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PHONON SPECTROSCOPY OF DEFECTS CORRELATED WITH THE DIFFUSION OF ZN INTO SI

J. STAIGER[1], P. GROSS[1], K. LASSMANN[1],
H. BRACHT[2], AND N.A. STOLWIJK[2]

[1]Universität Stuttgart, 1. Physikalisches Institut,
Pfaffenwaldring 57, D-70550 Stuttgart
[2]Universität Münster, Institut für Metallforschung,
Wilhelm-Klemm-Straße 10, D-48149 Münster

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ABSTRACT

We analyse by phonon spectroscopy low lying phonon scattering states from defects that are introduced by the diffusion of Zn into thick Si wafers.

INTRODUCTION

The two Γ_8-holes bound to a substitutional double acceptor in a diamantine semiconductor at low temperatures would form a sixfold degenerate ground state were it not for the hole-hole interaction that within T_d splits it into at most 3 states: Γ_1, Γ_3, and Γ_5 [1]. The ordering of these states may be according to Hund's rule with Γ_1 (J=0) highest or it may be inverted (i.e. the S-like Γ_1 lowest) by a strong attractive central potential [2]. The (near) degeneracy of this ground state multiplet may add the complication of a Jahn-Teller effect [3] which may increase the number of possible scattering resonances.
The level separations of the ground state multiplets of double acceptors in Ge were found by optical methods to lie in the range of meV where phonon spectroscopy with superconducting tunnel junctions is a direct spectral method with high sensitivity and resolution. Such experiments applied to Ge:Zn and Ge:Be [4] have essentially confirmed the optical results: A non-degenerate ground state and a rather broad ($\approx$ 1.4 meV) excited state at 2.4 meV for Ge:Zn and for Ge:Be a triplet with zero stress separations below .3 meV. Including also the optical data for the Hg and Mg double acceptors in Ge a simple relationship between binding energy and ground state splitting is not obvious. The reason may be a delicate interplay of the concurrent mechanisms enumerated above.
In Si the situation is even more complicated by the tendency of the corresponding elements to associate with other defects or to reside on interstitial sites [5,6,7]. Recent Hall and DLTS-measurements [8,5] have confirmed older work in that Zn may prevail as a substitutional double acceptor in Si under appropriate conditions. From IR-absorption due to transitions between ground and excited states [9,10] it was concluded in addition that the double acceptor ground state is a multiplet of at least three states with separations in the meV range and additional splittings under uniaxial stress. However, position and total number of these states are not unequivocal from these optical data. Therefore, measurements involving only transitions within the ground state multiplet are of interest.

EXPERIMENTAL

In this paper we analyse by phonon spectroscopy low lying phonon scattering states that are introduced by the diffusion of Zn into thick Si wafers [11]. Zn was diffused from an elemental source into originally n-type Si ([P] = $5 \cdot 10^{12}$ cm^{-3} and, for partial compensation, [P] = $1.1 \cdot 10^{15}$ cm^{-3}) by annealing at about 1000°C. The predominant configuration of Zn in Si is the substitutional double acceptor Zn_s. Partial compensation by a deep donor (possibly Zn_i) is found right after the diffusion and eliminated after an additional heat treatment at 600°C for 15 minutes. Concentration-depth profiles of Zn_s were determined after this 600°C anneal on simultaneously diffused high-ohmic samples of same thickness using the spreading-resistance technique [11, 12]. Some of the non-compensated, annealed samples with higher concentration were measured by IR-absorption and predominant Zn_s was found [13] with a ground state multiplet with separations as reported in [18].

At the cryogenic temperatures of our experiments the acceptors compensated by the phosphorous or the diffusion-induced donors could be neutralized by white light. Uniaxial stress up to 170 MPa was applied in <100>, <110>, or <111> directions along the length of the typically 2x5x15 mm^3 samples for the investigation of symmetries from stress-induced splittings and shifts.

