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SEMI-EMPIRICAL STUDIES ON ELECTRONIC STRUCTURES
OF A BORON-DOPED GRAPHENE LAYER – IMPLICATIONS
ON THE OXIDATION MECHANISMX. MA, Q. WANG,* L.-Q. CHEN, W. CERMIGNANI, H. H. SCHOBERT and
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Abstract—The electronic structures of pure and boron-doped graphene layers have been investigated using the semi-empirical Molecular Orbital Package (MOPAC) and large clusters of carbon atoms. It is shown that boron-doping on the edge and internal lattice sites of the graphene layer produces very different effects on the electronic structure around the edges. It is found that the substitutional boron atoms on the edges dramatically alter the density distribution of high energy electrons along the edges and the substitutional boron atoms in the deep internal lattice sites do not produce any significant effect on the density distribution along the edges. Based on the results obtained, a model is proposed for describing the oxidation process in boron-doped graphite. The mechanism of oxidation inhibition due to boron-doping of a graphene layer is chemical inhibition via the reduction of electron density with high energy at surface sites, and consequently, a reduction in the total number of active sites for gasification of the carbon. © 1997 Elsevier Science Ltd

Key Words—A. Natural graphite, B. oxidation, C. molecular simulation, D. electronic structure, D. surface properties.

1. INTRODUCTION

Since boron has been found to be a unique and efficient dopant for improving the oxidation resistance of graphite [1–4], there have been many studies on the synthesis [5,6], oxidation behavior [7,8], atomic and electronic structures [9–14], and possible ordered ground states [15] of boron-doped graphite. Based on their experimental observations, Jones and Throter [3] proposed three possible mechanisms to explain the role of boron in oxidation inhibition of graphite: (1) physical blockage of the surface active sites by a B_2O_3 barrier layer formed on the surface during oxidation; (2) chemical inhibition via electron transfer between carbon and substitutional boron atoms on the internal graphite lattice sites, which increases the activation energy for the C–O₂ reaction; and (3) boron doping resulting in the improvement of graphite crystallinity, and thus a decrease in the total number of accessible active surface sites for oxygen. One of the main objectives of this paper is to investigate the electronic density redistribution of a graphene layer as a result of boron substitution using the semi-empirical Molecular Orbital Package (MOPAC), which will shed some light on the mechanism, or mechanisms, mainly responsible for the oxidation inhibition of boron-doped graphite.

Substitutional boron can occupy either a surface or an internal lattice site of graphene layers. Experimentally, the oxidation rates of boron-doped

graphite are usually measured as a function of the overall boron content, which includes both surface and internal bulk boron atoms [3]. It is unclear whether internal and surface boron atoms contribute equally to the oxidation inhibition. Therefore, in this paper, the differences in the effectiveness of oxidation inhibition between surface and internal bulk boron substitution will be studied within an individual graphene layer.

The paper is arranged as follows: Section 2 describes the model and simulation procedures, the results are presented and discussed in Section 3, and the conclusions are given in Section 4.

2. THE MODEL

In our previous work [14], a cluster with 54 atoms arranged in a honeycomb structure was used to model the surface structure of a graphene layer. There are six edges in the cluster and only one active site on each edge. However, the cluster is still small compared to the typical size of the graphite crystallite used in experiments. In order to make the cluster a more realistic mimic of the surface structure of the graphene layers that comprise graphite, a new cluster with 56 carbon atoms having four active sites on the edge studied was designed as shown in Fig. 1. There are two long edges, labeled as top and bottom, and two short edges, labeled as left and right. On the top edge, there are four surface active sites, 4, 6, 8 and 10. The carbon atoms on the active sites of the bottom and two short edges are saturated by

