

Photoionization cross sections of a two-electron donor center in silicon*

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A simple model is presented for calculating the photoionization cross-section spectra of a two-electron center in silicon. A hydrogenlike wave function is used for the ground state of the singly ionized one-electron center, and a heliumlike wave function for the ground state of the neutral two-electron center. A test of this model is provided by comparison with the observed photoionization cross-section spectra of sulfur centers in silicon, using trial wave functions obtained previously from variational calculations of the bound-state electronic energy levels. The experimental spectra were obtained by the photocapacitance transient method for sulfur-doped silicon p^+-n junction diodes. Good agreement between theory and experiments is obtained without the use of empirical-effective-field ratios. Structures below the extrinsic edge in the spectra of the neutral centers were observed and are attributed to two-step photothermal transitions. The peak at about 0.285 eV is attributed to an optical transition from the $[1s(A_1), 1s(A_1)]$ ground state of the neutral two-electron center to the $[1s(A_1), 1s(T_2)]$ excited state, with a subsequent thermal excitation into the conduction band as the second transition step.

I. INTRODUCTION

Impurity centers such as substitutional group-V or group-III elements in silicon could be pictured as hydrogenlike centers embedded in a dielectric medium. When occupied, the center is neutral and there is an electron (or a hole) bound to the core or nucleus of net charge $+e$ ($-e$). These are one-electron or one-hole centers. Impurity centers such as substitutional sulfur, interstitial magnesium, or substitutional zinc, in silicon are two-electron or two-hole centers. They may be pictured as heliumlike centers embedded in a dielectric medium. When fully occupied, the center is neutral and there are two electrons (holes) bound to the core or nucleus of net charge $+2e$ ($-2e$). If one of these two electrons (holes) is excited into either the conduction band or the valence band of the host semiconductor, the center becomes singly ionized, with one electron (hole) bound to the core or nucleus of net charge $+2e$ ($-2e$).

There are many published works, both theoretical and experimental, on the electronic structures¹⁻⁷ and on the photoionization cross-sections^{4,8-13} of the one-electron or one-hole centers. In comparison, there are relatively few reported works on two-electron or two-hole centers.¹⁴⁻¹⁹

In the case of the one-electron or one-hole centers, three theoretical models have often been used to calculate the photoionization cross-section spectrum. These are the hydrogenic model,⁸ the δ -function potential model,¹⁰ and the quantum-defect model.¹¹ In addition, there is also a simple model which uses plane waves for the continuum states and hydrogenlike trial wave functions for the ground state.⁴ This last model, the δ -function

potential, and the quantum defect models all predict photoionization cross-section spectra similar to experimentally observed data in that the spectra rise from zero at threshold energy to a maximum, and then fall off gradually at higher photon energies. In contrast, the hydrogenic model, which uses scaled hydrogen wave functions for both the bound and the continuum states, predicts a spectrum which is maximum at threshold energy and falls off relatively rapidly as the photon energy is increased.

Although there are reported calculations for the photoionization cross-section spectra of atomic helium atoms or heliumlike ions,²⁰ as far as we know, no such calculations have been reported for the solid-state analogs of the heliumlike centers in semiconductors.

In this paper, we present a simple model for calculating the photoionization cross section of a two-electron heliumlike center in semiconductors. A test of this model is provided by comparison with the observed photoionization cross-section spectra of the two-electron sulfur centers in silicon, using wave functions obtained previously from variation calculations of the electronic energy-level structures.¹⁹

We also report here the observation of the $[1s(A_1), 1s(A_1)]$ to $[1s(A_1), 1s(T_2)]$ optical transition for the first time at neutral sulfur donor centers in silicon.

