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EXCITED DONOR STATES IN SULFUR AND SELENIUM DOPED SILICON

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Excited states of deep centers in Si:Se have been studied using junction space charge techniques. Assuming singly and doubly charged centers, structures at the edge of the photoionization cross section spectra have been interpreted as Rydberg series. In addition, internal transitions between states originating from the valley-orbit splitted ground states are seen. The temperature dependence of the spectra is in agreement with photothermal excitation processes. The electron capture into the shallower center is dominated by a cascade capture process well described by a two stage capture model.

If a donor level in silicon is mainly constructed from states in the conduction band, its ground state is split because of the multivalley nature of the conduction band and thus generating excited states. In addition the Coulombic tail of the potential may give rise to a set of excited states commonly referred to as the Rydberg series. Whereas both types of excited states have been observed for several shallow donors in silicon, little information is available on excited states at deep donor states [1, 2].



Fig.l Temperature dependence of the capture cross section for the B-center in Si:Se and Si:S In this paper we present data on excited states in Si:S and Si:Se. Both sulfur and selenium create two dominant donor levels at about E_C -0.5 eV (Accenters) and E_C -0.3 eV (B-centers) [3, 4, 5]. It will be shown that all centers including the midgap levels have excited states.

Detailed investigations of the thermal properties of the Bcenters clearly reveal that the temperature dependence of their electron capture cross sections σ_n^t , Fig.(1), is best understood in terms of a two step capture model previously proposed by Gibb et al [6]. Within the framework of this model, the electron capture cross sections given by $\sigma_n^t = AT^{-2} \exp(E_1/kT)$ where A is a temperature independent factor and E₁ the energy spacing between the conduction band and the lowest state, accessible in a cascade capture process. From the data presented in Fig.(1) values of 17 and 14 meV are obtained for sulfur and selenium, respectively. Since these values are in fair agreement with the effective-mass binding energy of the 2p₀ state this result strongly suggests that the 2p₀ state is the lowest accessible state in the cascade capture process. The energy spacing, E₂, from the 2p₀ state down to the ground state is then obtained [6] as the activation energy in an Arrhenius plot of the thermal emission rates (log $e_n^t - 1/T$). E₂ is found to be 0.286 eV for selenium and 0.302 eV for sulfur. Knowing the temperature dependence of σ_n^t the Gibb's free energy ΔG_n can be calculated at different temperatures using the detailed balance relationship $e_n^t = \sigma_n^t v_{th} N_c \exp(-\Delta G_n/kT)$. Values of 0.301 eV (independent of temperature) and 0.30 - 0.31 eV (weakly depending on temperature) are obtained for selenium and sulfur, respectively.

The spectral distribution of the photoionization cross section of electrons $\sigma_{\rm BB}^{\rm O}$ for the B-center in Si:Se is shown in Fig.(2a) at two different temperatures. The values of ΔG_n and E_2 obtained from thermal measurements are marked with arrows and the corresponding tran-



Fig.2 $\sigma_{\text{OB}}^{\text{O}}$ in Si:Se a) temperature dependence b) energy level scheme

sitions are shown in Fig.(2b). The structure in the spectra observed for energies smaller than ΔG_n are due to photothermal ionization processes. The electron is first transfered optically from the ground state to an excited state and then thermally excited into the conduction band. All excited states of the Bcenters are situated so close to the conduction band that thermal emission processes are much faster than optical processes even at 40 K. The optical spectra are therefore not thermally activated, Fig.(2a).

The structure between ΔG_n and E_2 may be interpreted as Coulomb excited states of a singly charged center. Further out in the infrared region a narrow and clearly resolved peak (T) is seen. The halfwidth of this peak (1.7 meV) strongly suggests that it is caused by an internal transition. The energy spacing between the peak and ΔG_n is 31 meV (33 meV for Si:S). This value is to be compared with 34 meV for the energy difference between the 1sT₂ state and the conduc-

tion band for shallow donor-like centers such as phosphorous and arsenic. These results suggest that the B-centers are singly charged centers in both sulfur and selenium doped silicon.

In contrast to the spectra of $\sigma_{\rm NB}^{\rm o}$, the photoionization cross sections of electrons, $\sigma_{\rm NA}^{\rm o}$, for the A-center in Si:Se show a pronounced temperature dependence in the low energy part of the spectrum due to

a deeper split-off state, Fig.(3a). Such a T_2 state may originate from a doubly charged center. In order to investigate this matter in more detail we replot the spectrum between 0.53 and 0.59 eV on an



Fig.3 σ_{nA}^{o} in Si:Se: a) temperature dependence, b) expanded edge region, c) energy level scheme

expanded scale in Fig.(3b). By multiplying the energies of the Rydberg series for a Z = 1 center with $Z^2 = 4$ good agreement has been obtained between the energies of the $2p_{\pm}$, $3p_{\circ}$ and $4p_{\pm}$ excited states and the energy position of the peaks in this part of the spectrum. In this way, a binding energy ∆G of 570 meV for the A-center (590 meV in Si:S) is deduced. Subtracting 44 meV for the energy of the $2p_0$ state from ΔG gives a value of 526 meV.(E2 in Fig.(3a)) which in the case of Si:Se is in excellent agreement with the value of E2 derived from thermal measurements. Knowing the energy value for $\triangle G$ it is readily seen that the T₂ split-off state is situated 143 meV (163 meV in Si:S) below the conduction band edge which explains why this part of the spectrum is thermally activated.

As seen from Figs.(2) and (3) the energy positions of the Tpeaks are independent of temperature. If the excited states of the A- and B-centers are effective mass-like this would imply that both centers are pinned to

the conduction band which is in agreement with thermal data at least for the B-centers. The spectra of the photoionization cross sections of holes for the A-center do not show any clearly resolved structure. Their temperature dependence is not in contradiction to what has been said above.

References

- C.T. Sah, T.H. Ning, L.L. Rosier and L. Forbes: Solid State Commun. <u>9</u> (1971) 917.
- T.H. Ning and C.T. Sah: Phys. Rev. B <u>14</u> (1976) 2528.
- H.G. Grimmeiss, E. Janzén and B. Skarstam: J. Appl. Phys. <u>51</u> (1980) July
- H.G. Grimmeiss, E. Janzén and B. Skarstam: J. Appl. Phys. <u>51</u> (1980) August

- 5) H.G. Grimmeiss and B. Skarstam: to be published.
- 6) R.M. Gibb, G.J. Rees, V.W. Thomas, B.L. Wilson, B. Hamilton, D.R. Wight and N.F. Mott: Philos. Mag. <u>36</u> (1977) 1021.