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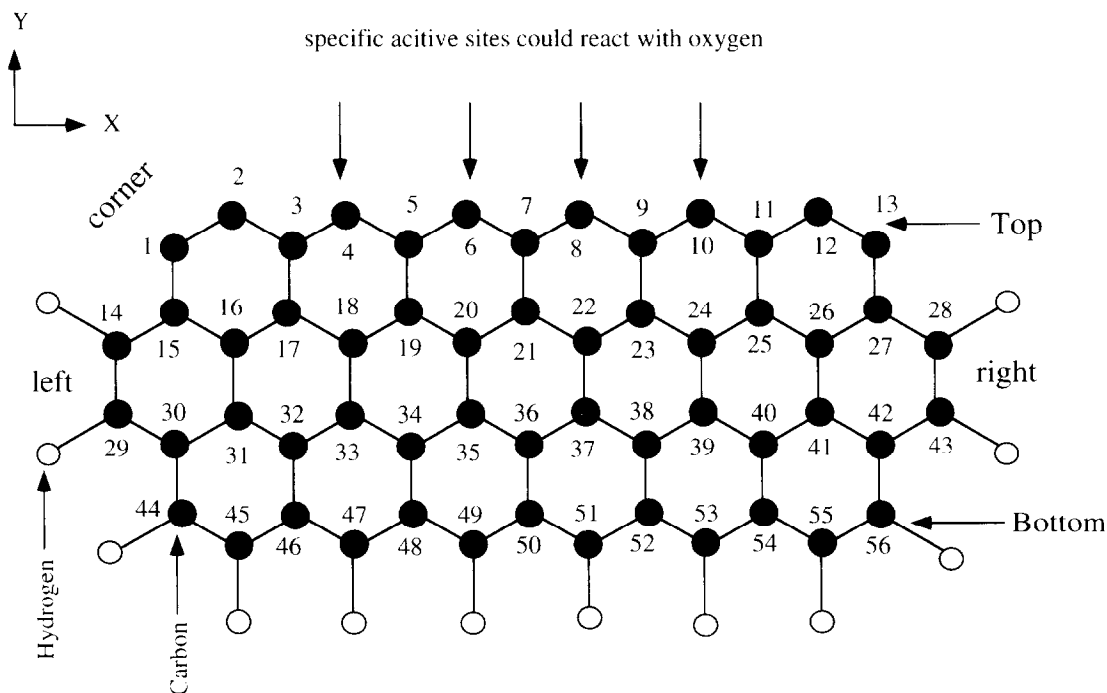


Fig. 1. The atomic arrangement in the designed carbon cluster.

hydrogen atoms. The hydrogen saturation on the bottom, left and right edges of the cluster is made to simulate the behavior of internal bulk, or unreactive, carbon sites in a graphene layer. On the other hand, the hydrogen atoms have been left off the top edge of the cluster in order to simulate the most reactive carbon sites present in the layer. In order for the oxidation reaction between carbon and oxygen to take place, hydrogen would have to be extracted from the carbon surface. Hence, the cluster model shown in Fig. 1 accurately describes all the important

features at the surface of the graphene layer during oxidation. There are a number of other steps involved in the oxidation process including removal of hydrogen (or other) surface species, splitting of molecular oxygen, and diffusion of reacting species to and from the surface of the graphene layer. Even though these steps will affect the overall reaction rates or activation energies of oxidation, they are ignored in this paper in order to fully understand site reactivity in boron-doped graphene layers. Therefore, the carbon atoms on the top edge (sites

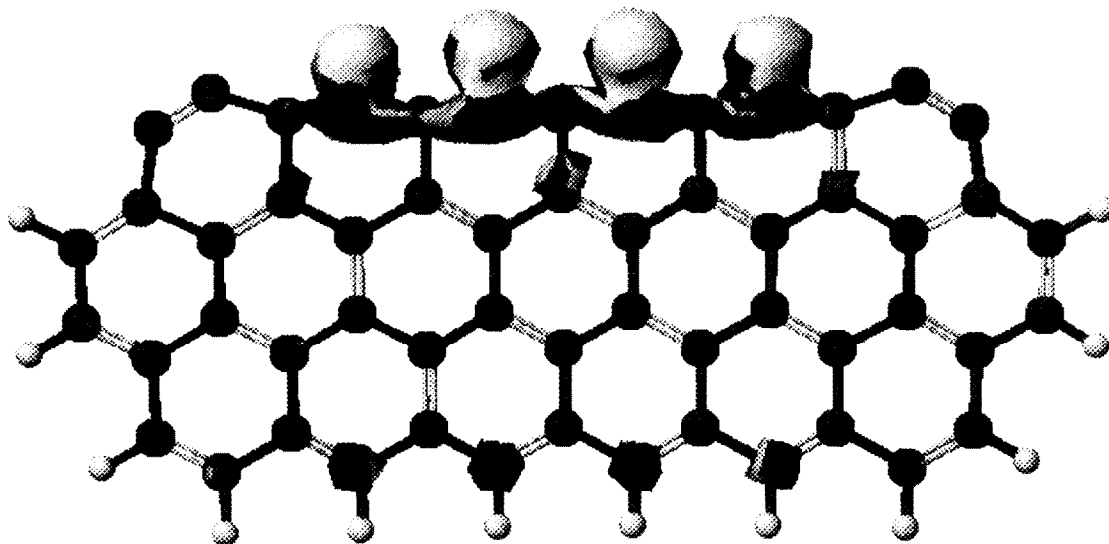


Fig. 2. The electron density distributions of the pure carbon cluster.