Phonons were generated and detected by 1 mm^2 superconducting tunnel junctions made from Al or Sn evaporated onto opposite side faces of the samples. The spectral range of phonon energies is given by the properties of the Al and Sn junctions as phonon generators and detectors: For the Sn generator, Al detector configuration (short cut [Sn→Al]) it extends from ≈0.3 meV (Al detector threshold) to 1.2 meV (limit of reabsorption for phonons of energies larger than the Sn generator gap). For the Al generator, Sn detector configuration ([Al→Sn]) it extends above 1.2 meV, the Sn detector threshold. Reabsorption within the weak coupling superconductor Al is small enough to allow quasimonochromatic phonon emission up to at least 14 meV [14].

RESULTS

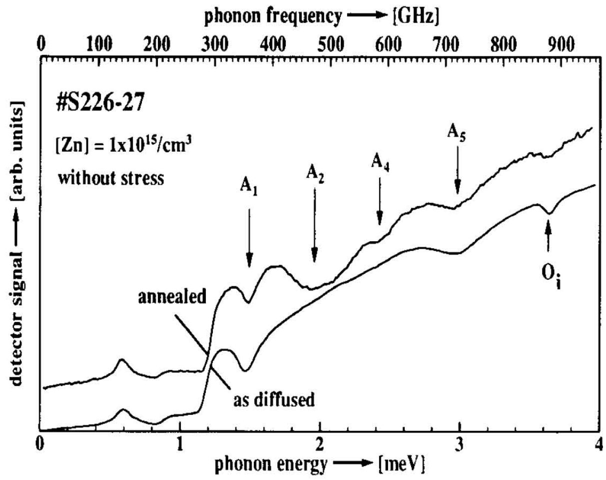

Fig. 1 Phonon scattering spectra beyond 1.2 meV ([Al→Sn] configuration) for a sample in the as diffused state and then after 600°C annealing to remove a deep compensating donor. Concentration of Zn_s^0: $1 \cdot 10^{15}$ cm^{-3}. O_i indicates the resonance of interstitial oxygen present in the sample at concentrations below 10^{16} cm^{-3}.

Depending on the sample conditions and parameters at zero stress a number of lines up to about 3.4 meV was observed of which the most distinct are labeled A_1 through A_9. Some of these are visible in Fig. 1 beyond the Sn detector threshold at 1.2 meV for a sample in the as diffused state and also after annealing. (O_i is due to a resonance of interstitial oxygen [15].) Since the annealing removes the partially compensating deep donor and thus increases the concentration of Zn_s^0 we attribute A_2 and A_4 to Zn_s^0. A_1 and A_5 vary in depth independently from each other and also from A_2 and A_4 under varying experimental conditions and thus should belong to two other defects, possibly to the complexes Zn(X1) and Zn(X2) of [16]. Only if A_5 is weak and narrow a line A_6 can be distinguished as shown in Fig. 2. From the correlation with sample conditions this line seems also to be associated with Zn_s^0.

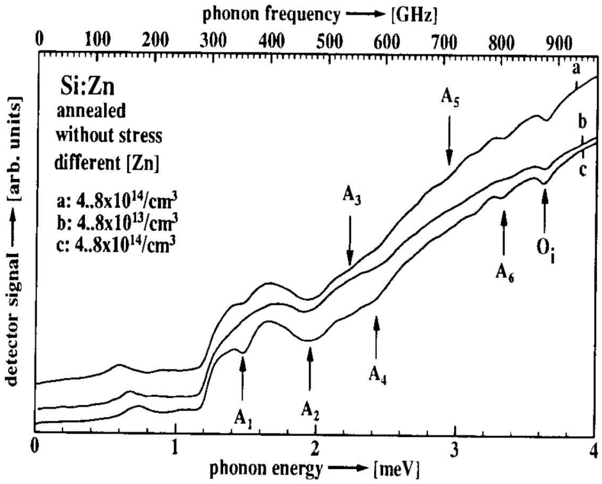

Fig. 2 Phonon scattering spectra for three non-compensated, annealed samples with differing concentrations of Zn_s^0 showing additional lines A_6 and A_3. A_3 seems to be correlated with A_1.

Line A_8 appears after neutralizing donors and acceptors in an annealed P-compensated sample by bandgap radiation (Fig. 3). This line is also found in non-compensated, annealed material without illumination and therefore also attributed to Zn_s^0.

