Role played by N and N-N impurities in type-IV semiconductors

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Ab initio all-electron Hartree-Fock calculations within the molecular-cluster model are performed to analyze the role of N impurities, both isolated and complex, in type-IV semiconductors. The results are used to investigate the structural and electronic properties. For isolated impurities the N atom distorts in the ⟨111⟩ direction towards a vacancy leading to a final local C_{3v} symmetry. The N atom forms sp^2 bonds with the host atoms and leaves an unoccupied N lone pair. For N_2 both N atoms tend to form similar sp^2 bonds and move away from each other in the ⟨111⟩ direction without N-N bond formation. For the case of N_2^+, localized N-N hole states are obtained. A detailed picture at the orbital level is given. These achievements should also be important for amorphous hydrogenated semiconductors.

I. INTRODUCTION

In the last four decades the study of impurities in semiconductors has been very intense due to their important technological interest. In this present paper we aim at an explanation of the role played by nitrogen in type-IV semiconductors. Both isolated (N) and complex (N_2) impurities will be considered in diamond (C), silicon (Si) and germanium (Ge). In distinction from its isovalent counterparts P and As, which introduce shallow states in the gap of Si and Ge, N introduces deep states. This is peculiar to N which more strongly perturbs semiconductor materials of type IV.

Interest in the electronic properties of nitrogen impurities in diamond, in particular, is closely related to several technological applications ranging from low friction surface, to high-temperature optoelectronic devices.[1] In fact, the study of N in diamond has been the subject of several theoretical works using different techniques.[2–6] Messmer and Watkins[7] analyzed this problem and have used the extended Hückel theory within the molecular-cluster model. More recently, Kajihara[8] considered the distortions of the lattice due to substitutional N using a large unit cell scheme with *ab initio* pseudo potential to calculate the total-energy minimum.

N in silicon has also been the subject of both experimental and theoretical work. Experimentally it has been studied using deep-level transient spectroscopy,[9] Hall effect,[10] IR absorption,[11] electron paramagnetic resonance EPR,[12,13] etc. In particular, Brower[14] showed from EPR measurements that substitutional N has a local C_{3v} symmetry with distortion from the T_d symmetry along the ⟨111⟩ direction. This was confirmed theoretically by Schultz and Messmer[15] from generalized valence bond calculations and by Snyder and Corbett[16] from third-order effective-core Moller-Plesset perturbation theory calculations. In both studies it was concluded that the off-center minimum is obtained only after the geometrical relaxation of the first Si neighbor that moves in the ⟨111⟩ opposite direction. This aspect will be discussed in great detail in this present paper.

Opposite to diamond and silicon, N in germanium has not received attention though there are a few experimental[17–19] and theoretical[20] investigations for the case of amorphous germanium. As far as we know our present work is the first study of N in crystalline Ge.

Although the emphasis of this paper is on crystalline systems, most conclusions, we believe, can be extended to amorphous systems because, as we shall discuss later in this paper, nitrogen seems to have a general behavior for binding chemically in covalent semiconductor systems. There is considerable interest in N impurities in *a*-Ge:H and *a* −Si:H. N is expected to have a very low doping efficiency in *a*-Si:H because it presents tetravalent sites with low stability.

According to Spear and LeComber[21] the amorphous semiconductors tetrahedrally coordinated and doped with atoms of group II and V show properties that are very similar to those of crystalline systems and, also, the 8-N rule of Mott is not valid. This has been confirmed by some recent experiments.[22]

All systems considered here show a very high nitrogen concentration both in amorphous and crystalline phases, hence, the possibility of complex formation such as N_2 should not be discarded. In fact, theoretical studies of As_2 and P_2 were already considered.[23] Here we give detailed attention to both N and N_2 in C, Si and Ge.

