Electrical and optical properties of vanadium-related centers in silicon

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Vanadium-doped silicon was investigated using junction space-charge techniques. Three energy levels were observed at $E_c-0.21$ eV (A level), $E_c-0.48$ eV (B level), and $E_v+0.36$ eV (C level). The enthalpies of electron capture are 4 and 16 meV for the A and B levels, respectively. The corresponding enthalpy of holes is 88 meV for the C level. It is believed that electron capture into the A and B levels is due to a cascade process. Changes in the Gibbs free energy as a function of temperature were calculated for all three levels. The good agreement of the Gibbs free energies with the optical threshold energies suggests negligible lattice relaxations. A structure in the low-energy part of the spectral distribution of the electron photoionization cross sections of the B level is assumed to be due to excited states and shown to be in good agreement with effective-mass theory.

I. INTRODUCTION

Transition metals (TM) in silicon are considered to be of particular interest since their electronic properties are widely used in semiconductor electronics. One would therefore expect that the electronic properties of TM have been studied in detail and that their energy positions in the forbidden energy gap as well as their donorlike or acceptorlike behavior are reasonably established. While this is in fact true for some of the TM such as gold,[1] platinum,[2] and iron,[3] the electronic properties of quite a number of TM in silicon are still not fully understood. One such example is vanadium.

The first studies of vanadium were performed by Fahrner and Goetzberger.[4] Later Hopkins *et al.*[5] reported on three vanadium levels at $E_v+0.42$ eV, $E_c-0.225$ eV, and $E_c-0.46$ eV which they studied by deep-level transition spectroscopy (DLTS).[6] It should be noted that the energy positions of these levels were obtained from Arrhenius plots of thermal emission rate without corrections for possible capture barriers. In 1981 Lemke[7] repeated some of the DLTS measurements and observed a donor level above the valence band with an enthalpy of about 0.31 eV, another donor level at $E_c-0.43$ eV, and an acceptor level at $E_c-0.18$ eV. The value of the acceptor level is reported to be an enthalpy whereas the energy position of the level at $E_c-0.43$ eV was obtained as a thermal activation energy from an Arrhenius plot of the thermal emission rate of electrons.

The only optical study of vanadium-doped silicon has recently been performed by Daliev *et al.*[8] They applied both photoconductivity and DLTS measurements and found four vanadium related levels at $E_c-0.22$ eV, $E_c-0.45$ eV, $E_c-0.52$ eV, and $E_v+0.41$ eV. A level at $E_c-0.55$ eV was also observed by Lemke[7] but he believed that the level most probably was caused by gold.

Since no comprehensive optical studies of vanadium in silicon are available and most of the energy positions have been obtained from unspecified thermal activation energies, an attempt was made to remeasure some of the electronic parameters of vanadium in silicon. In this paper we therefore report on detailed studies of thermal emission and capture rates as well as photocurrent and photocapacitance measurements in vanadium-doped silicon. Our measurements allowed us to calculate changes in the Gibbs free energy, enthalpy, and entropy due to electron or hole excitation of each of the vanadium-related levels. It is shown that these energies are in good agreement with the optical data and that previous assignments of the energy levels should be reconsidered.

II. EXPERIMENTAL DETAILS

The samples used were either p^+-n or n^+-p diodes implanted with vanadium. The diodes were prepared without metallization using a localized oxidation of silicon (LOCOS) technology. The p-type and n-type doped silicon wafers had a free-carrier concentration of about 10^{15} cm^{-3}, respectively. The p^+- and n^+-type regions were annealed at 1100 °C for 2 h after boron and arsenic implantation, respectively. After the annealing process vanadium ^{51}V was implanted onto the front side of the silicon wafers with an energy of 300 keV and a dose of 10^{13} cm^{-2}, and diffused into the n- and p-type regions by heating the samples to 1100 °C for 30 min. The vanadium was finally electrically activated by rapid thermal annealing at 1250 °C for 30 s in a nitrogen ambient resulting in a concentration of electrically active vanadium-related

centers of about 10^{14} cm^{-3}.

