Energetic stability and charge states of 3*d* transition metals in diamond: Towards a diamond based diluted magnetic semiconductor

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Abstract. Energetic stability of magnetically ordering dopants in diamond holds the prospect of achieving a diamond based diluted magnetic semiconductor which, in addition to diamond's extreme properties may successfully be considered for spintronic device applications. However, one of the problems to be addressed is that of predicting the most energetically stable lattice configurations or charge states in which such dopants can remain electrically or optically active, and at the same time induce magnetic moments when incorporated into diamond. We report *ab initio* DFT calculations on the formation energies of isolated 3*d* transition metal impurities at various lattice sites and charge states in diamond, and show that these impurities introduce deep donor and acceptor levels in the band gap of diamond. We further show that their formation energies as well as the magnetic ordering properties are critically dependent on the position of the Fermi level in the diamond band gap, with formation energies across the 3*d* series being lower in *n*-type or *p*-type diamond compared to intrinsic diamond, thus predicting that co-doping with impurities such as boron, nitrogen or phosphorus will considerably enhance their stability in diamond.

1. Introduction

Understanding of energetic properties of defects in semiconductors is fundamental for the development of semiconductor based technology. In particular, the magnetic properties of Diluted Magnetic Semiconductors (DMS) depend on the energetic positions of defect induced impurity levels which arise from interactions between the impurity and the host semiconductor. The energy of the induced defect levels in the host semiconductor's band gap, together with the on-site correlation energy determine the electrical activity of an impurity defect and the behavior of its charge or spin states in the presence of other impurities within the semiconductor matrix [1].

Impurity defects in semiconductors occur in multiple charge states, and usually introduce defect levels in the host band gap due to transitions between different charge states of the defect center. The experimental detection of these levels often forms the basis for identification of the defect, and therefore prediction of these levels for magnetically ordering impurities in diamond is an important priority for the development of a diamond based DMS [2].

Diamond based DMSs have been predicted to possess high Curie temperatures and are expected to offer superior performance in high temperature, high power and high frequency applications due to diamond's excellent physical and electrical properties [3]. In particular, diamond's extraordinary intrinsic carrier mobilities, high thermal conductivity, radiation hardness, chemical inertness and high

breakdown field makes it an ideal material for fabrication of semiconducting devices with a wide range of applications. However, it is essential to understand not only their formation energies, defect levels, and spin properties, but also the influence of charge state, Fermi level and co-doping on these properties, while at the same time exhibiting useful magnetic ordering. Therefore, an important priority is to determine which charge states of these transition metal ions are stable, and under what doping conditions. This is crucial in evaluating whether these defects may possess useful ground state magnetic ordering when incorporated into diamond, since each charge state may correspond to a different spin configuration, some of which may order magnetically in their ground state, while others not.

Previous studies on the energetic stability of transition metal defects in diamond have focused mostly on those metals transition metals (Mn, Fe, Ni, Co, Cr) which are commonly used as catalysts during High Pressure-High Temperature (HP-HT) growth of synthetic diamond; however, no explicit explanation exists as to why some of these transition metals are preferentially incorporated into diamond containing other impurities, such as nitrogen or boron [3]. In this study, we consider the formation energies of isolated 3*d* transition metals in diamond at various lattice sites and charge states, and demonstrate that their energetic stability is dependent on the charge states, and therefore also on the position of the Fermi level. Their spin configuration and magnetic ordering will also be determined, allowing us to predict candidate transition metal dopants which may successfully be considered for spintronic applications.

2. Method

Ab initio DFT calculations have been performed for 3*d* transition metal-doped diamond using a pseudopotential plane wave approach, as implemented in the CASTEP code [4]. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) [5] was used, with Ultrasoft Vanderbilt pseudopotentials [6] in reciprocal space representation, and a plane wave cut-off energy of 310 eV. Optimized $4 \times 4 \times 4$ Monkhorst-Pack grid sampling [7] for integration over the Brillouin zone (32 k-points in the irreducible wedge of the Brillouin zone) was employed for geometry optimization, together with a $48 \times 48 \times 48$ FFT grid for electron density representation [8]. Increasing the number of k-points or plane wave cut-off energy resulted in insignificant changes in total energy and structural relaxation (less than 10^{-4} eV and 10^{-3} Å, respectively).

