Calculations of Electrical Levels of Deep Centers: Application to Au-H and Ag-H Defects in Silicon

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First-principles local-density formalism cluster theory is used to determine the structure of Au- and Ag-hydrogen complexes in Si. The theory, with an empirical correction, is then applied to extract their donor and acceptor levels and these are compared with capacitance transient spectroscopic measurements. Assignments of these levels to specific H defects are then made. Models for the defects responsible for the neutralization of the electrical activity of the Au and Ag centers are proposed.
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The interaction of hydrogen with transition metals (TM) has recently become of great interest [1–4]. The presence of hydrogen has three effects on the electronic levels of the TM impurity. It can shift these levels, introduce additional ones, or it can remove them completely from the band gap achieving passivation [1]. However, in no case are these effects completely understood. One problem is that first-principles techniques which can determine the structure of the complex cannot predict the donor $(0/+)$ and acceptor $(-/0)$ levels with the required precision. To overcome this some empirical correction is necessary usually to the band gap used in the calculation [5,6]. We find that by employing an empirical correction in a different way, these levels can be calculated to within about 0.2 eV and as such the theory can be used to predict the electrical activity of Au- and Ag-hydrogen defects [7].

The donor level with respect to E_v is the difference between the ionization energy of the defect and that of bulk Si. If the wave function of the defect is localized within the cluster and does not overlap the surface, then, in principle, the ionization energy of the defect can be calculated by the cluster method. However, as the valence band wave functions are always extended throughout the cluster and affected by the surface, the bulk ionization energy cannot be calculated by the method. To circumvent this problem, we compare the ionization energy of the defect, I_d, with that of a standard defect, I_s. The position of the donor level, $E(0/+)_d$, is then given by $E(0/+)_d = E(0/+)_s + I_d - I_s$, where the donor level of the standard defect, $E(0/+)_s$, is taken from experiment. In the same way the electron affinities can be used to determine the acceptor levels. In practice we take the standard defect to be the carbon interstitial, C_i, which is known to assume the same structure in all charge states [8]. This has $(0/+)$ and $(-/0)$ levels at $E_v + 0.28$ eV

and $E_c - 0.1$ eV, respectively [9]. The ionization energies and electron affinities are calculated by applying Slater's transition state argument [10,11]. Using the relaxed geometry appropriate to the transition state takes into account, to first order, the difference in structures between the neutral and ionized clusters. This method is remarkably accurate. For example, by comparing the total energies of relaxed neutral and ionized molecules, the ionization energy of the water molecule is found to be 13.37 eV. The Slater method applied to the molecule relaxed with a net charge of $+\frac{1}{2}e$ is 13.31 eV while the experimental value is 12.59 eV [12].

An important point is that by comparing the ionization energies of defects calculated in the same sized cluster, we can reduce a systematic shift in the calculated levels caused by overlap of the wave function with the cluster surface. The shift in the level position caused by the surface, to first order, depends only on the asymptotic part of the wave function, Ψ_λ, and is given by $\int \Psi_\lambda^2(\mathbf{r})V(\mathbf{r})\,d\mathbf{r}$. Here, V is the difference between the potential for an infinite solid and a finite cluster and is the same for the defect and the standard if each were embedded in identical clusters. Now, if the energy level of the defect is close to that of the standard then the asymptotic decay of the highest occupied wave functions will be similar as these decays are related to the distance between the levels and the band edges. Moreover, as the total charge of the defects are the same, i.e., $+\frac{1}{2}e$ for donor levels, then the amplitudes of the wave functions outside the defect cores are expected to be the same if the wave functions possess the same symmetry. Hence, the first order shift in ionization energy of the defect will be the same as that of the standard.

The electronic levels are found by embedding the defect in either tetrahedral 131 $(Si_{71}H_{60})$ or trigonal 134 $(Si_{68}H_{66})$ H-terminated atom clusters. The wave

function basis consists of N Cartesian s, p Gaussian orbitals sited on each atom. N independent d orbitals were sited on the TM impurity. The charge density is fitted to M Gaussian functions. In this study, (N, M) are Au(6, 12), Ag(7, 14), Si(4, 5), and H(2, 3). Three extra functions, located midway between each bonded pair of atoms, excluding the H-atom terminators, were added to the basis for the wave function and the charge density. The clusters were relaxed, as described previously [13], in either the $+\frac{1}{2}e$, $-\frac{1}{2}e$, or $-\frac{3}{2}e$ charge state to obtain the $(0/+)$, $(-/0)$, or $(=/-)$ electrical levels. Calculations on large clusters and basis gave similar $(0/+)$ levels for the lattice divacancy.

