Formation energy and electronic structure of silicon impurities in diamond

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The formation energies and electronic structures of three kinds of Si impurities in diamond are studied using the modified neglect of differential overlap method and the discrete-variational local-density-functional method with cluster models. The results show that it is difficult for all of the silicon impurities (interstitial, substituting, and pair-interstitial) to be formed in diamond, and that there is local density of states within the band gap for the interstitial silicon and the pair interstitial, but not for the silicon substitution impurity in diamond. It is suggested that the silicon impurities in diamond destroy locally the sp^3 hybrid of diamond, which results in changes in some intrinsic properties of diamond.

In experiments, people have found that in diamond films there are several possible forms of silicon impurities, such as the interstitial silicon atom[1] and pair-interstitial silicon atoms.[2] Recently, one of the two kinds of silicon impurity centers has been found by ion implantation of natural diamond with silicon, and the 1.685-eV line in cathode luminescence spectra is associated with this center.[3] The other is evidently observed in homoepitaxial growth of diamond. Previously, it has been suggested that plasma etching of the silica reactor walls in microwave-plasma chemical-vapor-deposition systems may also introduce silicon impurities.[4] But Ruan, Choyka, and Partlow have demonstrated that the majority of these Si impurities are believed to originate from the silicon substrates, not from the CVD reactor walls.[5]

The impurities in diamond may impact on the microstructure, electronic structure, and properties of diamond. So, it is desirable to understand and control the formation of some impurities in it, e.g., silicon impurities, so that potential applications of this material can be realized successfully. But, no paper to our knowledge reports studying the formation energies and electronic structure of Si impurity centers in diamond at present, as far as we know, and the nature of them is kept unknown.

In order to determine the nature of these Si centers, the formation energies and electronic structure have been calculated by using the discrete-variational local-density-functional (DV-LDF) method with cluster models. In our calculations, the Si substitution impurities, which are not found in experiments in the literature, are also investigated.

Cluster models are adopted here to study the Si impurity problems in diamond. The perfect diamond crystal is simulated by a cluster containing a certain number of the host atoms and with an appropriate boundary condition; the structure parameters of this cluster are taken from those of diamond in bulk. The Si-doped diamond crystal is simulated by other clusters, which are optimized by using the modified neglect of differential overlap (MNDO) method.[6]

The MNDO method is a semiempirical self-consistent computation or procedure for solving the Hartree-Fock-Roothan equations. This method may produce reliable

total energies as a function of atomic configuration for a cluster, and is used to optimize the configuration of minimum energy.

In this paper, similar to Ref. 7, for the chosen clusters $SiC_4C_{12}H_{36}$ (containing Si substitution impurity atom), $(SiC)C_4C_{12}H_{36}$ (containing Si interstitial impurity atom), and $(SiSi)C_4C_{12}H_{36}$ (containing two interstitial Si impurity atoms), we optimize their "core" configurations— SiC_4H_{12}, $(SiC)C_4H_{12}$, and $(SiSi)C_4H_{12}$ (see Fig. 1) by the MNDO method. Here, 12 H atoms (H_{12}) or 36 H atoms (H_{36}) are used to saturate the dangling bonds at the surface, 4 carbon atoms (C_4) are the nearest neighbors of the studied Si impurity and are called first-shell atoms, and the second-shell atoms of the impurity are the C_{12}. The structure parameters optimized are listed in Table I. Then for constructing a cluster, for example, $(SiC)C_4C_{12}H_{36}$, the structure parameters of $(SiC)C_4$ are taken from Table I, the C-C bond length between C_4 and C_{12} is taken as 1.54 Å, and C-H bond length between an atom C of the second-shell C_{12} and H_{36} as 1.1 Å.

In our calculations, two kinds of boundary conditions are added to clusters for different purposes.[8] The first one is the free boundary condition in which the problem of the saturation of the dangling bonds at the surface is not considered. It is used to calculate the binding energies of clusters; the obtained binding energy in this

TABLE I. The structure parameters optimized by the MNDO method.