II. PHOTOIONIZATION CROSS SECTION

The photoionization cross section for a two-electron neutral center is given in the electric dipole approximation by⁸

$$\sigma_I^{(0)}(\hbar\omega) = \left[\left(\frac{E_{\text{eff}}}{E_0} \right)^2 \frac{n}{\epsilon} \right] \frac{4\pi^2\alpha}{3} \\ \times \hbar\omega \sum_f |\langle f | \vec{r}_1 + \vec{r}_2 | i \rangle|^2 \\ \times \delta(E_f - E_i - \hbar\omega), \quad (2.1)$$

where n is the optical index of refraction, ϵ is the optical dielectric constant, E_{eff}/E_0 is the effective electric field at the center, $\alpha = e^2/\hbar c$ is the fine-structure constant. Here $|i\rangle$ is the initial ground state, and $|f\rangle$ is the final state where one of the electron is in the continuum state and the other electron is in the ground state of the singly ionized center. In our heliumlike model, the initial ground state for the two-electron center is assumed to be

$$|i\rangle = (1/\pi a^3) \exp[-(r_1 + r_2)/a], \quad (2.2)$$

and the final continuum state is written

$$|f\rangle = |\vec{k}\rangle = (2\pi b^3 V)^{-1/2} [\exp(-r_1/b + i\vec{k} \cdot \vec{r}_2) \\ + \exp(-r_2/b + i\vec{k} \cdot \vec{r}_1)], \quad (2.3)$$

where a is the effective Bohr radius of the two-electron neutral center, and b is that of the one-electron singly ionized center. Here V is the volume of normalization and \vec{k} is the wave vector which characterizes the electron in the continuum. The summation in Eq. (2.1) then becomes a sum over all the \vec{k} values. Using (2.2) and (2.3) to calculate the electric dipole matrix elements, we obtain

$$\sigma_I^{(0)}(\hbar\omega) = [(E_{\text{eff}}/E_0)^2 n/\epsilon] \frac{4\pi^2\alpha}{3} a^2 S^{(0)}(\hbar\omega), \quad (2.4a)$$

where the spectral dependence is contained in the dimensionless shape function

$$S^{(0)}(\hbar\omega) = 512 \left(\frac{2m^* a^2}{\hbar^2} \right) \hbar\omega \left(\frac{b}{a} \right)^3 \left(\frac{2}{b/a + 1} \right)^6 \\ \times \frac{[2m^* a^2/\hbar^2](\hbar\omega - E_I^{(0)})^{3/2}}{[1 + (2m^* a^2/\hbar^2)(\hbar\omega - E_I^{(0)})]^6}. \quad (2.4b)$$

Here $E_I^{(0)}$ is the one-electron ionization energy of the neutral center.

After the ionization of one of the electrons from the heliumlike neutral center, the center becomes singly ionized and is hydrogenlike. The photoionization cross section for the singly ionized or one-electron center is given by⁸

$$\sigma_I^{(+)}(\hbar\omega) = \left[\left(\frac{E_{\text{eff}}}{E_0} \right)^2 \frac{n}{\epsilon} \right] \frac{4\pi^2\alpha}{3} \\ \times \hbar\omega \sum_f |\langle f | \vec{r} | i \rangle|^2 \delta(E_f - E_i - \hbar\omega). \quad (2.5)$$

Using

$$|i\rangle = (1/\pi b^3)^{1/2} e^{-r/b} \quad (2.6)$$

for the initial ground state, and

$$|f\rangle = |\vec{k}\rangle = (1/V)^{1/2} e^{-i\vec{k} \cdot \vec{r}} \quad (2.7)$$

for the final continuum state, we find

$$\sigma_I^{(+)}(\hbar\omega) = [(E_{\text{eff}}/E_0)^2 n/\epsilon] \frac{4\pi^2\alpha}{3} b^2 S^{(+)}(\hbar\omega), \quad (2.8a)$$

with

$$S^{(+)}(\hbar\omega) \\ = 256 \left(\frac{2m^* b^2}{\hbar^2} \right) \hbar\omega \frac{[(2m^* b^2/\hbar^2)(\hbar\omega - E_I^{(+)})]^{3/2}}{[1 + (2m^* b^2/\hbar^2)(\hbar\omega - E_I^{(+)})]^6}, \quad (2.8b)$$

where $E_I^{(+)}$ is the ionization energy of the singly ionized center. Equations (2.8a) and (2.8b) had been obtained previously.⁴

