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APPLICATIONS OF MÖSSBAUER SPECTROSCOPY TO INVESTIGATIONS OF DEFECTS IN SEMICONDUCTORS

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ABSTRACT

A survey of applications of Mössbauer spectroscopy to semiconductor physics will be given, comprising discussions of useful Mössbauer isotopes, the type of experiments which can be conducted, and the information which can be obtained. Specific examples have been chosen to illustrate the potential of Mössbauer spectroscopy in studies of defects in semiconductors, for example the lattice location and electronic structure of 5 sp impurities in elemental and compound semiconductors; the solubility and diffusion from supersaturated solutions in silicon; and the complex behaviour of transition-metal impurities.

INTRODUCTION

Soon after the discovery of the Mössbauer effect [1], its potentialities to studies of impurities and defects in semiconductors were realized [2]. Several reviews on this topic have been published [3,4]. This review will focus on various types of experiments which can be conducted, the information which can be obtained, and the possible combination with other techniques. The examples given were selected to elucidate the potential and limitations of the method rather than to cover all recent progress in the field.

The observation of the Mössbauer effect, the resonant absorption of γ -radiation, is restricted to a limited number of Mössbauer isotopes with suitable ground state γ transitions. Among these, mainly isotopes of sp elements (^{67}Zn , ^{73}Ge , ^{119}Sn , ^{121}Sb , ^{125}Te , ^{129}I) and the 3d element iron (^{57}Fe) have been applied to studies of semiconductors. Two types of Mössbauer spectroscopy should be distinguished: 1) In absorption spectroscopy stable Mössbauer nuclei (e.g. ^{57}Fe) incorporated as probe atoms in the sample under study are analyzed by resonance absorption of external γ rays from a standard source. In this case an absolute number of probe atoms of 10^{16} - 10^{18} atoms/cm² is required. This corresponds to a minimum concentration of $\sim 10^{17}$ at/cm³ due to photoabsorption limitations in the maximum sample thickness (a few mm). 2) In emission spectroscopy

py the system under study is labelled by radioactive nuclei (e.g. ^{57}Co), which in their decay leads to the emission of the γ rays of interest. These are then analyzed against a standard absorber. In this case the useful number of probe atoms is in the range $>10^{11}$ atoms/cm². These probe atoms can be incorporated in the systems in different depths from very shallow (<1000 Å) up to mm. This leads to a large accessible concentration range of $>10^{12}$ atoms/cm³.

The absorption type Mössbauer spectroscopy is easy to interpret since the resonance absorption at the nucleus (e.g. ^{57}Fe) does not change the electronic configuration of the probe atom. In contrast, in emission-type experiments the probe atom may undergo a nuclear transmutation ($^{57}\text{Co} \rightarrow ^{57}\text{Fe}$). Thus the system is produced with a parent probe (e.g. ^{57}Co) but the electronic properties of the daughter probe (e.g. ^{57}Fe) are measured.

The basic parameters, which can be determined for a Mössbauer probe atom, are briefly described in the following: The isomer shift, δ , is proportional to the difference in electronic charge density at the Mössbauer nucleus of the source, $\rho_s(0)$, and absorber, $\rho_a(0)$:

$$\delta = \alpha(\rho_s(0) - \rho_a(0)). \quad (1)$$

Since accurate calibrations of the constant α have become available [5] for the Mössbauer isotopes considered here, the charge density at the Mössbauer nucleus is obtained. This quantity is interpreted in terms of the valence electron configuration of the probe. The presence of an electric field gradient at the Mössbauer nucleus leads to a splitting of the Mössbauer resonance via the electric quadrupole interaction. The presence (or absence) of an electric field gradient, its magnitude and direction, gives direct information on the local symmetry of the probe atom. Lattice dynamical information is obtained from the Lamb-Mössbauer factor, which probes the bonding strength of the probe atom to its surroundings:

$$f = \exp(-k^2 \langle x^2 \rangle), \quad (2)$$

where k is the wave number of the γ radiation and $\langle x^2 \rangle$ the mean squared vibrational amplitude of the probe. In certain cases, local motion (e.g., cage jumping, diffusion) of the probe atom can also be studied.

It should be emphasized that each distinct site occupied by probe atoms gives rise to a Mössbauer resonance. As will be demonstrated, even different charge states of a probe atom can often be distinguished. On the other hand, the limited resolution renders Mössbauer spectroscopy rather insensitive to the local surrounding beyond the nearest neighbour shell.

