PHYSICAL REVIEW B **71**, 075421 (2005)

N-type electric conductivity of nitrogen-doped ultrananocrystalline diamond films

Ying Dai,[1,*] Dadi Dai,[2] Cuixia Yan,[1] Baibiao Huang,[1] and Shenghao Han[1]
[1]*School of Physics and Microelectronics, State Key Laboratory of Crystal Materials, Shandong University, Jinan, 250100, People's Republic of China*
[2]*Department of Chemistry, North Carolina State University, Raleigh, North Carolina, 27695-8204, USA*

(Received 1 January 2004; revised manuscript received 20 September 2004; published 25 February 2005)

The electronic structures of several possible nitrogen-related centers on the diamond surface and in the diamond grain-boundary have been studied using density functional theory approaches with cluster models. The results indicate that the nitrogen-vacancy related complex may be the shallow donor center, and the complexes of nitrogen and dangling bond or nitrogen with a π bond may play the role of compensation centers. Three mechanisms of electric conductivity in ultrananocrystalline diamond films are proposed as the model to explain the recently reported experimental results of both *n*-type conductivity-temperature and nitrogen-concentration dependences.

DOI: 10.1103/PhysRevB.71.075421 PACS number(s): 72.20.−i, 71.55.−i

I. INTRODUCTION

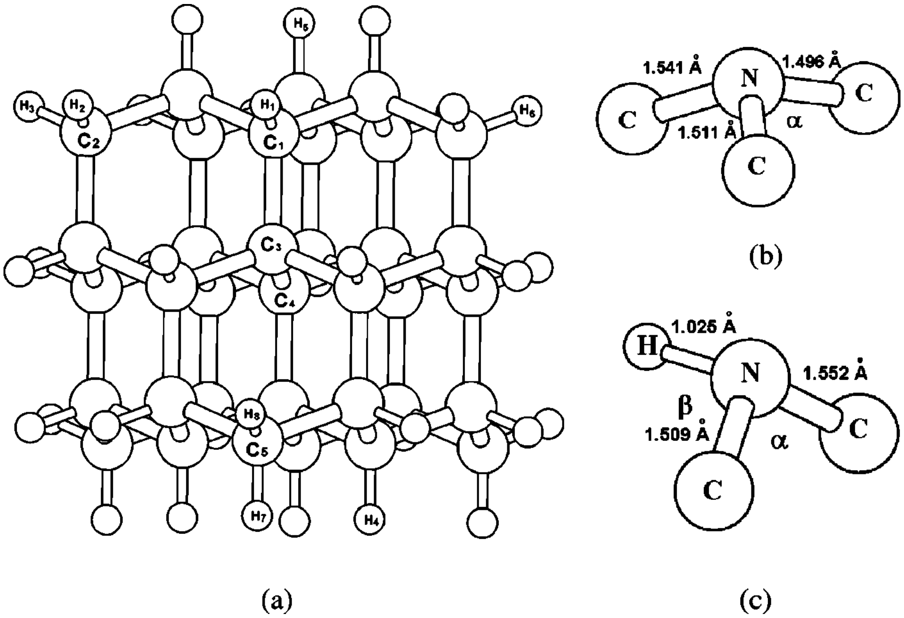
Diamond is a promising wide band-gap semiconductor that may in future rival silicon as the material of choice in the electronics industry because of its exceptional physical and chemical properties.[1] Although the synthesized diamond is already available in either polycrystalline or monocrystalline form, the utilization of the unique electronic properties of diamond is limited because of the unavailability of the *n*-type diamond. *n*-type diamond has been expected as a better electron emitter, photoemission, and ion or electron impact-induced emission, and could serve as a better inert electrode for electrochemical applications. Furthermore, the *n*-type diamond is necessary to realize new *p*-*n* junction related semiconductor devices. As a consequence, both theoretical and experimental efforts have been spent for years in searching practical *n*-type dopant of diamonds.[2–6] Nitrogen (N) is commonly found at different concentrations in natural diamond and can also exist in the synthesized diamond by introducing N during the chemical vapor deposition (CVD) synthesis of the diamond. By an analogy to substitutional phosphorous in silicon, one may have an intuition that nitrogen at a substitutional site might be a natural candidate to act as a donor in diamond.[7] However, N in diamond creates a deep donor state (~1.7 eV) in the gap below the lowest conduction band.[8] The theoretical study indicates that the high resistivity of N-doped diamond results from preferential formation of complex of threefold-coordinated nitrogen atom (N-sub) with a dangling bond (DB).[9] Consequently, the doping diamond with N is not expected to yield useful conductivities at room temperature. It is interesting to note that the recently reported experimental and theoretical results challenge the above traditional thinking of N doping of diamond. Namely, the *n*-type conductivity, which has been obtained so far in ultrananocrystalline diamond (UNCD) films doped N,[10] can reach as high as up to 143 $\Omega^{-1}\,\mathrm{cm}^{-1}$; and in the crystalline bulk diamond a defect of nitrogen and hydrogen complex N—H—N is much shallower than an isolated N donor.[4] Therefore, one may question whether N and the related complexes are effective donor dopants in bulk diamond and UNCD films. The grain-boundary (GB) conduction has been proposed responsible for the high *n*-type electrical conductivities[10] but the related transition mechanism for this noncrystalline semiconductor is unclear yet. The purpose of this paper is to investigate the related mechanism of *n*-type high conductivity in the UNCD films.

