PHOTOLUMINESCENCE FROM CHROMIUM-BORON PAIRS IN SILICON

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Silicon samples containing chromium-boron pairs exhibit characteristic luminescence
lines in the 1.5 μm wavelength region. The spectrum consists of a sharp structured
no-phonon line and low energy sharp in-band resonant mode replicas. The phonon energy
(13.6 meV) corresponds to a local vibration of the interstitial chromium.
In an uniaxial stress field the splitting of the no-phonon line is anisotropic and can
be explained consistent with the known trigonal symmetry of the Cr-B pairs. We discuss
the luminescence in terms of an excitonic recombination at an isoelectronic Cr-B pair,
where the hole of the exciton is deeply bound to the boron acceptor in the axially
symmetric field of the complex.

1. INTRODUCTION

Diffusion of transition metals into silicon
crystals results in a variety of different
electrically active levels in the forbidden
bandgap. Not only from the technological point
of view, but also with regard to deep level
calculations it is essential to investigate the
properties of these defects. Unfortunately the
sample preparation technique influences drasti-
cally defect reactions of the fast diffusing
transition metals and makes a comparison of re-
sults as obtained by different experimental
techniques on different samples very difficult.
On the other hand even if different experimen-
tal techniques are applied to the same sample
it is not obvious that the same defect is in-
vestigated.
The basic knowledge of the structure of the
transition metal complexes in silicon comes
from the pioneer work of Ludwig and Woodbury.[1]
By EPR-technique they determined the ground
state symmetry of many transition metals and de-
developed a simple crystal-field model, which ex-
plained all characteristic features of these
point defects in a straightforward manner. For
an interstitial transition metal all 4s elec-
trons are transferred to the 3d shell. A small
crystal-field splits the degenerated d-states
into a twofold e-level and a threefold t_2-level,
with the t_2-state lying lower in energy. The le-
vels are occupied according to Hund's rule, re-
sulting for the ground state in a high spin
state.
Due to their high diffusion constant, the inter-
stitial transition metals form complexes with
other impurities, especially with the shallow
acceptors. In these complexes the ionized accep-
tors bind the positive charged transition metal
ions in the nearest or next nearest interstitial
lattice site. The EPR parameters of these pairs
differ only slightly from the values measured
for the corresponding isolated interstitial me-
tal ion. The acceptor ion mainly disturbes the
symmetry of the cubic binding potential of the

transition metal. In nearly all these pairs, as
e.g. the Cr-B pairs, the LS-coupling of the tran-
sition metal ion remains valid. Cr-B pairs show
the same angular momentum J=5/2 as the intersti-
tial $Cr_i^+(d^5)$ ion. The g-value is isotropic and
the <111> axis of the complex is described by
the D-term.

Contrary to the picture of Cr_i and Cr-B pairs
derived from EPR measurements, the electrical
properties of these defects are quite controver-
sy. Many different energy levels attributed to
chromium were reported in the literature (see
e.g. Ref. [2]). Combining EPR and Hall effect
results measured in the same samples, Feicht-
inger and Czaputa [2] could correlate the Cr do-
nor transition $Cr_i^0(d^6) \rightarrow Cr_i^+(d^5)$ with the level
(E_c-0.22 eV) determined by electrical measure-
ments. DLTS measurements by Graff and Pieper [3]
yield the same chromium single donor level and
an additional one (E_v+0.29eV) in boron doped
material which could be identified with the Cr-B
pair donor level.

Photoluminescence from deep transition metal
complexes attracts currently much interest [4].
We found that chromium gives rise to character-
istic luminescence lines as in the cases of iron
and copper doped silicon samples. Contrary to
iron or copper, chromium diffuses not so fast,
therefore we put emphasis on sample preparation
and correlated our results with DLTS- and EPR-
measurements on the same samples. Results of
these investigations will be the subject of a
separate paper [5]. In the following we will
concentrate on the luminescence induced by Cr-B
pairs.

