Electronic Properties of Transition Metal related Defects in Germanium

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Abstract

The deep level properties of transition metal impurities of the iron group in germanium have been investigated using DLTS, in the case of Ti, Cr, Fe and Co using metal implanted wafers. For each metal distinct spectra have been observed with two to four levels, belonging to one defect in each case. The spectra and the carrier capture data show that the defects are double or triple acceptors, in agreement with the occurrence of the impurities on substitutional lattice sites. It was observed that the acceptors can be passivated by a hydrogen plasma treatment. New metal specific levels are tentatively assigned to metal-hydrogen complexes.

Introduction

Metal impurities in germanium have been quite intensively studied about 50 years ago. In that period electronic properties such as energy levels and carrier capture cross-sections of several transition metals were investigated using mainly Hall-effect and photoelectric measurements [1-4]. A general picture that emerged is that transition metals in germanium predominantly form multiple-acceptor centres introducing several deep levels in the band gap, which according to a simple valence bond model is in agreement with a preferential occurrence of the impurities on substitutional sites. Due to the perspective to apply germanium in advanced electronic devices, a renewed interest in the properties of defects and impurities in germanium has appeared in the last few years. This is e.g. the case for transition metal impurities, which may affect the carrier lifetime already at trace concentrations [3]. Since the early studies mentioned, deep level transient spectroscopy (DLTS) has become the preferential technique to study deep level centres in semiconductors. DLTS of metal-diffused germanium has been successful in the case of Cu, Ag, Au and Ni [4], however for most transition metals it is difficult in this way to obtain metal concentrations exceeding the unwanted contamination. We have recently shown that metal implantation of germanium wafers is a better approach, allowing to obtain distinct DLTS spectra for different transition metal impurities [5]. In the present paper a summary is given of data concerning the deep level system of metals of the iron group in germanium, obtained with DLTS. The focus will be on recent results obtained for Ti, Cr, Fe and Co using implanted wafers; the data are completed with results for Ni (diffused and implanted) and Cu (diffused).

Substitutional transition metal impurities

Implantations with Ti, Cr, Fe or Co were made on n-type and p-type germanium wafers (Umicore) with a Sb shallow donor concentration of 5×10^{13} cm^{-3} and a Ga shallow acceptor concentration of 1×10^{14} cm^{-3} respectively. For each metal a wafer with a low (5×10^{13} cm^{-2}) and a high (5×10^{14} cm^{-2}) implantation dose was prepared. The wafers received a 5 min post-implantation thermal annea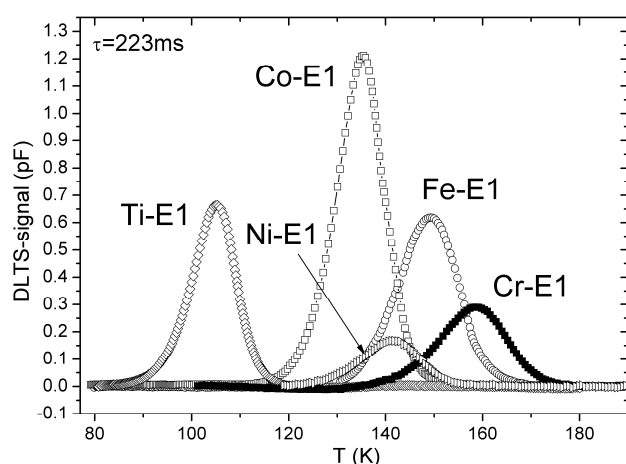l at 500°C to restore the implantation damage and to diffuse the impurities deeper into the wafer. Schottky diodes for DLTS were prepared by evaporation of Au (on n-type) or In (on p-type); the evaporation was preceded by a short etch.