It is known that some defects in diamond such as DB, vacancy, and graphitic carbon with π-type bonds have been identified by many experiment techniques.[11] Additionally, it has been observed that the defects in diamond, acting as donor centers, may lead to thermally activated conduction with the activation energies dependent upon the defect type.[12] Therefore, it becomes of interests to study the electronic properties of various N-related microstructures with DB, π-type bond, vacancy, and H in diamond.[4,11] In this work, we have analyzed the electronic structure of different N-related centers in diamond by using cluster model and density functional theory (DFT) approach. As a consequence, we have proposed a model of the mechanism of *n*-type electrical conductivity in UNCD films to explain the conductivity-temperature dependence, the experimental results reported by Bhattacharyya *et al.*[10]

II. COMPUTATIONAL DETAILS

The Amsterdam density functional (ADF2003) program is employed.[13] In our calculations, the 2*s*, 2*p* orbitals of C, N and 1*s* orbital of H are considered as valence shells for which the triple-ξ Slater type orbital plus polarization functions are employed. The VWN+Becke88+Perdew86 is selected as the exchange-correlation functional.[14–16] The single point energy has converged to 10^{-6} Hartree after self-consistent-field iterations. The coordinates of the atoms in the cluster models have been optimized using the convergence criterion of 10^{-3} Bohr on the displacement, 10^{-3} Hartree/Bohr on the gradient, and 10^{-6} Hartree on the energy, respectively.

$C_{35}H_{36}$ (I) shown in Fig. 1(a) is chosen as the basic cluster. Modifying the basic cluster derives the other clusters. The initial bond lengths of C—C and C—H adopted in the



(a) (b) (c)

FIG. 1. (a) Structures of the basic cluster $C_{35}H_{36}$(I), (b) local structure of N center at the surface of cluster $C_{34}N_1H_{35}$(II), (c) local structure of N center at the surface of cluster $C_{34}N_1H_{35}$(III).

calculations are 1.540 and 1.080 Å, respectively, The optimized average C—C bond length is about 1.542 Å and that of the C—H is about 1.105 Å. The binding energy of a C—H bond is about −12.29 eV.

III. RESULTS AND DISCUSSIONS

A. The electronic structure of N substitution for C (N-sub) at the surface of clusters

Based on the studies of impurities in diamond using the tight-binding approaches, Zapol *et al.*[11] found that the grain boundaries in UNCD films result in 40–50 % of threefold-coordinated atoms in the interface and the incorporation of nitrogen impurities in the grain boundary cost less energy than that in the bulk. We have thus chosen two cluster models with N-sub centers at the surface to simulate the N impurity in the grain boundary. One is the cluster $C_{34}N_1H_{35}$ (II), in which N atom substitutes the atoms C_1 and H_1 on the surface of the basic cluster $C_{35}H_{36}$ (I) [see Fig. 1(a)]. Another one is $C_{34}N_1H_{35}$ (III), in which N atom substitutes the atoms C_2 and H_2 on the surface of the basic cluster $C_{35}H_{36}$ (I). To make a clearer picture, the local N-related structures in $C_{34}N_1H_{35}$ (II) and $C_{34}N_1H_{35}$ (III) are shown in Figs. 1(b) and 1(c), respectively. In Fig. 1(b), the three N—C bond lengths are 1.541, 1.511, and 1.496 Å, respectively, and the angle α is 108.41°. In Fig. 1(c), the two N—C bond lengths are 1.509 and 1.552 Å and the N—H bond length is 1.025 Å, and the angles α and β are 107.46° and 110.57°, respectively. The calculated bonding energy of C—N in the clusters $C_{34}N_1H_{35}$ (II) and $C_{34}N_1H_{35}$ (III) are about −7.59 and −7.67 eV, respectively. The difference is as small as 0.08 eV, showing that their stabilities are almost same.