All calculations were carried out using a 64-atom diamond supercell constructed from $2 \times 2 \times 2$ conventional fcc unit cells with an optimized lattice constant of 3.569 Å, which is in close agreement with the experimental value of 3.567 Å. Full geometry optimization was performed without any symmetry or spin restrictions, with the transition metal (TM) atom in different charge states: (q = +2, +1, 0,-1, -2) placed at the divacancy (TM_{2V}), substitutional (TM_S), tetrahedral interstitial ($TM_{Td\text{-}i}$) or hexagonal interstitial ($TM_{Hx\text{-}i}$) sites in the diamond supercell. For each lattice site and charge state, various initial positions and spins of the TM atom were considered in order to systematically determine the most energetically stable configurations with respect to geometry and spin state.

To determine the energetically most favourable lattice site for the TM atoms in diamond, their formation energy (E_f) at each charge state and lattice site in the diamond supercell was calculated using the equation:

$$E_f[TM]^q = E_T[n_C,\, n_{TM}]^q - n_C\mu_C - n_{TM}\mu_{TM} + q(\varepsilon_V + \varepsilon_F)$$

where $E_T[n_C, n_{TM}]^q$ is the total energy of the supercell in a charge state q containing n_C carbon atoms and n_{TM} chromium atoms, with a chemical potential of μ_C and μ_{TM}, respectively, while ε_F is the Fermi energy measured relative to the energy of valence band maximum ε_V. The chemical potential of each atomic species was determined from their respective pure crystalline phases [9,10].

3. Results and discussion

3.1 Formation energy and chemical trends

Figure 1 presents the calculated formation energies of the isolated 3*d* transition metals in the neutral charge state at substitutional and divacancy lattice sites in intrinsic diamond, as well as the predicted formation energies of the most stable charge states in *p*-type boron doped ($E_V + 0.37$ eV) and *n*-type nitrogen doped ($E_C - 1.6$ eV) or phosphorus doped ($E_C - 0.6$ eV) diamond. We find that most 3*d* transition metals at these Fermi levels are stable at the divacancy site, while transition metals at the interstitial sites are highly unstable, indicating that the interstitial species are unlikely to be observed in significant concentrations for any position of the Fermi level. A distinctive trend of the calculated formation energies is seen across the series, with transition metals in the middle of the 3*d* series predicted to be energetically most stable compared to those early or late in the series – a result which can be explained by the filling of the *d* orbital and the relatively large free atomic radius of transition metals atoms compared to diamond's small lattice constant.

Importantly, the formation energy at any lattice site is strongly dependent on the charge state of the transition metal impurity or the position of the Fermi level and therefore on the type of diamond (intrinsic, *p*-type or *n*-type). We find that all the 3*d* transition metals have lower formation energies in *n*-type or *p*-type diamond compared to intrinsic diamond, with the double negative charge states in *n*-type diamond being considerably lower in energy compared to the neutral charge state, which is consistent with experimental results where transition metal ions are often observed in diamond containing nitrogen (which is a deep donor in diamond) [3]. Although complexes of transition metal impurities with these dopant impurities may form in diamond during growth or after annealing, it has previously been noted that [11,12] their role is to shift the Fermi level of the system, therefore influencing the charge states of these defects in the diamond crystal.

At the substitutional and divacancy lattice sites, the formation energies of the most stable charge states are comparable to that of phosphorus in diamond (~7 eV) which is a well known donor that is routinely incorporated into diamond by CVD methods, in concentrations of up to 2×10^{19} cm^3. This suggests that incorporation of transition metal impurities may also be achieved using similar non-equilibrium techniques or ion implantation, in agreement with recent experimental results for Cr [13] and Fe [14].