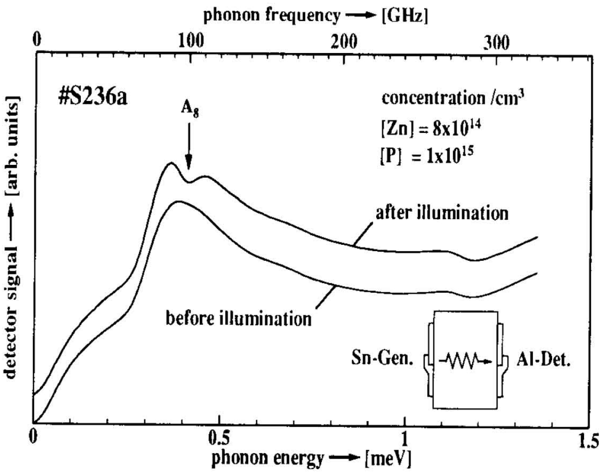

Fig. 3 Example for spectroscopy in the [Sn→Al]-configuration): Observation of a line A_8 beyond the Al-detector threshold (at $\approx$0.3 meV) after illumination of a partially P-compensated sample, i.e. after neutralization of P and Zn_s. In the [Al→Sn] configuration a line A_7 at 1.86 meV is visible in this P-compensated material only before illumination. It may be correlated with a Zn-P complex.

The changes in the spectra induced by bandgap illumination in partially compensated material are stable after switch off at the working temperature of $\approx$1 K. There is a characteristic difference between compensation by phosphorous and by the diffusion-induced donor: in the first case the changes are annihilated at a temperature below 77 K as expected for thermal excitation of the 44 meV donor P and in the second case at a temperature above 77 K and below 200 K, indicating a deeper donor. Neutralizing illumination deepens A_1 i.e. it should belong to a defect with acceptor character. The zero stress positions of the lines we attribute to Zn_s^0 are given below (in meV) and compared with the optical data from [9,18]:

This work:	.3 (A_8)	1.92 (A_2)	2.45 (A_4)			3.3 (A_6)	
[9]:		1.85	2.48	2.85	3.16		
[18]:		2.1			3.1	3.4	4.0

It is only for A_2 that all three data sets coincide; for the rest they are more or less at variance with each other. The energy of A_8 may be too small to be detectable optically. On the other hand, the selection rules for phonon transitions may leave levels undetected by phonon spectroscopy. E.g., transitions starting from the supposed thermally occupied, final state belonging to A_8 have not been found, in contrast to the case of the first and second excited rotational states of interstitial oxygen in Ge [17]. In any case: it seems clear from the three data sets that there are more than three states belonging to the Zn_s^0 ground state, i.e. more than would be expected if only Coulomb interaction between the two holes would be effective. In addition: the stress dependence of the level shifts and splittings should be distinctly nonlinear with such large level separations [1]. Instead, we find that all lines shift or split linearly under uniaxial stress in the three main directions as shown in Fig. 4 for different conditions in the <100> and <111> directions. Also in previous optical measurements [18] linear shifts and splittings have been found for stress in the <111> and <100> directions but a nonlinear dependence for stress in <110>. We do not find a large difference for the deformation potential constants in the <100> and <111> directions: A_2 shifts (splits) with 29 meV/GPa in <100>, 23 meV/GPa in <111> and in <110>, whereas Kaufmann et al. [18] find for the ground state splitting 12 meV/GPa in <111> and 78 meV/GPa in <100>.