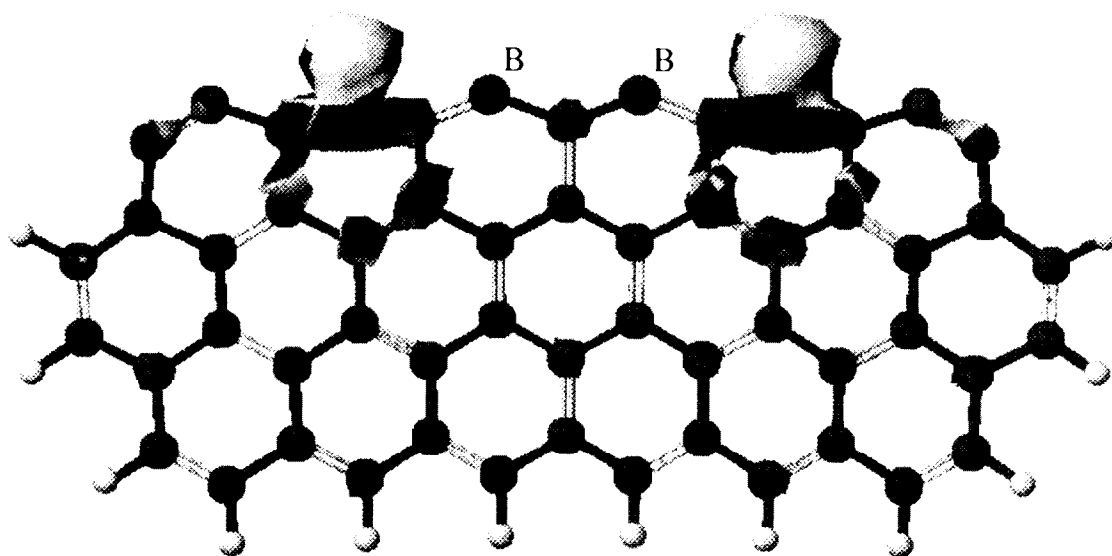


Fig. 3. The electron density distribution of the carbon cluster with two substitutional boron atoms on the surface sites 6 and 8.

4, 6, 8 and 10) and two up corners (sites 1, 2, 12 and 13) are open for simulating the bare surface of a graphene layer.

The geometric structure of the cluster is optimized by minimizing its energy, i.e. heat of formation. Minimum-energy geometries are stationary geometries for which the energy increases when the atoms are displaced in any direction. The bond length between, and the number of valence electrons on, those carbon atoms close to or on the top edge are slightly different from the corresponding bulk values. For example, the optimized bond length is 1.45 Å for the C7–C21 bond, as compared to the value 1.42 Å in the bulk. The number of valence electrons for the carbon atoms are 4.07 electrons on C7, while in the bulk the number is 4.00. The corresponding parameters for the carbon atoms close to the bottom edge of the cluster are closer to the bulk values, e.g. 1.42 Å for the C35–C36 and C36–C37 bonds, 1.43 Å for the C36–C50 bond, 3.99 electrons on C35 and C37, and 4.01 electrons on C36 and C50. These results show that the hydrogen saturation on the bottom, left and

right edges makes the behavior of carbon atoms more similar to those in the bulk, i.e. the carbon atoms close to the bottom edge can be used to approximate the internal bulk carbon atoms of the graphene layer.

The Computer Aided Chemistry (CACHe) work-system was used to calculate the electronic properties of designed clusters with and without substitutional boron atoms, by means of the semi-empirical Molecular Orbital Package (MOPAC, version 94). The AM1 potential parameters were employed to solve the Schrodinger equation for optimum geometry of the clusters, using the Mechanics (MM2) geometry as an initial input.