Using a combination of DLTS and single-shot measurements,[9] we were able to measure the thermal emission and capture rates over a large temperature range. Measurements of capture cross sections are often disturbed by the free-carrier tail from the neutral region into the space-charge region. This effect was suppressed in the evaluation of the capture cross sections by subtracting the strongly nonexponential part for long-filling pulses from the exponential part at short-filling pulses.

The influence of the electric field on the thermal emission (capture processes take place in the neutral region) was investigated using single-shot measurements. The basic idea of this technique was to take the difference between two transients recorded at two slightly different pulse voltages V_1 and V_2 and keeping the reverse bias V_R constant.[10] Only signals at a fairly constant electric field, i.e., from a small region of the space-charge region, were recorded. By varying the reverse bias it was possible to alter the electric field in the part of the space-charge region where the measurements were performed.

Most of the optical measurements were persued using a 0.5-m vacuum grating monochromator (Acton Research Corporation). By performing the measurements in vacuum (10^{-2} mbar), disturbances arising from atmospheric absorption lines were avoided. The resolution was about 1 meV. The photocurrent measurements were carried out in a double prism monochromator (Zeiss MM3) with a resolution of about 10 meV. The spectral distribution of the photoionization cross section of the A level in p^+-n diodes was measured using photoadmittance spectroscopy (PAS),[11] since the level was emptied in less than a second due to blackbody radiation. By applying PAS a capacitance signal is obtained which originates from a shift of the edge region due to a recharging of the center and is detected by a lock-in technique.

III. RESULTS

The three vanadium-related levels observed in our samples are labeled A, B, and C. The Arrhenius plot of the thermal emission rate of electrons, e_n^t, for level A is shown in Fig. 1. The emission rates were T^2 corrected and hence, the calculated activation energy of 204 meV is given by the sum $\Delta H_n + \Delta H_{cn}$ (Ref. 12), where ΔH_n is the change in enthalpy due to electron emission and ΔH_{cn} is the change in enthalpy due to electron capture, provided that the capture cross section of electrons σ_n^t can be approximated by

$$\sigma_n^t = \sigma_0 \exp(-\Delta H_{cn}/kT) . \quad (1)$$

As demonstrated in Fig. 2 where the logarithm of the capture cross section of electrons for level A is plotted versus $1000/T$, an approximation of the temperature dependence of the capture cross section by Eq. (1) seems to be reasonable. The data are well represented by a straight line from which a value of -4 meV is readily calculated for ΔH_{cn}. Together with the data presented in Fig. 1, a value of 208 meV is therefore obtained for the change in enthalpy ΔH_n of level A.

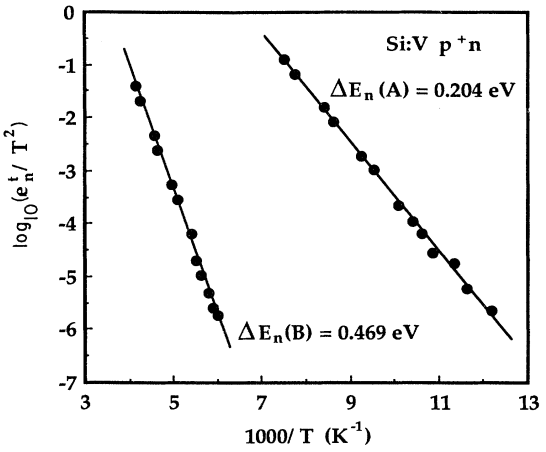

FIG. 1. Arrhenius plots of T^2-corrected thermal emission rates of electrons for the A and B levels in the upper half of the band gap. The energies given are the DLTS activation energies.

Considering the fact that the emission rates were measured in the presence of rather high electric fields, a careful check was performed in order to find out whether or not the data were influenced by field enhanced emission processes. However, measurements performed at different reverse bias showed very little variation compared with the scatter of the data.