II. METHOD OF CALCULATION

All calculations are made at the *ab initio* Hartree-Fock level within the molecular-cluster model. For isolated N we use the NX_4H_{12} (X=C, Si, and Ge) cluster while for the complex N_2 we use the $N_2X_6H_{18}$ (X =C, Si, and Ge) cluster. The H atoms are used to saturate the bonds, as usual. Having defined the molecular clusters the total energies are calculated using the all-electron Hartree-Fock method in the usual linear-combination-of-atomic-orbitals basis procedure. The basis adopted here is taken from Dunning and Hay[24] and consists of $(4s)$ contracted to $[2s]$ for H, $(10s5p)$ contracted to $[3s2p]$ for C, and $(12s8p)$ contracted to $[6s4p]$ for Si. For Ge the basis used is termed as MIDI in the literature[25] corresponding

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to a basis of $(12s9p3d)$ contracted to $[5s4p1d]$. The size of the basis set thus ranges from the smallest 69 (in the case of C_5H_{12}) to as much as 220 (in the case of Ge_8H_{18}) contracted-Gaussian-type functions The calculations are performed using the program system GAMESS[26] in its restricted Hartree-Fock option for closed-shell and unrestricted Hartree-Fock for open shell (all open-shell states calculated here are doublet states with only one open shell and negligible spin contaminations). In type-IV semiconductors, N introduces a localized state in the gap. The cluster model used here is quite appropriate. In fact it leads to the same result as those obtained by the *ab initio* large unit cell with 64 atoms per unit cell for the case of the single impurity.[8]

Before calculating the geometric structure of N in C, Si and Ge we have first optimized the structure of the pure systems X_5H_{12} in T_d (Ref. 27) and X_8H_{18} D_{3d} symmetries, with respect to the A_1 and A_{1g} vibrational modes respectively. This is necessary to avoid spurious forces in the N impurity when it is in the substitutional position. In the next section, the results of these calculations are presented and discussed.

III. RESULTS AND DISCUSSION

This section is conveniently divided into four parts. First we discuss the results for the structural and electronic properties of isolated N and next we discuss the same for N_2.

A. Structural properties of N in C, Si, and Ge

Utilizing the theoretical procedure described in the previous section we calculated the total energies of N in C, Si and Ge as a function of the distance in the ⟨111⟩ direction. For zero distance, T_d configuration, the N impurity for all these semiconductors introduces an antibonding a_1 orbital in the gap region. This orbital is occupied by only one electron, the donor electron of N, giving rising to a ground state of $^2A_1$ symmetry. This is a spatially nondegenerate state and, therefore, not subjected to Jahn-Teller forces. However, all three systems are found here to have minima off the T_d position and in all three cases the N atom distorts in the ⟨111⟩ direction towards an interstitial position leading to a final C_{3v} local symmetry. For diamond and silicon the off-center minimum is found only if the host atom relaxes in the ⟨111⟩ direction away from the impurity. Otherwise the T_d minima are preserved. For germanium distinctively, the off-center position is obtained even if the host atoms are fixed, but relaxation, as for the case of diamond and silicon, more favorably changes the energetics involved. This situation is in agreement with the previous theoretical results,[2–8,15,16] as described in the Introduction , for N in diamond. Figure 1 summarizes the situation for N in C. Three curves are shown : (a) N moving in the ⟨100⟩ direction which shows no minimum in this C_{2v} symmetry; (b) N moving in the ⟨111⟩ direction towards a vacancy but with all host atoms fixed which also shows no minimum; and (c) N moving in the ⟨111⟩ direction as in case (b) but now with the opposite host C atom allowed to relax in the opposite direction. A minimum is finally found corresponding to the displacement of N by 0.23 Å and the host C atom in the opposite direction by 0.36 Å. The calculated values for case (c) in C, Si, and Ge are given in Table I. It shows that the displacement of the host atom is equivalent to the displacement of the impurity but as discussed in opposite directions. For these coupled displacements the off-center position is more favorable than the T_d site by 1.0 eV for diamond, 0.7 eV for Si and 0.6 eV for Ge. Figure 1(d) complements the picture