In order to evaluate the cross sections from (2.4) and (2.8) for a given center, we need to know the effective Bohr radii a and b for the neutral and the singly ionized centers. At present these values are available only for sulfur centers in silicon.¹⁹ Sulfur has the same electronic core configuration as silicon which makes the problem of sulfur impurities in silicon much more susceptible to theoretical interpretation than other impurities.^{7,19} From variational calculations of the energy levels, the effective Bohr radii for sulfur centers in silicon have been determined to be $a = 8.1$ a.u. and $b = 7.3$ a.u.¹⁹

III. EXPERIMENTAL

Photoionization cross-section spectra were obtained by the photocapacitance transient method²¹ for sulfur-doped silicon $p^+ - n$ (p^+ denotes a heavily doped p -type region) abrupt junctions. This sensitive method allows cross sections in the range of 10^{-19} cm² or absorption coefficient of 10^{-3} cm⁻¹ to be readily measured. The device fabrication procedures have been described elsewhere.^{14,15} The low-temperature optical data were taken using a Janis Model DT liquid-helium Dewar fitted with Irtran II windows which transmit from about 0.4–15 μ m. The monochromatic infrared photon flux was derived from a blackbody radiation source and a Jarrell-Ash 0.5-m spectrometer. The $P+N$ junction was first zero biased so that the sulfur donor centers on the N side of the depletion region were filled with electrons. It was then switched to a reverse bias. The junction temperature was kept sufficiently low so that the trapped electrons in the junction depletion layer were frozen on the sulfur centers. These trapped electrons were then photoexcited into the conduction band by monochromatic infrared radiation. The decrease in the trapped electron concentration with time in the junction depletion layer due to photoexcitation was monitored by measuring the high-frequency (1 MHz)

junction capacitance using a Boonton Electronics Model 71A capacitance-inductance meter. Analyses of the capacitance transient as a function of the photon energy gave the photoionization cross-section spectrum.¹⁵

Two precautions should be noted while applying the photocapacitance transient method at low temperatures. One is the deionization effect at very low temperatures when the Fermi level on the *N* side of the junction gets within $k_B T$ of, or moves above the energy level of the shallow level donors. This is best illustrated with the thermally stimulated capacitance method which is a convenient and sensitive tool for scanning the depletion region²² and the edge²³ of a *pn* junction for the presence of defect or impurity centers. Figure 1 shows a typical thermally stimulated capacitance scan for a sulfur doped *P+N* diode. Peaks 4 and 5 are due to the thermal emission of electrons from the neutral and the singly ionized sulfur centers in the depletion region of the junction. These two centers were the subjects of the present and also of earlier^{14,15} studies. Peak 3 is due to the Fermi level crossing the shallow phosphorus donor energy level in the edge region of the junction. Peaks 1 and 2 are yet unidentified. Besides demonstrating the presence of defect or impurity centers, the thermally stimulated capacitance scan also gives the temperature range within which photocapacitance data for a center should be taken. For the neutral center, the temperature of the junction must be kept less than about 115 °K so that the thermal emission of the trapped electrons was negligible.¹⁴ At the same time, the temperature must be higher than about 54 °K in order that the effects of the

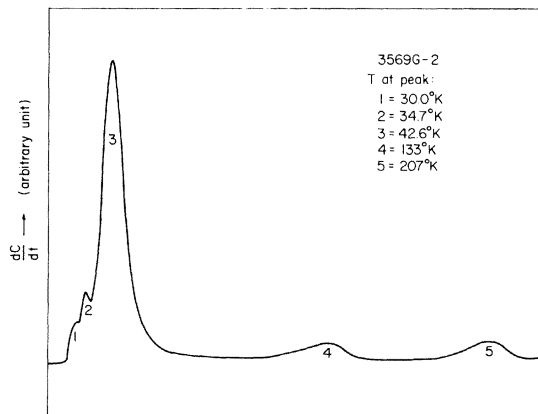


FIG. 1. Thermally stimulated capacitance for sulfur doped *p⁺-n* silicon diode. Peaks 1 and 2 are yet unidentified. Peak 3 is due to phosphorus donors in the edge region of the junction. Peaks 4 and 5 are due to neutral and singly ionized sulfur centers in the depletion region of the junction.

shallow phosphorus donors in the edge region of the junction (peak 3 in Fig. 1) would not be important.

