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ZINC AND ZINC-IMPURITY PAIRS IN SILICON

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ABSTRACT

In this report the properties of zinc as a dopant of silicon are reviewed. For the isolated impurity the data on solubility, diffusion, ionization levels and acceptor states are given, together with a brief discussion. Zinc participates in the formation of impurity complexes. Pairs formed between zinc and other acceptors, donors and hydrogen are described.

1. INTRODUCTION

Zinc is an active dopant in silicon. In its isolated form it occupies the regular substitutional site and, lacking two electrons to be an isovalent impurity, it acts as a double acceptor. Its first and second ionisation levels have been determined at about E_v + 0.30 eV and E_v + 0.60 eV, respectively, consistently over a long period of time, by many experiments. Being a well-identified centre, the zinc impurity offers the rare possibility to investigate the electronic structure of a deep double acceptor state. While the neutral zinc atom has electron configuration $3d^{10}4s^2$, the incorporation in the silicon crystal will introduce the competition with the formation of sp^3 hybridized covalent bonds. In fourfold coordination this would leave eight electrons for an incompletely filled 3d shell. For excited states the validity of a description in the effective mass approximation is an important issue for verification. Zinc has shown a pronounced tendency to form complexes with other impurities. As expected, pairs of positive donors with negative zinc acceptors are stabilized by the gain of electrostatic energy. Highly mobile interstitial transition metal impurities, such as manganese, iron, chromium and copper are active in the formation of these complexes. Other impurities involved in pair formation, though less definitively established, are the shallow acceptors boron, aluminium and gallium. Passivation of zinc centres by hydrogenation appears to be possible. Several other zinc related centres are just only detected in one technique, but lack all further characterization and identification. The studies of zinc related centres in silicon are in their very early stage.

2. ISOLATED ZINC

2.1. Solubility

Zinc has the low melting temperature of 419.5 °C, it boils at 907 °C. The solubility of zinc in silicon is determined by temperature and composition of the external phase. In contact with the liquid the segregation at the solid-liquid interface is controlled by the distribution coefficient k^{eq}. A general expression for k^{eq} is

$$k^{eq} = \gamma \exp[\Delta S/k] \exp[-\Delta H/kT]. \qquad (1)$$

The changes of entropy and enthalpy upon transfer of the impurity from external phase to silicon are given by ΔS and ΔH, respectively. For Si:Zn the values are given as $\Delta S/k = -2$ and $\Delta H = 1.5$ eV [1,2]. The liquidus curve in the silicon-zinc phase diagram deviates from a straight line

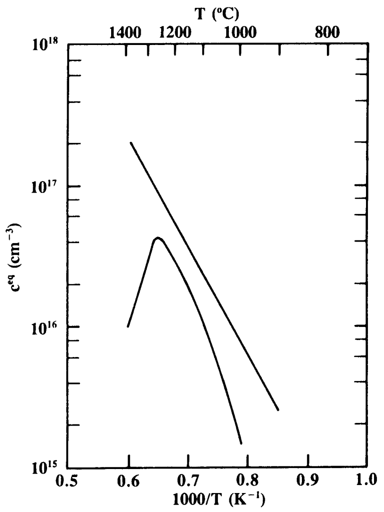

Figure 1. Solubility c^{eq} of zinc in silicon as a function of the reciprocal temperature 1000/T. After Refs. [4], [5] and [6].

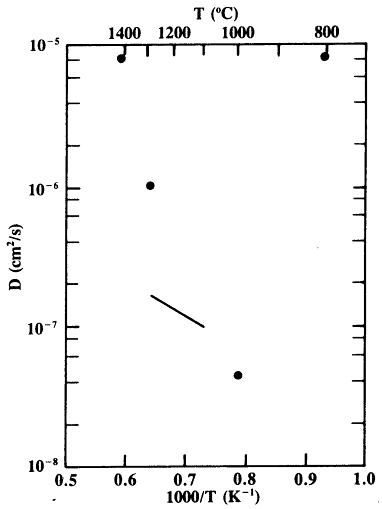

Figure 2. Diffusion constant D of zinc in silicon as a function of reciprocal temperature 1000/T. Data from Refs. [2], [9], [10], [11] and [12].