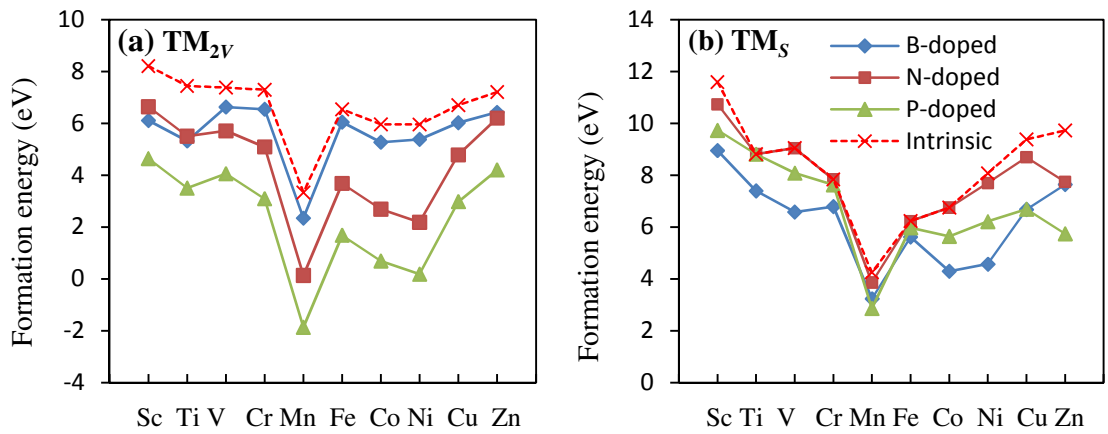

Figure 1. Predicted formation energies of 3*d* transition metals in intrinsic diamond as well as in *p*-type B doped (E_V + 0.37 eV) and *n*-type N doped (E_C -1.6 eV) or P doped (E_C - 0.6 eV) diamond at (a) divacancy, TM_{2V} (b) Substitutional, TM_S lattice sites. Data points correspond to the calculated formation energies; line shows the trend.

In *p*-type B doped and intrinsic diamond, the formation energy difference between substitutional and divacancy V, Cr, Mn, Fe and Co is relatively small (~0.5 eV), implying that these transition metals may be observed at both of these sites. This result is consistent with recent experimental data for Fe implanted diamond [14] in which 65 % of Fe ions were found to be located at the substitutional site, in agreement with our prediction of $(Fe_S)^{+1}$ being more stable by ~0.4 eV compared to $(Fe_{2V})^{+1}$ in *p*-type B-doped diamond.

3.2 Defect levels

Figures 2 and 3 illustrates the thermodynamic charge transition levels of 3*d* transition metals in diamond with respect to the valence band maximum and conduction band minimum at divacancy and substitutional lattice sites, respectively, for the charge states q = +2, +1, 0,-1, -2. It is seen that the majority of transition metals induce deep donor and acceptor impurity levels in the diamond band gap, thus highlighting the fact that electronic and magnetic properties of transition metals in diamond will be strongly dependent on their charge state. The deep nature of these levels is particularly important in achieving highly localized and controllable quantum states well isolated from decoherence sources, similar to the well-known $(N\text{-}V)^{-1}$ centre in diamond which is among the leading candidates currently being considered for spintronic and quantum computing applications [15].

In substitutional Sc, Ti, V Cr, and Mn, we find that the double acceptor (-1/-2) impurity levels occur as resonances inside the conduction band; the bands associated with these levels may hybridize with shallow donors, thus potentially influencing magnetic ordering properties, similar to theoretical predictions in transition metal-doped ZnO [16]