The calculated electronic structure of clusters $C_{35}H_{36}$ (I), $C_{34}N_1H_{35}$ (II), and $C_{34}N_1H_{35}$ (III) are summarized in Fig. 2, where the bottom of the conduction band E_c is defined as the lowest unoccupied energy level and the top of the valence band E_v is the highest occupied energy level. The results indicate that the N-related centers on the surface, as simulated by the clusters $C_{34}N_1H_{35}$ (II) and $C_{34}N_1H_{35}$ (III), intro-

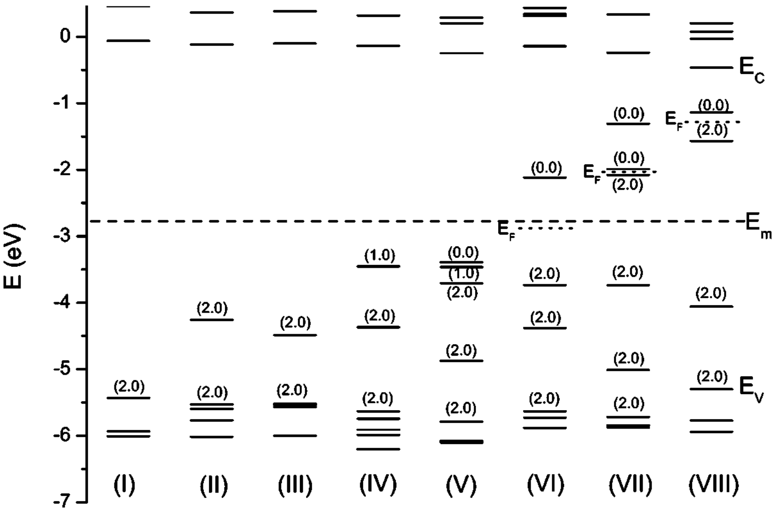


FIG. 2. Electronic structures of the N-related centers of (I) $C_{35}H_{36}$(I), (II) $C_{34}NH_{35}$(II), (III) $C_{34}NH_{35}$(III), (IV) $C_{34}NH_{34}D_1$(IV), (V) $C_{34}NH_{32}D_3$(V), (VI) $H_{33}N_1C_{34}{=}CH_2$ (VI), (VII) $C_{33}N(VD_4)H_{35}$ (VII), and (VIII) $C_{33}N(VH_4)H_{35}$(VIII). E_C is the bottom of conduction band. E_V is the top of valence band. E_m is the middle line of the energy gap. E_F is the Fermi level. The numbers in parenthesis are the electron occupations at the presented levels from the Mülliken population analysis.

duce the energy levels occupied by two electrons in between the middle of the gap (E_m) and the valence band (E_v), which suggests threefold coordinated N atom with three N—C bonds and a lone pair of electrons. Thus, this type of N-related local structures can play the role of neither effective donors (with the occupied levels near to the E_c) nor compensation centers (with the singly occupied or unoccupied levels below the donor levels) for *n*-type conductivity of diamond.

B. Electronic structure of complexes of nitrogen and dangling bond (N-DB) on the surface

To explore how the DB on the surface[17,18] or in the grain boundary[10,11] plays an effective role in electrical properties of the hydrogenated diamond,[19] we have performed electronic structure calculations of the clusters $C_{34}(N_1D_1)H_{34}$ (IV), in which an N is put on the surface as the N in the cluster $C_{34}N_1H_{35}$ (II) and the H_4 on the surface is removed [see Fig. 1(a)]. The result is shown in Fig. 2 (IV). The case of three DBs existing on the surface is represented by the cluster $C_{34}(N_1D_3)H_{32}$ (V), in which the N substitutes C_1 [as that in cluster $C_{34}N_1H_{35}$ (II)] and H_5, H_6 and H_7 are removed. The electronic structure, shown in Figs. 2 (IV) and (V), directly indicate that these kinds of N-DB related complex centers yield the states lower than the middle E_m of the energy gap and some of them are either singly-occupied or unoccupied. This implies that the N-DB centers cannot be the effective donors but may play the role of compensation centers for the coexisting donors.