causing appreciable temperature dependence of the activity coefficient γ. The solubility will therefore not follow Arrhenius behaviour. From equation 1, with $\gamma = 1$, the segregation coefficient at the melting point of silicon is calculated as $k_m^{eq} = 10^{-5}$. Following the empirical rule of Fischler [3] the maximum solubility is predicted as 10^{-6} in atomic fraction, corresponding to the concentration 5×10^{16} cm^{-3}. Both results are in agreement with experimental findings. Solubilities of zinc in silicon were determined measuring the hole conductivity induced by this acceptor dopant [4]. Results of solubility measurements are given in figure 1 [4-6].

2.2. Diffusion

Diffusion of impurities in a solid proceeds via thermally activated jumps over energy barriers. Such a process is generally represented by an Arrhenius relation

$$D = D_o \exp(-Q/kT). \tag{2}$$

The activation energy Q is related to the barrier height and the pre-exponential factor D_o involves the attempt jump frequency and jump distance. Several mechanisms for diffusion exist. Impurities moving via interstitial sites are characterized by high diffusion constants. Diffusion over substitutional sites is very slow. The magnitude of diffusion of zinc in silicon is intermediate between these cases and suggests an interstitial-substitutional exchange mechanism. In one of these models a highly mobile zinc atom on interstitial position can change place with a silicon atom on a regular lattice site, pushing the silicon atom into interstitial position. This kick-out mechanism, represented by

$$Zn_i \rightleftarrows Zn_s + I, \tag{3}$$

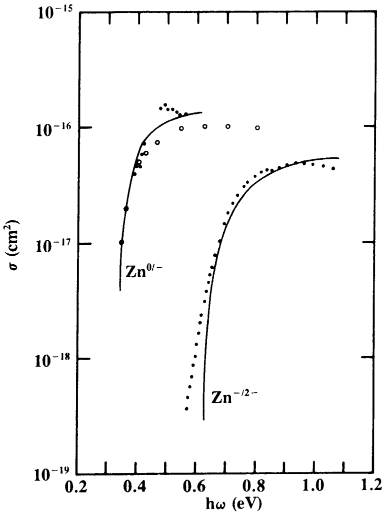

Figure 3. Photoionization cross sections σ for holes of the neutral and singly charged zinc centres as a function of photon energy hω. Data after Ref. [18].

was found to be dominant for the zinc in silicon diffusion [7,8]. The diffusion rate may be limited by the diffusivity of the interstitial impurity or by the flow of self-interstitials. The concentration of the intrinsic defect is affected by the crystal quality, such as dislocation density, or the conditions of the surface. This may explain the wide scatter of diffusion data in the literature. Data representing the rather limited literature of zinc in silicon diffusion are given in figure 2. Representative values for the parameters D_o and Q can hardly be given.

2.3. Ionization levels

Already in its first year of observation zinc was recognized as a substitutional impurity with a double acceptor behaviour [4,13]. From the Hall effect measurements the first and second hole ionization levels were determined at about $E_v + 0.30$ eV and $E_v + 0.60$ eV, respectively. These results were essentially confirmed in many following experiments using infrared absorption [14,15], photoconductivity [16], and several variants of the deep level transient spectroscopy (DLTS) [17-24]. A summary of the results obtained, showing some scatter between the data, is given in Ref. [24]. In view of the propensity of zinc of complexing with other impurities, the reported values are remarkably consistent. The photoionization cross sections for the excitation of holes to the valence band from the zinc levels as reported in Ref. [18] are shown in figure 3. By fitting the spectral dependence with the Lucovsky model the ground state binding energies were derived. In most of these experiments additional electronic levels were observed. These are attributed to zinc-related complexes.