A summary of the DLTS result obtained on n-type germanium is shown in Fig.1. For each of the metals one single band (labelled M-E1 with M indicating the metal) is observed, with different position depending on the metal. In the p-type samples one band appears in the case of Ti and Fe, while respectively two and three bands with similar amplitude are found in the Co and Cr implanted wafers (the hole traps are labelled M-Hi with i =1, 2 or 3). The DLTS results for p-type are summarized in fig.2. It is important to emphasize that the spectra of the higher and lower dose display the same bands for the same implanted metal, while different metals clearly result in different

Fig. 1. DLTS of metal implanted n-type germanium

spectra. The bands show exponentially decreasing concentration profiles which are consistent between n-and p-type for each metal. The Ni-E1 band which has been added in Fig.1 corresponds with a Ni-implantation which was made in different circumstances; this band is identical with the one observed earlier in Ni-diffused germanium [6].
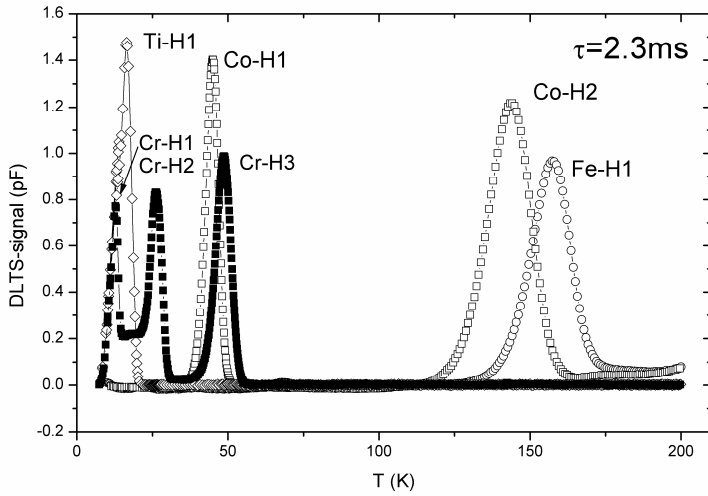
The signatures of the electron traps M-E1 extracted from the DLTS data and consisting of the apparent activation energy E_{na} of the emission and the apparent electron capture cross-section σ_{na} [7] are listed in Table 1. The true electron capture cross-sections σ_n have low values and could be directly measured by the variable pulse length method. The result of a similar measurement in the case of the Fe-E1 level is shown in Fig.3a,b as an example. The experimental data in Fig.3a have been fitted using a new procedure taking account of slow capture at the edge of the depletion layer and of a non-constant concentration profile [8]. Repeating the measurements at different temperatures, an exponential dependence of the capture cross-section on temperature $\sigma_n = \sigma_\infty \exp(-E_\sigma/kT)$ is found, as represented in the Arrhenius diagram of Fig.3.b. A similar temperature dependence, which is also observed for the other M-E1 bands except Ni, is in agreement with multiphonon capture against a repulsive barrier [9]. The corresponding σ_∞ and E_σ values are displayed in Table 1. The apparent activation energy of the M-E1 levels may now be corrected by the capture barrier E_σ yielding a value for the ionisation enthalpy: $\Delta H = E_{na} - E_\sigma$. The corresponding entropy change may be calculated as $\Delta S/k = \ln(\sigma_n/\sigma_\infty)$ [7]. The values of ΔH and ΔS are also included in Table 1. The signatures E_{pa}, σ_{pa} of the M-Hi levels are listed in Table 2. For most of the M-Hi levels the hole capture cross-section σ_p is too high in order to be measured directly. These observations are in general agreement with the expected behaviour for multiple acceptor centres. An overview of the energy levels of the transition metals of the iron-group obtained by DLTS is shown in Fig.4.

