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Electrical and optical properties of titanium-related centers in silicon

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Titanium-doped silicon was investigated using junction space-charge techniques. Apart from a midgap level at about $E_c-0.6$ eV, three energy levels were observed at $E_c-0.065$ eV (A level), $E_c-0.295$ eV (B level), and $E_v+0.255$ eV (C level) at 80 K. Electron excitation processes of the upper levels revealed values of 0.077 and 0.268 eV, respectively, for the change in enthalpy, as well as $2k$ and $-4k$, respectively, for the change in entropy. The corresponding values for holes of the C center are 0.258 eV and $0.5k$, respectively. The Gibb's free energy as a function of temperature was calculated for all three levels and found to be in good agreement with the threshold energies of the corresponding photoionization cross section. Only small, if any, lattice-relaxation effects are expected.

I. INTRODUCTION

Some of the transition metals (TM) in silicon have been studied recently in detail by using high-resolution spectroscopy.[1–4] Several of these TM such as Fe (Ref. 1) or Pt (Ref. 2) show considerably more complicated energy structures, both with regard to the ground states and excited states than, for example, the previously studied double donors sulfur and selenium[5] in silicon. Although the optical properties of these transition metals have been studied comprehensively, very little information is available about the optical properties of other TM in silicon such as, for example, titanium.

The recombination properties of titanium-related centers in silicon have previously been characterized electrically and reexamined recently.[6–8] In most of these studies, two titanium related centers have been observed, one in the upper half of the band gap at $E_c-0.28$ eV (which we label the B level) and another one in the lower half of the band gap at $E_v+0.25$ eV (C level). Recently a third titanium-related center has been reported[6,7] at $E_c-0.08$ eV (A level). The two deep levels have been suggested previously[8] to be different charge states of the same donor. In a recent paper, Mathiot and Hocine[7] claim that the level at $E_c-0.08$ eV is an acceptorlike version of the same center implying that titanium forms a center in silicon with three different charge states. In addition to the three charge states several papers[9,10] report on a fourth level, which has been noticed in titanium-doped silicon in the range from $E_c-0.51$ to $E_c-0.55$ eV (D level).

The purpose of this paper is to present spectral distributions of photoionization cross sections for the B and C levels. The results are compared with data obtained from our own or previously published electrical measurements. Absolute values of the enthalpy and entropy as well as the Gibbs free energy as a function of temperature are discussed for the A, B, and C levels. In addition, optical data of the D level are presented.

II. EXPERIMENTAL DETAILS

The samples used were either p^+-n or n^+-p diodes implanted with titanium. The diodes were prepared without metallization using a localized oxidation of silicon technology. The p-type- and n-type-doped silicon wafers, respectively, had a free carrier concentration of about 10^{15} cm^{-3}. The p^+- and n^+-type regions were annealed at 1100 °C for 2 h after boron and arsenic implantation, respectively. After the annealing process the titanium 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 titanium was finally electrically activated by rapid thermal annealing at 1220 °C for 60 s in a nitrogen ambient resulting in a concentration of electrically active titanium-related centers of about 5×10^{13} cm^{-3}.

The thermal emission rates were determined using junction space-charge techniques such as deep-level transient spectroscopy[11] (DLTS) and single-shot measurements.[12] By combining the different methods we were able to determine the corresponding emission rates and capture cross sections of the A, B, and C levels over a large temperature range. Special care was taken to avoid influences from the tail of the space-charge region on the capture processes. This is done most reliably in the analysis by including only measurements with short

pulses far from saturation.

All electric-field measurements were conducted using single-shot measurements. This aided us in the measurement of strictly exponential transients. The electric-field enhanced electron-hole emission from a thin slice of the space-charge region was studied by taking 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. By using this technique only signals at fairly constant electric fields were recorded.[13]

Some of the optical measurements were performed using a 0.5-m vacuum grating monochromator (Acton Research Corporation) to avoid disturbances from atmospheric absorption lines. For the same reason the globar light source and the collimating system were also evacuated. The resolution of the monochromator used was about 1 meV. The other optical measurements were preformed using a double prism monochromator. Stress introduced by improper mounting of the samples tends to smear out the features of the optical cross sections. This was avoided by mounting the samples on a gold-plated silicon chip which exhibits the same thermal expansion as the sample.