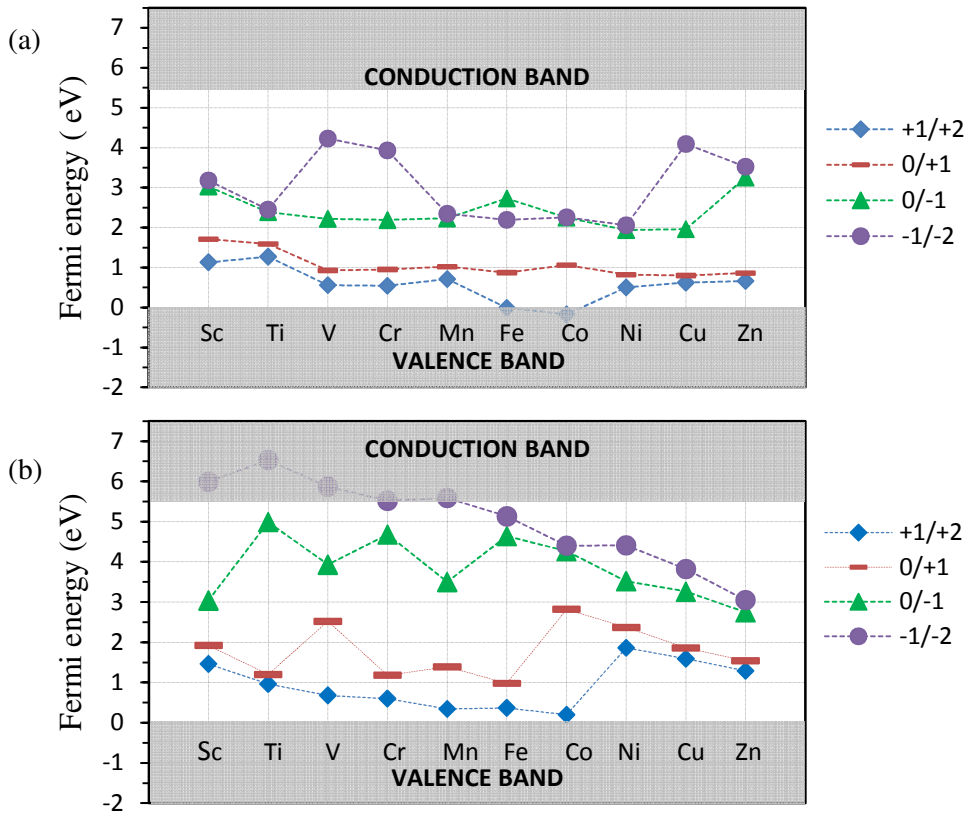

Figure 2. Thermodynamic charge transition levels of 3*d* transition metals at (a) divacancy and (b) substitutional lattice site sites in diamond, relative to the valence band maximum and conduction band minimum.

To determine which 3*d* transition metals and charge states are likely to lead to collective magnetic ordering in diamond, Table 1 summarizes the induced magnetic moments and point symmetries of the most stable charge states in different types of diamond as given in Figure 1. Importantly, the magnitude of the induced magnetic moment generally depends on the doping site and charge state, with the majority of the 3*d* transition metals at any lattice site inducing non-vanishing magnetic moments, thus indicating that incorporation of these impurities into diamond may lead to collective magnetic ordering [17]. However, to determine the nature of this magnetic ordering, impurity-impurity interaction also need to be taken into account in order to obtain the magnetic ground states and magnetic stabilization energies for the most stable charge states. Previous theoretical studies on the magnetic ordering of transition metals in diamond have predicted that ferromagnetic ordering in Mn-doped diamond is unlikely [9], while Co has been predicted to order ferromagnetically with a small magnetic moment of $0.4\mu_B$ per Co atom [18].

Based on the results of this study we predict that V, Cr, and Fe may successfully be considered due to their relatively low formation energies − which means they may be incorporated into diamond at reasonable concentrations, together with non-zero magnetic moments in most of their stable charge states in diamond (Table 1). We predict that $(V_{2V})^{+2}$ and $(Fe_S)^{+2}$ will be of particular interest which in addition to their favourable formation energies, also possess integer magnetic moments per impurity ion − which is a necessary condition for half-metallic ferromagnetic ordering [19], hence may attain up to 100% spin polarisation when doped into diamond.

