The electronic properties of transition metal hydrogen complexes in silicon

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Abstract

The electrical levels of various combinations of transition metal-H_n defects in Si are calculated using spin-polarised local density functional cluster theory with an empirical correction. The shifts of these levels with H can be understood through a displacement and splitting of the gap t_2 manifold of states due to the impurity. Passive defects are identified.

Key words: transition-metal impurities, H, Si, complexes, *ab initio* theory.

Introduction

The transition metals Au, Ag, Pt and Pd form substitutional defects in Si with a simple energy level structure. They possess donor or $(0/+)$ levels around $E_v + 0.35$ eV and, in the case of Au and Ag, acceptor or $(-/0)$ levels at $\sim E_c - 0.55$ eV. Pt and Pd have $(-/0)$ levels around $E_c - .23$ eV and double donor $(+/++)$ levels around $E_v + .1$ eV.

From a theoretical viewpoint, the energy levels are understood to rise from the t_2 manifold lying deep in the gap and occupied by 3 electrons for neutral Au and Ag and 2 for Pt and Pd. Most calculations do not give the correct Si band gap and there

is then a problem in calculating these levels. We show here that using a combination of first principles theory and an empirical correction to the level position, the donor and acceptor levels can be found to within about 0.2 eV. The method we use is described below and applied to a number of deep level defects as well as to Ag, Au, Pd and Pt impurities. We also investigate the effect of bringing H atoms up to the impurity and compare these with experimental results using capacitance transient spectroscopic techniques on Si doped with Ag, Au, Pd and Pt into which hydrogen has been introduced.

A density functional cluster scheme, applied to large H-terminated clusters, is used to first deduce the structure of the defect [1], but an extension to this procedure must be sought if the electrical levels are required. The $(0/+)$ level with respect to E_v is the difference between the ionisation energy of the defect and that of bulk Si. If the wavefunction of the defect is localised within the cluster, then in principle the ionisation energy of the defect can be calculated by the cluster method. However, as the valence band wavefunctions are always extended throughout the cluster and affected by the surface, the bulk ionisation energy cannot be calculated by the method. To circumvent this problem we compare the ionisation energy of the defect, I_d, with that of a standard defect, I_s (taken to be C_i), with localised levels. The $(0/+)$ level is then the sum of $I_s - I_d$ and the $(0/+)$ level of C_i, *i.e.* 0.28 eV. In the same way the electron affinities can be used to determine the acceptor level relative to that of C_i.

By comparing the ionisation energies of defects in this way, we can eliminate a systematic shift in the calculated levels caused by the cluster surface. This follows as the wavefunction for the ionised defect will decay exponentially away from the centre of the cluster, and the shift in the level position caused by the surface, to first order, then depends only on the asymptotic part of the wavefunction. Clearly, this decay is related to the depth of the level from the band edges and the shift would be the same for the standard defect if the latter possessed the same energy level and the same total charge within the core. In the same way, the error in estimating the Hubbard U-parameter would be the same as in the standard defect if U depended only on the asymptotic part of the wavefunction. Thus we expect that the error in estimates of the levels to increase with the separation between the defect level and that of the standard. In practice, the ionisation energies and electron affinities are calculated from the Kohn-Sham levels by relaxing the transition state corresponding to an additional $1/2$ electron or hole. In this way the effect of a change in structure between the ionised and neutral defects is treated to first order. This technique supersedes an earlier one based on scaling the band gap although the two methods give rather similar results [2].

The clusters used either contained 131 atoms ($Si_{71}H_{60}$) with T_d symmetry centred on an atom, or 134 ($Si_{68}H_{66}$) atoms with D_{3d} symmetry and centred on the middle of a bond. The latter was used for 'trigonal' defects like H_{BC}, V_2 etc. Usually, the clusters were relaxed with the H atoms fixed. However, for vacancy-like defects, eg

VP, V_2 and VO, the clusters were prerelaxed to force a strong reconstruction across the Si dangling bonds and all atoms were then relaxed. Second acceptor levels of defects can also be found by comparing the second electron affinities with that of PtH_2. The $(--/-)$ level of this defect is believed to lie between 0.045 eV and 0.1 eV below E_c and we assume a value of 0.07 eV.