DISCUSSION

We have made an arbitrary classification of Mössbauer probes as 1. Shallow (covering constituents, isovalent impurities, and shallow dopants). 2. Deep-level impurities (e.g., Cd, Te, I in Si). 3. Transition metal impurities (e.g. Co, Fe in Si). This classification enables a natural choice of appropriate examples but has also bearings on the preparation of Mössbauer systems since the class 1 probes tend to have high solubilities and low diffusion constants whereas the reverse holds for the class 3 probes.

1. SHALLOW PROBES

Under this headline we treat Mössbauer probe atoms incorporated as constituents, isovalent impurities or shallow dopants in

group-IV as well as in compound semiconductors. This subfield constitutes the centre of gravity (in terms of publications) of the research in recent years. The isotopes relevant here are ^{67}Zn , ^{73}Ge , ^{119}Sn , ^{121}Sb , ^{125}Te , and ^{129}I where the four underlined isotopes cover more than 90% of the activity. Interestingly, these four isotopes represent the 5sp period from the group-IV to VII elements. Most of the systems which have been studied could in principle have been prepared during the growth of the crystals. However, for practical reasons many systems are prepared by ion implantation and/or diffusion.

As a first example we discuss results for Sb donors in Si. Mössbauer absorption spectroscopy can be carried out on the stable isotope ^{121}Sb for concentrations of 10^{18} - 10^{19} Sb atoms/cm³ [6], i.e., in the high doping range (n^+). In order to study the properties of Sb in Si in more detail, Mössbauer emission experiments were carried out on Si containing ion implanted radioactive ^{121}Te (decaying to ^{121}Sb). A subsequent laser annealing treatment produces a supersaturated solution of ^{121}Te on substitutional sites in Si [6]. Thus, the dependence of the ^{121}Sb isomer shift on the position of the Fermi level controlled by additional dopants could be measured. Minute differences in charge density ($\Delta\rho(0)=0.6 \text{ a}_0^{-3}$) were found to characterize the ionized and neutral Sb donors, respectively. Similar measurements enabled a systematic investigation of the electronic configuration of Sb probe atoms on V and VI sites in a series of III-V and II-VI compounds [6]. The prominent feature of these investigations are rather similar valence configurations of the Sb probes, irrespective of their dopant character.

Williamsson et al. have investigated Sn doped GaAs and $\text{Ga}_{1-x}\text{Al}_x\text{As}$ compounds grown with isotopically enriched, stable ^{119}Sn by various methods [7,8]. The doping concentration was in the range 10^{18} - 10^{19} atoms/cm³ which is typically necessary for absorption experiments. The fraction of Sn atoms occupying Ga sites in GaAs (as determined by Mössbauer spectroscopy) was shown to correlate exactly with the electrical activity (as determined via the

Fig. 1. ^{119}Sn Mössbauer spectra of Sn doped $\text{Ga}_{1-x}\text{Al}_x\text{As}$ for three different values of x .

Fig. 2. Relative intensities of the DX center related components 2+3.

Hall effect) [7]. Several non-substitutional components were also studied. Besides trivial components (e.g., β -Sn precipitates), two components which seem related to the DX centers were found in $\text{Ga}_{1-x}\text{Al}_x\text{As}$. Figure 1 shows ^{119}Sn Mössbauer spectra for various values of x . Component 1 originates from Sn atoms on substitutional Ga or Al sites. Components 2+3 (which actually could be one, quadrupole split component) grow abruptly in intensity around $x=0.30$ (figure 2), correlated with the appearance of DX centers. Due to the ambiguity in the interpretation of the data, the presence or absence of large lattice relaxations in DX centers can not yet be concluded [8], but further work is presently being undertaken by several groups [9,10].

As already mentioned, Mössbauer emission type experiments are complicated by the fact that the system is prepared with a parent isotope, but it is the properties of the daughter probe which are measured. However, this can be utilized 1) to obtain information - although indirectly - on an element which does not possess a Mössbauer isotope and 2) to achieve an unusual lattice location of the probe atom. As discussed above, doping of GaAs with Sn during crystal growth leads to a preferential incorporation of Sn on Ga-sites as a donor and not on As-sites as an acceptor, although Sn is normally considered an amphoteric dopant in the III-V compounds. However, when Mössbauer emission spectroscopy is performed with ^{119}Sn after the decay of ^{119}In and ^{119}Sb parent isotopes respectively, a site-selective incorporation on III- and V-sites can be achieved [11]. In this way the electronic configuration and the lattice dynamical properties of Sn atoms on both substitutional sites in a series of III-V compounds have been studied [11,12].