Once the temperature dependence of the thermal emission rate and the capture cross section is known, the change in Gibbs free energy ΔG_n is easily calculated as a function of temperature using the detailed balance equation[13]

$$e_n^t = \sigma_n^t v_{\text{th}} N_c \exp(-\Delta G_n/kT) . \quad (2)$$

Here v_{th} is the average thermal velocity of electrons and N_c is the effective density of states in the conduction band. Considering that[14]

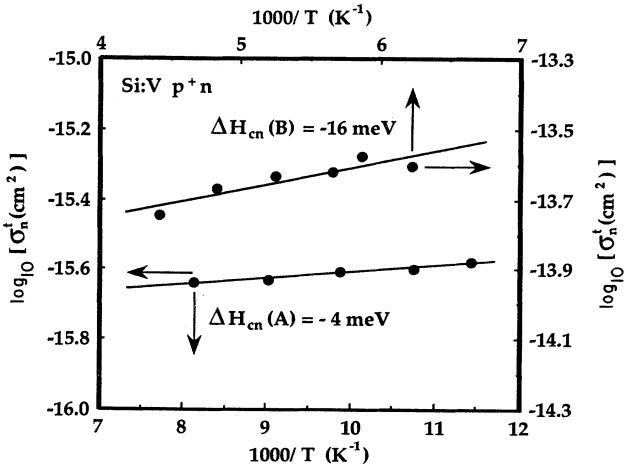

FIG. 2. Arrhenius plots of the electron-capture cross sections for the A and B levels in the upper half of the band gap. The energies given are the changes in enthalpy due to the capture of electrons.

$$\Delta G_n = \Delta H_n - T\,\Delta S_n \ , \tag{3}$$

where ΔS_n is the total change in entropy, one would expect a linear temperature dependence of ΔG_n as long as ΔS_n is temperature independent. Figure 3 shows that this is obviously true within the temperature range of the measurements. However, it should be noted that from the third law ΔS_n must go to zero as T goes to zero. A plot of ΔG_n against T, therefore, cannot be a straight line of the nonzero slope right down to $T=0$.[15] Nevertheless, it is expected from general thermodynamic relations that both ΔH_n and ΔS_n can be taken as constant over a certain temperature range if a plot of ΔG_n vs T is linear over the same range. With these considerations in mind a value of 207 meV is obtained for ΔH_n from Fig. 3 and a value of $2.3k$ for ΔS_n.

The optical properties of level A were studied by photoadmittance measurements.[11] The spectral distribution of the photoionization cross section of electrons is shown in Fig. 4. Although the spectrum exhibits some structure we were unable to show in what way this structure is related to the energy structure of the center. From the spectrum of Fig. 4 a threshold energy slightly below 0.2 eV is deduced at 77 K in good agreement with the data presented in Fig. 3.

The second level observed in vanadium-doped silicon was also found in the upper half of the band gap, but at a larger binding energy. From the T^2-corrected Arrhenius plot of the thermal emission rate of electrons (Fig. 1) an activation energy of 469 meV was obtained for level B. As in the case of level A, a rather weak temperature dependence of the capture cross section of electrons was observed (Fig. 2) giving a value of about -16 meV for ΔH_{cn}. The change in enthalpy of level B is therefore calculated to be about 485 meV. Using Eq. (2) and calculating ΔG_n as a function of temperature a linear dependence is found (Fig. 3). Performing a similar analysis as in the case of level A, values of 483 meV and $2.1k$ are found for

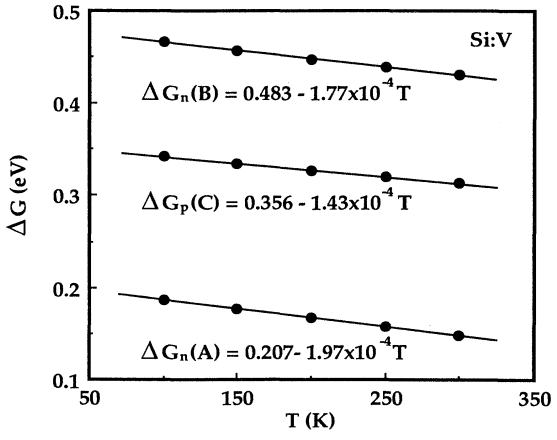

FIG. 3. Temperature dependence of the change in Gibbs free energy, $\Delta G_{n,p}$, for the A, B, and C levels, required to excite electrons and holes to the conduction and valence band, respectively.