After a short description of our sample prepar-
ation technique we present the general features
of the Cr-B pair luminescence. More detailed
measurements of the finestructure of the no-
phonon line, the temperature dependence of the
intensity and the splitting in an uniaxial
stress field point to a model of an exciton

bound to an axial Cr-B complex, which will be discussed in section 3.5.

2. SAMPLE PREPARATION

Starting material for the chromium diffusion was dislocation and swirl free n- or p-type silicon in the concentration range from 10^{13}-10^{18} cm^{-3}. Almost all samples were prepared from float-zone (FZ) silicon, only a few from Czochralski (Cz) material. The results were identical in both sample types. Typical sizes of the samples were 7x5x0.3 mm^3 or 7x2x2 mm^3. The latter ones were used for the uniaxial stress measurements. The samples were chemically etched (HNO$_3$/HF) and then a thin high purity chromium film was evaporated on both sides of the samples. The difficulty to diffuse chromium in silicon was pointed out by Graff and Pieper [3]. Oxides and nitrides of chromium prevent the diffusion in silicon. To avoid these passivating surface layers we used evacuated quartz ampoules to diffuse our samples. To get a homogene chromium doping the diffusion time was chosen as long as one hour. After diffusion the samples were cooled down by quenching the whole ampoule in water at room temperature. We used different diffusion temperatures in the range between 900 and 1200°C to vary the chromium concentration from 10^{13} to 2×10^{15}cm^{-3} [5].

Our samples were measured by DLTS and EPR for determination of the Cr$_i$ and Cr-B pair concentrations and to check the quality of the samples. Photoluminescence spectra were recorded from a lot of chromium doped samples obtained from different groups and doped by different techniques (sandwich technique [3] and ion implantation). As for the luminescence measurements no difference was found due to different sample preparation techniques.

Table 1: labeling and spectroscopic parameters of the Cr-B pair luminescence.

line	transition	λ(μm)	hν(eV)	remarks
CrB$_1^0$	no-phonon	1.4700	0.8432	fine-
CrB$_2^0$	no-phonon excited states	1.4695	0.8435	structure
CrB$_3^0$		1.4692	0.8436	of the
CrB$_4^0$		1.4687	0.8439	CrB^0-line
CrB$_5^0$		1.4680	0.8443	
CrB^1	1.loc.mode	1.493	0.8302	
CrB^2	2.loc.mode	1.518	0.8160	
CrB$^{0\Gamma}$	0$^\Gamma$ phonon	1.588	0.780	
*		1.634	0.758	

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1 General features of the luminescence, due to chromium-boron pairs

At liquid helium temperatures chromium doped p-type silicon samples exhibits a characteristic luminescence spectrum. It appears at low energies whereas simultaneously observed near-band-gap lines are due to excitons bound to boron acceptors.

Details of the experimental setup used for these photoluminescence measurements were described elsewhere [6,7].

The "deep" luminescence spectrum presented in Figure 1 is located approximately 300 meV below the silicon bandgap. The spectrum consists of a narrow no-phonon (NP) transition, CrB^0, and two equi-spaced broader lines at lower energies labeled CrB^1 and CrB^2 with an energy spacing of 13.6 meV or 27.3 meV, respectively, from the princple CrB^0-line. We shall show in this paper that the spectrum is due to a recombination at Cr-B pairs. The labeling used anticipates our Cr-B interpretation. Line CrB$^{0\Gamma}$ results from an electron-hole recombination at the Cr-B pair with the emisson of an 0$^\Gamma$-phonon. The CrB^1-and CrB^2-lines are typical of all transition metal induced luminescence spectra recently investigated (for a survey see Ref. 4). These lines originate from optical transitions with the simultanious excitation of a vibration of the luminescent center. The phonon energy of 13.6 meV does not correspond to the usual momentum conserving phonon energies measured e.g. in the recombination spectra of shallow bound excitons. If we compare the phonon energies of different transition metal induced spectra, the energies seem to be mainly sensitive to the vibration of the interstitial transition metal.
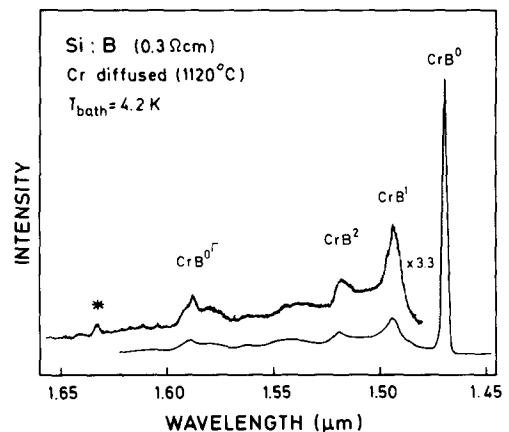

