

Calorimetric Absorption Spectroscopy of Deep Donors in Silicon at mK Temperatures

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High resolution calorimetric absorption spectroscopy (CAS) at mK temperatures is shown to confirm perfectly the well known Rydberg series of excited states from the deep donors Se^+ and S^+ in silicon. Superior to the standard methods CAS is able to quantitatively determine the radiative efficiency of any measured optical transition. Our experiments show clearly that the excited donor-levels decay completely nonradiative into the ground state, in accordance with the already known observation that no D^+ -correlated emission could be observed.

Our results are somewhat in contradiction with the theoretical explanations, as the electronic structure of the chalcogen donors indicates - at least for the higher excited energy levels - the absence of any lattice relaxation and, thus, of a direct multiphonon mechanism for the decay. By comparing the half width of the absorption lines, and thus the lifetime of the excited states, with the oscillator strength of the absorption, a new model for the term sequence of the donor levels is proposed in which not directly observable levels as long living meta stable storage centres.

1. Introduction

Sulfur, selenium, and tellurium give rise to various deep donor centres /1/ in silicon. They are often incorporated in a substitutional place, either neutral or ionized, and have been thoroughly investigated by Fourier-transform or photo thermal ionization spectroscopy (PTIS) /2/. From these measurements it is known that chalcogens show very pronounced Rydberg series of excited states. Up to now, no corresponding luminescence has been found. From theoretical considerations, however, it has been reported /3/ that the lattice relaxation of these centres in silicon is small and amounts to about 10 meV only. An open question is therefore what kind of relaxation mechanism acts in the chalcogen donors.

In the present paper we report on a study to determine quantitatively the quantum efficiency of optical transitions between excited states and the ground state of Se^+ and S^+ centres in Si by using the calorimetric absorption spectroscopy (CAS) at mK temperatures. This method turned out to be most effective for measuring radiationless transitions quantitatively. Based on a comparison of the width of the detected spectral lines with the oscillator strength of the absorption structure a model will be discussed which seems suitable to understand the relaxation mechanism in chalcogen centres in Si.

2. Experimental Setup

Calorimetric absorption spectroscopy (CAS) bases on the increase of the sample temperature by emission of phonons during the nonradiative recombination to thermal equilibrium of an excited system. The sample is monochromatically illuminated, and a CAS spectrum is taken by measuring the change of sample temperature in dependence on excitation wavelength. Additionally, the transmitted light was registered calorimetrically (called CTS), leading to the possibility to determine the quantum efficiency, i.e. the radiative decay part of an excited state. Since the sensitivity of CAS/CTS increases drastically with decreasing temperature, we performed our experiments at mK temperatures using a $^3\text{He}/^4\text{He}$ -dilution refrigerator. The experimental setup is described in detail in Ref./4/, the growth and doping procedure of the samples is given in Ref./5/.

3. Experimental Results

The energy level scheme of isolated substitutional chalcogen donors is well known and is represented in the insert of Fig.1. Theoretically, it is based on the effective mass theory (EMT) for a single conduction band minimum modified by valley - orbit splitting in a tetrahedral crystal field. Selection rules for optical transitions in this model are also indicated. Fig.1 shows CAS P_{CAS} and optical absorption spectra P_{abs} of Se^+ or S^+ doped silicon. By a calculation described in detail in Ref. /4/ P_{abs} has been determined in absolute values from the measured CTS spectrum regarding the influence of reflectivity. The energy scale is set to zero for the transition from the $1s(A_1)$ ground state of the donor centre to the conduction band. According to literature the ionization energy yields 613.5 meV for S^+ and 593.5 meV for Se^+ , respectively. The CAS and P_{abs} spectra reveal all the fine structures of the modified Rydberg series previously observed in absorption /1/ and PTIS /2/. Additionally, due to an enhanced resolution a number of new lines has been detected which agree perfectly with theoretical predictions of the $3s(T_2)$ and $4s(T_2)$ states.

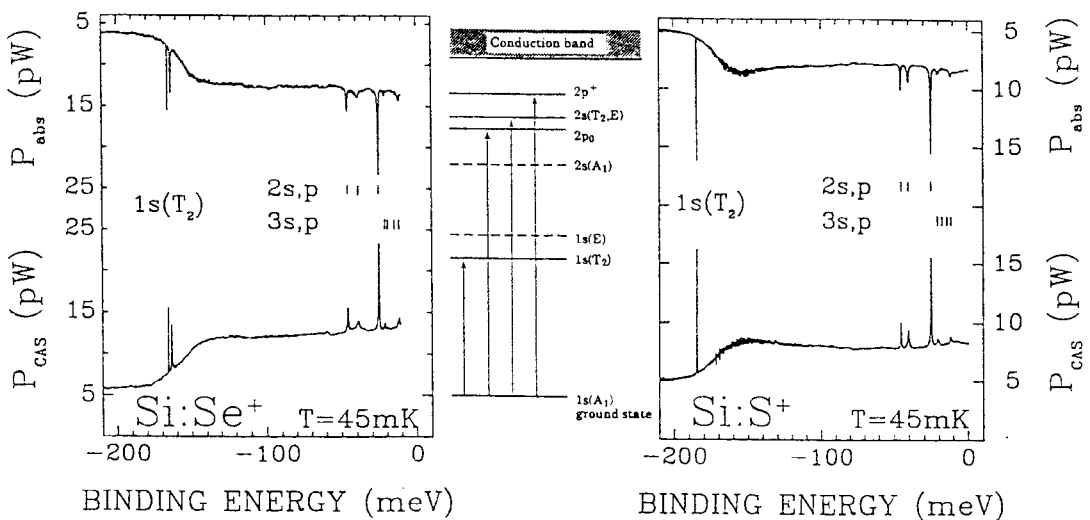


Fig.1: CAS spectrum (lower curves) and optical absorption (P_{abs}) for Se^+ and S^+ doped silicon, respectively. In the insert a term scheme for D^+ centres in Si is shown. Detected optical transitions are marked by an arrow.