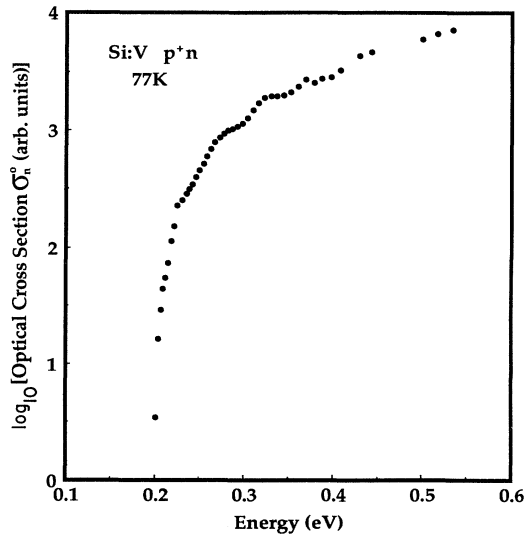

FIG. 4. Spectral distribution of the photoionization cross section of electrons (A level) at 77 K.

ΔH_n and ΔS_n, respectively.

It should be noted that although the temperature dependence of the electron-capture cross section was approximated by Eq. (1) in the above analysis, this does not imply that the capture cross section could not have a different temperature dependence. We demonstrate this in Fig. 5 by plotting the logarithm of the capture cross section versus $\log_{10}T$. From this presentation it would seem that the capture cross section is proportional to T^{-1} and, hence, might be caused by a cascade capture process.[16,17] This, in turn, would imply that level B is a donor level with narrow spaced excited states close to the conduction band. Figures 2 and 5 show that junction space-charge measurements, in general, are not accurate enough to reveal the correct temperature dependence of capture processes. However, as long as the analysis is performed consistently, the same ΔH and ΔS values are

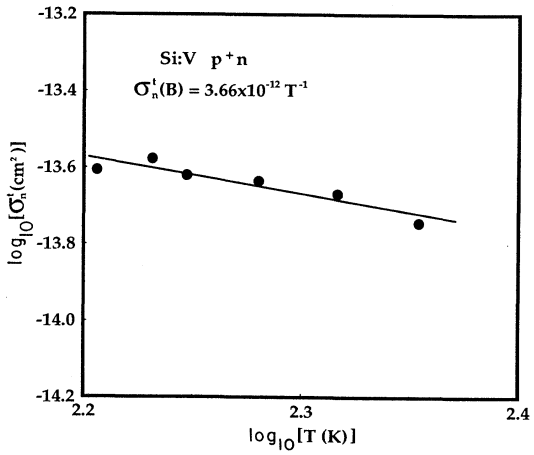

FIG. 5. Temperature dependence of the electron-capture cross section for the B level.

obtained irrespective which temperature dependence of the capture cross section is assumed.[10]

Indications for excited states of level B are indeed found in the optical spectra. Figure 6 shows the spectral distribution of the photoionization cross section of electrons for three different temperatures. All spectra which have been obtained by photocapacitance measurements exhibit at least two clearly resolved peaks at 433 and 457 meV. Whereas the energy positions of the peaks seem to show only a small temperature independence, it is quite clear that the peak intensities, in particular, the one at 433 meV, are strongly temperature dependent. Expansions of the spectra taken at 48 and 98 K are shown in Fig. 7. Since the structures observed were fairly reproducible, an attempt was made to analyze the spectra in more detail. Such an analysis, however, is not straightforward and complicated by the fact that the peaks are rather broad and that only a limited number of peaks with high intensity is observed. It is therefore difficult to decide whether the center is neutral or charged. Assuming a neutral center, a binding energy of the ground state was obtained which was much smaller than the value of ΔG_n at 48 K. Furthermore, such an analysis suggested that the peak at 457 meV was due to transitions into the $2p_{\pm}$ state and, hence, that this peak is much stronger than the $2p_0$ peak which is not often observed for centers of similar binding energy. It appeared therefore to be more correct to assume that the spectra are due to a singly charged center. An assignment of the peaks based on this assumption (Fig. 7) is in very good agreement with effective-mass theory (EMT) (Refs. 18 and 19) and results in a binding energy of the ground state of 479 meV at 48 K which is in excellent agreement with the ΔG_n value of 475 meV obtained from Fig. 3. It should be noted that the optical binding energy ΔG^o is related to the total change in Gibbs free energy ΔG by the relation $\Delta G^o = \Delta G + kT \ln g$, where g is the degeneracy of the energy level.[20]