In order to compare with energy levels observed in the early Hall-effect measurements (in most cases using melt-doped crystals), we use the ΔH values for the M-E1 levels and the E_{pa} values for the M-Hi

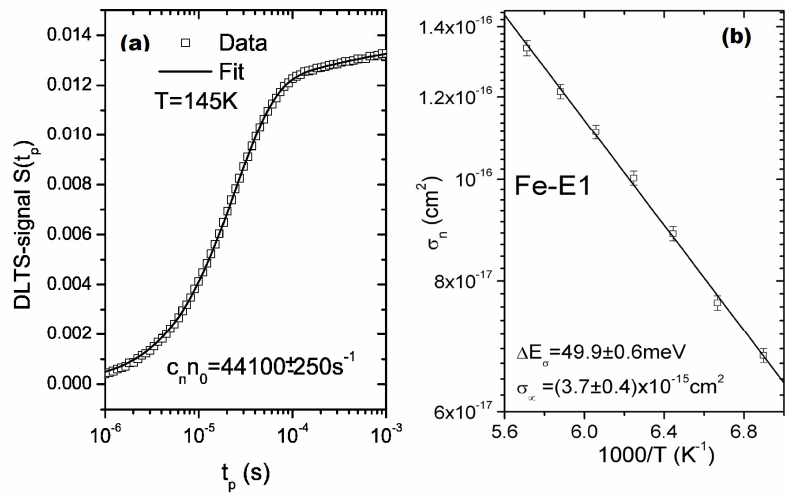Fig.2. DLTS of metal implanted p-type germanium

Fig. 3. Electron capture cross section measurement of Fe-E1 level;
(a): isothermal measurement of capture rate; (b): temperature dependence of capture cross-section

levels. Reliable Hall-effect data are available for Fe, Co, Ni and Cu which are in very good agreement with the data in Table 1 and 2. The good agreement for Fe and Co also strengthens our confidence in the adopted implantation procedure and in the new data for Ti and Cr.

The M-E1 and M-Hi levels are for each case attributed to the metal impurity on a substitutional site. The specificity and reproducibility of the spectra of the implanted samples, with almost no secondary features due to contaminants, allows to unambiguously assign the levels to the metal species implanted. Moreover the very similar concentrations of the different levels belonging to the same metal and for the same implantation condition, indicate that in each case only one single defect is involved.

The old Hall-effect data already indicated that the metal impurities in germanium form multiple acceptors. This is substantiated by the DLTS measurements. The M-E1 levels correspond with a low value of the electron capture cross-section which is thermally activated (it may be noted that this is also the case for the electron traps belonging to Ag and Au in germanium [4]). This indicates that we are concerned with multiphonon capture against a repulsive barrier, as would be the case for capture into a negative charge state of the defect. The assignment to acceptor levels is further supported by the absence of an electric field enhanced shift of the M-E1 bands. The hole capture cross-sections of most of the M-Hi levels on the other hand are much higher and could therefore not be measured directly, which is in agreement with hole capture into a negatively charged acceptor state. The observation of field-enhanced emission for several of the M-Hi bands is also in agreement with the latter assignment. Exceptions in this respect are the Cr-H1 and Co-H1 bands which are attributed to donor states. In summary: Ti, Fe, Co and Ni form double acceptors, Cr and Cu form triple acceptors. In the case of Cr and Co a donor level is also present close to the valence band. The level system of Cr is similar to that of Cu, Ag and Au [4] (in the case of Cu the lowest level is considered rather an overcharged acceptor [10]).
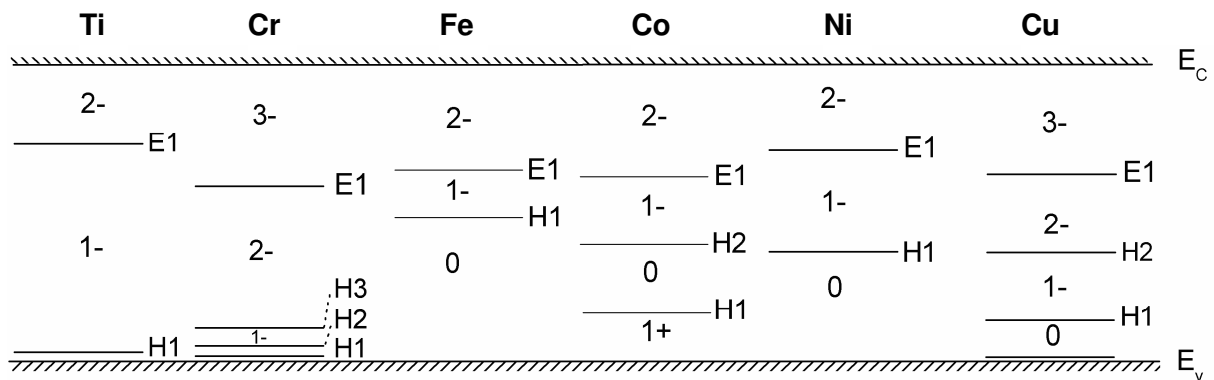
Fig. 4. Energy levels and charge states of transition metal centres in germanium