Structure parameters	SiC_4H_{12}	$(SiC)C_4H_{12}$	$(SiSi)C_4H_{12}$
a (Å)		1.56	1.90
b (Å)		1.64	2.37
c (Å)		1.83	1.90
α (°)		121.0	111.0
β (°)		110.8	111.0
l (Å)	1.86		

boundary condition is closer to the binding energy of the bulk than that in the other boundary conditions.

In order to calculate accurately the electronic structure of the doped diamond crystal with silicon impurities by cluster models, the problem of the dangling bonds mentioned above must be considered. We chose the second kind of boundary condition to clusters in which the dangling bonds at the surface are saturated by hydrogen atoms H_{36} or H_{12}.

The binding energies and electronic structure of the clusters are calculated by a more sophisticated method, the DV-LDF method.[9,10] It is a kind of molecular-orbital-calculation method and is based on LDF theory. Since it has been described in detail elsewhere, we do not give a further description here. In our calculations, the exchange-correlation potential[11] is taken to be of the von Barth–Hedin form, with the parameters taken from Moruzzi, Janak, and Williams.[12]

(a) SiC4
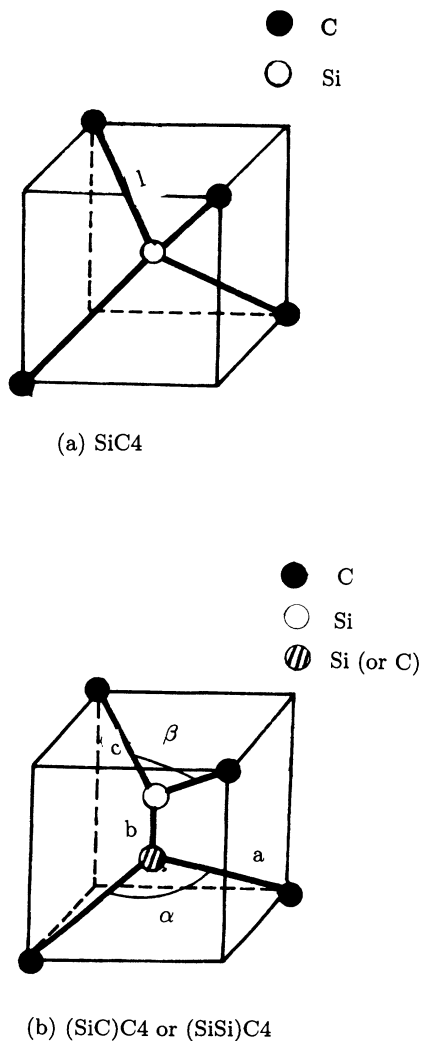

(b) (SiC)C4 or (SiSi)C4

FIG. 1. Cluster models which are optimized by the MNDO method. Hydrogen atoms saturating the dangling bonds are not drawn.

Formation energies of silicon impurities in diamond

In order to know the formation ability of the three kinds of Si impurity centers as mentioned above, it is significant to calculate the formation energies of the silicon impurities.

In cluster models, the formation energy of an impurity can be expressed approximately as[8,13]

$$E^F = E^b(\text{impurity cluster}) - E^b(\text{perfect cluster}),$$

where $E^b(\text{impurity cluster})$ is the binding energy of a cluster containing silicon impurities, and $E^b(\text{perfect cluster})$ is the binding energy of a cluster-simulated perfect crystal. In this paper, we have

$$E_M^F = E^b(\text{impurity cluster}) - E^b(\text{perfect cluster}); \quad (1)$$

here $M = $ Si, SiC, and SiSi.