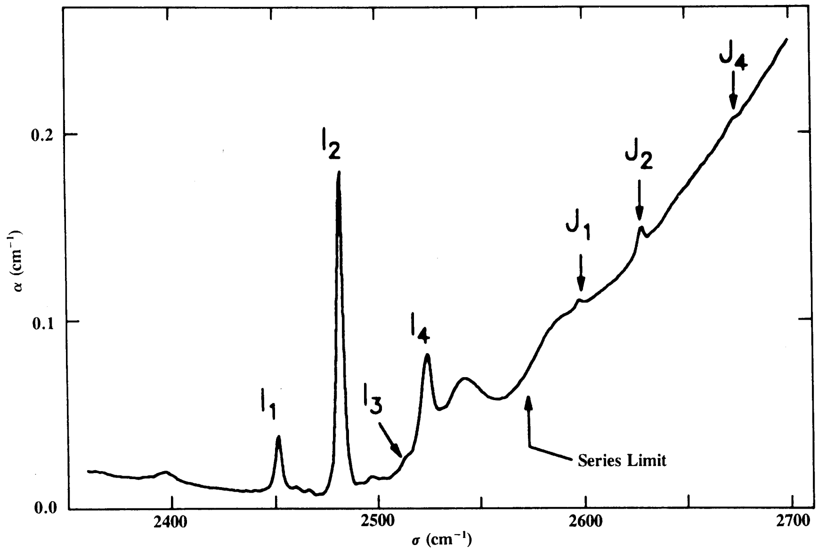

Figure 4. Optical absorption α of Zn^0 (lines I) and the complex Zn(X2) (lines J) due to excitation to bound effective-mass like states. Data after Ref. [27].

Table 1. Optical absorption energies E_a and total ionization energies E_i for the double acceptors Zn^o and Be^o, for centre Zn(X2) and for the single acceptor B^o. Theoretical EMT binding energies E_b are also given. All energies in meV.

Transition	Zn^o		Zn(X2)		Be^o		B^o		EMT
	E_a	E_i	E_a	E_i	E_a	E_i	E_a	E_i	E_b
I_1	303.92	319.42	322.21	337.71	176.6	192.1	30.38	45.88	15.5
I_2	307.81	319.21	325.98	337.38	180.3	191.7	34.49	45.89	11.4
I_3	311.71	319.01							7.3
I_4	313.04	319.04	331.51	337.51	185.6	191.6	39.57	45.57	6.0

2.4. Acceptor states

A much more precise value for the optical ionization energy is obtained by the observation of ground to bound excited state transitions in the neutral impurity. Such experiments have recently been reported using high resolution, ≈ 0.06 meV, Fourier transform spectroscopy [25-27]. A spectrum of absorption lines, labeled I_1 to I_4, observed at low temperature, is shown in figure 4. The excitation energies corresponding to these absorptions, E_a, are given in table 1. For the excited states, with holes in extended orbits, the binding energies E_b can well be calculated in the effective mass theory (EMT). Adding the respective values one obtains the ionization energy $E_i = E_a + E_b$. The constant result, as given in table 1, demonstrates the validity of the analysis. To high precision the first ionization level Zn^o/Zn^- of the acceptor is determined as 0.3192 eV. In the figure this value is indicated as the series limit. The spectrum consisting of the lines J_i, $i=1,2,4$, also shown in figure 4, is attributed to the Zn(X2) complex; for further details see section 3.3.

3. ZINC−IMPURITY PAIRS

3.1. Zinc-donor pairs

Donor-acceptor pairs are a familiar form of small impurity complexes. Their formation is favoured by the electrostatic attraction between negative acceptor impurity and positively charged donor. Being an acceptor, zinc can form impurity pairs of this kind by trapping a donor impurity. Transition element donors of the 3d series, which are fast interstitial diffusers, are good candidates for this process. Indeed, the observation of impurity pairs between zinc and vanadium, chromium, manganese, iron and copper has been reported. Investigations, mainly by deep level transient spectroscopy (DLTS) and electron paramagnetic resonance (EPR), have revealed the microscopic electronic aspects of these centres.