Table 1. Deep level parameters and assignment of electron traps due to transition metal impurities in n-type germanium

band	E_{na} eV	σ_{na} cm^2	σ_{∞} cm^2	E_{σ} eV	ΔH eV	$\Delta S/k$	level
Ti-E1	0.228	1.1×10^{-14}	8.7×10^{-16}	0.027	0.201	2.6	Ti$^{-/2-}$
Cr-E1	0.366	1.8×10^{-14}	2.2×10^{-17}	0.056	0.310	6.9	Cr$^{2-/3-}$
Fe-E1	0.342	2.6×10^{-14}	3.7×10^{-15}	0.050	0.292	2.0	Fe$^{-/2-}$
Co-E1	0.325	1.1×10^{-13}	2.3×10^{-15}	0.010	0.315	3.9	Co$^{-/2-}$
Ni-E1	0.310	7.7×10^{-15}	1.9×10^{-16}	0.001	0.309	3.6	Ni$^{-/2-}$
Cu-E1	0.324	1.3×10^{-15}	3.4×10^{-17}	0.065	0.259	3.6	Cu$^{2-/3-}$

The triple acceptor nature of the column Ib metals Cu, Ag and Au with $d^{10}s^1$ configuration may be qualitatively explained by a tetrahedral bonding model for the substitutional impurity, in a similar way as a column III element such as Ga is expected to be a single and a column IIb element such as Zn is expected to be a double acceptor [1]. This kind of explanation seems less straightforward for transition metals with a partially filled 3d-shell, nevertheless also for these elements the acceptor multiplicity is in general agreement with the occupation of the atomic 4s-shell. In any case, the multiple acceptor action of elements having less than 3 electrons in the outer shell has been considered to support the viewpoint that they are substitutional [11].

Table 2. Deep level parameters and assignment of hole traps due to transition metal impurities in p-type germanium

band	Ti-H1	Cr-H1	Cr-H2	Cr-H3	Fe-H1	Co-H1	Co-H2	Ni-H1	Cu-H1	Cu-H2
E_{pa} (eV)	0.025	-	0.042	0.088	0.345	0.086	0.254	0.217	0.037	0.322
σ_{pa} (cm^2)	1.6×10^{-14}	-	4.1×10^{-14}	1.7×10^{-13}	2.1×10^{-12}	7.2×10^{-13}	1.8×10^{-14}	6.2×10^{-13}	6.4×10^{-14}	1.6×10^{-12}
level	Ti$^{0/-}$	Cr$^{+/0}$	Cr$^{0/-}$	Cr$^{-/2-}$	Fe$^{0/-}$	Co$^{+/0}$	Co$^{0/-}$	Ni$^{0/-}$	Cu$^{0/-}$	Cu$^{-/2-}$

The $\Delta S/k$ data in Table 1 in principle bear information concerning the bonding configuration. Only for Ni a detailed model is available from ESR measurements: the metal atom is displaced from the substitutional lattice position making bonds with two Ge neighbours, while the other two Ge neighbours form a reconstructed bond [12]. The configurational entropy change for the Ni^{2-} to Ni$^-$ transition may then be calculated in a similar way as for the *5d* analogon Pt in silicon for which the same bonding model applies [13], yielding $\Delta S_{conf} = 0.7k$. The vibrational part of the entropy change may be estimated as $\Delta S_{vib} = 2.5k$ [14], yielding a total of $\Delta S = 3.2k$, which is in fair agreement with the experimental value of $\Delta S = 3.6k$ for the Ni$^{-/2-}$ level.