1   Results

Calculations were carried out for the standard defect C_i, and C_i-P, the T-centre (C_s-C_iH), H at a bond centred site (H_{BC}), H at anti-bonded lattice site, H_{AB}, VO, VP, V_2, Au, Ag, Pt, Pd, AuH_n, AgH_n, PdH_n and PtH_n and the results are given in Table 1 where they are compared with experimental values.

In general the calculated electrical levels of light impurities are within about 0.2 eV of the experimental results where available. Whereas the donor and acceptor levels of C_s-C_iH, C_iP, VP, VO and even V_2 are within 0.2 eV of the experimental values, it is surprising that the 0/+ level of H_{BC} is found so close to the observed level given that the theory is expected to be worse when the level moves far away from that of C_i. For Ag, Au, Pd and Pt, all in low spin configurations, we find the $(-/0)$ and $(0/+)$ levels to be deep in the gap and within 0.2 eV of the observed values. We now investigate the effect of adding H atoms to these defects.

1.1   Au and Ag hydrogen defects

There are two likely sites for H next to the TM impurity. Either H lies inside the vacancy or outside with approximate trigonal symmetry. The energy difference between these structures is a sensitive function of basis size and previously [2] we reported preliminary results using a modest sized basis. We have now repeated these with a much larger basis described above and find, in contrast with the previous results, that the most stable structures are generally with the H atoms outside the vacancy. However, the energy differences are not large. For example, in the case of Au-H, the energy of H anti-bonded to a Si neighbour (AB site) is lower by 0.23 eV than when H lies inside the vacancy at an AB site. Structural details are reported in [7]. Here we concentrate on the electrical activity of the various defects.

The electrical levels are determined by the shift and splitting of the t_2 manifold. In each case we assumed that a low spin state results from the addition of H. Since the wavefunction of the added electron is distributed over several shells of atoms, it is unable to completely screen the additional proton. This results in a downward shift of the t_2 manifold and opens the possibility for a second acceptor level. However, the t_2 manifold is split by the presence of H and this can result in an upward

Defect	$E(0/+)$ Calc.	$E(0/+)$ Observed	$E(-/0)$ Calc.	$E(-/0)$ Observed	Ref.
VP	0.2	-	0.45	0.43	
VO	0.0	-	0.13	0.18	
V_2 (C_{2h})	0.42	0.23	0.51	0.43	
C-CH	0.24	?	0.20	0.20	
C_iP	0.36	0.48	0.60	0.38	
H_{BC}	0.94	1.0	-	-	
H_{AB}	-	-	0.78	?	
V_2O	-	-	0.47	-	
Ag	0.46	0.37	0.60	0.56	ref. [3]
AgH	0.36	0.28 (H2) ?	0.45	0.45 (E2) ?	ref. [3]
AgH_2	0.33	0.38 (H3)?	0.50	-	ref. [3]
AgH_3	0.0	-	0.13	-	
AgH_4	0.0	-	0.97	-	
Au	0.21	0.35	0.66	0.54	ref. [4]
AuH	0.36	0.21 (G2)?	0.62	~ 0.53 (G4)?	ref. [4]
AuH_2	0.28	0.47 (G3) ?	0.62	-	ref. [4]
AuH_3	0.0	-	0.26	-	
AuH_4	-	-	1.4	-	
Pd	0.52	0.31	0.22	0.23	ref. [5]
PdH	0.53	0.55 (H280)?	0.39	0.29 (E160) ?	ref. [5]
PdH_2	0.0	-	0.39	0.43 (E200) ?	ref. [5]
PdH_3	0.0	-	1.0	1.0 (H140) ?	ref. [5]
PdH_4	-	-	0.53	-	
Pt	0.23	0.35	0.36	0.23	ref. [6]
PtH	0.52	0.4 (H210) ?	0.42	-	ref. [6]
PtH_2	0.0	-	0.45	0.50 (E250)?	
PtH_3	0.0	?	1.4	0.9 (H150)	ref. [6]
PtH_4	-	-	1.0	-	

Table 1

Electrical levels, eV, of deep centres. $(0/+)$ is referred to E_v and $(-/0)$ to E_c. Tentative assignments are indicated by ?.