3. RESULTS AND DISCUSSION

3.1 Density of high energy electrons and reactivity

Since oxidation of an atom is an electrophilic reaction in which the oxygen atom draws electrons from the atom, the ability of the atom to donate electrons involving in the reaction with oxygen can be considered to be oxidation reactivity of the atom. The more electrons the atom has in the reaction with oxygen, the easier the atom reacts with oxygen, and the higher oxidation reactivity the atom possesses. In bulk graphite, only the electrons occupying the states around the Fermi surface would contribute to the oxidation reaction [9]. In a larger carbon cluster with edges and corners, the electrons in the highest occupied molecular orbital (HOMO), and those orbitals close to the HOMO, are considered to make the main contribution to the oxidation reaction [16]. Therefore, the oxidation reactivity of the atoms depends on the populations of their electrons in the HOMO and the orbitals close to the HOMO. Such

Table 1. Reactivities (R) of four surface active sites for various cases

Site #	R^a	R^b	R^c	R^d
4	0.820	1.680	0.534	0.920
6	1.100	0.074	1.153	1.000
8	1.100	0.074	0.261	1.000
10	0.820	1.680	1.659	0.920

^a Pure graphite cluster.

^b The graphite cluster with two boron substitutions on sites 6 and 8.

^c The graphite cluster with two boron substitutions on the shallow internal lattice sites 19 and 21.

^d The graphite cluster with two boron substitutions on the deep internal lattice sites 35 and 37.

populations can be used as an index of the oxidation reactivity (R). In MOPAC, this reactivity (R) can be characterized through the coefficient C_j^i [16,17]

$$R = \sum_j 2 \sum_i (C_j^i)^2 \quad (1)$$

where C_j^i is the coefficient of LCAO (linear combination of atomic orbitals) on molecular orbital j , and i labels the atomic orbitals s , p_x , p_y and p_z , respectively. The summation runs over the high occupied molecular orbitals including the HOMO. In our model, the four highest occupied orbitals were taken into account to determine R . It should be emphasized that the electron density distributions presented below are also calculated for only those electrons occupying the four highest occupied orbitals, unless otherwise specified.

3.2 Pure graphene layer

The electron density distribution calculated from the four highest occupied orbitals in a pure carbon cluster is shown in Fig. 2, where the carbon atoms are represented by large dark circles and the hydrogen atoms are denoted by small light circles; the volume of the shaded regions around an atom, for instance, atoms 4, 6, 8 and 10, refers to the density of high energy electrons on this atom, and the light and dark colors within these regions represent high and low values for the electron density: if there is no shaded region around an atom, say, atom 36, it implies that this atom has no valence electrons on the four highest molecular orbitals; and the convention of using the volume of shaded region to represent electron density will be used consistently in the other figures. According to Fig. 2, most of the electrons with high energy are predominantly localized on the four surface active sites (4, 6, 8 and 10). The oxidation reactivities (R) on these sites are calculated and listed

in Table 1. These values are much higher than those on other sites which are almost zero. It implies that, in an oxidizing environment, oxygen atoms will most likely first attack the carbon atoms at these hydrogen-free active sites. The reactivities of the carbon atoms on the corner sites (i.e. 1, 2, 12 and 13) are almost zero, and thus they are considered to be relatively inactive to an oxidation reaction even though they do not contain hydrogen. By comparing the reactivities on the four active sites, i.e. 4, 6, 8 and 10, listed in Table 1, we found that the reactivities on the 6 and 8 sites are greater than those on other two sites. This may imply that the carbon atoms on edge sites which are furthest away from the corner sites possess the greatest reactivity, i.e. the carbon atoms located at the middle of a edge of graphene layer are more susceptible to oxidation. The suggestion from the MOPAC simulation for the pure carbon cluster seems to be consistent with previous predictions [3].

3.3 Boron dopants at surface sites

In order to study the effect of boron doping, we replace the carbon atoms on two (6 and 8) of the four surface active sites with two boron atoms, and the resulting density distribution of high energy electrons is shown in Fig. 3. One may notice a significant reduction in the density of high energy electrons on these sites as a result of boron substitution. The corresponding oxidation reactivities are calculated and listed in the second column of Table 1, which indicates a dramatic decrease on sites 6 and 8. However, the decrease in R on sites 6 and 8 is accompanied by an increase in R on the other two active sites, 4 and 10. Therefore, oxidation will most likely take place on the remaining active sites, and significantly slows down only if all the remaining active sites are replaced by boron atoms. Figure 4