III. RESULTS

Our samples showed all four levels previously observed in titanium-doped silicon. The enthalpy of three of these levels were determined by measuring the temperature dependence of both the thermal emission rate e^t and capture rate c^t. From detailed balance it is known[14] that the thermal emission rate of electrons is given by

$$e_n^t = c_n^t N_c \exp(-\Delta G_n / kT) , \tag{1}$$

where k is the Boltzmann constant, N_c is the effective density of states in the conduction band, and ΔG_n is the change in Gibbs free energy needed to excite an electron from the energy level into the conduction band. Similar considerations are valid for hole transitions. Since[15]

$$\Delta G_n = \Delta H_n - T \Delta S , \tag{2}$$

it follows from Eq. (1) that

$$e_n^t = c_n^t N_c \exp(\Delta S / k) \exp(-\Delta H_n / kT) , \tag{3}$$

where ΔH_n is the change in enthalpy and ΔS the total change in entropy observed during excitation. Provided the capture rate is temperature independent, it is evident from Eq. (3) that the activation energy obtained from an Arrhenius plot of the thermal emission rate reveals the change in enthalpy ΔH_n and not the change in Gibbs free energy ΔG_n as often assumed. It is also evident that the capture rate c_n^t cannot be calculated from an Arrhenius plot of e_n^t unless the change in entropy ΔS is known. Since ΔS in most cases is not known from other investigations, the capture rate can be obtained only from direct measurements. ΔS is often of the order of several k and in such cases $\exp(\Delta S / k)$ represents a factor larger than 10^2, which implies, if c_n^t is calculated from the preexponential factor of Eq. (3), that the calculated c_n^t value may differ by more than two orders of magnitude from the real capture rate.

The relation of the capture rate with the capture cross section σ_n^t is given by

$$c_n^t = \sigma_n^t v_{\text{th}} , \tag{4}$$

where v_{th} is the thermal velocity of electrons. σ_n^t is often temperature dependent and if this temperature dependence can be expressed as

$$\sigma_n^t = \sigma_0 \exp(-\Delta H_{cn} / kT) , \tag{5}$$

by rewriting Eq. (3) one obtains

$$e_n^t = A T^2 \exp[-(\Delta H_n + \Delta H_{cn}) / kT] , \tag{6}$$

where A is a temperature-independent constant and ΔH_{cn} is the change of enthalpy due to the electron capture. Hence, from an Arrhenius plot of $\log_{10}(e_n^t / T^2)$ versus $1/T$ the activation energy

$$E_{\text{DLTS}} = \Delta H_n + \Delta H_{cn} \tag{7}$$

is obtained, which implies that ΔH_n can only be calculated if ΔH_{cn} is known. Once ΔH_n is determined, ΔS can be calculated using Eq. (2) since ΔG_n is readily obtained from Eq. (1).

It has already been pointed out previously[16] that there is a simplier way of analyzing the data by calculating ΔG_n for different temperatures from Eq. (1) using the absolute values of e_n^t and σ_n^t and plotting the obtained ΔG_n values versus T. Following Eq. (2) the slope of such a line gives ΔS and the extrapolated value of ΔG_n at $T = 0$ reveals ΔH_n. It should, however, be noted that it is often not trivial to measure absolute values of capture rates correctly.[17,18] The change of the optical Gibbs energy ΔG_n^0 is given by[19]

$$\Delta G_n^0 = \Delta G_n + kT \ln g , \tag{8}$$

where g is the degeneracy factor of the energy level. For small g values and in the absence of lattice relaxation effects it can therefore be expected that ΔG_n is close to the optical binding energy, at least at lower temperatures. Hence a plot of ΔG_n versus T represents in many cases a reasonable approximation for the temperature dependence of the binding energy of an energy level. The normally quoted ΔH_n values differ from the ΔG_n^0 values by $T(k \ln g - \Delta S)$ and can therefore in general not be used for a direct comparison of thermal and optical data if the optical data have not been taken at very low temperatures.