C. Electronic structure of complexes of nitrogen and π bond (N-π) on the surface

It is known that some graphitic carbon defects may exist on the grain boundary in polycrystalline diamond and the π-type bonds may be the key to interpret the electronic properties of UNCD films.[10,11] We have performed the calculations for the cluster $H_{33}N_1C_{34}{=}CH_2$ (VI), in which N substitutes carbon atom such as in cluster $C_{34}N_1H_{35}$ (II) and the atoms H_7 and H_8 (connected to C_5) are replaced with a CH_2. The results is shown in Fig. 2 (VI). The nitrogen atom interacts with the π-type bond and form a complex center that introduces two types of levels in the energy gap. The Fermi level E_F, defined as the energy level occupied with single electron, lies below the E_m. Therefore, these defects are not the donor centers either but may play the role of compensation center for donors when the surface N-π complexes coexist with some of the donor centers in the sample.

D. Electronic structure of nitrogen-vacancy (N-*V*) complexes

The nitrogen-vacancy (N-*V*) complexes have been considered as one of the most important defects of diamond.[20,21] In the present work, we have examined the electronic structure of the nitrogen-vacancy complexes by the calculations of two simulating clusters. One is $C_{33}N_1VH_{35}$ (VII), in which the vacancy replaces the C_4 in the cluster (I) [Fig. 1(a)], and the N substitutes the atoms C_1 and H_1 on the surface of the basic cluster $C_{35}H_{36}$ (I). Another one is $C_{33}N_1(VH_4)H_{35}$ (VIII), the same as $C_{33}N_1VH_{35}$ (VII), but the vacancy is hydrogenated by four H atoms with C—H bond distance fixed at about 0.932 Å. The obtained electron structures of these two clusters are given in Fig. 2, (VII) and (VIII) respectively.

From Fig. 2, it is found that (i) the Fermi level E_F pinned by the gap states produced by the vacancy-related centers is closer to the conduction bottom E_C than that caused by others. Thus, we may conclude that these vacancy-related defects play the role of donor centers in the *n*-type conductivity of diamond. Our conclusion can be further supported by the experimental observations that defects in diamond may result in the appearance and act as donor centers,[12] and that large quantity of the N-*V* complexes may be formed in nitrogen doped CVD diamond.[22] (ii) The donor levels produced by the fully hydrogenated-vacancy-related centers are shallower than that without hydrogenation. Thus this type of centers should be one of the possible donor origin that are responsible for the *n*-type high conductivity of UNCD films, and the others play the role of compensation center for donors, if they coexist in samples.

E. The mechanism of *n*-type electric conductivity in UNCD films

The experimental results indicate that the UNCD films consists of pure sp^3 carbons and a disordered mixture of sp^2 and sp^3 carbons on the ~0.5-nm-wide grain boundaries. It has been proposed that the grain boundary conduction is responsible for the high electrical conductivity in these films.[11,22] In addition, the theoretical results indicate that incorporation of N impurities into the grain boundary is easier than incorporation of N into the bulk diamond.[5] Therefore, it is reasonable to expect more N atoms incorporated in the grain boundary than that in the grains, and the electronic structure of these N-related centers results in the mechanism of the high conductivity in UNCD films. To further explore the relationship between the electronic structure and the donor and acceptor characters, we have plotted the density of states (DOS) for the clusters (IV)–(VIII) in Fig. 3(a). The reason only the clusters (IV)–(VIII) were chosen is that the possible active donor or acceptor states appear only in these clusters [see Fig. 2] within the experimental temperature range 4.2–300 K.[10] The active donor/acceptor states are noted by "act" in Fig. 3(a). The donor level is the energy level near E_F with single or double electron occupation, and the acceptor level is that below E_F with single or zero occupation.