The first observation of such centre was the MnZn pair by magnetic resonance [28]. Figure 5 is an illustration of the result, revealing information on fine and hyperfine structure. While figure 5 gives the spectrum for the magnetic field B parallel to a <111> crystal direction, the full angular dependence studies were made. Analysis of data using the spin hamiltonian formalism determines the interaction constants. The more important of these are given in table 2. From the observed <111> axial angular patterns the spectrum is concluded to arise from a centre with trigonal symmetry. For an impurity pair this is a probable configuration. The spectrum consists of the transitions between states with electronic quantum numbers from $m_S = +5/2$, down to $m_S = -5/2$, and requires electron spin $S = 5/2$ for its full description. Manganese can act as double donor; $Mn^{\circ} \rightleftarrows Mn^{2+} + 2e^{-}$. It favours the electronic configuration $[Ar]3d^5$, with half-filled d shell and without bonding to the crystal. Spin alignment, following Hund's rule, results in spin $S_{Mn} = 5/2$. The double acceptor zinc has the ionized configuration $[Ar]3d^{10}4s4p^3$, on a substitutional site with bonding to four silicon neighbours. The spin of this Zn^{2-} state is $S_{Zn} = 0$. In this pair configuration $(MnZn)^{\circ} = Mn^{2+}_{int} \cdot Zn^{2-}_{subst}$ the observed electron spin $S = 5/2$ for the pair finds an evident explanation. The hyperfine interaction parameters with the manganese ion (isotope ^{55}Mn, nuclear spin $I=5/2$, 100% natural abundance) are given in the original literature [28] as $A_{\parallel} = -154.2$ MHz and $A_{\perp} = -150$ MHz. The interaction appears to be nearly isotropic, with $a = (A_{\parallel}+2A_{\perp})/3 = -151.4$ MHz, indicating only a small influence of the trigonal fields in the centre. A comparison with the isolated manganese impurities in the silicon crystal can therefore be made.

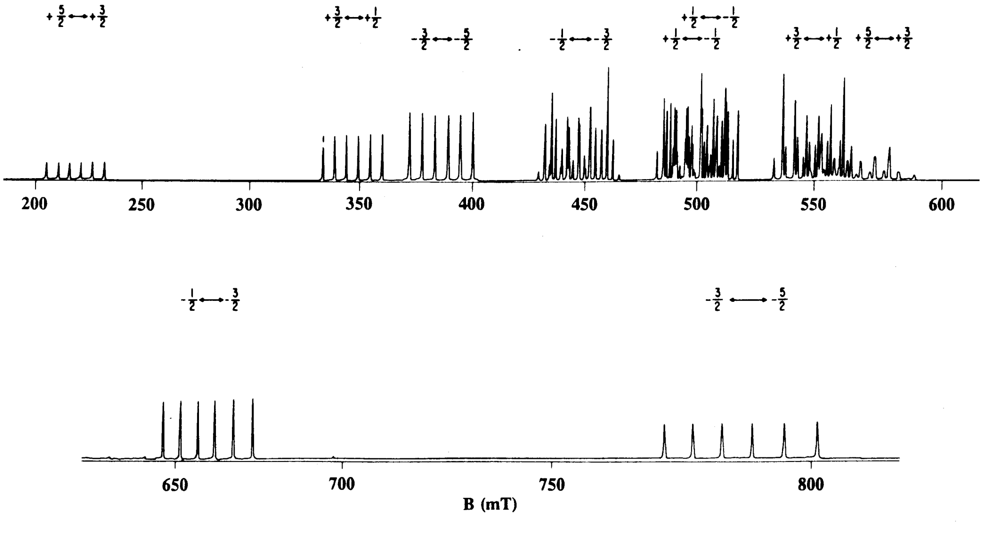

Figure 5. Electron paramagnetic resonance spectrum of the neutral centre MnZn in silicon, for magnetic field direction parallel to <111>. Different sets of lines correspond to different orientations of the trigonal centre in the crystal. Data after Ref. [28].

For interstitial Mn^{2+}, the reported value is a = −160.21 MHz; for substitutional Mn^{2-}, a = −121.5 MHz, with both cases referring to $3d^5$ and S = 5/2. As additional bonding in the pair is likely to lead to some delocalization of the d electrons and therefore reduction of the hyperfine strength, the measured value for the pair is consistent only with manganese on an interstitial site. In the pair model the spin density is highly localized on the manganese ion. The hyperfine interaction with this impurity is strong and easily visible through the sixfold splitting of the resonance lines, see figure 5. No spin density is localized in the model on the zinc ion. In agreement with the model the spectrum shows no resolved zinc hyperfine structure. Although the interaction is measurable, it is about 50 times smaller than for manganese, indicating some, but small delocalization. The absence of orbital momentum in the electron configuration is consistent with the observed g-values, which are close to the free electron value g = 2.