Comparing the CAS spectra to those of the P_{abs} spectra in fig.1 we are able to determine the quantum efficiency in absolute values. Within the experimental error the equality of the two values proves a complete nonradiative recombination of the $1s(T_2)$ state to the $1s(A_1)$ term in both Se^+ or S^+ centres, and also for the higher excited states close to the conduction band. This is fully consistent with the fact that no corresponding luminescence has been found up to now.

Since the donor concentrations of our samples are known and the absorption coefficient can be drawn from our experiments it is possible to determine the oscillator strength for dipole transition and to calculate the radiative lifetimes τ_r of the excited states. The value of τ_r amounts to several μs for all observed excited states. This lifetime would correspond to a homogeneous absorption linewidth in the order of $1\mu\text{eV}$. The observed linewidth, however, is almost three orders of magnitude bigger and lies in the range between 0.1 and 0.5 meV. Since the crystals have a small donor concentration of less than 10^{14} cm^{-3} and the host lattice is of nearly perfect quality we can exclude inhomogeneous linewidth broadening effects. Thus, from the large linewidth an estimated lifetime τ_l of only a few ps results. Such a discrepancy in the two calculated lifetimes is well known in literature and is often explained by fast nonradiative relaxation mechanisms.

4. Discussion

In contradiction to theoretical expectations nonradiative processes apparently play a dominant role in the recombination of excited chalcogen donors in silicon. Three kinds of nonradiative recombination processes in semiconductors are known: Auger processes, phonon cascade processes and multi phonon emission processes (MPEP).

Since in our experiments the excitation is resonant with the energy differences between the ground state and the different excited states of the S^+ and Se^+ centres and, no free carriers are excited at mK temperatures by thermal effects. Two step radiative excitation of free carriers is also very unlikely as the donor doping is moderate and the lifetime τ_l of the excited defect states is small. Therefore, Auger processes can be excluded. The same holds for cascade processes, as the energy distance to the ground state is larger than one optical phonon energy.

A necessary supposition for MPEP is a lattice relaxation in the vicinity of the defect. In the case of chalcogen donors in silicon the electronic structure of the higher excited shallow states is in perfect agreement with calculations by EMT, suggesting the absence of lattice relaxation. For the valley orbit split ns states theoretical calculation [3] predicts relaxation, but the determined value of a Huang-Rhys factor of about 0.2 is too small to explain a complete nonradiative decay.

The key to understand the nonradiative character of the transitions comes from the difference between the estimated radiative lifetime τ_r , from absorption spectroscopy, and the lifetime τ_l determined from the half width of the spectral lines. It becomes clear that we have to assume energy levels lower than those observed in absorption, to which a fast decay occurs. These levels must have a very long lifetime to allow MPEP processes to occur. Thus, we have

to look for levels which exist in the energy level system, but have a highly forbidden transition probability to the ground state.

In the case of the $1s(T_2)$ term a possible candidate for such a level is the $1s(E)$ level of the valley-orbit-split ground state (see fig. 1). Transitions from this level to the $1s(A_1)$ ground level are EMT and symmetry forbidden, no direct experimental data of the term positions exists and it cannot be assumed a priori that it is situated above the $1s(T_2)$ state. Theoretical calculations /6/, however, predict the $1s(E)$ term to be energetically above the $1s(T_2)$ level and existing experimental data have been discussed in similar ways /7,8/. For D^0 centres such a term sequence was determined from stress experiments /7/, but the situation might be different for D^+ donors. Fano resonance experiments /8/ show a reversed sequence for D^0 and D_2^0 centres - D_2^0 having a lower $1s(E)$ state - and are thus not conclusive for the D^+ donors. In this case there is no possibility for such experiments, due to the large energetic distance ($S^+ = 184\text{meV}$, $\text{Se}^+ = 164\text{meV}$) to the conduction band edge.

Thus, for D^+ centres it cannot be excluded that the $1s(E)$ level might be located below the $1s(T_2)$ term. Then it can act as a storage centre, from which the nonradiative transitions start (Fig.2). In addition for the higher excited levels such a storage centres can be formed by the $2s(A_1)$ term which is less than one optical phonon energy below the higher $2s,p$ states.

Our experimental results **do not prove** the term sequence shown in Fig.2, but this model is able to explain the analogous behaviour of the $1s(T_2)$ and the higher excited levels -their complete nonradiative decay- and the discrepancy in the two calculated lifetimes.

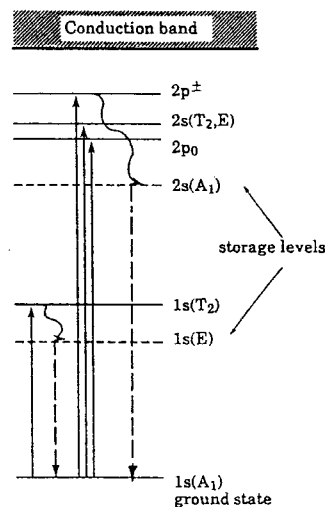


Fig. 2
A new model for the term sequence of D^+ centres in silicon.

In any case, the discussion of our results lead to the consequence that the reoccupation time of the ground state must be as long as the lifetime of the storage centres. Saturation spectroscopy could be used to measure such a long lifetime leading to a final proof for our assumption.

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