Level B was also observed when measuring the short-circuit current of a vanadium-doped p^+-n diode. The spectrum of the short-circuit current obtained from such a diode at 77 K is exhibited in Fig. 8. Two major and two minor thresholds are observed. The signal giving the smallest threshold energy at about 0.55 meV was difficult to measure and was therefore not studied further. This signal may originate from level D mentioned by Daliev *et al.*[8] and could be caused by gold as suggested by Lemke.[7] The main threshold at about 0.64 eV is in fair agreement with the binding energy of level B since the sum of both energies gives a value of 1.12 eV which is close to the band gap of silicon at 77 K. If the signal originates from level B then the spectrum is due to the photoionization cross section of holes at least for photon energies between about 0.64 and 0.7 eV.[9] The two minor thresholds are difficult to assign but may be caused by levels A and C.

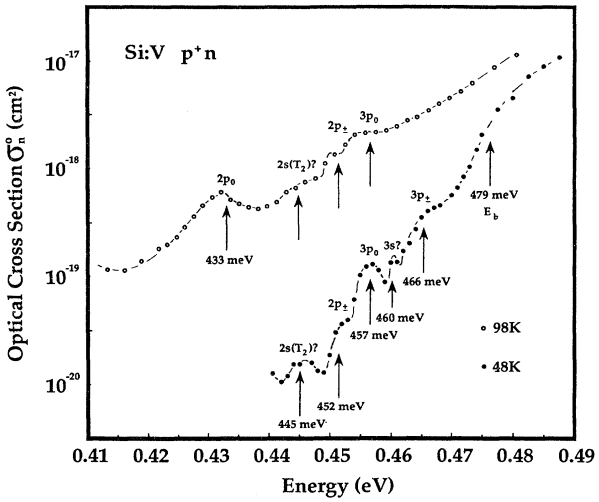

FIG. 7. Part of Fig. 6. The peaks are labeled according to EMT. The arrows indicate transitions from the ground state into the corresponding excited states (see text).

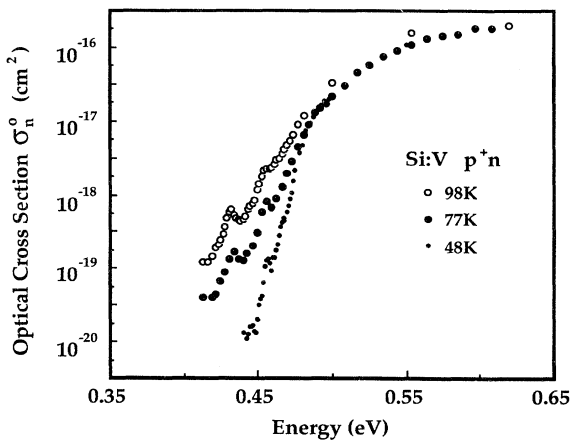

FIG. 6. Spectral distribution of the photoionization cross section for electrons (B level), measured at 48, 77, and 98 K. The cross sections are given in absolute values.

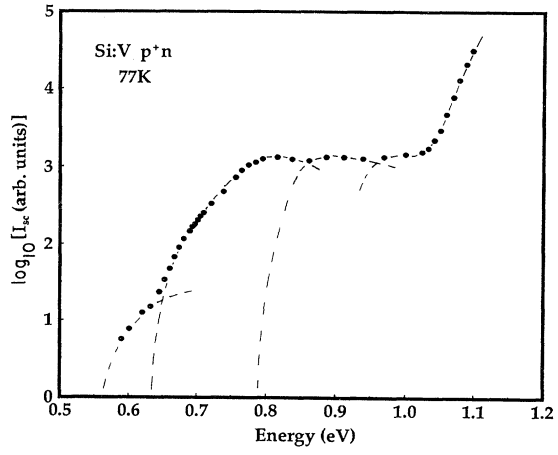

FIG. 8. Spectral distribution of the short-circuit current, I_{sc}, in p^+-n diodes, at 77 K. Thresholds possibly caused by levels A, B, and C as well as by a midgap level, are indicated.