Figure 1 : Typical luminescence spectrum of chromium diffused boron-doped silicon. The lines are named CrB with an additional upper index in accordance with our interpretation. Line CrB^0 is the no-phonon transition, the lines with indices 1 and 2 are due to excitations of local vibrations of the complex and the CrB$^{0\Gamma}$-line is the 0$^\Gamma$-phonon replica of the CrB^0-line.

All the CrB-lines shown in Fig.1 are associated with the same complex, they show up in all samples containing Cr-B pairs with the same relative intensities and exhibit the same behaviour in an uniaxial stress field.

The spectral positions of all lines corresponding to the Cr-B pairs are summarized in Table 1. The CrB^0-line consists of several sharp finestructure lines (their positions are also given in Table 1). The behaviour of these lines will be discussed later.

Compared to the copper induced lines [6] the luminescence intensity of the CrB-lines was very weak even in our best samples. The intensity of the CrB^0-line increases at liquid helium temperatures linearly with laser power. Only at the highest laser excitation intensities ($\sim 10W/mm^2$) the luminescence intensity saturates, due to the limited concentration of the centers. This is a common feature in bound exciton luminescence (see e.g. discussion in Reference 7).

The CrB-lines were found only in boron doped starting material after chromium diffusion. The luminescence intensity depends on the boron as well as on the chromium-concentration, which was varied by different diffusion temperatures. We determined the interstitial chromium and Cr-B pair concentrations by DLTS measurements and found within experimental error a linear correlation between the luminescence intensity of the CrB-lines and the Cr-B pair concentration.

As in the case of the Fe-B pairs, there is an equilibrium between the interstitial chromium-, boron- and Cr-B pair-concentrations which can be varied by changing the temperature. In DLTS- as well as EPR- measurements the pairs anneal out between 100 and 200°C depending on the interstitial chromium and substitutional boron concentration. By increasing the boron concentration the annealing temperature increases. The same quantitative behaviour was found in our luminescence measurements [5].

3.2 Finestructure of the CrB^0-line

The CrB^0-line exhibits a pronounced finestructure if measured in high resolution. In principle we can distinguish five finestructure components which show an increase in intensity to lower energies. In Figure 2 high resolution spectra are given of the CrB^0 finestructure lines at different bath temperatures. We labeled the components with an additional lower index CrB_1^0, CrB_2^0,... to indicate various electronic states in the NP transitions. The spectral positions of these components are given in Table 1.

With increasing bath temperature the intensity ratios of the finestructure lines change. By lowering the bath temperature the high energy components decrease compared to the CrB_1^0-line. Due to the low intensity of the CrB^0-line it was unfortunately not possible to measure at low laser excitation. Therefore bath temperature and
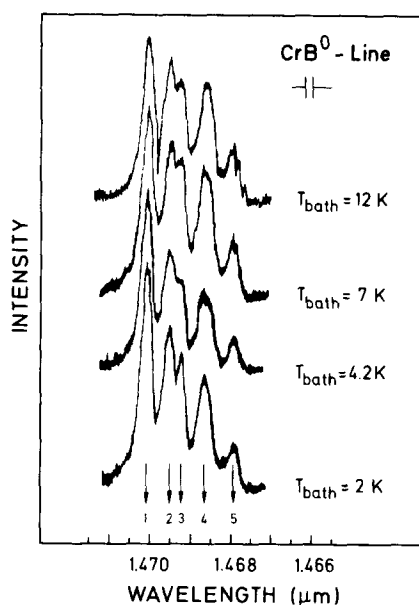