Most probably the same centre has also been observed in deep level transient spectroscopy [19]. Figure 6 demonstrates the observation of the MnZn related emission near T = 100 K. A donor level at E_v + 0.18 eV is derived for the centre. It is consistent with the observation of the pair in a neutral charge state in the magnetic resonance experiment. Both constituents of the pair have donor or acceptor activity and can be observed themselves separately in the DLTS experiment. In figure 6 the Zn and Mn signals are also observable. By monitoring the time dependence of the intensities of Mn-, Zn- and MnZn-related peaks the reaction kinetics can be followed. Such experiment was carried out in more detail for vanadium, which similar to manganese, is also a double donor. In the experiment the equilibrium was established in the reaction

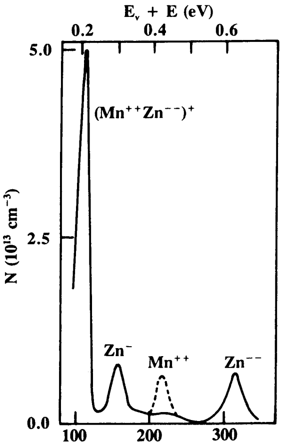

Figure 6. DLTS spectrum observed in silicon double-doped with zinc and manganese. After Ref. [19].

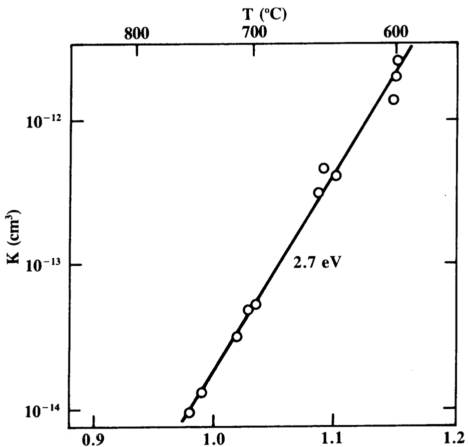

Figure 7. Temperature dependence of the equilibrium constant K for the donor-acceptor pairing reaction between zinc and vanadium in silicon. After Ref. [19].

$$V^{2+} + Zn^{2-} \rightleftarrows VZn, \tag{4}$$

then frozen by quenching and measured at low temperature. In a mass action description

$$[VZn]/[V][Zn] = K(T) = K_o \exp(U/kT) \tag{5}$$

the temperature dependent reaction constant K(T) was determined. The result is displayed in figure 7. The slope gives $U = 2.7$ eV, which reflects a considerable binding energy and stability of the pair. The value can be put in perspective by comparison to the result $U = 0.65$ eV reported for the well-known Fe^+B^- pair [29]. The enhancement by an almost exact factor 4 for the VZn pair is a good confirmation of its double donor-double acceptor character.

Another system for which results from different sources are available is zinc-chromium. The DLTS measurement has revealed the formation of CrZn pairs with an associated acceptor level at $E_c - 0.10$ eV [19]. The simple rule that double acceptor plus single donor gives single acceptor seems to be obeyed. Also in magnetic resonance such pairs were observed, actually two different ones [30,31]. By the controlled intentional introduction of the nuclear magnetic isotopes ^{67}Zn, $I = 5/2$, and ^{53}Cr, $I = 3/2$, to a high enrichment, the hyperfine structure was enhanced, allowing better studies. In both cases the involvement of one zinc and one chromium atom each was established for the centres. The two centres differ in their geometrical structure. One centre, labeled Si-NL35, has trigonal symmetry and could well correspond to a pair formed by a substitutional zinc atom with a chromium atom on a nearest interstitial site along <111>. The other centre, with spectrum