Figure 1 shows a T^2 corrected Arrhenius plot of the thermal emission rate of electrons obtained for the shallow titanium related A level close to the conduction band. The electron-capture cross section was found in agreement with previous results[7] to be rather temperature independent and the calculated activation energy $E_{\text{DLTS}} = 0.077$ eV is therefore close to the change in enthalpy. The capture rate is expected to depend exponentially on the pulse width. Due to tail effects, however, deviations are often observed for longer pulses. Subtracting the signals obtained for larger pulse widths, an exponential dependence is observed for the A level

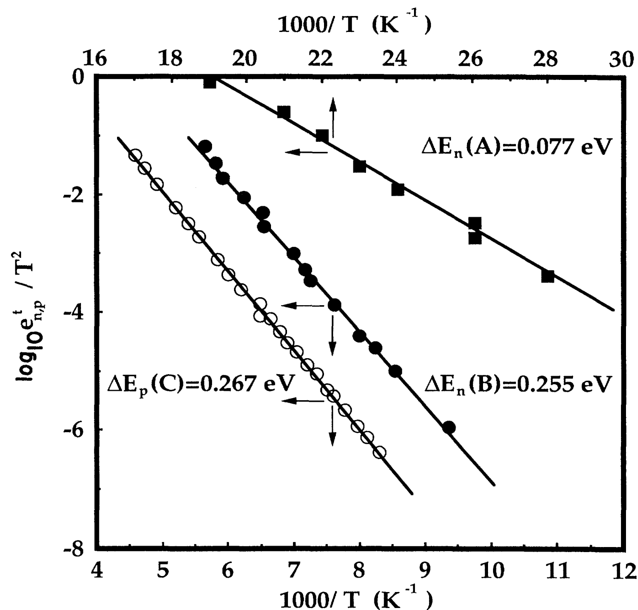

FIG. 1. Arrhenius plots of the T^2 corrected thermal emission rates for the energy levels A, B, and C. The energies given are DLTS activation energies for electrons in the case of the A and B levels and for holes in the case of the C level (see text).

over almost two orders of magnitude. Similar results have been obtained for the other levels.

Using Eq. (1) and the measured e_n^t values, together with a temperature-independent electron-capture cross section of 1.6×10^{-15} cm^2, ΔG_n was calculated at different temperatures [Fig. 2(a)]. A value of 0.077 eV was obtained for the extrapolated ΔG_n value at $T=0$ K in agreement with the ΔH_n value obtained from the Arrhenius plot presented in Fig. 1. The value of $\Delta H_n=0.08$ eV is in good agreement with the value previously reported,[7] although the absolute values of the thermal emission rate are in our case slightly larger than those quoted in Ref. 7. From the slope of the straight line [Fig. 2(a)] an entropy change of about $2k$ is calculated.

Similar measurements were performed on the C level. Using both DLTS and single-shot measurements the thermal emission rate for holes was measured over about five orders of magnitude (Fig. 1). From the T^2 corrected Arrhenius plot an activation energy of $E_{\rm DLTS}=0.267$ eV was obtained. Since the thermal emission rate e_p^t was found to have very little dependence on the applied electric field, no further studies on the field dependence of the hole emission rate were performed. The hole-capture cross section showed a slight increase with increasing temperature (Fig. 3), suggesting a multiphonon-emission process rather than a cascade capture process. The capture barrier was calculated to be about $\Delta H_{pc}=10$ meV, thus giving an enthalpy change of $\Delta H_p=0.257$eV for the lowest observed titanium-related energy level.

Using Eq. (1) and the regression lines presented in Figs. 1 and 3 for the C level, ΔG_p was calculated for different