The other precaution is that the photocapacitance transient signal depends on the absolute incident photon flux on the device. The optical emission rate from the background radiation must be subtracted out.²⁴ For centers whose ionization energies are larger than about 0.32 eV, the background emission rate is negligible. For the case of neutral sulfur centers in silicon, the background emission rate is small, but not negligible; and the lowest cross section that could be accurately measured was about $5 \times 10^{-19} \text{ cm}^{-2}$.

IV. RESULTS AND DISCUSSIONS

Figure 2 shows the one-electron photoionization cross-section spectrum of the two-electron neutral sulfur center in silicon. The theoretical curve is calculated using Eqs. (2.4a) and (2.4b), and the effective Bohr radii of $a = 8.1 \text{ a.u.}$ and $b = 7.3 \text{ a.u.}$ which were determined from variation calculations of the energy levels.¹⁹ The low-energy ($< E_I$, $= 0.315 \text{ eV}$) tail is attributed to two-step photothermal excitation processes in which one of the bound

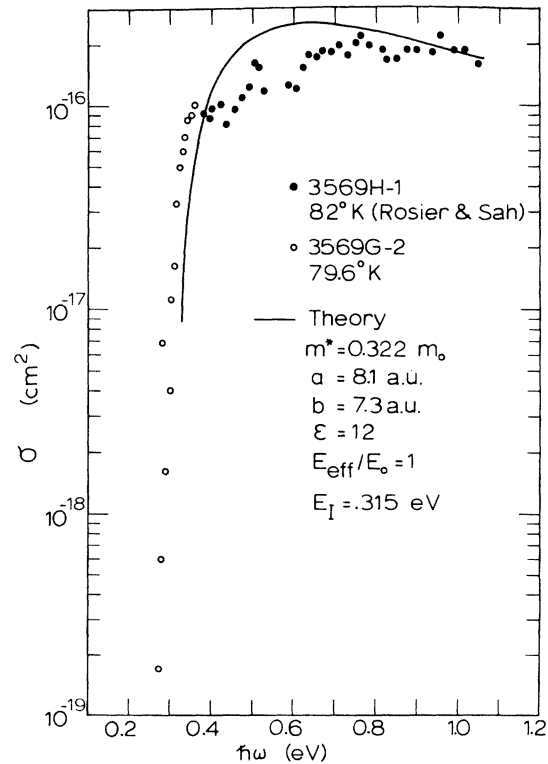


FIG. 2. Photoionization cross section of neutral sulfur centers in silicon. The solid dots were taken from Ref. 15.

electrons in the ground state is first optically excited to an excited state and then thermally excited from the excited state into the conduction band. Such two-step photothermal processes have been observed in one-electron centers of many semiconductors.^{25, 26}

The s states of a donor center in silicon are split by the valley-orbit interaction into a singlet A_1 , a doublet E and a triplet T_2 state.¹⁻⁴ The A_1 state is s -like, the E states are d -like and the T_2 states are p -like. Therefore, electric dipole transition between the $1s(A_1)$ state and the $1s(T_2)$ state is allowed by the usual selection rules of $\Delta l = 1$ and $\Delta m = \pm 1$. However, such a transition is expected to be weak, since the dipole matrix element comes entirely from intervalley overlaps of the wave functions. Excited $1s$ levels of the one-electron donor centers have been observed for shallow-level group-V impurities in silicon^{5, 27-29} and for deep-level singly ionized sulfur in silicon.²⁵ For two-electron donor centers, such as interstitial magnesium or substitutional sulfur in silicon, optical transitions from the $[1s(A_1), 1s(A_1)]$ ground state to the $[1s(A_1), np]$ excited states have also been observed, but transitions from the ground state to the $[1s(A_1), 1s(T_2)]$ excited state have either not been observed or not been definitely identified before.^{16, 17}