Table I gives the calculated acceptor (relative to E_c) and donor levels (relative to E_v) of several deep level defects as well as the experimental activation energies. The agreement is within about 0.2 eV. The ionization energy of the vacancy-oxygen pair (A center), VO, falls more than 0.28 eV below that of C_i and, thus, the defect does not possess a $(0/+)$ level consistent with experiment. However, the calculated donor level of VP lies at $E_v + 0.2$ eV and probably is too deep by this amount as no donor level has been reported for this defect. The H-C_iC_s defect gives a prominent luminescent line (the T line) and is known to possess an acceptor level at $E_c - 0.2$ eV [14], but the donor level is unknown. The calculated levels for both C_i-P and the divacancy, V_2, lie within 0.2 eV of those observed. Remarkably, the theory gives a donor level of H_{BC} to be close to that observed even though the level is well separated from that of the standard defect C_i. H_{AB} is a deep acceptor at midgap consistent with the inverted ordering of H related levels. It is of interest to note that the $(-/0)$ levels of V_2O and V_2 are very similar and highlights a problem with deep level transient spectroscopy (DLTS) in being able to distinguish levels of such similar defects.

To describe second acceptor levels, the electron affinities of negatively charged defects must be compared with each other. We use as a standard the PtH$_2$ defect which is known to possess a second acceptor level lying between the P donor level at $E_c - 0.043$ eV and the $(-/0)$ level of C_i [15]. We take this value to be $E_c - 0.073$ eV. The

$(=/-)$ level of V_2 is then at $E_c - 0.35$ eV and close to $E_c - 0.23$ eV assigned to the defect previously [16].

We now consider Au and Ag defects. Neutral Au and Ag have an electronic configuration t_2^3 but are slightly distorted T_d defects with the impurity moving 0.03 Å along [100] for Au and 0.01 Å for Ag. The resulting C_{2v} symmetry is consistent with EPR experiments on Ag [17,18] and optical absorption studies on Au [19,20]. The Au-Si and Ag-Si lengths are all between 2.6 Å and 2.7 Å. We also find small adiabatic reorientation barriers of 0.11 eV for Au_s^0 and 0.14 eV for Ag_s^0. These are upper limits to the barrier, and tunneling probably plays an important role as reorientation can occur at cryogenic temperatures [19]. The donor and acceptor levels are given in Table II and again are within 0.2 eV of those found by DLTS [21].

We now apply this theory to the complexes of substitutional TM impurities with hydrogen. There are three likely positions for the H atom. These are (a) when H sits at an antibonding, AB, site to a Si neighbor of the TM impurity; (b) AB sited to the TM impurity; and (c) bond centered, BC, sited between the impurity and Si. For the AuH_1 defect, configurations (b) and (c) are less stable than (a) by 0.23 eV and 0.47 eV, respectively. This result is sensitive to basis size and a smaller basis reverses this ordering [22]. The H stretch vibrational frequencies for the three configurations are given in Table III along with experimental results [23]. Agreement is best for the configuration (a) but the sense of the small shifts arising with different charge states is not reproduced. The H-reorientation barrier among the equivalent $\langle 111 \rangle$ directions is 0.41 eV for (a) and 0.23 eV for (b). The observed barrier is athermal and presumably must proceed by a tunneling mechanism. Local density functional calculations usually overestimate barrier energies [24]. For structures (a) and (c), the shift in frequency on replacing ^{28}Si with ^{29}Si is $\lesssim 1$ cm^{-1} for each charge state. For configuration (b) where H is bonded to the impurity, the shift is negligible. Thus, although the energy and vibrational mode calculations favor configuration (a), the observed low reorientation barrier favors configuration (b).