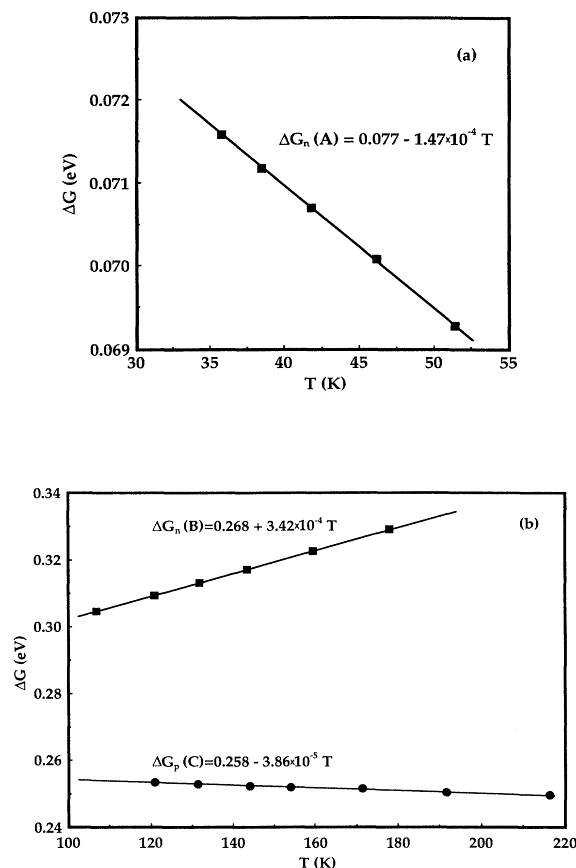

FIG. 2. (a) Temperature dependence of the Gibbs free energy for level A. (b) Temperature dependence of the Gibbs free energy for levels B and C. The ΔG values are presented according to Eq. (2) (see text).

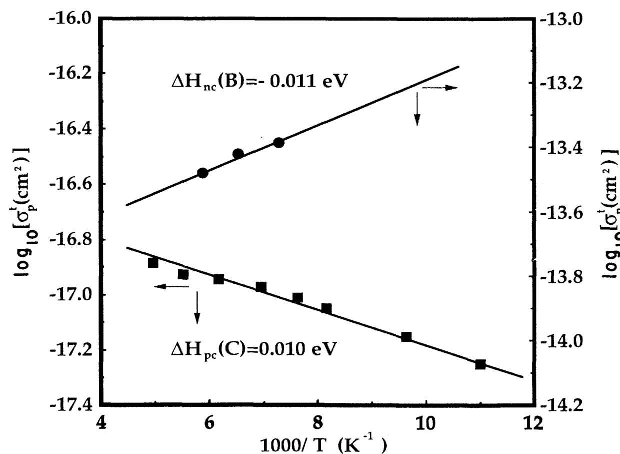

FIG. 3. Arrhenius plots of the capture cross section for electrons (B level) and holes (C level). The energies are calculated changes of enthalpy due to the capture of electrons (B level) and holes (C level).

temperatures and plotted versus T [Fig. 2(b)]. Extrapolating the calculated ΔG_p values to $T=0$ K, a value of $\Delta H_p=0.258$ eV was obtained, which is in reasonable agreement with the value deduced from the Arrhenius plots. The slope of the line shown in Fig. 2(b) for ΔG_p gives a value of about $0.5k$ for the change in entropy which is in good agreement with previous values observed for other deep centers in silicon.[20]

Considering the ΔG_p values obtained for the lowest titanium-related energy level one would expect an optical threshold energy of about 0.255 eV at 77 K for the photoionization cross section of holes, σ_p^0. However, the threshold energy deduced from the spectral distribution of σ_p^0 reveals a slightly larger value of 0.27 eV (Fig. 4), if only the experimental data at 77 K are taken into account. The best fit to the spectral distribution was obtained by using $\sigma^0(h\nu)=a(h\nu-E_{TH})^{5/2}/h\nu^3$, an expression suggested for doubly forbidden optical transitions not involving excited states[21] (dashed curve in Fig. 4), which resulted in a threshold energy of 0.273 eV. Although no further studies were performed, the slight difference between ΔG_p and the optical threshold energy may originate either from a somewhat larger degeneracy factor or a small lattice relaxation effect. The photoionization cross sections were obtained from transient photocapacitance measurements. As shown in the inset of Fig. 4 all transients studied were singly exponential.