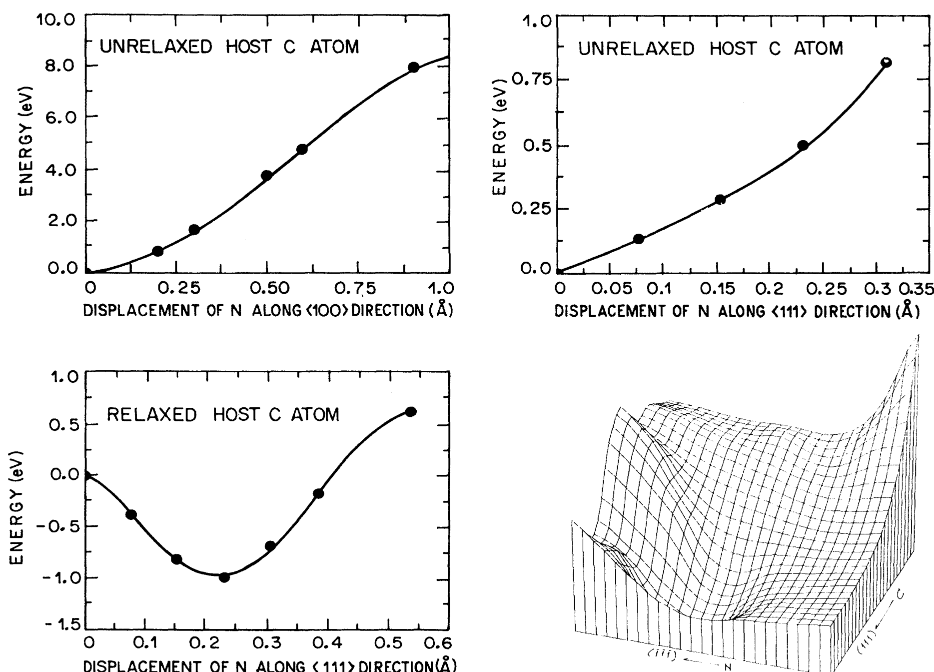

FIG. 1. Calculated total-energy curves for displacement of N in diamond (see text).

TABLE I. The calculated structural (in Å) and energetic (in eV) changes due to N impurity in C, Si, and Ge. (See text.)

	C	Si	Ge
N(⟨111⟩)	0.23	0.47	0.49
X(⟨$\overline{111}$⟩)	0.36	0.46	0.48
ΔE	1.0	0.7	0.6

by showing the total-energy surface for coupled displacements of N in C.

B. Electronic properties of N in C, Si and Ge

Figure 2 shows a schematic representation of the orbital formation after substitutional N in type-IV semiconductors without structural distortion. At the left, X represents the host atom with its s and p orbitals that make up the valence and conduction bands. At the right, we show the atomic orbitals of the nitrogen impurity. At the center, we show the floating orbitals arising from the vacancy orbitals of the crystal. After that we finally show the semiconductor when doped with N in a vacant position with a hyperdeep bonding a_1 orbital, a t_2 orbital in the valence band, a a_1^* antibonding orbital lying in the gap, and a t_2^* antibonding orbital which is resonant in the conduction band. The orbital configuration results in $a_1^2 t_2^6 a_1^{*1} t_2^{*0}$ leading to a spatially nondegenerate $^2A_1$ ground state. When the system distorts to the off-center ⟨111⟩ position the occupied t_2 orbital splits into a_1+e where this a_1 orbital becomes a N lone pair resonant in the valence band but moving towards the top of the band. The singly occupied a_1^* orbital moves in the gap and in the equilibrium off-center position this orbital loses the nitrogen s character and becomes essentially a p_z orbital of the relaxed host atom. The next effect is the formation of a sp^2 bonding of the N atom with three host atoms and the formation of a lone pair in N and a dangling bond in the fourth host atom. To show that this is a general role played by N in type-IV materials, we analyze next the bond-order matrices. In Table II we show the bond-order matrics involving the N atom, the host atom (X), and the relaxed host atom (Y). In the tetrahedral position, the bonds are stronger the larger the atomic number of the impurity. At the C_{3v} equilibrium conformation the N-X bond increases and the final bonds have all nearly the same values. As stated before there is a considerable weakening of the N-Y bond with nearly no bonding at all characterizing the hybridization of sp^2 of N with three X atoms. The N p_z orbital is a lone pair in the valence region and the p_z orbital of the Y host atom is held responsible for the a_1^* orbital lying in the gap. For the C:N case, the N-Y bond order is negative indicating a node of the a_1^* orbital in the ⟨111⟩ direction.