In order to explain the experimental results[10] based on Fig. 3(a), we have suggested a model as shown in Fig. 3(b). (1) The number of the effective donors (D_e) is larger than that of compensation-effective acceptors (A_e) to ensure the conductivity to be *n* type. (2) E'_C and E'_V denote for the mobility edges[23] of the conduction and the valence bands, respectively, which are the characteristics of disordered emiconductors. (3) The localized D_e-band states are induced mainly by the nitrogen-vacancy related centers. (4) The Fermi energy level (E_F) is pinned within the range of the D_e band. Consequently, three conduction mechanisms have been proposed as follows within an appropriate range of tempera-

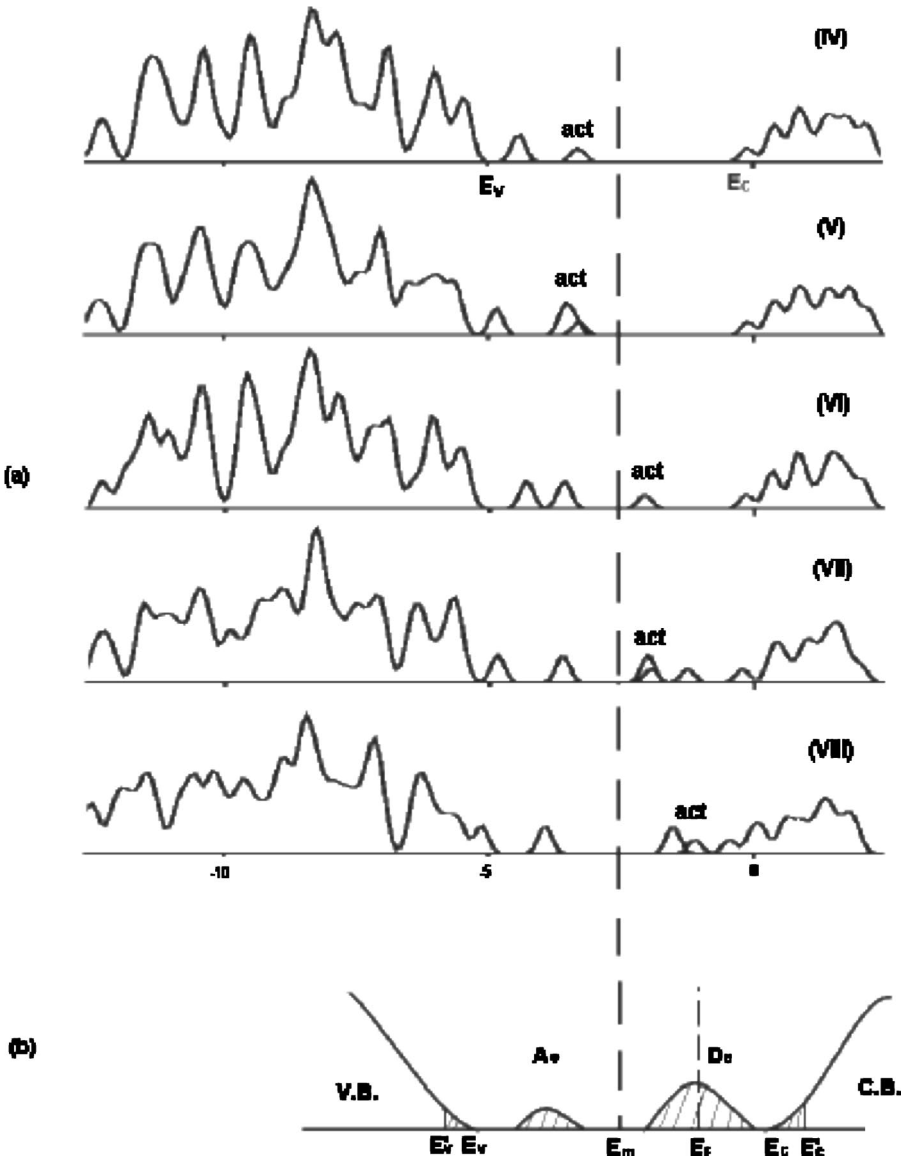


FIG. 3. (a) IV-VIII: the DOS of the clusters (IV)–(VIII). (b) Schematic of effective donor D_e and acceptor A_e bands for a sample of UNCD films with *n*-type conductivity. E'_C and E'_V denote for the mobility edges of the conduction and valence bands respectively, E_C and E_V are the bottom of conduction band and the top of valence band respectively. E_F is Fermi level. The possible active donor/acceptor states are denoted by "act."