Figure 2 : High-resolution spectra of the finestructure of the CrB^0-line at different bath temperatures. The components are labeled from 1 to 5. For the line positions see Table 1.

sample temperature may be different and it is not possible to decide whether the finestructure components thermalize according to their spectroscopic spacing or not. Finestructure lines with indices two and three show temperature-independent intensity ratios. This indicates a transition from the same initial state into different ground states.

In all our samples we found the same finestructure with the same intensity ratios of the components. This indicates that all the lines belong to one optical center. Also in samples doped with different chromium isotopes no variation in the relative intensities of the components was observed.

3.3 Temperature dependence of the CrB^0-line

We measured the CrB^0-line intensity as a function of temperature to deduce the electronic level scheme of the corresponding electronic transitions. The temperature of our cryostat could be varied between 4.2 and 100K allowing an excitation power of 50mW without raising the sample temperature. Due to the weakness of the Cr^0-line only the total intensity of all finestructure components could be measured The intensity of the CrB^0-line is plotted in Figure 3 in a logarithmic scale against the reciprocal temperature. The experimental points were fitted with the familiar expression for I(T) (see Ref. 6). The parameters derived from the

fitting process are given in the figure caption of Figure 3. Due to the weakness of the signal, the uncertainty of the obtained energy values is large. We determine an ionization energy of approximately 20 meV. Another excited state approximately 8 meV above the CrB^0-line is needed to give a reasonable fit to the data. In the temperature dependent measurements we did not succeed in finding a line at a corresponding energy even at our highest temperatures. In uniaxial stress measurements, however, at high temperatures and stress along $\langle 100 \rangle$ a luminescence line approximately 8 meV above the stress induced components of the CrB^0-line could be observed.

A level scheme explaining the temperature dependence of the CrB^0-line intensity is shown in the insert of Figure 3. A level 300 meV below a bandedge is required to explain thermal data and luminescence intensities consistently.
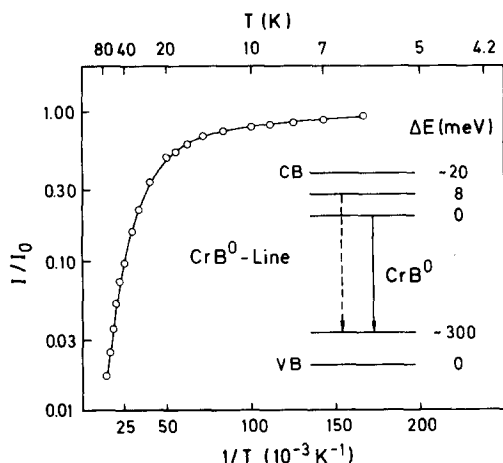

Figure 3 : Temperature dependence of the CrB^0-line intensity. A least square fit (full line) was performed using the following expression which refers to a three-level electronic system. $I(T)/I(0)=[1+C_1\exp(-E_1/kT) + C_2\exp(-E_2/kT)]^{-1}$ Fit parameters are $E_1 \sim 20$ meV, $C_1 \sim 2000$, $E_2 \sim 8$ meV, $C_2 \sim 40$. In the insert a level scheme is given which combines the spectroscopic transition of the CrB^0-line with the thermal data and the known donor level of the Cr-B pairs.

3.4 Uniaxial stress splitting of the CrB^0-line

The CrB^0-line shows – as is expected for this pair luminescence – an anisotropic splitting, if an uniaxial stress is applied to the center in the main crystallographic directions (Figure 4). Due to the small intensities and, therefore, bad resolution it was not possible to completely resolve the finestructure splitting under stress. Hence in Figure 4 on left hand side only the shifts and splittings of the whole CrB^0-line are given.