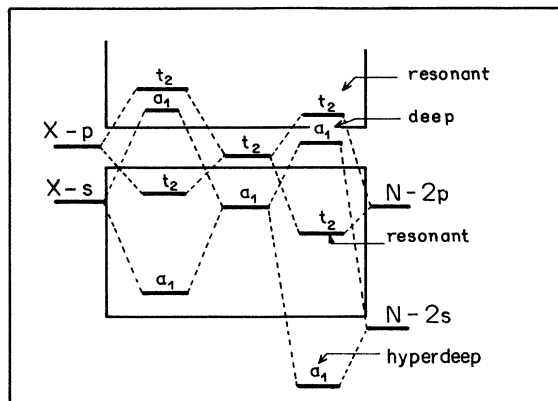

FIG. 2. Schematic representation of a N substitutional in a type-IV semiconductor.

TABLE II. Calculated bond order between the impurity (N) and the host (X) atoms and the impurity and the relaxed host (Y) atoms.

	C:N	Si:N	Ge:N
T_d[N-X]	0.03	0.14	0.24
C_{3v} [N-X]	0.27	0.29	0.37
[N-Y]	−0.52	∼0.0	∼0.0

It is now our contention that this behavior of N substitutional in type-IV materials is very general. That this is not a general behavior of sp impurities in semiconductors may be seen by consideration of type-VI impurities such as oxygen. It is well known that Si:O distorts in the ⟨100⟩ C_{2v} direction whereas N distorts in the ⟨111⟩ C_{3v} direction.

Nitrogen is special insofar as it prefers sp^2 bonds with three host atoms leaving a lone pair and a dangling bond that repel each other and makes no chemical bond. We believe that this is a general behavior present not only in the crystalline phase, considered here, but also in the case of amorphous hydrogenated semiconductors.

C. Structural properties of N_2 in C, Si and Ge

Using the same theoretical procedure used in the study of the isolated N impurity we calculated the complex N_2 impurity in C, Si and Ge. The N atoms are initially introduced in the substitutional position leading to a D_{3d} symmetry for the cluster $N_2X_6H_{18}$ (X=C, Si, or Ge). The ground state is a $^1A_{1g}$ state. As in the case of N we first calculated the variation of the total energy corresponding to independent displacements of the two N atoms in the ⟨111⟩ direction. In all three semiconductor systems considered the lowest energy is found to correspond to a symmetric displacement in opposite directions of the two N atoms thus preserving the D_{3d} symmetry. Figure 3 shows the total-energy curves for the three cases: diamond, silicon and germanium. In this figure

TABLE III. The calculated structural relaxation and corresponding energy gain for N_2 impurities in C, Si, and Ge.