The greatest advantage of Mössbauer absorption spectroscopy is that the concentration range ($>10^{17}$ probe atoms/cm³) and the sample type (homogeneously doped thick crystals) is suitable for the application of complementary techniques, like channeling/RBS, Hall effect measurements, EPR or IR measurements. In certain cases (e.g., the DX centers in $\text{Ga}_{1-x}\text{Al}_x\text{As}$) a correlation with DLTS measurements is being pursued. Presently, efforts are made in Aarhus to apply simultaneous DLTS and Mössbauer spectroscopy to studies of Sn- and Sb-vacancy related defects in Si.

We end this section by an example of Mössbauer emission spectroscopy on Sb doped Si. When Sb is ion implanted into Si to concentrations below $\sim 1 \times 10^{20}$ cm⁻³ perfect substitutional systems can be produced by rapid thermal annealing at temperatures of 700-1050°C [13]. These systems can not be studied by Mössbauer absorption spectroscopy because the absolute number of probe atoms in the doped layers (only a few 1000Å) is too low. Instead, Mössbauer emission spectroscopy on radioactive ^{119}Sb (decaying to ^{119}Sn) added to a higher dose of stable, ion implanted ^{121}Sb has been carried out [13,14].

The diffusion of Sb in Si can be modelled assuming diffusion only via neutral and double-negatively charged vacancies for donor concentrations below $\sim 2 \times 10^{20}$ cm⁻³ [15]. The diffusion via the double-negatively charged vacancies causes an n^2 concentration dependent diffusivity, where n is the carrier concentration. Recently, however, Hall effect and RBS/channeling measurements have shown that the diffusivity depends on the fourth power of the carrier concentration for concentrations between $\sim 2 \times 10^{20}$ and 5×10^{20} cm⁻³, where 5×10^{20} represents the highest doping level which can be achieved with a P-background doping (see figure 3) [14]. Mössbauer emission spectra of ^{119}Sb added to an Sb solution with background P-doping levels of 9×10^{19} and 4×10^{20} cm⁻³ are shown in figure 4.

Fig. 3. Total diffusion coefficient for Sb in Si as a function of the background doping. The lines are fits to a power law, the exponent, s , is indicated.

Fig. 4. ^{119}Sb Mössbauer spectra for two background doping levels. The corresponding points in Fig. 1 are marked by arrows.

The spectrum a (corresponding to a diffusivity in the n^2 region) consists of a line from substitutional Sb atoms and a small line from surface precipitated Sb atoms only. From such spectra it is estimated that ~6% of the Sb atoms are contained in these surface precipitates, the rest is in exact substitutional positions. The spectrum b (corresponding to a diffusivity in the n^4 region) shows additionally a component the intensity of which corresponds to an Sb fraction of ~80%. The n^4 dependence of the diffusivity is correlated to the appearance of this component. The component has been tentatively assigned to a fast-diffusing Sb-V-P complex.

2. DEEP LEVEL SP IMPURITIES

This class covers group II, VI, and VII impurities in Si and analogous systems in compound semiconductors. As an example we discuss experiments on the system Te in Si. Impressive progress has been made in recent years towards an understanding of chalcogen impurities in Si [16]. The application of Mössbauer spectroscopy has produced valuable information [17,18].

Mössbauer absorption experiments on ^{125}Te diffused (or incorporated during growth) into Si should be feasible, but no such experiment has been reported. Three different Te isotopes ($^{119\text{m}}\text{Te}$, $^{125\text{m}}\text{Te}$, and ^{129}Te decaying to ^{119}Sn , ^{125}Te , and ^{129}I , respectively) can be utilized in Mössbauer emission experiments. The Groningen group has implanted these isotopes into Si crystals with different background doping levels (n^+ , i , and p^+ [17,18]. After ion implantation the samples were laser annealed to produce a supersaturated solution of Te in Si. The ^{119}Sn Mössbauer emission spectra after ^{119}Te implantation consist of single lines and the isomer shift and Debye temperature were independent of the background doping. The line is well-known to originate from substitutional Sn atoms, which