For comparison, the spectral distribution of σ_p^0 was

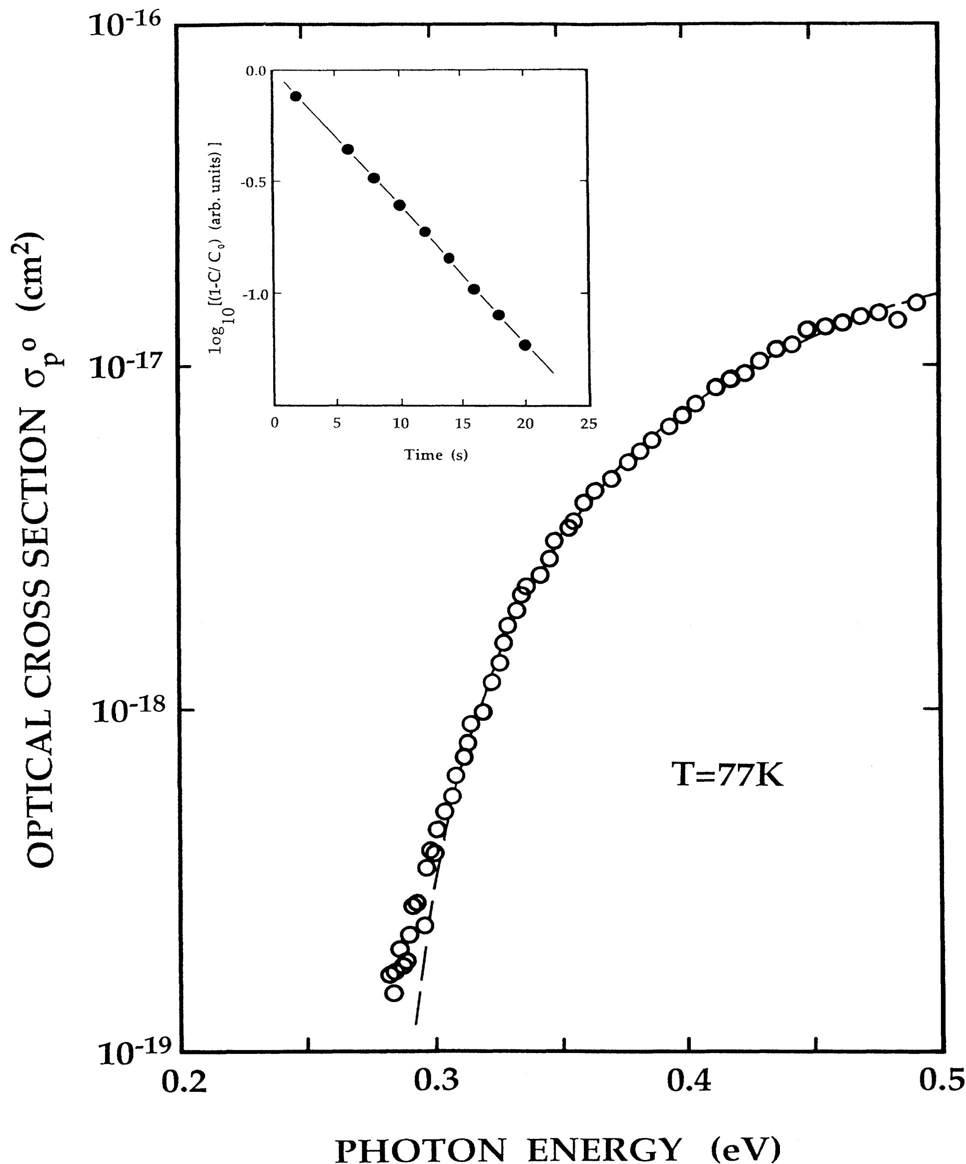

FIG. 4. Spectral distribution of the photoionization cross section for holes (C level) at 77 K. The cross sections are given in absolute values. The inset shows the time dependence of a photocapacitance transient obtained with a photon energy of 0.44 eV.

also measured in n^+-p diodes using the photocurrent storage effect[12] (Fig. 5). The data obtained from this measurement method are in good agreement with the photocapacitance measurements resulting in a threshold energy of 0.270 eV when using a similar approximation as in Fig. 4 (dash-dotted curve in Fig. 5). Since these studies also included measurements at higher energies, a second threshold was observed at about 0.6 eV. Extrapolating the σ_p^0 values, obtained at lower energies, to higher energies and subtracting these values from the measured data, the dashed line was obtained with a threshold energy of 0.51 eV, which can probably be attributed to the energy distance of the level from the valence band. Although this method is not very accurate, it nevertheless proves that an additional level is present in our samples which probably is identical with the previously reported energy level at $E_c - 0.6$ eV.[9,10]