At low temperatures (T=4.2K) only a shift of the CrB^0-line was measured when the stress was aligned along a $\langle 100 \rangle$ crystal direction. At higher temperatures excited lines show up. Their stress dependence is indicated by dashed lines in Figure 4. The spectrum on the right hand side corresponds to a stress of 1.7 kbar and shows the two excited lines together with the ground state component.

Twofold different splittings arise in the other main directions. At higher temperatures and for $\tilde{X}\|[110]$ again a weak line shows up, thermalizing with the low temperature component (also indicated by dashed lines in Figure 4).

In the interpretation of the stress splittings we shall neglect the large anisotropic center-of-gravity shifts. The low temperature splitting is then consistent with an axial defect in a $\langle 111 \rangle$ crystallographic direction:
No splitting occurs in the $\langle 100 \rangle$ stress direction. If, however, the stress is applied in $\langle 111 \rangle$ direction the optical transitions correlated with centers orientated parallel to the stress will be split apart from those transitions of the still equivalent three remaining axes. An intensity ratio 1:3 is expected if no thermalization occurs between the optical transitions of differently orientated centers. The typical spectrum at the right hand side of Figure 4 was recorded at 3.1 kbar and shows the expected intensity ratio. Inserted in the spectrum is a schematic plot of the polarizations of the stress split components. Measured polarizations are indicated by solid bars, the dashed ones are the values calculated by Kaplyanskii [8] for an σ-oscillator. The theoretical data are in accord with the experimental values.
If the uniaxial stress is applied along a $\langle 110 \rangle$ direction, there is no straightforward interpretation of the line splittings. Unfortunately the magnitude of the splittings is even at highest stress in the order of the finestructure zero-field-splittings. From Kaplyanskii's table we expect a twofold splitting with an 1:1 intensity ratio. To reconstruct the experimental spectrum given for a stress of 3.6 kbar in Figure 4, we superposed two identical finestructure spectra (characterized by solid and dashed lines) split apart exactly by the difference of the CrB_1^0- and CrB_4^0-finestructure lines. As is indicated in the spectrum by bars, the intensity ratio of the stress components fits nicely to that calculated for a trigonal center.
The splitting in $\langle 111 \rangle$ direction is 1.4 times larger than in $\langle 110 \rangle$ direction, this is in accordance with the factor of 1.3 derived from Kaplyanskii's table.

An isotropic center-of-gravity shift is expected for a trigonal center, contrary to the measured stress splittings of the CrB^0-line. In $\langle 100 \rangle$ stress direction the largest shift occurs, becoming successively smaller for the $\langle 110 \rangle$ and $\langle 111 \rangle$ directions. The magnitude and behaviour of these shifts correspond exactly to the silicon conduction band splittings in an uniaxial stress field.
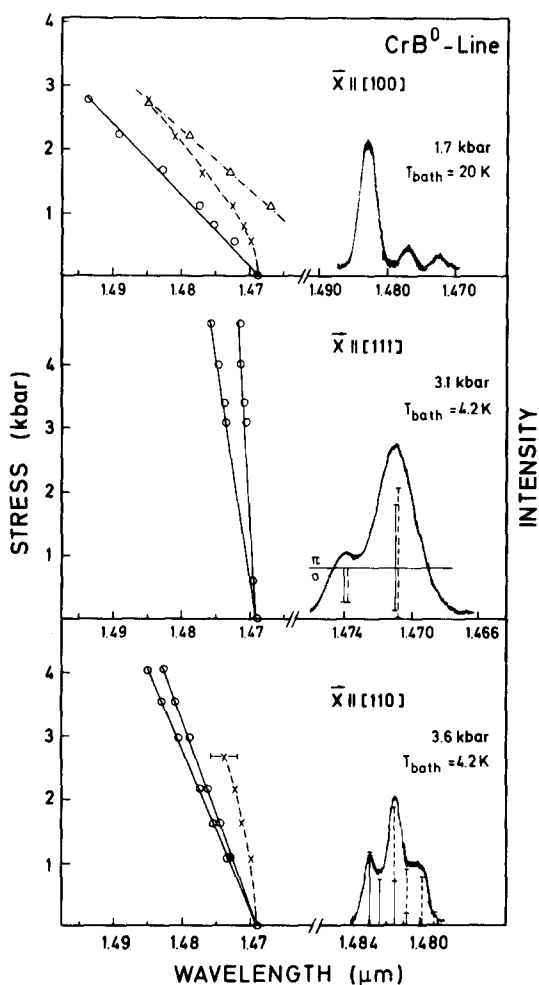
Figure 4 : Splitting of the CrB^0-line for uniaxial stress $\vec{X}$ along the main crystallographic directions.
Left hand side: splitting pattern in dependence of the applied stress.
Right hand side: Spectra showing typical stress splittings are given (mention the different scales for the different stress directions).
For detail see text.