have no levels in the band gap. Since the nuclear transmutations are not expected to alter the lattice position of the impurity, it was considered established that the laser annealing leads to a substitutional incorporation of the Te atoms as also supported by channeling measurements. The ^{125}Te Mössbauer emission spectra from ^{125}mTe implants also consist of a single line for all three doping levels. But as can be seen from Table I, the isomer shifts and the Debye temperatures do depend on the doping level. Table I also gives the Debye temperatures for substitutional Sn^0 and Sb^+ in Si, which agrees with that of ^{125}Te in $p^+-\text{Si}$. This indicates that the Te atom is in the Te^{++} charge state, which is isoelectronic to Sb^+ and Sn^0 . The lower Debye temperature and the higher charge density ($\Delta\rho(0) = 12 \text{ a}_0^{-3}$) at the Te nucleus in $n^+-\text{Si}$ suggest that the Te atom is more negatively charged, presumably in the Te^0 state. In conclusion the Mössbauer results show that Te can be brought on substitutional sites in Si. Furthermore different charge states of Te could be identified from their Mössbauer parameters.

Table I

Isomer shifts (relative to: CaSnO_3 for ^{119}Sn , GaSb for ^{121}Sb , SnTe for ^{125}Te , and CuI for ^{129}I) and Debye temperatures for Sn, Sb, Te and I on substitutional sites in Si.

Impurity	Charge state	Isomer shift (mm/s)	Debye temp (K)	Ref.
^{119}Sn	Sn^0	1.79(3)	234(5)	[13]
^{121}Sb	Sb^+	0.39(5)	243(6)	[6]
^{125}Te	Te^0	0.14(1)	207(3)	[17,18]
	(Te^+)	0.06(1)	-	
	Te^{++}	-0.13(1)	232(3)	
^{129}I	I^0	2.15(4)	155(7)	[17,18]
	I^+	2.34(1)	170(3)	
	I^{++}	0.94(1)	196(3)	

The ^{129}I Mössbauer spectra from ^{129}Te implants are very different in n^+- and $p^+-\text{Si}$. In $n^+-\text{Si}$ the Mössbauer resonance is quadrupole split demonstrating that the substitutional site occupied by the ^{129}Te mother is not inherited by the ^{129}I daughter. The electric field gradient was proposed to result from a Jahn-Teller relaxation of the I^0 atom away from the substitutional site in Si. Also for I three different charge states could be distinguished by their isomer shifts and Debye temperatures (see Table I).

Additionally, ^{129}I Mössbauer spectra recorded around 80K in $n^+-\text{Si}$ indicate that the I^0 performs fast jumps between equivalent sites within the lifetime of the Mössbauer level (24 ns). In contrast to the cases discussed above this is a local motion as distinguished from a participation in the normal lattice vibrations.

Thus in cases where the electronic configuration and the dynamical properties become charge-state dependent, detailed information can be obtained by Mössbauer spectroscopy.

3. TRANSITION METAL IMPURITIES

The last class of systems we want to mention are the transition metal impurities in Si. Mössbauer absorption spectroscopy can

be performed with ^{57}Fe , whereas emission spectroscopy uses the parent isotope ^{57}Co . Although these systems have been studied extensively over the years, little progress has been made towards an identification of these impurities on well-defined substitutional or interstitial lattice sites.

Mössbauer absorption spectroscopy on ^{57}Fe in Si is hampered by the low, interstitial, solubility (essentially zero at 300K, $\sim 10^{16}$ atoms/cm³ at 1500K) of most transition metals in Si [19]. On the other hand, fast cool-down from high temperatures freezes in this interstitial solution [19]. However, the concentration is marginal for an absorption experiment and no results have been published so far.

The high temperature solubility is more than sufficient to apply Mössbauer emission spectroscopy to ^{57}Co in Si. However, Co cannot be kept on interstitial or substitutional sites at 300K even after rapid quenching. Investigations of the complexing and precipitation behaviour of ^{57}Co have been conducted mainly by the Göttingen [20] and Leuven groups [21].

Ion implantation has been widely used to circumvent the low solubilities. However, for implantation temperatures at or above 300K Co and Fe seem to be effectively trapped by their own radiation damage, the defects of which are partly mobile. As expected the recorded Mössbauer spectra are strongly dose-concentration dependent. An example from low-dose implantations (10^{12} – 10^{13} cm⁻²) of Co in Si is shown in Figure 5 [21]. At the lowest concentrations a doublet with a large intensity appears in a narrow temperature interval around 750K. This doublet was proposed to originate from Co-dimers (from comparison with rare-gas matrix-isolated Co-dimers). The dimers represent the first step towards precipitation which occurs at slightly higher temperatures, possibly during the ordering of the Si lattice.