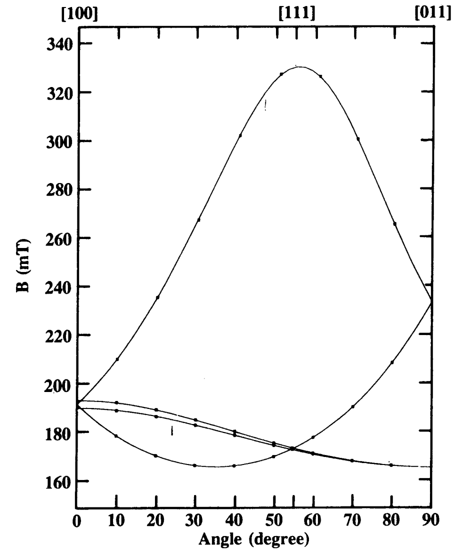

Figure 8. Angular variation for the trigonal Si:CrZn centre, spectrum Si-NL35, for rotation of the magnetic field in the $(0\bar{1}1)$ plane, at X-band frequency. After Ref. [30].

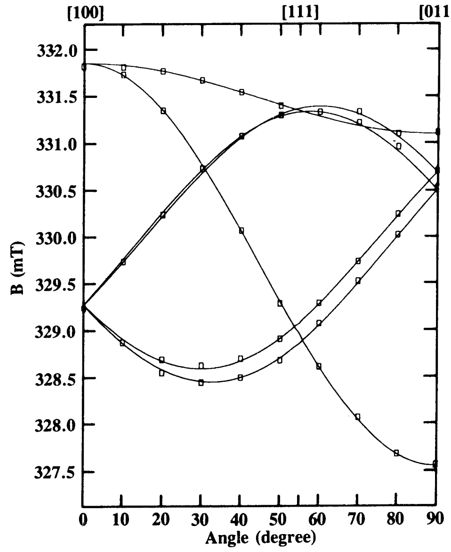

Figure 9. Angular variation for the orthorhombic Si:CrZn centre, spectrum Si-NL36, for rotation of the magnetic field in the $(0\bar{1}1)$ plane, at X-band frequency. After Ref. [31].

label Si-NL36, has orthorhombic-I symmetry and could arise from a pair with constituents separated at a further distance. Angular dependence patterns on the basis of which the symmetry of the paramagnetic centres is found are given as figures 8 and 9 for the centres Si-NL35 and NL36, respectively. One might speculate that the two centres with chemical identity differ only in their geometrical arrangements of atoms and that transformations between the two species are possible. Such atomic bistability is well documented for iron-shallow acceptor pairs, for example by the trigonal and orthorhombic iron-aluminium pairs [32,33]. Presently it is still unclear whether the ZnCr pairs represent a new case of such atomic bistability.

Other 3d transition metals involved in pairing reactions with zinc are iron and copper. Results as following from DLTS studies are summarized in figure 10 [19]. Some parameters describing the magnetic resonance for zinc and its impurity pairs are collected in table 2.

3.2. Zinc-acceptor complexes

Although no detailed information about structure is known, the formation of pairs between zinc and the shallow acceptor dopants is reported frequently in the literature [4,13,17,24]. The reports are based on observations by the Hall effect or DLTS. In general, the disappearance of the shallow acceptor level is observed with simultaneous appearance of a new electronic level. For boron a level at E_v + 0.09(2) eV is found [4,13,24], or at E_v + 0.167 eV [17]; for gallium the level is at E_v + 0.083 eV [4]. As regards the atomic model of a complex only speculative ideas, involving interstitial zinc or vacancies, have been forwarded. On the basis of reaction kinetics the centre Zn_3B was proposed [17].