TABLE I. Electrical levels (in eV) of deep centers. $(0/+)$ is with reference to E_v and $(-/0)$ to E_c.

| | $(0/+)$ | | $(-/0)$ | | |
	Calc.	Obs.	Calc.	Obs.	Refs.
VO	0.00	⋯	0.13	0.18	[35]
VP	0.20	⋯	0.58	0.43	[36]
V_2 (C_{2h})	0.42	0.23	0.51	0.43	[16]
HC$_i$C$_s$	0.24	⋯	0.20	0.20	[14]
C$_i$P	0.36	0.48	0.60	0.38	[37]
H$_{BC}$	0.94	1.00	⋯	⋯	[38]
H$_{AB}$	⋯	⋯	0.78	0.56^a	[39,40]
V_2O	⋯	⋯	0.47	⋯	

^{a}Muon spin-resonance experiments.

TABLE II. Electrical levels (in eV) of Au- and Ag-hydrogen defects. $(0/+)$ is with reference to E_v and $(-/0)$ to E_c.

| | $(0/+)$ | | $(-/0)$ | | |
	Calc.	Obs.	Calc.	Obs.	Refs.
Au	0.21	0.35	0.66	0.56	[4,21]
AuH$_1$	0.36	0.21 ($G2$)	0.62	0.54 ($G4$)	[4,29,31]
AuH$_2$	0.28	0.47 ($G3$)	0.62	0.58 ($G4'$)	[4,29,31]
AuH$_3$	0.00	⋯	0.26	0.28	[33]
AuH$_4$	⋯	⋯	1.40	⋯	
Ag	0.46	0.37	0.60	0.56	[41]
AgH$_1$	0.36	0.28 ($H2$)	0.45	0.45 ($E2$)	[41]
AgH$_2$	0.33	0.38 ($H3$)	0.50	0.5 ($E6$)	[27,41]
AgH$_3$	0.00	⋯	0.13	⋯	
AgH$_4$	0.00	⋯	0.97	⋯	

TABLE III. Hydrogen stretch modes (in cm^{-1}) for three configurations (see text) of AuH_1. D values in parentheses. Observed values from Ref. [26].

$(AuH_1)^q$	$q = 0$	$q = -1$	$q = -2$
Expt.	1787.7 (1292.9)	1813.3 (1310.9)	1827.1 (1319.4)
Config. (a)	1947.4 (1401.1)	1890.5 (1359.6)	1893.2 (1361.4)
Config. (b)	2014.5 (1427.3)	1980.0 (1402.8)	2118.0 (1500.2)
Config. (c)	2419.0 (1726.2)	2500.8 (1783.5)	2454.3 (1748.9)

For AuH_2 and AgH_2 defects with C_{2v} symmetry, configuration (a) is more stable than (b) or (c). This structure is the same as that suggested by magnetic resonance on PtH_2 defects [15]. AuH_2 defects have been detected by infrared absorption studies [23]. For the configuration (a), Table IV shows that the separation in frequencies between the symmetric (A_1) and antisymmetric (B_1) modes is much closer to experiment than the separations in configurations (b) and (c).

The electrical levels are determined assuming that a low spin state results from the addition of each H atom. The addition of one H atom lowers and splits the t_2 level into a filled a_1 level lying below a half filled e level. The lowering of the t_2-manifold is offset by the splitting so that the differences in the donor and acceptor levels from those of the TM impurity are quite small. Table II gives these levels for configuration (a). The $(=/-)$ levels of AuH_1 and AgH_1 lie at $E_c - 0.22$ eV and $E_c - 0.36$ eV, respectively. The levels found for configuration (b) are very similar. For example, the $(0/+)$, $(-/0)$, and $(=/-)$ levels of AuH_1 lie at $E_v + 0.37$ eV, $E_c - 0.76$ eV, and $E_c - 0.36$ eV, respectively.

A second H atom, added in configuration (a), results in an additional electron occupying the e manifold which is pushed downward and splits with the upper level being occupied. Thus, once again there are only small shifts in the donor and acceptor levels on going from say AgH_1 to AgH_2. The e manifold is filled for $(AuH_2)^-$ and $(AgH_2)^-$, and a second acceptor level can arise only from a new state entering the gap. The calculations give no hint for such states and hence the dihydrogen defects do not possess $(=/-)$ levels.