Recently, low dose implantation of ^{57}Co in Si at low temperatures, where most defects are immobile, has been claimed to lead to a population of substitutional and tetrahedral interstitial sites, respectively [22].

Fig. 5. ^{57}Fe Mössbauer spectra from RT implantations of ^{57}Co into Si for three different doses. The samples were subsequently annealed to 475 °C.

CONCLUSION

By Mössbauer spectroscopy the hyperfine interaction and lattice dynamical parameters of specific probe atoms can be unambiguously determined. Detailed information on the local surroundings of the probe atoms can be obtained comprising information on the electronic configuration, the symmetry, and the vibrational behaviour of the probe atoms. Despite numerous applications to problems concerning defects in semiconductors it is fair to state that the impact of Mössbauer spectroscopy in this field has been limited. Nevertheless, recent progress in dedicated applications utilizing various complementary techniques on the same problem have put the potential of Mössbauer spectroscopy into sharper focus. Although restrictions due to the limited number of suitable Mössbauer isotopes prevent a universal application of this method, it may contribute in a unique way whenever direct microscopic information on a well-identified probe is of value.

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REFERENCES

- 1) R.L.Mössbauer, *Naturwissenschaften*, 1958, 45, 538
- 2) P.C.Norem, G.K.Wertheim, *J.Phys.Chem.Solids*, 1962, 23, 1111
- 3) G.Weyer, *Hyp.Int.*, 1986, 27, 249
- 4) D.L.Williamson, *Hyp.Int.*, 1988, 40, 249
- 5) A.Svane, E.Antoncik, *Phys.Rev.B*, 1987, 35, 4611 and references therein.
- 6) G.J.Kemerink, H.Andreasen, H. de Waard, G.Weyer, *J.Phys.C*, 1988, in press
- 7) D.L.Williamson, P.Gibart, B.El-Jani, K.N.Guessan, *J.Appl.Phys.*, 1987, 62, 1739
- 8) P.Gibart, D.L.Williamson, B.El-Jani, P.Basmaji, *Phys.Rev.B*, 1988, 38, 1885
- 9) G.L.Zhang, D.Mo, D.D.Boerma, L.Niesen, *Hyp.Int.*, to be publ.
- 10) G.Langouche, H.Bemelmans, J.Odeurs, G.Borghs, M.de Potter, W.Deraedt, M.Van Rossum, this conf.
- 11) G.Weyer, J.W.Petersen, S.Damgaard, H.L.Nielsen, J.Heinemeier, *Phys.Rev.Letters*, 1980, 44, 155
- 12) O.H.Nielsen, F.K.Larsen, S.Damgaard, J.W.Petersen, G.Weyer, *Z.Phys.B*, 1983, 52, 99
- 13) A.Nylandsted Larsen, F.T.Pedersen, G.Weyer, R.Galloni, R.Rizzoli, and A.Armigliato, *J.Appl.Phys.*, 1986, 59, 1908
- 14) A.Nylandsted Larsen, P.Tidemand-Petersson, P.E. Andersen, G.Weyer, *Proc.Third Int.Conf.Shallow Impurities in Semiconductors*, Linköping, Sweden, 1988
- 15) R.B.Fair, M.L.Manda, J.J.Wortman, *J.Mater.Res.*, 1986, 1, 705
- 16) H.G.Grimmeis, E.Janzen, in "Deep Centers in Semiconductors", ed. S.T.Pantelides, 1986 (Gordon and Breach Science Publishers, New York) 87
- 17) H.de Waard, G.J. Kemerink, *Physica B*, 1983, 116, 210
- 18) H.de Waard, G.J.Kemerink, L.Niesen, D.Boerma, *Hyp.Int.*, 1983, 14, 37 & 54, and refs. therein
- 19) E.Weber, *Appl.Phys.A*, 1983, 30, 1
- 20) D.Gilles, W.Schröter, *Mat.Sci.Forum*, 1986, 10-12, 169 and refs. cited herein
- 21) G.Langouche, M.de Potter, D.Schroyen, *Phys.Rev.Lett.*, 1984, 53, 1364 and references cited therein.
- 22) G.Langouche, M.De Potter, *Nucl.Instrum.Methods B*, 1987, 19-20, 322