Finally, in order to estimate the importance of the metal impurities with respect to minority carrier lifetime in germanium, the directly measured capture cross-sections may be extrapolated to room temperature. The data are summarized in Fig. 5. The σ_n data suggest that Co and Ni will be the most efficient lifetime killers in p-type Ge. Only few values of σ_p could be measured, the high values nevertheless indicate that the effect of transition metal impurities on hole lifetime in n-type germanium may be important. The data in Fig.5 complete data which have been obtained by other techniques [3].
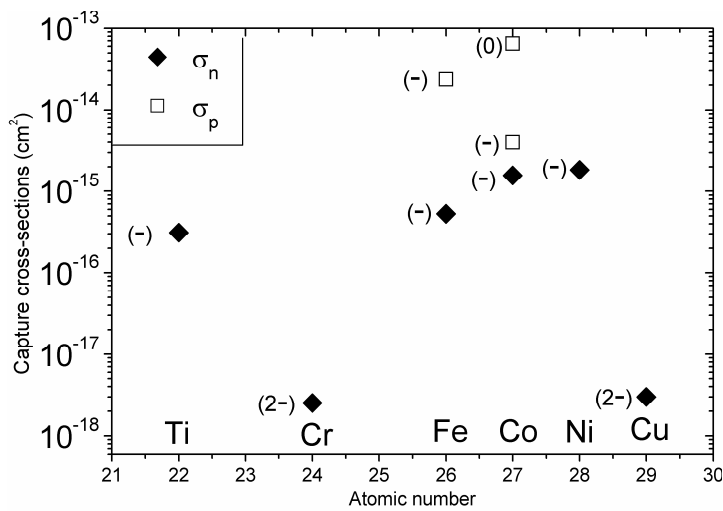

Fig. 5. Capture cross-sections at 300 K of transition metals in germanium. The charge state of the defect before capture is indicated between brackets

Hydrogen passivation of transition metal impurities

The triple acceptor Cu in germanium may be partially or completely passivated by bonding with hydrogen. The levels of the double acceptor Cu-H and of the single acceptor Cu-H$_2$ have been well established [15]; in this model the Cu-H$_3$ complex is electrically inactive. It remained unclear however whether the multiple acceptor states of other transition metals may also be passivated by hydrogen. In order to study this problem, transition metal implanted n- and p-type germanium wafers have been hydrogenated in a direct hydrogen plasma equipment, typically at 200°C during 4 hours [16]. The general observation using DLTS is that three different spatial ranges can be distinguished below the treated surface, as shown in Fig.6 for the case of a p-type Co implanted germanium wafer [17]. In a first range extending to a depth of about 5 μm no deep levels are found, indicating that the metal centres are completely passivated. It may be remarked that on the contrary no difference in shallow dopant concentration is observed within the accuracy of the capacitance voltage profiling. In a second range between about 5 and 12 μm, several traps are observed which are assigned to irradiation damage due to the direct plasma. The most interesting observation in this range is however the occurrence of several metal specific electron and hole traps which are tentatively assigned to metal-hydrogen complexes: one for Ti, three for Cr, two for Fe and Co [16]. No systematic ordering of the level positions with respect to the levels of the substitutional metals
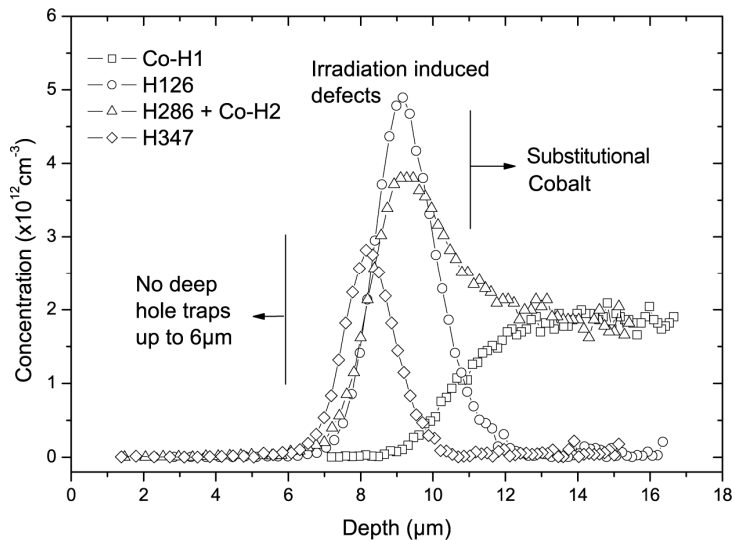
Fig. 6. Depth profile of deep level centres in Co implanted and plasma hydrogenated germanium; H126, H286, H347 refer to DLTS bands due to irradiation damage