The energy level at about $E_c - 0.6$ eV is also observed in the spectral distribution of the photoionization cross section obtained from measurements of the short-circuit current[12] in n^+-p diodes giving a threshold of 0.585 eV (dotted curve) (Fig. 5). This energy probably corresponds to the energy distance of the D level from the conduction band. Adding this value to the threshold energy obtained from the storage effect, a value of about 1.1 eV is obtained, which is close to the band-gap energy. The second threshold observed in Fig. 5 for the short-circuit current at about 0.8 eV (0.783 eV due to the solid curve) is difficult to assign since the energy distances of the B and C levels from the nearest energy bands are very similar.

Thermal emission and capture rates as well as optical emission rates of the B center were also studied. Since both DLTS and single-shot measurements were applied the temperature dependence of the thermal emission rate could be studied over about five orders of magnitude giving an activation energy of $E_{\mathrm{DLTS}} = 0.255$ eV (Fig. 1). The electron-capture cross section σ_n^t decreased slightly with increasing temperature (Fig. 3) and exhibits therefore a different temperature dependence than the hole capture process of the C level. The enthalpy of the capture process, ΔH_{cn}, obtained from an Arrhenius plot of σ_n^t, was found to be about -11 meV, resulting in a change of the enthalpy $\Delta H_n = 0.266$ eV for the thermal emission of the B level.

A similar result for ΔH_n was obtained when using Eq. (1) and calculating ΔG_n for different temperatures. Plotting the ΔG_n values versus T [Fig. 2(b)] a value of 0.268 eV is obtained for ΔH_n by extrapolating the data to 0 K. The slope of the regression line corresponds to a change of entropy of about $-4k$.

The data presented in Fig. 2(b) for the B level suggest that the photoionization cross section spectrum of electrons should have a threshold energy of about 0.295 eV at 77 K if no lattice relaxation occurs. Figure 6 shows that this is indeed observed.

The spectral distribution of the short-circuit current was also studied in p^+-n diodes. In the case of n^+-p diodes (Fig. 5) three thresholds were observed. For energies less than about 1 eV the spectral distributions are very similar in both n^+-p and p^+-n diodes, although the relative signal strength due to the two energy levels is different. Interestingly, the threshold energy for the one-photon electron-hole pair generation seems to be different in the two types of diodes, implying that the threshold energy for the one-photon pair generation is shifted about 40 meV to higher energies in the n^+-p diodes.

Attempts were made to measure the optical cross section of electrons for the C level and the optical cross section of holes for the B level. Photocapacitance measure-

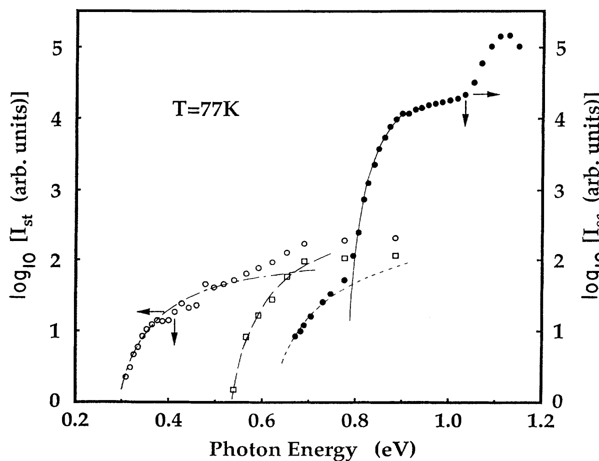

FIG. 5. Spectral distribution of the short-circuit current I_{sc} (solid circles) and the photocurrent storage effect I_{st} (open circles and squares) measured for holes in n^+-p Si:Ti diodes at 77 K. The open squares have been obtained by subtracting the dash-dotted curve from the open circles.