Defect	$E(--/-)$ Calc.	$E(--/-)$ Obs.	Ref.
V_2	0.35	0.23 ?	
AgH	0.36	0.09 (E3) ?	ref. [3]
AuH	0.22	0.19 (G1) ?	ref. [8]
AgH_2	0.0	-	
AuH_2	0.0	-	
PdH	~ 0.0	-	
PdH_2	~ 0.0	-	
PtH	0.12	-	
PtH_3	0.0	-	

Table 2
$(--/-)$ levels of deep centres, relative to E_c, in eV. Tentative assignments are indicated by ?.

movement of the higher levels.

In the case of Ag, the addition of one H atom, with approximate trigonal symmetry, leads to downward shift in the donor level and an upward shift in the acceptor level. This is because the t_2 level is split into an a_1 (filled) level lying below a half-filled e level. The lowering of the t_2 manifold is then compensated by the splitting. A second H atom results in an additional electron occupying the e level and the shift in the level is dominated by a downward shift in the manifold although this is reduced by an upward shift caused by a symmetry induced splitting of the e level. Adding a third H fills the e level and the t_2 manifold is pushed below the valence band top. Thus AgH_3 and AuH_3 do not possess any donor levels. However, it appears that an empty level, due, we believe to the $5s$ and $6s$ levels of Ag and Au, creeps into the band gap. We place the resulting $(-/0)$ levels of AgH_3 and AuH_3 at 0.13 and 0.26 eV below E_c. It may be that these levels are in reality much more shallow and thus substitutional Ag and Au can be passivated by three H atoms.

Experimentally, the levels for Ag [3] and Au [4,8] hydrogen defects are rather similar. For the former impurity, the H2 level at 0.28 eV $(0/+)$ and E2 at 0.45 eV $(-/0)$ have been assigned to Ag-H, while the G2 level at 0.21 eV and G4 at $\sim$ 0.53 eV have been assigned to the $(0/+)$ and $(-/0)$ levels of Au-H. Although the calculated values for AgH and AuH are in fair agreement with these assignments, we cannot rule out an assignment to AgH_2 and AuH_2. However, the calculated $(--/-)$ levels for AgH and AuH are reasonably close to E3 (0.09 eV) and G1 (0.19 eV) respectively, while AgH_2 and AuH_2 do not appear to possess $(--/-)$ levels. This is probably the result of the filling of the t_2 manifold. We thus conclude that the observed levels are due to a single H atom complexed with the impurity.

The H3 level at 0.38 eV has been assigned to the $(0/+)$ level of AgH_2 while the G3

level at 0.47 eV to a Au-H_2 defect. Although this is consistent with our calculations, there are no reports of associated $(-/0)$ levels. We place these close to E2 and G4. The absence of these levels places doubts on the assignments.

Both defects Ag and Au can be passivated and our calculations suggest that AgH_3 and AuH_3 are candidates given our errors can be around 0.2 eV. However, we describe below a different defect which is electrically inactive. AuH_4 and AgH_4 defects possess deep acceptor levels reminiscent of H_{AB}.

1.2 Pt and Pd hydrogen defects

PtH and PdH have donor and acceptor levels lying deeper in the gap than those of Pt and Pd respectively. Adding a second H atom, however, results in a rapid drop in the t_2 manifold and the donor levels are pushed into the valence band. The acceptor levels are, however, hardly affected. The $(--/-)$ level of PdH_2 appears to be very shallow. PtH_3 and PdH_3 defects are particularly interesting as the donor levels are absent and the acceptor levels are very deep. It seems that there is strong affinity to fill the t_2 manifold. These $(-/0)$ levels are calculated to lie 1.4 eV and 1.0 eV below E_c although of course the error in the estimates increases with the depth. PtH_4 and PdH_4 also possess deep acceptor levels probably related to the $5s$ and $6s$ levels being brought into the gap.