The first, $E^b(\text{CC}_4\text{C}_{12})$ is calculated, and we obtain $E^b(\text{CC}_4\text{C}_{12}) = 5.62$ a.u., and so the average binding energy of the carbon atoms in the cluster CC_4C_{12} is about 9.0 eV. This value is 1.7 eV higher than the one from experiment, so the calculation is reasonable and effective. Next, we calculate the binding energies $E^b(\text{SiC}_4\text{C}_{12})$, $E^b[(\text{SiC})\text{C}_4\text{C}_{12}]$, and $E^b[(\text{SiSi})\text{C}_4\text{C}_{12}]$ of $\text{SiC}_4\text{C}_{12}$, $(\text{SiC})\text{C}_4\text{C}_{12}$, and $(\text{SiSi})\text{C}_4\text{C}_{12}$, respectively, and the obtained values are 5.09, 5.28, and 5.03 a.u. Then, according to formula (1), the formation energies of the silicon impurities are $E_{\text{Si}}^F = -15.88$ eV, $E_{\text{SiC}}^F = -9.02$ eV, and $E_{\text{SiSi}}^F = -14.48$ eV. These negative formation energies imply that it is not easy to form these silicon impurity centers in diamond. Furthermore, we see that the formation of silicon substitution and pair-interstitial impurities is more difficult. Perhaps, it is the reason that the substitution Si impurity center has not been found in experiment up to now.

Electronic structure

We have also calculated the electronic structure of the silicon impurities in diamond. Figure 2(a) shows the total density of states (TDOS) of cluster $\text{CC}_4\text{C}_{12}\text{H}_{36}$, the band gap is about 8.0 eV, close to the value of 7.3 eV obtained by Briddon, Jones, and Lister[15] with their cluster model. Figure 2(b) is the TDOS of $\text{SiC}_4\text{C}_{12}\text{H}_{36}$ cluster, with the band gap being slightly wider than 8.0 eV, and there is no local density of states (LDOS) within the band gap. We may understand this phenomenon as below: silicon and carbon belong to the same column in the Periodic Table of elements, and the valence electron distribution of Si is similar to that of carbon. When a silicon atom replaces a carbon atom of diamond, this silicon atom is called balance electron impurity (BEI). As is known, the condition that BEI results in a binding state within the band gap is $J \gg E$ (here J is the potential energy, and E is the kinetic energy), which does not seem to be fulfilled here.

For the silicon interstitial impurity, the TDOS of cluster $(\text{SiC})\text{C}_4\text{C}_{12}\text{H}_{36}$ displays a peak of LDOS within the band gap [as shown in Fig. 2(c)], and the composition of

TABLE II. The analyses of LDOS in Fig. 2.

	$(SiC)C_4H_{12}$		$(SiSi)C_4H_{12}$
Position of local states of (Hartree)	-1.90	-0.20	-0.13
Main composition of the local states (%)	46 Si_{3p}	70 Si_{3p}	40 $Si_{3p} + 13\ C_{2p}$

this peak mainly consists of a $3p$ shell of silicon (see Table II). For the impurity center of pair-interstitial silicon atoms, there are two peaks of LDOS within the band gap, which mainly consist of Si $3p$ orbits [Fig. 2(d), Table II].

Table III lists the number of valence electrons of related atoms for the $CC_4C_{12}H_{36}$, $SiC_4C_{12}H_{36}$, $(SiC)C_4C_{12}H_{36}$, and $(SiSi)C_4C_{12}H_{36}$ clusters. By comparing the number of valence electrons of atoms at the centers in clusters, we see that both the substitution silicon atom and interstitial silicon atoms lose one electron or so, and the total number of lost electrons of the pair-interstitial silicon atoms are also about one electron. Further, comparing the number of valence electrons of the first- and the second-shell atoms in various clusters, we find that for the clusters containing silicon atoms, the number of valence electrons of the first-shell atoms has a large change, but the changes in the second-shell atoms are few, which implies the interaction between Si impurities and the first-shell atoms is rather strong, but weak between Si impurities and the second-shell atoms; that is, Si impurities spread their influence mainly within the first-shell atoms. Thus, it is reasonable for us to choose these clusters, which contain the second-shell atoms, to study the electronic structure of silicon impurities in diamond.