Luminescence lines found at higher temperatures correspond either to the electronic splitting of finestructure components or belong to an high energy excited level of the CrB^0-line. This excited line was only observed in <100> direction and increases in intensity with increasing stress magnitude. The zero field position of this line can be determined by extrapolating the data points in Figure 4 linearly back to zero stress. We found an energetic position approximately 8 meV above the CrB^0-line, which is in agreement with the result derived from the temperature dependence of the CrB^0-line.

The uniaxial stress splitting of the CrB^0-line

was interpreted by the orientational splitting of a trigonal center. The electronic transition is a so called σ-oscillator, with an initial state splitting similar to a shallow donor e-or t_2-level.

3.5 Discussion

After chromium diffusion in silicon samples we found at liquid helium temperatures a new luminescence spectrum, centered around 0.84 eV. The spectrum shows the typical properties of other recently found spectra resulting from optical transitions in transition metal complexes. At high energies a no-phonon transition preceeds two low energy lines. These lines are equi-spaced and can be attributed to the excitation of one or two, respectively, local modes of the optical center in the luminescence transition.
The phonon energy is well above those found for other heavier transition elements in silicon (Fe, Cu, Zn)[4].

From sample preparation and correlation of the CrB^0-line intensity with the Cr-B pair concentration as determined by DLTS- and EPR- measurements on the same samples, we identify the luminescence center as due to Cr-B pairs.

The uniaxial stress splitting of these lines is explainable by an axial complex along the <111> main crystal direction in agreement with the symmetry of the Cr-B pairs determined by EPR.[1] One state of the optical transition is correlated with the indirect conduction band minima. This points to a model in which an electron is weakly bound to the Cr-B complex.
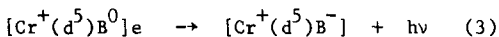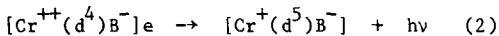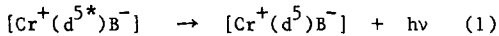By temperature dependent luminescence measurements we derived an ionization-energy of approximately 20 meV of this weakly bound particle, which is drastically lower than the spectroscopic binding energy (326 meV). This discrepancy indicates an excitonic recombination at an isoelectronic binding center. From the above mentioned energies we obtain a localization energy of ~0.3 eV for the primarily bound particle, in good agreement with the donor level position $E_v + 0.29$ eV of the Cr-B pairs [3]. We therefore ascribe the luminescence process to an exciton localized at an isoelectronic Cr-B pair, where the hole of the exciton is deeply bound to this complex.

Going into detail the finestructure of the CrB^0-line exhibits a lot of information about the nature of the recombination process. Although many of the finestructure lines thermalize, we have to postulate a splitting of the excitonic ground state to account for non-thermalizing finestructure components. This is unusual for excitons bound to "classical" isoelectronic centers, but resembles very much excitonic spectra found in III-V semiconductors. In GaAs and GaP chromium e.g. gives rise to a complex luminescent system with a no-phonon line consisting of several finestructure components. White [8] proposed a model to explain the electronic transitions of these complexes, where an exciton

is bound to these "isoelectronic" centers in the following way: One particle of the exciton is bound in the d-shell of the transition metal, whereas the other is only shallow bound in the coulomb field of the deeply bound particle. A number of excited states in the initial as well as in the final state of the optical transition is due to coupling of the exciton angular momenta to the d-shell states of the binding center. Adopting White's explanation for the Cr-B pair luminescence in silicon, we will discuss several specific models.