Structures below the extrinsic edge of neutral sulfur centers in silicon are evident in Fig. 3 which shows the photoionization cross-section tail region for three temperatures. As discussed in the preceding section, the upper temperature is limited by the thermal emission rate and the lower temperature is limited by the effect of the phosphorus donors in the edge region of the junction. The slight scattering of the data in Fig. 3 at about 0.292 eV is due to atmospheric absorption in our experimental system which is not enclosed. The peak at about 0.285 eV is attributed to a photothermal process via the $[1s(A_1), 1s(T_2)]$ excited state. This identification is based on the observation that this peak lies about 30 meV below the extrinsic edge¹⁹ (315 meV). This agrees very well with the theoretical value of about 32 meV from a heliumlike excited energy level spectrum.¹⁹ That the excited energy level spectrum for a two-electron neutral donor center in silicon is heliumlike has been observed experimentally not only for a substitutional neutral sulfur in silicon,¹⁷ but also for interstitial neutral magnesium in silicon.¹⁶

There appears to be very little temperature dependence of the magnitude of the peak at 0.285 eV, indicating that the second thermal step of the two-step photothermal process was so fast at these relatively high temperatures that the ionization process was rate limited by the $[1s(A_1), 1s(A_1)]$ to

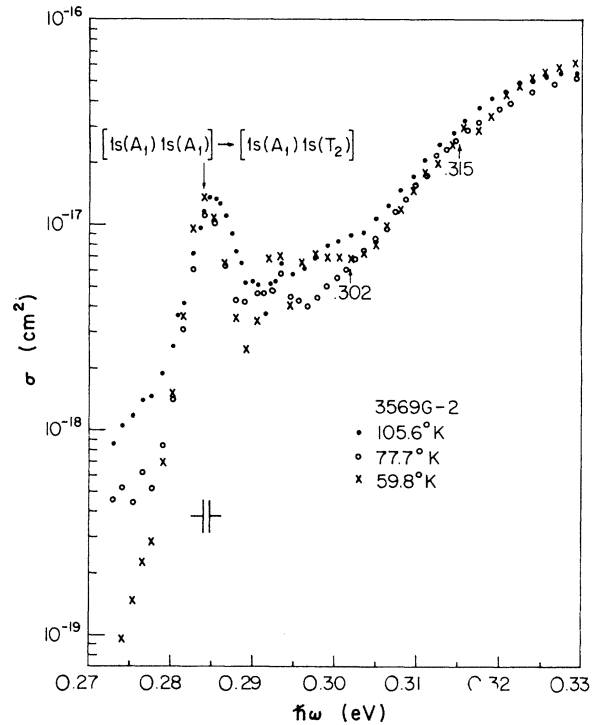


FIG. 3. Low-energy tail of the photoionization cross section of neutral sulfur centers in silicon. The arrows indicate the ionization energy (0.315 eV) and the thermal activation energy (0.302 eV). The 0.285-eV peak is attributed to photothermal transition via the $[1s(A_1), 1s(T_2)]$ excited state.

$[1s(A_1), 1s(T_2)]$ optical transition. This point could be further substantiated by the following considerations. Consider the thermal capture and emission of electrons at the phosphorus donor centers in silicon. The low temperature capture cross section has recently been measured by Norton *et al.*³⁰ At 20 °K, they found $\sigma_n = 3 \times 10^{-12}$ cm². Since the energy level structure of the excited states of a heliumlike neutral donor center in silicon is about the same as that of the shallow-level group-V impurities in silicon,¹⁹ it is reasonable to assume that the capture cross section for the neutral sulfur center is about the same as that for phosphorus impurities. The corresponding emission rate at thermal equilibrium could be obtained from the relation³¹

$$e_n = \sigma_n \langle v \rangle N_C \exp(E_T - E_C/k_B T), \quad (4.1)$$

where $\langle v \rangle = (8k_B T/\pi m_N)^{1/2}$ is the average thermal velocity of the electrons, N_C is the effective density of state, E_T is the trap energy level, and E_C is the conduction-band edge. At 20 °K, $N_C = 4.716 \times 10^{17}$ cm⁻³, and using $E_C - E_T = 32$ meV for the $[1s(A_1), 1s(T_2)]$ state, we have $e_n = 6.2 \times 10^4$ sec⁻¹.