tures in accordance with the theory of noncrystalline semiconductors.[23]

(1) Considering the electron excitation from beyond the mobility edges into nonlocalized states at E'_C, we write the *n*-type conductivity as

$$\sigma = \sigma_{\min} \exp\left(-\frac{E'_C - E_F}{kT}\right) \tag{1}$$

in which k is the Boltzmann constant $\sigma_{\min}$ is the minimum conductivity[23] and for all noncrystalline semiconductors

$$\sigma_{\min} = 610/\alpha \quad (\text{in unit of } \Omega^{-1}\,\text{cm}^{-1}), \tag{2}$$

where a is the distance (in Å) between the potential wells. For diamond a equals 3.56 Å and thus $\sigma_{\min} \approx 170\ \Omega^{-1}\,\text{cm}^{-1}$, which is very close to the conductivity value of $143\ \Omega^{-1}\,\text{cm}^{-1}$ around the highest temperature range reported in Ref. 10, and therefore the electric conductivity higher than $143\ \Omega^{-1}\,\text{cm}^{-1}$ should become possible.

(2) Considering the electron excitation into the localized states at the band edge E_c and hopping between the levels close to E_C, we write the *n*-type conductivity as

$$\sigma = \sigma_1 \exp\left(-\frac{E_C - E_F + W_1}{kT}\right), \tag{3}$$

where W_1 is the activation energy for hopping, σ_1 is about 10^{-1} of $\sigma_{\min}$. This type of conductivity may be found in the range of temperatures lower than that described in Eq. (1).

(3) At low temperatures the conductivity behaves as

$$\sigma = \sigma_2 \exp\left(-\frac{W_2}{kT}\right), \tag{4}$$

where $\sigma_2 \leqslant \sigma_1$ and W_2 is the activation energy for hopping of electrons at the energy near E_F and σ_2 depends strongly on the concentration of donors (N_D).

According to Eqs. (1), (3), and (4), we have summarized the typical temperature dependence for the N-doped UNCD films in Fig. 4, which clearly shows two features. (1) For a

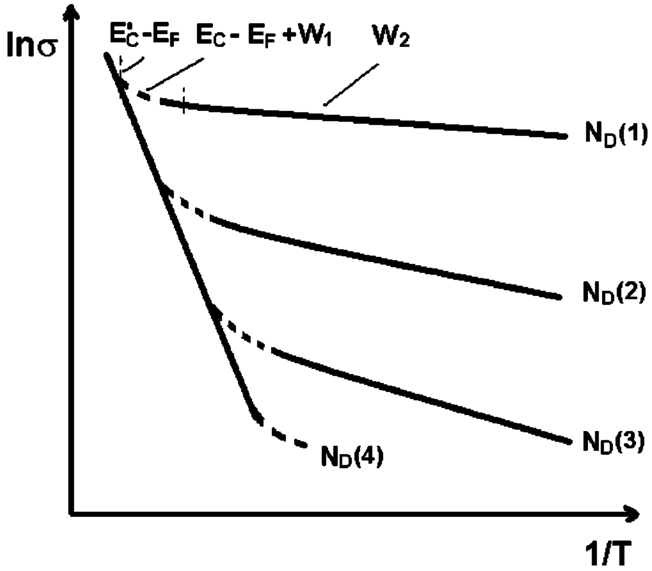


FIG. 4. Illustration of the temperature and nitrogen-concentration dependences of conductivity expected on the model of Fig. 3(b). $E'_C - E_F$, $E_C - E_F + W_1$ and W_2 represent the activation energies in Eqs. (1), (3), and (4), respectively. $N_D(1) > N_D(2) > N_D(3) > N_D(4)$.

given sample there are three temperature regions each with a different activation energies, e.g., $E'_C - E_F' > E_C - E_F + W_1 > W_2$. (2) Only in the temperature range characterized by W_2, the conductivity depends strongly on the concentration of donors D_e. Both features are in good agreement with the experiment in which the high *n*-type conductivity 143 Ω^{-1} cm^{-1} was observed.[10] As a consequence, the higher conductivity than 143 Ω^{-1} cm^{-1} can be achieved in principle for heavy N-doped UNCD films.