appears however. In the case of Cr, levels at 0.10 and 0.03 eV above the valence band show a hierarchy with respect to the triple acceptor levels of the substitutional metal, which is similar as for the Cu-H levels with respect to Cu (it may be remembered that the level system of substitutional Cr and Cu is also similar); the levels are therefore tentatively assigned to the Cr-H complex. For the other levels no definite assignment could be made so far. Finally, in a third range beyond 12 μm the levels from the substitutional metal impurities are observed again.

REFERENCES
[1] W.W. Tyler, *J. Phys. Chem. Solids*, **8**, (1959), 59
[2] S.M. Sze and J.C. Irvin, *Solid State Electron.*, **11** (1986) 599
[3] E. Simoen, C. Claeys in: *Germanium-Based Technologies: From Materials to Devices, ed. C. Claeys, E. Simoen* (Elsevier, Amsterdam, 2007)
[4] P. Clauws and E. Simoen, *Mater. Sci. Semicond. Proc.*, **9**, (2006), 546
[5] P. Clauws, J. Van Gheluwe, J. Lauwaert, E. Simoen, J. Vanhellemont, M. Meuris and A. Theuwis, *Physica B*, **401-402**, (2007), 188
[6] G. Huylebroeck, P. Clauws, E. Simoen and J. Vennik, *Solid State Commun.*, **82**, (1992), 367
[7] P. Blood and J.W. Orton, *The Electrical Characterization of Semiconductors: Majority Carriers and Electron States* (Academic Press, London, 1992)
[8] J. Lauwaert, J. Van Gheluwe and P. Clauws, Rev. Sci. Instr., **79**(9), (2008)
[9] C.H. Henry and D.V. Lang, *Phys. Rev. B*, **15**, (1977), 989
[10] R.E. Mc Murray Jr, *Solid State Commun.*, **52**, (1985), 1127
[11] R. Newman and W.W. Tyler, *Solid State Phys.*, **8**, (1959), 49
[12] G.W. Ludwig and H.H. Woodbury, *Phys. Rev.*, **113**, (1959), 1014
[13] S.D. Brotherton and J.E. Lowther, *Phys. Rev. Lett.*, **44**, (1980), 606
[14] J.A. Van Vechten and C.D. Thurmond, *Phys. Rev. B*, **14**, (1976), 3539
[15] E.E. Haller, G.S. Hubbard and W.L. Hansen, *IEEE Trans. Nucl. Sci.*, **NS-24**, (1977), 48
[16] J. Lauwaert, J. Van Gheluwe and P. Clauws, *Mater. Sci. Semicond. Proc.*, (2008), to be published
[17] J. Lauwaert, J. Van Gheluwe and P. Clauws, *Physica B*, **401-402**, (2007), 210