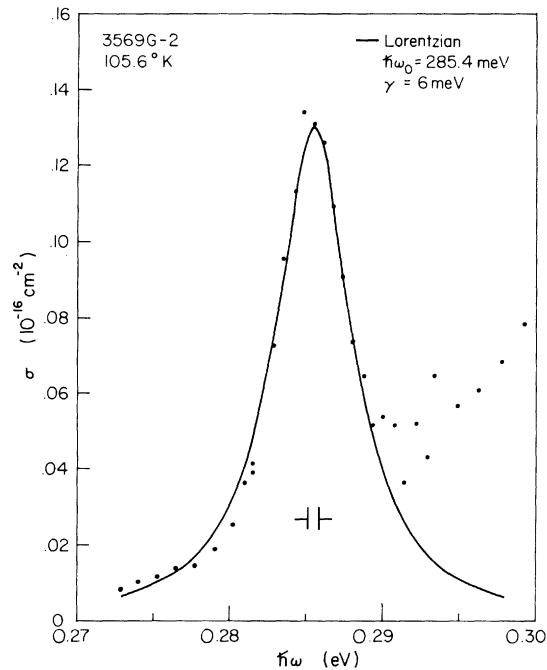


FIG. 4. Linear plot of the 0.285-eV peak, indicating a Lorentzian line shape with half-width of 6 meV.

This thermal emission rate would be much larger at higher temperatures. Thus, we should not expect appreciable changes in the 0.285-eV peak in Fig. 3 as the temperatures were changed from 105 to 60 °K where the photocapacitance transient time constant was typically 10^2 – 10^3 sec. Nevertheless, temperature effects were observed at the low energy side of this peak.

Figure 4 is a linear plot of the 0.285-eV peak at 105.6 °K. It shows a Lorentzian line shape with half-width $\gamma = 6$ meV. Typical resolution of the experimental apparatus in this low-energy tail region is 0.6 meV.

The photoionization cross-section spectra of the singly ionized sulfur centers in silicon have been studied in detail before.^{15,25} The experimental data are reproduced here in Fig. 5 to compare with the theoretical spectrum calculated from Eqs. (2.8a) and (2.8b) using the effective Bohr radius value of $b = 7.3$ a.u. previously determined from variation calculations of the energy levels.¹⁹ The low-en-

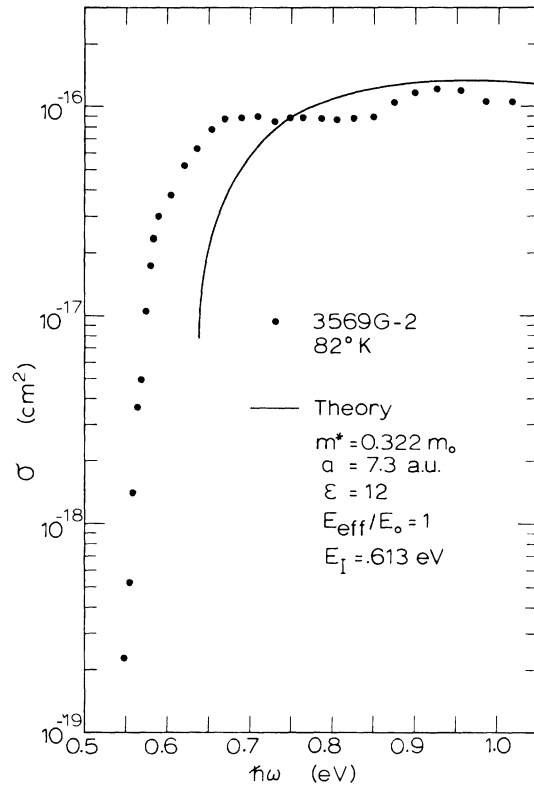


FIG. 5. Photoionization cross section of singly ionized sulfur centers in silicon. The experimental values were taken from Ref. 15.

ergy tail in Fig. 5 again was traced to two-step photothermal processed via excited states.

It is interesting to note in Figs. 2 and 5 that good agreement between the theoretical photoionization cross-section spectra and experiment is obtained for both the neutral and the singly ionized centers with an effective field ratio of 1. Such an effective field ratio is consistent with the recent observations of Blakemore *et al.*^{12,32} who found that an effective-field ratio of approximately unity was required to fit the observed photoionization cross-section spectra of In in Si and Mn in GaAs, and of Grimmeiss and Ledebor³³ who found an effective field ratio of about unity in fitting observed photoionization cross-section spectra of O in GaAs, Au in Si, and Zn in Si.

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