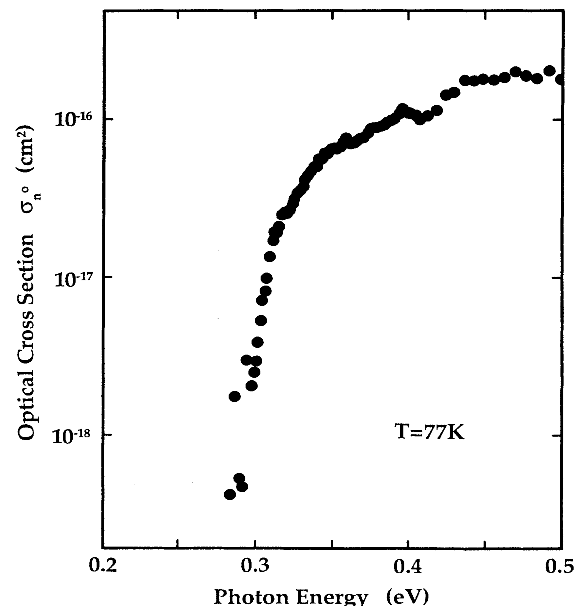

FIG. 6. Spectral distribution of the photoionization cross section for electrons (B level) at 77 K. The cross sections are given in absolute values.

ments, however, showed that $\sigma_p^0 \gg \sigma_n^0$ for the C level and $\sigma_n^0 \gg \sigma_p^0$ for the B level. Hence the C level could not be emptied and the B level could not be filled with electrons optically to a degree which was sufficient enough to perform reliable measurements.

IV. DISCUSSION

The results presented in this paper suggest that lattice relaxation effects connected with the energy levels studied are small if not negligible. This is in agreement with other transition-metal impurities in silicon such as Au, Ag, and Pt, which all seem to have very small Frank-Condon shifts.[2-4] Junction space-charge measurements in general and our measurements in particular do in general not reveal the charge state of an energy level and it is therefore not known from such measurements which charge state of an energy level is changed due to a particular excitation process. Since it has been suggested previously that probably all four energy levels studied in this paper are titanium related, it was of particular interest for us to show which of these energy levels are coupled. However, due to the symmetry in energy position of the three deep energy levels with respect to the band edges and the proximity of the fourth level to the conduction band none of the known measurement techniques could be used to study the coupling of any of these energy levels. Mathiot and Hocine compared the heights of the DLTS peaks due to the three deep energy levels in Si:Ti and found that the heights of three peaks were very similar. It has therefore been concluded that the three energy levels are associated with different charge states of the same defect, i.e., titanium. However, Brotherton *et al.*[22] have shown previously in the case of chalcogens that energy levels with different binding energies sample different parts of the space-charge region and different heights of the corresponding DLTS peaks are therefore expected in spite of the fact that the concentrations of the levels are similar. Although there are good reasons to believe that the four levels studied in titanium-doped silicon all originate from titanium and that at least three of them originate from the same defect, we nevertheless believe that this has still to be explicitly shown.

Several of the properties observed in titanium-doped silicon, however, support the suggestion that probably three of the energy levels are likely due to the same defect. Assuming that the midgap level is caused by a different center and following previous assignments,[7] one would expect that the threshold energy of the short-circuit current in n^+-p diodes is predominantly caused by electron excitations from the C level into the conduction band, considering that this process involves the largest part of the space-charge region and that two electrons have to be excited into the C level before the B level will participate in the generation of the short-circuit current. Consequently, the A level will play a minor role in these excitation processes and, hence, the generation of electron-hole pairs involving one photon is expected to occur close to the band-gap energy without major interference from the A level. On the other hand, in p^+-n diodes the threshold and signal intensity is expected to depend on the concentration of unoccupied A and B levels since most of the C levels are completely occupied with electrons. One would therefore expect that the generation of the short-circuit current involving only one photon starts at a smaller photon energy in p^+-n diodes than in n^+-p diodes due to photothermal excitation processes involving the A level. Considering the data presented in Fig. 5 there is no doubt that the third threshold of the short-circuit current in p^+-n diodes at about 1.0 eV occurs at a smaller photon energy than in n^+-p diodes with a threshold at about 1.05 eV.

At 80 K the energy distance of the C level from the nearest energy band is about 30 meV smaller than in the case of the B level. In n^+-p diodes one would therefore expect a slightly larger threshold energy for the short-circuit current (at about 0.8 eV) than in p^+-n diodes. This is in qualitative agreement with the experimental data.