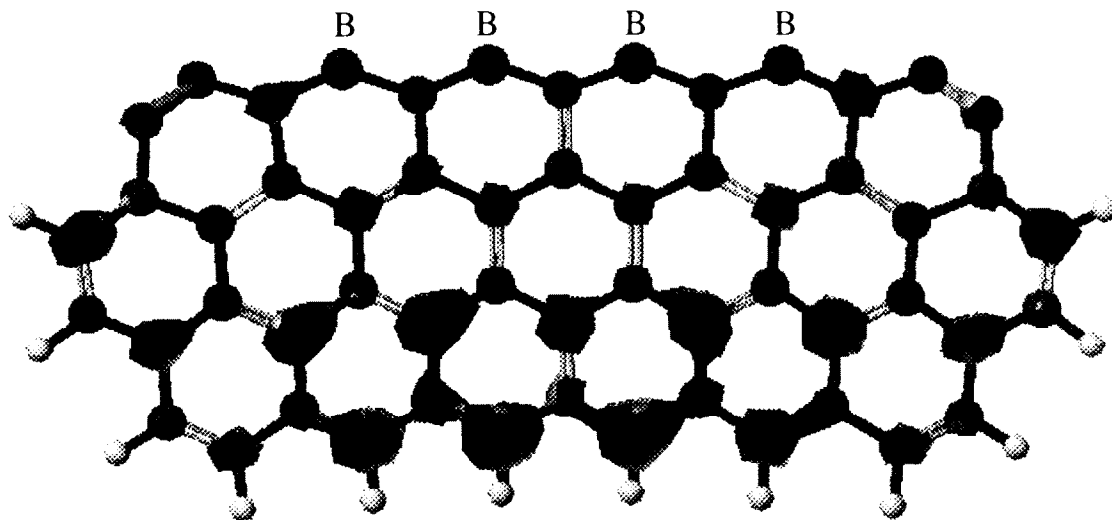


Fig. 4. The electron density distributions of the carbon cluster with four substitutional boron atoms on the surface specific active sites 4, 6, 8 and 10.

shows that when all of the surface active sites are occupied by substitutional boron atoms, the density of high energy electrons on all the originally active sites is dramatically reduced. At the same time, there is an increase in the density of high energy electrons at internal sites in the graphene layer which are, however, much less accessible to surface oxygen. Therefore, boron substitution for carbons on edge sites improves the oxidation resistance of the graphene layer by reducing the total number of surface active sites.

It was also found that substituting boron atoms for carbons on the nearest neighbor sites to the active sites can also reduce the density of high energy electrons on the active sites. For example, Fig. 5

shows that by replacing the carbon atoms on sites 5 and 7 with boron atoms, the density of high energy electrons on the active site 6 is significantly reduced (Fig. 5(a)), while replacement of carbons on sites 5 and 9 by boron atoms reduces the density of high energy electrons on the active sites 4 and 10 (Fig. 5(b)). Similar to the case in Fig. 3 (where two carbon atoms on the surface active sites are replaced by boron atoms), the remaining active sites show higher reactivity with oxygen than the pure graphene layer. Therefore, any reduction in the oxidation rates must be due to the decrease in the number of surface active sites by the boron substitution.

It is shown in Fig. 3 that the addition of surface boron atoms to the graphene layer results in a