Experimentally, in Pt doped hydrogenated p-Si, a level at $E_v+.4$ eV (H210) is formed below 400K, which upon annealing is converted into a deep acceptor, at $E_c - .9$ eV (H150) [6]. This defect dissociates into Pt above 530K. In n-Si, two levels at E_c -.18 eV (E90) and $E_c - .5$ eV (E250) are formed around 300K but these dissociate above 600K. At lower annealing temperatures around 300K, they convert into H(150). However, H(150) converts into H(210) in p-Si and E(250) in n-Si above about 500K. The emission rate of E(90) increases with electrical field suggesting it is a donor. The H(150) acceptor is formed where the H concentration is maximum and a rough estimate is that this centre contains 2 to 3 times as much H as E(90) and E(250). The latter anneal out at slightly different temperature indicating that they are distinct defects –as are E(250) and H(210).

The results in Table 1 suggest that the deep acceptor, H(150), is likely to be PtH_3 or PtH_4. There are no associated donor levels. Only PtH has a deep donor and we assign this to H(210). This suggests that E(250) is the $(-/0)$ level of PtH_2 as this defect is believed to be distinct from H(210). This leaves the $(-/0)$ level of PtH to be detected. The calculations give no support to the idea that the *donor level* around $E_c-.18$ eV (E90) is a Pt-hydrogen defect. Nor could this level be the $(--/-)$ level in this region detected in EPR [9]. However, its character and location suggests a $(0/+)$ level associated with bond centred H trapped near an unknown neutral Pt related complex.

EPR experiments [9] demonstrate that the PtH_2 defect has a (-/0) level between 0.23 and 0.87 eV below E_c. We place it at $E_c - .45$ eV and identify it with E(250). However, disturbingly there are no DLTS levels reported for the $(--/-)$ level of PtH_2.

More levels have been detected for $Pd-H_n$ defects [5]. A suggested correspondence between the Pt and Pd levels allows us to tentatively assign the H(280) and E(200) levels to PdH and PdH_2 respectively, and H(140) to the deep acceptor level of PdH_3. The presence of an additional DLTS level, namely E(160) at $E_c - .29$ eV, which is close to the calculated $(-/0)$ level of PdH suggests that this is the acceptor level missing in PtH. Thus the two levels E(160) and H(280) should be correlated. Two hole traps H(45) and H(55) around 0.08 eV may be due to double donor levels of PdH where the H is separated by different distances from Pd. Similarly, *if* E(60) is a *donor* level analogous with the Pt related E(90) level, then it must be related to H_{BC} close to a neutral defect. Apparently Pd can be passivated in contrast with what has been reported for Pt. The calculations do not show that substitutional Pd or Pt can be passivated but we now describe a defect which is inactive.

1.3   Void and Multivacancy Defects

Transition metal impurities have a large atomic radius and are readily attracted to voids or multivacancies. Indeed, there have been several studies of the gettering effect of voids [10]. Within the void, there is a possibility of a molecular hydride species being formed as for example, AuH, AgH, PtH_2 and PdH_2. The molecular species are known to be thermally stable, *e.g.* AuH has a dissociation energy of 3.1 eV. To investigate their properties within Si, calculations were carried out on clusters containing a decavacancy whose surface is saturated with H. The ionisation energies and electron affinities of TMH hydrides inserted into this microvoid demonstrated that these defects possess no gap levels and as such represent a means by which the impurity is passivated. However, whereas it is known that voids form in plasma treated or H-implanted material, it is unclear whether they, or multivacancy centres, can be produced by wet etching.

2   Conclusions

The calculations of the electrical levels of the TM-H defects have allowed us to assign several observed levels to defects containing up to 3 H atoms. Whereas AuH_3 and AgH_3 may be passive, it seems that substitutional Pd and Pt cannot be inactivated by H. However, molecular hydrides of all the metal impurities are passive when inserted into microvoids. The calculations highlight several levels which remain to be detected, *e.g.* the $(-/0)$ levels of AuH_2, AgH_2 and PtH. The observation

of shallow donor levels E(90) and E(60) in Pt and Pd doped material respectively suggests to us that H does not simply aggregate around substitutional TM impurities.

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