	C	Si	Ge
ΔR (Å)	0.38	0.59	0.85
ΔE (eV)	4.0	2.5	1.3

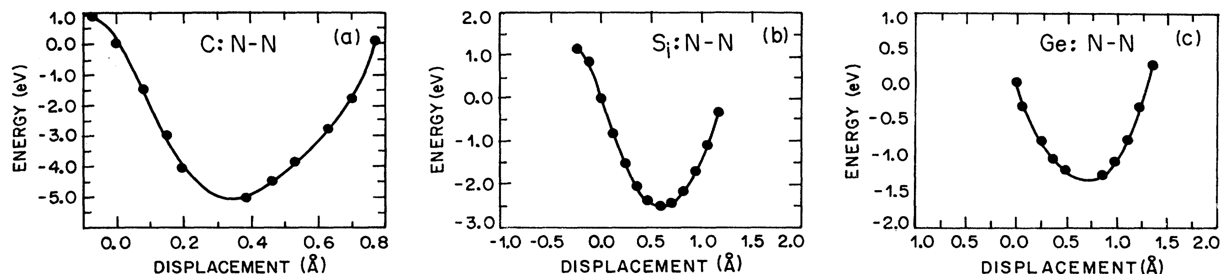

FIG. 3. Calculated total-energy curves for independent displacements of two N atoms in the ⟨111⟩ direction (see text).

the displacement are given as a percentage of the half-bond distance of the pure crystal. The three minima are obtained in nearly the same relative displacements (45% for C, 50% for Si, and 68% for Ge) but corresponding to large and different absolute displacements (0.38 Å for C, 0.59 Å for Si, and 0.85 Å for Ge). These results may be well understood analyzing the corresponding lattice parameters and covalent radii. As the covalent radius of N is smaller it must move longer in type-IV semiconductors with larger lattice parameter.

The minimum total energy for N_2 as obtained above shows that each N atom moves in the ⟨111⟩ direction away from each other and towards vacant positions of the crystal. This movement towards interstitial position is obtained also in the case of isolated N. This repulsion of the N atoms in N_2 shows that formation of N_2 impurities in type-IV semiconductors if it occurs should correspond to an unstable state. It also shows that N should have a high solubility in semiconductors.

Ge:N_2 presents the largest calculated structural relaxation but the lowest energetic gain compared to the initial crystalline positions. These energy gains are 4.0 eV for C:N_2, 2.5 eV for Si:N_2, and 1.3 eV for Ge:N_2. These results are summarized in Table III.

The highest occupied orbital is of a_{1u} symmetry and it is occupied by two electrons in the N_2 impurity case. At the minimum energy this a_{1u} orbital has a strong p_z N character. If the impurity is now in a positive charge state, N_2^+, we find that there is a lower symmetry solution corresponding to a localized hole state; i.e., a broken symmetry solution corresponding to asymmetric N and N^+ atoms. The spatial point-group symmetry decreases from D_{3d} to C_{3v} because there is no longer inversion symmetry. Figure 4 shows a contour plot of the total-energy surface that clearly illustrates the broken-symmetry solution. At the minimum, one N stays at nearly the same position of the neutral case, whereas the other moves by 0.42 Å from the initial substitutional position.

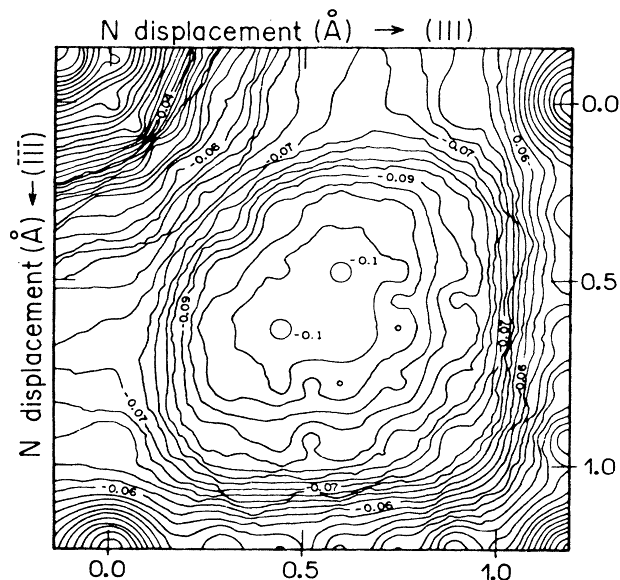

FIG. 4. Contour plot of the calculated total-energy surface for coupled displacements of each N in N_2^+ along the ⟨111⟩ direction. Contour spacing is 0.004 hartree.