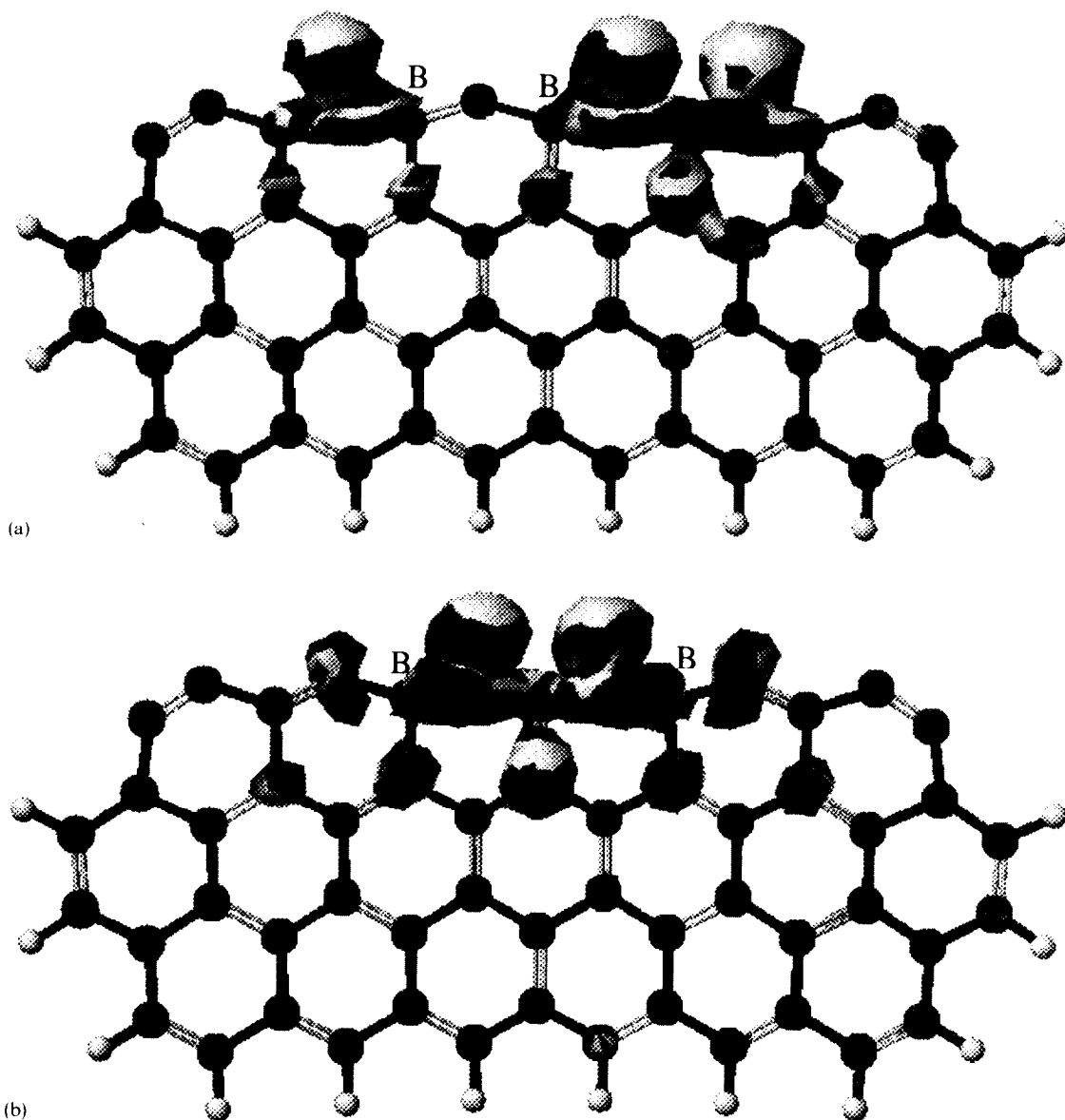


Fig. 5. The electron density distribution of the carbon cluster with two substitutional boron atoms on the shallow surface sites: (a) 5 and 7; (b) 5 and 9.

decrease in the density of high energy electrons around the boron atoms (sites 6 and 8) and an increase in the density of high energy electron around neighboring carbon atoms (sites 4 and 10). This situation can also be seen at the different sites in Fig. 5(a) and (b). Since the high energy electron density distribution is related to the oxidation reactivity of carbon atoms, and indirectly to the activation energy of the oxidation reaction, the simulation might imply different effects of boron substitution on the activation energy of the oxidation reaction depending upon the local structure. This is supported by experimental data. It was shown by Jones and Thrower [3] that doping mesophase pitch carbon-fibers at 2450 C with low boron concentration resulted in an increase

in the activation energy for fiber oxidation, and once the boron concentration increased over 1000 ppm a noted decrease in the energy of activation was also observed. Allardice and Walker [18] showed similar measurements that doping graphitic carbon with boron at approximately 1000 ppm level lowered the activation energy for oxidation. It is possible that the cause of this variation in activation energy is due to the final distribution of boron in the graphite at different boron-doping concentration levels.