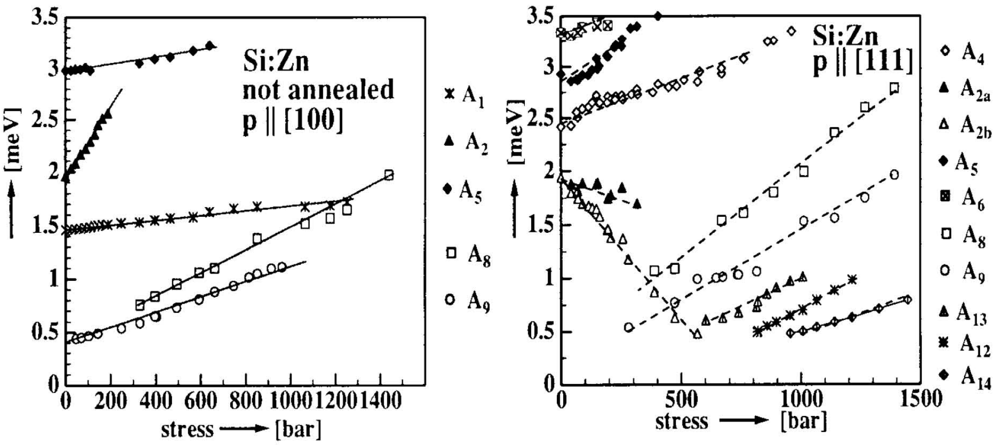

Fig. 4 Stress dependence of various lines in the <100> and <111> directions. In this special <111>-sample A_1 was rather weak.

For most lines the widths are of the order .1 meV and compare well with those observed for single and double acceptors in Ge and single acceptors in Si and thus should be determined by

lifetime broadening which is also consistent with the observed deformation potential constant. The stress coupling constant of A_1 in <100> is only 2.2 meV/GPa, and correspondingly this line is relatively narrow. This suggests that A_1 may not be due to an electronic transition.
Zn is apparently an effective recombination center in Si: illumination of the samples, though producing the above mentioned changes in the depth of the various absorption lines, did not result in significant changes of the resistivity as compared to analogous situations for single acceptors in Si [19]. This may be the reason that we could not observe a phonoconductivity signal corresponding to Zn^+ which could have produced by the illumination.

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REFERENCES

1) Mathieu, H., Camassel, J., Ben Chekroun, F.: Phys. Rev., 1984, B29, 3438
2) Thewalt, M.L.W., Labrie, D., Booth, I.J., Clayman, B.P., Lightowlers, E.C., Haller, E.E.: Physica, 1987, 146B, 47
3) Averkiev, N.S., Ashirov, T.K., Gutkin, A.A.: Sov. Phys. Semicond., 1981, 15, 1145 and 1983, 17, 61
4) Beate Altreuther, Diplomarbeit Uni Stuttgart, 1987
5) Weiss, S., Beckmann, R., Kassing, R.: Appl. Phys., 1990, A50, 151
6) Ammerlaan, C.A.J., Altink, H.E., Gregorkiewicz, T.: Sol. State Comm., 1990, 75, 115
7) Peale, R.E., Muro, K., Sievers, A.J.: Phys. Rev., 1990, B41, 5881
8) P. Stolz, Thesis, Erlangen 1990
9) Merk, E., Heyman, J., Haller, E.E.: Sol. State Comm., 1989, 72, 851
10) Dörnen, A., Kienle, R., Thonke, K., Stolz, P., Pensl, G., Grünebaum, D., Stolwijk, N.A.: Phys. Rev., 1989, B40, 12005
11) Bracht, H., Stolwijk, N.A., Mehrer, H., Yonenaga, I.: Appl. Phys. Lett., 1991, 59, 3559
12) Grünebaum, D., Czehalla, Th., Stolwijk, N.A., Mehrer, H., Yonenaga, I., Sumino, K., Appl. Phys. 1991, A53, 65
13) A. Dörnen and B. Kaufmann, private comunication
14) Gienger, M., Groß, P., Laßmann, K.: Phys. Rev. Lett., 1990, 64, 1138
15) Dittrich, E., Scheitler, W., Eisenmenger, W.: Jpn. J. Appl. Phys., 1987, Suppl. 26-3, 873
16) Stolz, P., Pensl, G., Grünebaum, D., Stolwijk, N.: Mat. Sci. and Eng, 1989, B4, 31
17) Gienger, M., Glaser, M., Laßmann, K.: Sol. State Comm., 1993, 86, 285
18) Kaufmann, B., Dörnen, A., Lang, M., Pensl, G., Grünebaum, D., Stolwijk, N.: Proc. 16th Int. Conf. Defects in Semicond., 1991 Mat. Sci. Forum 1991, 83-85, 197
19) Burger, W., Laßmann, K.: Phys. Rev. 1986, B33, 5868