Although it is clear from DLTS measurements that the Cr-B pair forms a deep donor state, no detailed information exists whether the donor action occurs in the chromium d-shell or at the boron ion. Comparing this problem with the analog one of the Fe-B pairs, there is now evidence for a capture process at the acceptor ion in the complex [9].

Cr-B pairs are found by EPR in the ground state configuration $[Cr^+(d^5)B^-]$. By laser illumination of the samples possible excitations could be:

$$[Cr^+(d^{5*})B^-] \rightarrow [Cr^+(d^5)B^-] + h\nu \quad (1)$$

$$[Cr^{++}(d^4)B^-]e \rightarrow [Cr^+(d^5)B^-] + h\nu \quad (2)$$

$$[Cr^+(d^5)B^0]e \rightarrow [Cr^+(d^5)B^-] + h\nu \quad (3)$$

Transition (1) corresponds to an electronic transition in the d^5 configuration. We discard this transition as an explanation for our Cr-B luminescence, because we do not expect such a large excited state splitting to explain the finestructure of the CrB^0-line. The D-term describing the d^5 ground state splitting was determined to be only in the order of 0.01 meV [1], and it would be hard to explain an excited state splitting a factor of 100 larger. For the same reason we discard transition (2) which corresponds directly to White's model.
We favour transition (3) to be the one occuring in the emission of the CrB^0-line. The ground state splitting of the d^5-state is comparable to the line width of the finestructure components, even the splitting of the non-thermalizing lines CrB_2^0 and CrB_3^0 is in accord with the magnitude of the D-term splitting. The initial state structure of the optical transition (3) is due to the acceptor hole splitting along the complex axis. The coupling of the shallow bound electron to this hole state results in excitonic states in accord with the work of Morgan and Morgan.[10]
At the moment no decision is possible concerning the quantum numbers of the states. Detailed measurements of the stress splitting of the finestructure lines are required to verify this model.

4. SUMMARY

Chromium-boron pairs in silicon give rise to a characteristic luminescence spectrum consisting of a high energy no-phonon transition CrB^0 and two low energy local mode replicas. The typical local mode energy of the chromium complex is 13.6 meV. The optical transition is explained by an excitonic recombination at an isoelectronic Cr-B pair. We correlate the 0.3 eV level found by temperature dependent measurements with the known donor state $(E_v+0.29$ eV) of Cr-B pairs. Uniaxial stress measurements show the trigonal symmetry of the binding center.
A tentative model for this excitonic recombination was presented: A deeply bound acceptor like hole which is influenced drastically by the Cr-B axis, recombines with the shallow bound electron in this complex.

References

[1] G.W. Ludwig and H.H. Woodbury, in "Solid State Physics", ed. F. Seitz and D. Turnbull (Academic Press), Vol.13 (1962) p.223
[2] H. Feichtinger and R. Czaputa, Appl.Phys. Lett. 39, 706 (1982)
[3] K. Graff, H. Pieper, in "Semiconductor Silicon 1981", ed. H.R. Huff and R.J. Kriegler, The Electrochemical Society (1981), p.331
[4] See R. Sauer and J. Weber talk given in this conference
[5] H. Conzelmann, K. Graff and E. Weber, to be published
[6] J. Weber, H. Bauch and R. Sauer, Phys. Rev. B 25, 7688 (1982)
[7] J. Weber, W. Schmid, R. Sauer, Phys.Rev. B 21, 2401 (1980)
[8] A.M. White, Solid State Comm. 32, 205 (1979)
[9] K. Wünstel, K.H. Froehner and P. Wagner this conference
[10] J.v.W. Morgan and T.N. Morgan, Phys Rev.B 1 739 (1970)