Vacancy-Hydrogen Complexes in Germanium

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Abstract

Local-density-functional pseudopotential theory is used to investigate the structural, electronic and vibrational properties of vacancy-hydrogen complexes in germanium. The results are compared with recent infrared absorption data from proton and deuteron implanted Ge. The acceptor and donor levels of the VH_n defects are derived semi-empirically from the relaxed structures.

Key words: Ge, H, vacancy, complexes, *Ab Initio* theory

Introduction

The tendency for the vacancy to act as a trap for hydrogen has been well studied in many semiconductors over recent years. The structure and vibrational properties of vacancy-hydrogen complexes in silicon have been systematically investigated both theoretically[1–3] and experimentally[1,5,4] resulting in reliable assignments of many of the local vibrational modes. We discuss the results of infrared experiments on ion-implanted Ge and *ab initio* modelling. A full report on techniques used will be published at a later date.

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Results

The relative frequencies of the vibrational stretch modes of the VH_n, n=2,3,4 defects in germanium were observed to be very similar to those identified in silicon with a constant factor mapping Si stretch frequencies onto their counterparts in Ge. The vibrational modes for VH in Ge have not yet been observed. There also remains some doubt as to the assignment of the stretch modes to VH_3. It is uncertain whether these modes arise from VH_3 or V_2H_6. The annealing data shows these modes to arise from a defect which is more stable than VH_4 which may suggest that they originate from V_2H_6 rather than VH_3.

The calculated local vibrational modes (LVM's) for the neutral charge states of the VH_n complexes and the effects of deuteration are compared with experiment in Table 1. The assignments of those vibrational modes arising from mixed isotopic defects are tentative.

Neutral VH gives rise to a partially occupied electronic doublet in the forbidden gap. The resulting Jahn-Teller distortion to C_{1h} symmetry is effected by a rebonding by pairs of the Ge dangling bonds across the gap. The reconstructed bond length in the relaxed defect was calculated to be 2.78 Å in the relaxed structure (cf. 2.4 Å for bulk Ge). The high electron density in the region between the two paired atoms repels the H atom so that the Ge-H bond moves 4° out of the [111] axis. The Ge-H bond was found to be 1.541 Å as compared to 1.52 Å in molecular GeH_4. The Ge atom bonded to the hydrogen moves outwards from the vacancy by 0.32 Å along [111].

The relaxed dihydrogen-vacancy defect was found to have C_{2v} symmetry. The reconstructed Ge-Ge bond length was found to be 2.79 Å. The effect of the additional H atom in the defect results in a shortening of the Ge-H bond length to 1.531 Å. The symmetry of the VH_3 defect was assumed to be C_{3v}. The relaxed defect then has three equivalent H atoms each with a Ge-H bond length of 1.536 Å. The angle made between the Ge-H bonds and the $< 111 >$ directions was found to be 6.2°. An orbital-singlet level was found deep in the gap occupied by a single electron.

VH_4 has four equivalent H atoms (T_d symmetry) each bonded to a Ge atom with a bond length of 1.526 Å in VH_4. The Ge atoms move outwards from the vacancy by 0.33 Å along [111] from their ideal sites. VH_4 was found to possess an energy gap free from defect levels.

Also calculated were the vibrational modes for both VH_3^- and neutral V_2H_6. The effect of the addition of an electron to VH_3 was to shorten all Ge-H bond lengths by 0.7% resulting in modest increases in the frequencies of the E and A symmetry vibrational modes by 6 and 25 cm^{-1} respectively. V_2H_6 was found to have the shortest Ge-H bond length of 1.52 Å. Two stretch modes of A_{2u} and A_{1g} symmetry were found at 2131 and 2129 cm^{-1} respectively. Two doublet E_u and E_g modes

were found at 2128 and 2120 cm^{-1} respectively. The A_{1g} and E_g modes are infrared inactive. The splitting between the I-R active A_{2u} and E_u modes was found to be 3 cm^{-1}, substantially smaller than that calculated difference between the A and E modes in VH_3.

Preliminary calculations using a method described elsewhere[7] were used to find the acceptor and donor levels. Acceptor levels were calculated for VH, VH_2 , VH_3 and were all found to lie within 0.35 eV of the valence band edge. The donor levels were calculated for VH and VH_3 and lie close to the valence band .

The reorientation barrier was calculated by optimising the energy of a VH_3 defect with one of the H atoms constrained to be equidistant from two unhydrogenated Ge atoms. The difference in energy between this configuration and the unconstrained VH_3 was calculated to be 0.30 eV.

	VH	VD			
	2017(?)	1435(?)			
	VH_2	VHD	VD_2		
s	2102(1993)	2090(?), 1486(1437)	1495(1444)		
a	2078(1980)		1478(1433)		
	VH_3	VH_2D	VHD_2	VD_3	
s	2098(2025)	2088(2023), 1477(1456)	2077(2018), 1484(1461)	1491(1465)	
a	2067(2015)	2067(2013)	1471(1453)	1471(1454)	
	VH_4	VH_3D	VH_2D_2	VHD_3	VD_4
s	2187(-IR)	2168(2084)	2149(2080)	2128(2075)	
a	2107(2062)	2107(2062 or 2066)	2107(2066),1499(1486)	1499(1487)	1499(1489)
s		1511(1491)	1524(1499)	1539	1554(-IR)

Table 1
Calculated and observed stretch frequencies of VH_nD_m. Experimental frequencies are given in parentheses. Assignments of experimental absorption lines to VH_2D, VHD_2, VH_3D, VH_2D_2, VHD_3 are tentative. s=total symmetric, a= non-total symmetric, -IR=infrared inactive.

Concluding remarks

In summary, the vibrational modes were found to be between 99 and 95 % of the observed data. The errors were found to increase for the defects with fewer hydro-

gen atoms. Using this trend we predict that the VH defect will possess an A_1 mode at around 1885 cm^{-1}.

The infrared active stretch modes for V_2H_6 are found at higher frequency than those in VH_3 by a modest amount ($< 2\%$). We expect the stretch modes VH_3^- to be shifted upwards in frequency with respect to neutral VH_3.

The Kohn-Sham levels show a similar pattern to that found in silicon : the addition of hydrogen atoms acts to move the defect levels from the gap. All the calculated acceptor and donor levels are predicted to lie in the lower half of the bandgap.

The calculated adiabatic barrier for the reorientation of VH_3 is somewhat larger than the observed barrier in silicon (87 meV). We therefore propose that the movement of the hydrogen atom across the VH_3 defect is effected by tunneling from an excited state similar that described for the reorientation of O_2^- in KI[6].

References

[1] B.Bech Nielsen, L. Hoffmann, M. Budde, R. Jones, J. Goss, S. Oberg, Mat. Sci. For. **196**, 933 (1995).

[2] S. K. Estreicher, Mater. Sci. Engr. Reports **14**, 317 (1995).

[3] H. Xu, Phys. Rev. B **46**, 1403 (1992).

[4] P. Stallinga, P. Johannesen, S. Herström, K. Bonde Nielsen and B. Bech Nielsen, Phys. Rev. B (1998), in press.

[5] L. M. Xie ,M. W. Qi and J. M. Chen, J. Phys. Cond. Mat. **3**, 8519 (1991).

[6] R. H. Silsbee, J.Phys. Chem. Solids. **28** , 2525 (1967).

[7] R. Jones, A. Resende, S. Öberg and P. R. Briddon, Proceedings of the E-MRS Spring Meeting, 16-19 June 1998 Strasbourg, France (Submitted).