Table 1. Induced magnetic moments together with the point symmetries for the most stable charge states (q) od 3d transition metals in diamond at fermi levels corresponding to *p*-type B doped ($E_V + 0.37$ eV) and *n*-type N doped ($E_C - 1.6$ eV) or P doped ($E_C - 0.6$ eV) diamond at (a) divacanc (b) Substitutional, lattice sites

	(a) DIVACANCY SITE			(b) SUBSTITUTIONAL SITE		
	Charge state, Magnetic Moment (μ_B) and symmetry			Charge state, Magnetic Moment and Symmetry		
	B-doped	N-doped	P-doped	B-doped	N-doped	P-doped
Sc	(+2) 0.1 D_{3d}	(-2) 0.6 D_{3d}	(-2) 0.6 D_{3d}	(+2) 1.0 C_{2v}	(-1) 0.0 T_d	(-1) 0.0 T_d
Ti	(+2) 0.0 D_{3d}	(-2) 0.0 D_{3d}	(-2) 0.0 D_{3d}	(+2) 0.0 C_s	(0) 0.0 C_{3v}	(-1) 1.0 T_d
V	(+2) 1.0 C_{2h}	(-1) 0.0 C_2	(-2) 1.2 D_{3d}	(+2) 0.1 C_{3v}	(0) 1.0 T_d	(-1) 2.0 T_d
Cr	(+2) 2.5 D_{3d}	(-2) 2.5 D_{3d}	(-2) 2.5 D_{3d}	(+2) 0.5 C_{3v}	(0) 2.0 T_d	(-1) 1.0 T_d
Mn	(+2) 3.0 D_{3d}	(-2) 3.0 D_{3d}	(-2) 3.0 D_{3d}	(+1) 0.0 T_d	(-1) 0.0 T_d	(-1) 0.0 T_d
Fe	(+1) 1.0 D_{3d}	(-2) 2.0 D_{3d}	(-2) 2.0 D_{3d}	(+2) 1.0 T_d	(0) 0.0 T_d	(-1) 1.0 C_{3v}
Co	(+1) 0.0 C_s	(-2) 1.0 C_2	(-2) 1.0 C_2	(+1) 0.0 T_d	(0) 1.0 C_{3v}	(-1) 0.0 T_d
Ni	(+2) 0.0 D_{3d}	(-2) 0.0 D_{3d}	(-2) 0.0 D_{3d}	(+2) 0.0 T_d	(-1) 3.0 T_d	(-2) 2.0 T_d
Cu	(+2) 0.3 D_{3d}	(-1) 0.0 D_{3d}	(-2) 1.0 D_{3d}	(+2) 0.5 T_d	(-2) 1.0 T_d	(-2) 1.0 T_d
Zn	(+2) 0.1 D_{3d}	(-2) 1.8 D_{3d}	(-2) 1.8 D_{3d}	(+2) 0.0 T_d	(-2) 1.8 T_d	(-2) 1.8 T_d

4. Conclusion

The energetic stability of 3*d* transition metals and their defect levels in diamond in diamond at different lattice sites and charge states have been investigated using *ab initio* pseudopotential DFT methods. At each lattice site, the formation energies of the transition metals are predicted to be lower in *p*-type (B-doped) or *n*-type (N- or P-doped) diamond compared to intrinsic diamond. Significantly, the formation energies and magnetic moments are shown to be critically dependent on the charge state, and therefore on the position of the Fermi level and type of diamond (intrinsic, *n*-type or *p*-type).

Majority of the transition metals are found to be energetically stable at the divacancy site in any charge state, with the formation energy of transition metals in the middle of the 3*d* series being lowest at any lattice site.

Most of the transition metals are found to induce deep donor and acceptor impurity levels in the diamond band gap, thus indicating that the electronic and magnetic properties of transition metals in diamond will be strongly dependent on their charge state. The magnitude of the induced magnetic moments is also found to depend on the doping site and charge state, with the majority of the 3*d* transition metals at any lattice site inducing non-vanishing magnetic moments, thus indicating that incorporation of these impurities into diamond may lead to collective magnetic ordering.

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