The distributions of valence electrons of Si impurity atoms are given in Table IV. From this table, the number of electrons on the $3s$ shell of the substitution Si are 1.43, and those on the $3p$ shell are only 1.64. So, in this case, the silicon atom does not keep the sp^3 hybrid. Similar to those mentioned above, both the interstitial Si and pair-interstitial silicon atoms do not remain a sp^3 hybrid, but do remain a sp^2 hybrid. We conclude that although silicon crystal is of diamond-type crystal structure, when silicon impurities atoms inlay into diamond crystal the bond structure between the silicon atom and its nearest-neighbor carbon atom is not a sp^3 hybrid but a sp^2 hybrid, so the silicon atoms destroy the structure of diamond locally, and change some intrinsic properties of diamond.
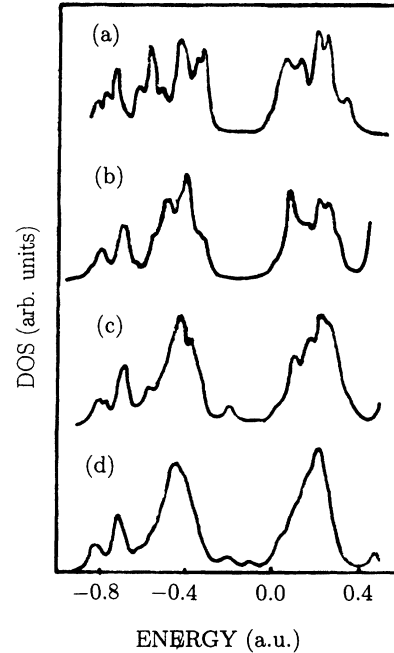

FIG. 2. The TDOS of clusters. (a) $CC_4C_{12}H_{36}$, (b) $SiC_4C_{12}H_{36}$, (c) $(SiC)C_4C_{12}H_{36}$, and (d) $(SiSi)C_4C_{12}H_{36}$.

In summary, after optimizing the structure of clusters, which are used to simulate Si-doped diamond by using the MNDO method, we employ the DV-LDF method to investigate the formation energy and electronic structure of Si impurities in diamond. The results are as follows.

(1) It is difficult for all of the silicon impurities (interstitial, substituting, and pair-interstitial silicon atoms) to be formed in diamond. Among them, the formation ability of the silicon substituting impurity is the poorest.

(2) The total density of states of clusters show that there are local densities of states from silicon impurities within the band gap for the interstitial and pair-interstitial silicon atom centers in diamond, but on local densities of states from silicon impurities for the substituting impurity.

(3) The silicon impurities in diamond destroy locally the sp^3 hybrid bond structure of diamond, the affect some of the intrinsic properties of diamond.

(4) The changes in the number of valence electrons related to atoms in clusters display that the cluster models used here are suitable to mimic the Si-doped diamond and to calculate the local electronic structure.

TABLE III. The number of valence electrons of related atoms in cluster.

	$CC_4C_{12}H_{36}$	$SiC_4C_{12}H_{36}$	$(SiC)C_4C_{12}H_{36}$	$(SiSi)C_4C_{12}H_{36}$
Atom at cluster center	4.00	3.07	3.18 Si 4.14 C	3.59 Si 3.52 Si
First-shell atoms	4.25	4.51	4.38	4.49
Second-shell atoms	3.91	3.91	3.91	3.91

TABLE IV. The distribution of valence electrons of Si impurities.

Valence orbit	$SiC_4C_{12}H_{36}$	$(SiC)C_4C_{12}H_{36}$	$(SiSi)C_4C_{12}H_{36}$	
$3s$	1.43	1.15	1.37	1.37
$3p$	1.64	2.03	2.22	2.16

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