D. Electronic properties of N_2 in C, Si and Ge

To analyze the electronic properties of the above systems we first show in Fig. 5 a schematic representation of

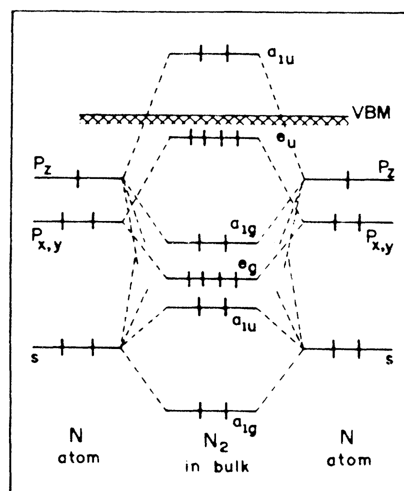

FIG. 5. Schematic orbital representation of substitutional N_2 in a type-IV semiconductor.

the orbital formation for N_2 in type-IV semiconductors. At the leftmost and rightmost parts of this figure we show the atomic orbitals of N under a D_{3d} crystal field. In total we shall have 16 electrons corresponding to the 10 electrons of the two N atoms and six electrons from the host obtained when the bonds are broken in the double vacancy. The central part of the figure then shows the resulting orbital energy scheme. There is a hyperdeep a_{1g} orbital obtained from the atomic 2*s* orbitals, the a_{1u}, e_g, a_{1g}, and e_u orbitals that are resonant in the valence band and a deep orbital a_{1u} which, as the others, is doubly occupied. This a_{1u} orbital that arises from the antisymmetric combination of the p_z orbitals lies in the gap region and the final state is a nondegenerate $^1A_{1g}$ state. The basic distinction of this case compared to the isolated N impurity is that, whereas in the latter, the orbital in the gap arises from orbitals of the host atoms in the N_2 case, the resonant a_{1g} and the gap a_{1u} orbitals are bonding and antibonding combinations of the N atoms. So in the N_2 case the orbital involved in the electronic process is related to the impurity and not the host atoms. At the total-energy minimum the electrons of the a_{1u} orbital are equally shared by the N atoms and locally the a_{1u} is a combination of two lone pairs. Therefore, each N atom energetically favors a threefold coordination. In the N_2^+ case, the a_{1u} orbital becomes a_1 with p_z character of N^1, occupied by only one electron, whereas the bonding a_{1g} orbital becomes the other a_1 orbital with p_z character of N_2. Each N atom acquires its own characteristic lone pair. Energetically it becomes more favorable to accommodate one electron in one of the two N atoms leaving the other unoccupied, thus localizing the hole.

IV. SUMMARY

In this paper we have discussed the role of nitrogen impurities, both isolated and complex, in type-IV semiconductors. For the isolated N impurity we find in all cases a distortion along the $\langle 111 \rangle$ direction towards a vacancy position. We discuss that this is a natural consequence of N of forming sp^2 bonds leaving one lone pair. This is not found generally in *sp* impurity as, for instance, O in Si distorts in the $\langle 100 \rangle$ direction.[28] This general aspect found here for the crystalline systems should also be important in amorphous type-IV semiconductors. For the case of N_2 both nitrogens form sp^2 bonds with the host atoms and thus the nitrogens move in opposite directions leading to a very weak, if any, N-N bond. It is thus expected that N should have high solubility in semiconductors. For $N_2{}^+$, each N atom having its own lone pair, it is favorable energetically to break the inversion symmetry localizing the hole in one of the two N atoms. From the orbital point of view, the basic distinction between the isolated and the complex impurity is that while for N the a_1 orbital in the gap comes from the host atoms, for N_2 it comes from the bonding combination of the N atomic orbitals. For $N_2{}^+$ this combination that comes from the inversion symmetry is lost and the hole localizes in only one N atom. Restoring the inversion symmetry that is present in the Hamiltonian is energetically not very important and goes beyond the one-particle picture as discussed in the literature.[29]

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