.

For the relatively shallow donors in silicon, one can use thermal population of the deepest excited 1s(E), $1s(T_2)$ states[20] at the expense of thermal broadening and shifts of the 1s(E), $1s(T_2) \rightarrow np$ transitions. Obviously, such an approach cannot be applied for deep donors in semiconductors. In this work, we have determined the energies of the deepest excited states of a neutral Mg donor in Si (binding energy of 107.5 meV) at elevated temperatures up to 150 K. This is very likely close to the upper temperature limit of this method.

A specific nonequilibrium spectroscopy, used in our experiments on observation of donor stimulated emission spectra, provided data of the even-parity states involved in the laser action. By this approach, energies of the 1s(E) and $1s(T_2)$ states of all group-V donors in silicon have been accurately defined. Similar information has been obtained for the excited $2\Gamma_8^+$ state of boron acceptor in silicon, which serves as a terminating state of lasing transitions under resonant optical pumping.[24] The values for the binding energies of the 1s-ground-split even-parity states of the hydrogen-like group-V shallow donors obtained from the spectra of the THz stimulated emission are closer to the theoretically values[8] when compared with the values derived by absorption spectroscopy at elevated temperatures and by electronic Raman spectroscopy. This approach is, however, possible only for impurities providing stimulated emission under optical pumping.

The $ns(A_1)$-type excited states are hardly accessed by the spectroscopic techniques used in this work. The $1s(A_1) \rightarrow ns(A_1)$ transitions can be observed in interband photoluminescence when a bound exciton transfers a portion of its energy to a donor electron, shifting the measured energy of the excitonic line.[18,19] We suppose that the observed spectral features at positions corresponding to transitions into the $3s(A_1)$ states[8] in the heavily doped Si:P and Si.Sb samples can be attributed to the above mentioned states.

In the case of Si:Mg there are no thorough theoretical calculations of the VOS states. The only known empirical estimate has been made by Ho and Ramdas[21] as 56.24 ± 3 meV. This estimate used the fact that the ground state $1s(A_1)$ and the splitted state 1s(E) are mixed by valley-orbit interaction. Under uniaxial stress the binding energies of both, the $1s(A_1)$ state and one of the components originating from the unstressed 1s(E) state, have a non-linear dependence of the binding energy on the stress with the VOS shift as a key parameter. Thus, the authors used the experimentally measured dependence of the energy of the $1s(A_1)-np$ transitions in silicon doped by shallower, group-V donors on stress, in order to scale the VOS shift expected for the deeper Mg° donor. Their estimate of the energy of the VOS state (i.e., 1s(E)) of about 56 meV is more close to the helium-like model than our value of 47.4 meV. In turn, the binding energy of the 1s(E) state for substitutional, deeper double donors (S, Se, Te) in silicon is above 30 meV which is even less. The $1s(T_2)$ states for the group-VI donors are also shallower than those for magnesium. Thus, the position of the 1s VOS ground state for substitutional, deeper donors is more close to the hydrogen-like model rather than to the helium-like one. As it is seen in Figure 3, the maximum of absorption from the VOS states of neutral Mg in Si is shifted from the trend line for the group-V donors. The possible reason of such a discrepancy can be caused by two-electron interaction, obeying Pauli exclusion principle. Thermal population of such two-electron system depends on partial contributions from both ortho- and para-states. We suppose that under described experimental conditions, the ortho-states dominate due to three times larger spin degeneracy.

We note here that there is a slight discrepancy between some values even when different authors derive them from the same experimental data, such as in refs. [25,26]. The reason is the different value of the reference energy, namely ground state 1s (A_1), which is slightly different in their assumptions. Also, one reason for the difference between the theoretical values[8] and our data for the states derived from low temperature spectra, is apparently the different values for the ground state binding energy, since we have used the slightly larger values from ref. [25], namely Si:P (45.5 meV[8] vs. 45.578 meV[25]); Si:Sb (42.7 meV[8] vs. 42.763 meV[25]); Si:As (53.7 meV[8] vs. 53.758 meV[25]) that made all our values smaller.

We note also that impurity lines are known to undergo not only thermal broadening but also shifts of their line center at elevated temperatures (**Figure 6**). Such a shift may be not monotonous and even change its direction as our data demonstrate. This is why binding energies of excited states derived from absorption spectra at elevated temperature can deviate from their undisturbed (low lattice temperature) values.

Additionally, our study has revealed a few transitions in the high excited odd-parity states in the absorption spectra of Si:As, namely $1s(A_1) \rightarrow 4f_0$; $5f_0$; $6h_\pm$ which have not been reported before. Their binding energies are 1.67 ± 0.01 meV ($4f_0$); 1.67 ± 0.01 meV ($5f_0$); and 0.88 ± 0.02 meV ($6h_\pm$).

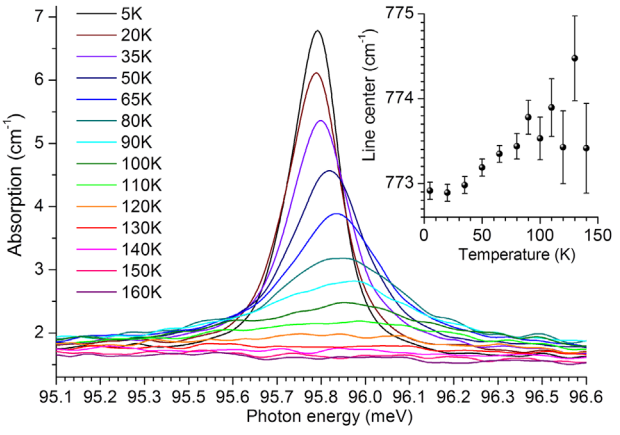

Figure 6. Temperature-related evolution of the $1s(A_1) \rightarrow 2p_0$ Mg° transition in silicon (Si:Mg 138-2). Note the significant shift of the line center position with temperature up to 100 K (inset).

In conclusion, several experimental techniques have been applied for observation of even-parity states in research grade silicon doped by the group-V donors and magnesium. Those methods include low temperature absorption spectroscopy, Raman scattering, variable temperature spectroscopy as well as spectroscopy of optically pumped THz silicon lasers. Such a combination has allowed to obtain new and refine existing data on binding energies of different even-parity excited states of shallow donors in silicon.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

impurities, infrared spectroscopy, Raman spectroscopy, silicon

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