All our vanadium-doped samples showed a level in the lower half of the band gap. The T^2-corrected Arrhenius plot of the thermal emission rate of holes of this third level (C) is presented in Fig. 9. By combining DLTS measurements with single shot studies we were able to measure the emission rate of holes over more than five orders of magnitude in n^+-p diodes. From these measurements an activation energy of 447 meV was obtained. The capture cross section of holes exhibited a rather pronounced temperature dependence with an activation energy of about 90 meV (Fig. 10). In spite of the scatter, the data clearly show an increase of the capture cross section with increasing temperature which is distinctly different from the corresponding temperature dependences of the capture cross section of electrons for levels A and B. From the Arrhenius plots of the emission rate and capture cross section an enthalpy of 359 meV is obtained.

Taking the regression lines of Figs. 9 and 10, ΔG_p of level C was calculated as a function of temperature (Fig. 3). The data suggest an enthalpy of 356 meV and an entropy of $1.7k$ in the temperature range studied. From Fig. 3, one would expect a threshold energy of about 0.35 eV for the photoionization cross section of holes, σ_p^o, at 77 K. A value close to 0.35 eV is indeed observed as shown in Fig. 11 exhibiting the photoionization spectrum of holes at 77 K. It should be noted that the spectrum of σ_p^o is very smooth in the threshold region showing no indication for any kind of structure.

IV. DISCUSSION

In agreement with previous reports,[5,7] our data suggest that at least three vanadium-related centers exist in silicon. At low temperatures, their energy positions are $E_c-0.207$ eV, $E_c-0.483$ eV, and $E_v+0.356$ eV. However, based on the measurements performed it is not possible to decide whether all three levels are different charge states of the same defect or whether they originate from different centers. If it is assumed that the center at

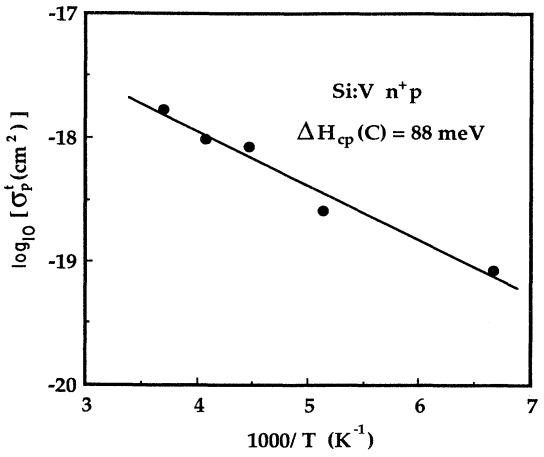

FIG. 10. Arrhenius plot of the hole-capture cross section for the C level in the lower half of the band gap. The energy is the total change in enthalpy due to the capture of holes.

$E_c-0.483$ eV is a singly charged center, then it is most probable that the center at $E_c-0.207$ eV is the neutral version of the same defect and that both levels belong to the same donor. This model is supported by the fact that the photoionization cross-section spectra of electrons in both cases exhibit structures which, compared with the photoionization cross-section spectrum of holes for level C, obviously are not caused by a scatter of experimental data. The smooth spectra observed for e_p^o in the case of level B as well as level C suggest that all three levels are caused by donors. Previous studies of chalcogen donors in silicon[21] have shown that the overall spectra of photoionization cross sections of electrons exhibit a much steeper rise in the threshold region than corresponding spectra of hole transitions. A comparison of Figs. 4, 6, 8, and 11 shows that the same properties are observed for the vanadium-related centers if all three levels are caused by donors. The spectra reported by Daliev *et al.* exhibit

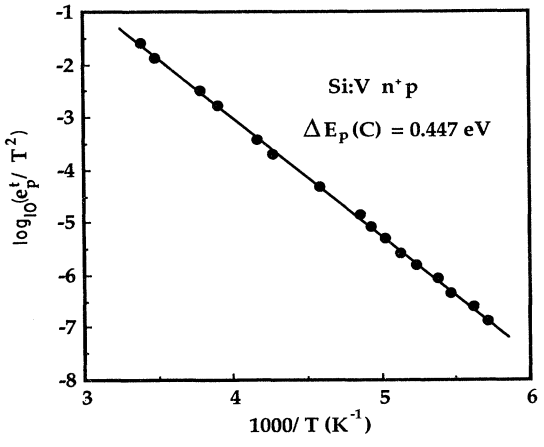

FIG. 9. Arrhenius plot of the T^2-corrected thermal emission rate of holes for the C level in the lower half of the band gap. The energy given is the DLTS activation energy.