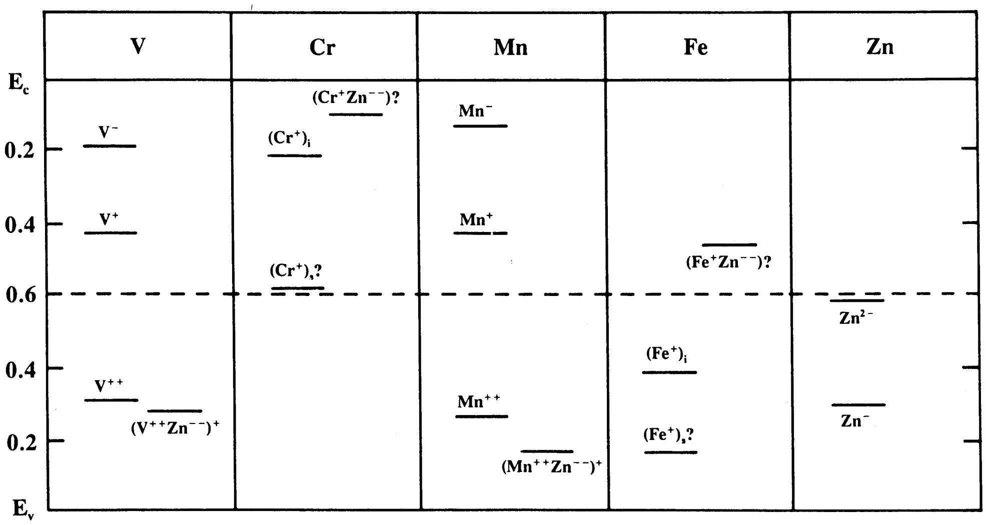

Figure 10. Energy level diagram for zinc, the 3d transition elements vanadium, chromium, manganese and iron, and their complexes. After Ref. [19].

Table 2. Spin Hamiltonian constants of EPR spectra of zinc-related centres in silicon.

Centre/ spectrum	Symmetry	Spin	Principal g-values			Reference
Zn^-	cubic	1/2	2.050			[28,34,35]
$(MnZn)^o$	trigonal	5/2	2.001	1.996		[28]
CuZn/NL34	monoclinic-I	1/2	1.9980	2.0872	1.9912	[30]
CrZn/NL35	trigonal	3/2	1.9972	2.0004		[30]
CrZn/NL36	orthorhombic-I	1/2	1.9856	1.9903	2.0119	[30,31]
NL37	monoclinic-I	1/2	2.0164	2.0507	1.9981	[30]
FeZn/NL38	trigonal	3/2	2.1520	2.0328		[30]

3.3. Zinc-hydrogen complexes

Hydrogenation is a new method of improving control over electrically active centres. Also for zinc in silicon the interactions with hydrogen were investigated [23]. Samples doped with zinc, measured by the deep level transient spectroscopy, showed the familiar Zn acceptor levels. As figure 11 shows, new levels, labelled Zn(X1) and Zn(X2), were present in addition. These

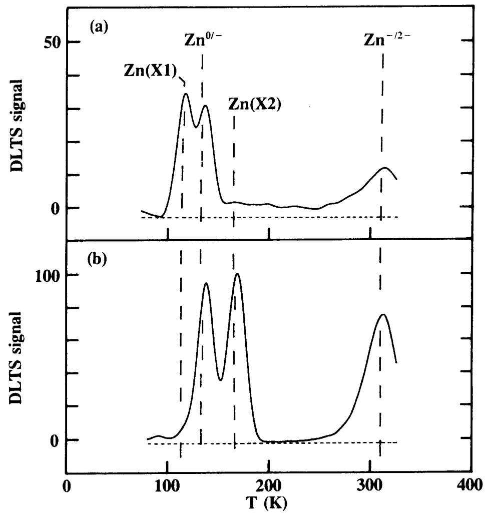

Figure 11. Deep level transient spectra of silicon subjected to zinc diffusion at (a) 900 °C and (b) 1000 °C, and after hydrogenation. Dotted curves indicate the absence of active levels after hydrogenation. Data from Ref. [23].

complexes, which were shown to be related to one zinc atom, have ionisation energies of 230 and 320 meV, respectively. Probably, the lines J_1 to J_4 observed in optical absorption, see figure 4, are associated with the Zn(X2) complex. Upon treatment in a hydrogen plasma all electrical levels disappear. This is indicated in figure 11 by the dotted line. New levels from zinc-hydrogen associates are not present. By heat treatment in the range 444-616 °C the zinc acceptors are reactivated. This process follows first-order kinetics with an activation energy of 2.2 eV. Also the Zn(X1) centres are recovered, but their reactivation is not described by simple kinetics. Centre Zn(X2) is not stable at temperatures above 400 °C.

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