In the framework of this tentative model it is also evident that the hole capture at the C level is not supposed to involve excited states whereas the electron capture of the B level may well employ excited states. If this is true one would expect that the electron-capture cross section decreases with increasing temperature,[23] whereas the hole capture cross section may increase with increasing temperature if multiphonon-emission processes are involved.[24] Figure 3 shows that this is indeed the case. It is worth noticing that our emission rates and capture-cross sections are in fair agreement with the data published by Wang and Sah.[8]

Further support of the model is obtained from the photoionization cross-section data. It has previously been shown for chalcogens in silicon[25] that photoionization cross sections due to $0/+$ or $+/++$ transitions exhibit much sharper thresholds than $+/0$ or $++/+$ transitions. Comparing the spectra presented in Figs. 4 and 6 it is quite evident that the threshold of σ_n^0 is considerably sharper than the one for σ_p^0.

At present we have no explanation for the negative change of the total entropy observed for the electron excitation of the B level. Negative changes of entropy have been observed previously in II–VI compounds.[16] They have been explained by a possible temperature dependence of some of the pressure coefficients contained in the expression for the total change of entropy. Although the origin of the negative change in entropy of the B level is not yet known, it nevertheless explains some confusion in the literature. Mathiot and Hocine[7] pointed out an inconsistency in the electron-capture cross section which they believed was not noticed by Wang and Sah.[8] Neglecting the entropy term Mathiot and Hocine calculated the electron-capture cross section from the preexponential factor of Eq. (3) and found that this value was a factor of about 70 smaller than the value measured by Wang and Sah. The authors claimed that the discrepancy arose from an incorrect analysis of the capture cross section in Ref. 8. They resolved the discrepancy by assuming an additional capture barrier, which finally resulted in an energy position of the B level at $E_c - 0.30$ eV.

As pointed out earlier capture cross sections cannot be calculated from the preexponential factor of Eq. (3) as

long as ΔS is unknown. From our analysis we suggest a value of about $-4k$ for ΔS, which implies that any capture cross section calculated from the preexponential factor would be a factor of about 55 too *small* if the entropy term is neglected. The discrepancy arises therefore not from an erroneous analysis of the experimental data by Wang and Sah but from an incorrect application of Eq. (3) in Ref. 7.

In the case of the hole capture Mathiot and Hocine found for the C level that their own measured capture cross section was a factor of 3–4 smaller than the one they calculated from the preexponential factor Eq. (3), without taking into account the entropy term. Our measurements suggest a value of about $0.5k$ for ΔS in connection with the hole capture. Any capture cross section calculated from the preexponential factor should therefore be a factor of about 2 too *large* if the entropy term is neglected. The good agreement between the calculated values using our ΔS values and the measured values shows that the results obtained for the C level in Ref. 7 are consistent and in good agreement with our own data.

Regarding the midgap level in titanium-doped silicon we have no explanation for its origin and will therefore not speculate whether or not this energy level is titanium related. Several midgap levels have been observed in silicon which originate from both impurities and process induced defects. Further studies have to be performed to unravel the chemical nature of this particular midgap level.

V. CONCLUSION

A comprehensive study of four energy levels observed in titanium-doped silicon has been performed. In addition to a midgap level three energy levels were observed with energy positions of $E_c-0.065$ eV, $E_c-0.295$ eV, and $E_v+0.255$ eV at 80 K. Electron excitation processes for levels in the upper half of the band gap revealed values of 0.077 and 0.268 eV, respectively, for the change in enthalpy as well as $2k$ and $-4k$, respectively, for the change in entropy. The corresponding values for hole excitation process of the lower energy level are $\Delta H_p=0.258$ eV and $\Delta S=0.5k$. The Gibbs free energy ΔG as a function of temperature was calculated for all three levels. The ΔG_n value of the B level was found to be in good agreement with the threshold energy of the corresponding photoionization cross section, whereas the threshold energy of the photoionization cross section for holes of the lower energy level was slightly larger than the corresponding ΔG_p value. These results suggest that only small, if any lattice relaxation effects are expected for these energy levels. Due to the symmetry in energy positions of two of these levels and the proximity of the upper energy level to the conduction band no evidence could be provided whether or not the three energy levels are coupled, i.e., whether they are different charge states of the same defect or not.

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