Adding a third H fills the e manifold which is now pushed below E_v. Thus AgH_3 and AuH_3 do not possess any donor levels. However, it appears that an empty level, due to the $5s$ and $6s$ levels of Ag and Au, respec-

TABLE IV. Hydrogen stretch modes (in cm^{-1}) for three configurations (see text) of AuH_2 (C_{2v}) complexes. Observed values from Ref. [26].

| | AuH_2 | | AuHD | AuD_2 | |
	(A_1)	(B_1)		(A_1)	(B_1)
Expt.	1803.3	1785.6	1792.5	1298.6	1304.4	1292.1
Config. (a)	1974.7	1970.5	1972.6	1419.2	1420.6	1417.8
Config. (b)	1988.4	1743.0	1884.6	1303.6	1406.2	1237.5
Config. (c)	2060.6	2013.6	2037.6	1461.9	1475.5	1449.2

tively, creeps into the band gap. We place the resulting $(-/0)$ levels of AgH_3 and AuH_3 at 0.13 eV and 0.26 eV below E_c.

In conclusion, the calculations show that AuH_n and AgH_n, $n = 1, 2$ defects, possess $(0/+)$ and $(-/0)$ levels close to Au and Ag, while only the monohydrides possess $(=/-)$ levels. The trihydride defects possess shallow acceptor levels.

DLTS studies have led to a number of levels assigned to AuH_n and AgH_n defects. There are two uncertainties in identifying these levels: first, the number of H atoms associated with each level and second its character. Annealing and defect profiling studies have shown that the $G1$ (at $E_c - 0.19$ eV), $G4$, and $G2$ levels due to Au hydrogen arise from the same defect [25]. The location of the levels (see Table II) and their emission cross sections suggest that they correspond to $(=/-)$, $(-/0)$, and $(0/+)$, respectively. This has been supported by minority carrier transient spectroscopic measurements [26]. The deep penetration of these defects is taken to imply that they possess one H atom. Similar considerations show that in the Ag case the $E3$ (at $E_c - 0.09$ eV), $E2$, and $H2$ levels are due to $(=/-)$, $(-/0)$, and $(0/+)$ levels of AgH_1 [27]. Such assignments agree with our calculations (Table II). We can exclude AuH_2 and AgH_2 as being responsible for these levels as these defects do not possess a $(=/-)$ level.

Table II shows that the levels of the Au- and Ag-hydrogen defects $G3$ and $H3$ are close to the calculated donor levels of AuH_2 and AgH_2, respectively. Using a model for the depth dependence of the concentration of the defects [28], Yarykin et al. [27] argue that these levels should be assigned to AuH_2 and AgH_2. There has been some changes of view as to their character [29], but the most recent opinion [27] is that they are donor $(0/+)$ levels. This agrees with our calculations. Our results also imply that the corresponding $(-/0)$ levels are very close to those of AuH_1 and AgH_1, respectively. Evidence for these $(-/0)$ levels has been more difficult to obtain. However, an early DLTS [30] and a recent Laplace-DLTS study [31] on Au-doped Si show a level $G4'$ at $E_c - 0.58$ eV while the difference in the concentrations of $E2$ and $E3$ in the surface region is taken to imply the existence of the $(-/0)$ level of AgH_2 labeled $E6$ [27]. The $G4'$ and $E6$ levels are close to the calculated $(-/0)$ levels.

Both Au and Ag can be passivated by hydrogen [1,2] and our calculations suggest that AgH_3 and AuH_3 are candidates given our errors can be around 0.2 eV. However, in the case of gold, a level at $\approx E_c - 0.28$ eV [32] arises after a long room temperature anneal [33], and this is close to the calculated $(-/0)$ level of AuH_3. If this level arises from this defect, then the passive defect cannot be due to substitutional Au complexed with H atoms.

Molecular hydrides AuH or AgH are chemically stable with dissociation energies ≈ 3.1 eV and large ionization energies. If these formed within a void whose surface is passivated by H, then the defects would be electrically

inactive. Calculations were carried out on a decavacancy, containing AuH and AgH and whose inner surface was passivated by H [34]. The resulting ionization and electron affinity were such that no gap levels are present and such defects are then passive. However, whereas it is known that voids form in plasma treated or H-implanted material, it is unclear whether they, or a multivacancy complex containing Au and Ag, can be produced by wet chemical etching.

In summary, the calculations have allowed us to determine the structure and electrical activity of TM-hydrogen defects. This has allowed us to assign the observed DLTS levels to specific defects. AuH_3 and AgH_3 defects have filled t_2-manifolds lying in the valence band and lack donor activity. They possess shallow $6s$ and $5s$ acceptor levels. Molecular hydrides of the metal impurities are passive when inserted into voids or passivated multivacancy centers.

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