IV. CONCLUSIONS

The electronic structure calculations of the diamond using the cluster models with DFT approaches indicate that the N-*V* complexes may play the role of the shallow donors while N-DB complexes as the compensation centers. For the N-doped UNCD films of *n*-type conductivity, three mechanisms have been proposed for three temperature ranges, by which the experimental results of conductivity-temperature dependence can be well explained. The mechanism of the highest conductivity 143 Ω^{-1} cm^{-1} is induced by the electron excitations into the states of conduction band.

ACKNOWLEDGMENTS

The work is supported by the National Science foundation of China (Grant No. 10374060), the Natural Science Foundation of Shandong Province (Grant No. Y2003A01), the Ministry of Science and Technology of China (Grant No. 973, 2001CB610504), and the Youth Fund of Shandong University.

---

*Electronic address: daiy60@sdu.edu.en

[1] C. Nebel, Nat. Mater. **2**, 431 (2003).

[2] S. Koizumi, H. Ozaki, M. Kamo, Y. Sato, and T. Inuzuka, Appl. Phys. Lett. **71**, 1065 (1997).

[3] I. Sakaguchi, M. N.-Gamo, Y. Kikuchi, E. Yasu, and H. Haneda, T. Suzuki, and T. Ando, Phys. Rev. B **60**, R2139 (1999).

[4] T. Miyazaki, H. Okushi, and T. Uda, Phys. Rev. Lett. **88**, 066402 (2002).

[5] Z. Teukam, J. Chevallier, C. Saguy, R. Kalish, M. Barbe, F. Jomard, A. Tromson-Carli, C. Cytermann, J. E. Butler, M. Bernard, C. Baron, and A. Deneuville, Nat. Mater. **2**, 482 (2003).

[6] Y. Dai, D. Dai, D. Liu, S. Han, and B. Huang, Appl. Phys. Lett. **84**, 1895 (2004).

[7] G. S. Woods (unpublished).

[8] R. Kalish, Diamond Relat. Mater. **10**, 1749 (2001).

[9] S. A. Kajihara, A. Antonelli, J. Bernholc, and R. Car, Phys. Rev. Lett. **66**, 2010 (1991).

[10] S. Bhattacharyya, O. Auciello, J. Birrell, J. A. Carlisle, L. A. Curtiss, A. N. Goyette, D. M. Gruen, A. R. Krauss, J. Schlueter, A. Sumant, and P. Zapol, Appl. Phys. Lett. **79**, 1441 (2001).

[11] P. Zapol, M. Sternberg, L. A. Curtiss, T. Frauenheim, and D. M. Gruen, Phys. Rev. B **65**, 045403 (2001).

[12] A. Reznik, V. Richter, and R. Kalish, Diamond Relat. Mater. **7**, 317 (1998).

[13] Amsterdam Density Functional (ADF2003), Department of theoretical Chemistry, Vrije Universiteit, De Boelelaan, Amsterdam, the Netherlands.

[14] S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).

[15] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).

[16] J. P. Perdew and Y. Wang, Phys. Rev. B **33**, 8800 (1986).

[17] B. D. Thoms, J. N. Russell, Jr, P. E. Pehrsson, and J. E. Butler, J. Chem. Phys. **100**, 8425 (1994).

[18] D. D. Koleske, S. M. Gates, B. D. Thoms, J. N. Russell, Jr., and J. E. Butler, J. Chem. Phys. **102**, 992 (1995).

[19] Y. Dai, B. Huang, and D. Dai, Diamond Relat. Mater. **12**, 15 (2003).

[20] A. Wotherspoon, J. W. Steeds, B. Catmull, and J. Butler, Diamond Relat. Mater. **12**, 652 (2003).

[21] T. A. Kennedy, J. S. Colton, and J. E. Bulter, Appl. Phys. Lett. **83**, 4190 (2003).

[22] J. Birrell, J. A. Carlisle, O. Auciello, D. M. Gruen, and J. M. Gibson, Appl. Phys. Lett. **81**, 2235 (2002).

[23] N. F. Mott and E. A. Davis, *Electronic Properties in Non-crystalline Materials*, 2nd ed. (Clarendon Press, Oxford, 1979) pp. 23,219,30.