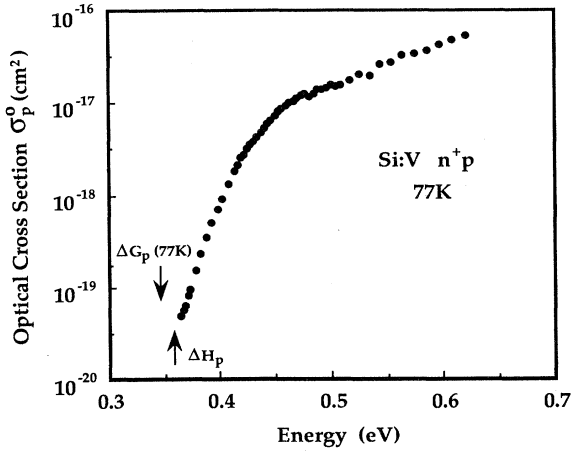

FIG. 11. Spectral distribution of the photoionization cross section for holes (C level), at 77 K. The cross sections are given in absolute values.

a similar behavior.[8] Though we have no direct evidence, our data are nevertheless best understood if it is assumed that the three levels observed are due to donors and that at least two, if not all three of them are different charge states of the same defect.

Further support for this model is obtained from the temperature dependence of the capture cross sections. Whereas in the case of levels A and B the temperature dependence of the electron capture supports a cascade capture process, a similar interpretation of the hole capture of level C is not possible. It is also noted that the capture enthalpies of electrons for levels A and B are small while the hole-capture barrier of level C is much larger, in agreement with previous results published by Lemke.[7]

It is worth mentioning that the total change of entropy obviously approaches zero first at rather low temperatures since the binding energy of level B at 48 K is only slightly smaller than the change of enthalpy obtained from an extrapolation of ΔG_n. This observation is in agreement with the plot of $\log_{10}(e_n^t/T^2)$ vs $1/T$ which is a straight line over as much as five orders of magnitude. One would expect a deviation from a straight line already for a small temperature dependence of ΔS_n since ΔS_n contributes to the preexponential factor as $\exp(\Delta S_n/k)$.

The tentative assignment presented in Fig. 7 is in very good agreement with EMT. If it is true that one of the peaks originates from transitions into the $2s(T_2)$ state then one would expect that the $1s(T_2)$ peak is also observed. However, due to experimental difficulties we were unable to extend our measurements to such small energies.

The large capture barrier of holes observed for level C once again demonstrates how important it is to study free energies instead of thermal activation energies for the evaluation of level positions. Similar reservations are valid for enthalpies, in particular, when thermal measurements are compared with optical studies which are not performed at very low temperatures.

The absolute values of hole-capture cross sections obtained for level C are in reasonable agreement with those obtained by Lemke[7] although the energy positions of the three levels observed by the author differ by 30–50 meV from our data. Similar deviations in the energy positions are observed for the data presented by Hopkins *et al.*,[5] with the exception of the $E_c-0.479$ eV level where the agreement is quite good.

V. CONCLUSIONS

Three vanadium-related centers in silicon were studied in detail. From the temperature dependence of thermal emission rates and capture cross sections the Gibbs free energies were calculated as a function of temperature. Extrapolating these values to $T=0$, the energy positions of the three centers are $E_c-0.21$ eV, $E_c-0.48$ eV, and $E_v+0.36$ eV and the corresponding total changes of entropy are $2.3k$, $2.1k$, and $1.7k$, respectively, which is well within the range previously observed for other defects in silicon[22] and germanium.[23] Photoionization cross-section spectra of electrons propose that at least the centers at $E_c-0.207$ eV and $E_c-0.483$ eV are donors. A more detailed analysis of the spectrum for the $E_c-0.483$ eV center suggests that the spectrum originates from a charged center. Without direct evidence a model has been discussed assuming that all three centers are donors and that at least two of the centers are different charge states of the same defect.

ACKNOWLEDGMENTS

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