3.4 Boron dopants at internal sites

In order to compare the difference in the effectiveness of oxidation inhibition between boron atoms on the graphite edge sites and those in the internal

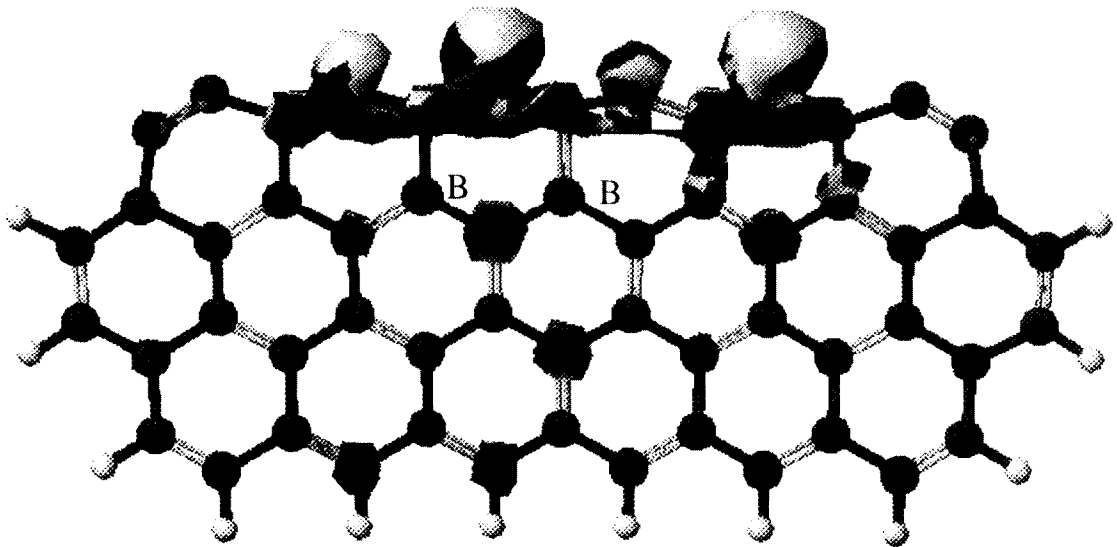


Fig. 6. The electron density distributions of the carbon cluster with two substitutional boron atoms on the shallow internal lattice sites 19 and 21.

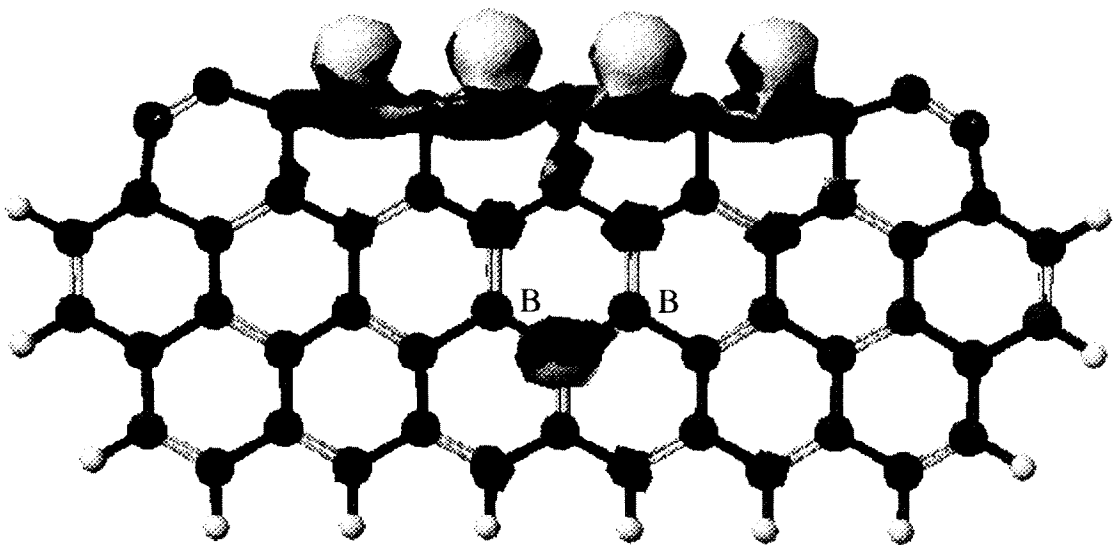


Fig. 7. The electron density distributions of the carbon cluster with two substitutional boron atoms on the deep internal lattice sites 35 and 37.

lattice sites, we also investigated the changes in the density of high energy electrons as a result of boron substitution in the internal lattice sites of the graphene layer. We distinguish two types of internal lattice sites: a) the shallow internal lattice sites near

the surfaces or edges, such as sites 19, 21 and 23; and b) the deep internal lattice sites like the sites 35 and 37.

When the near-surface carbon atoms on sites 19 and 21 were replaced by boron atoms, there is a

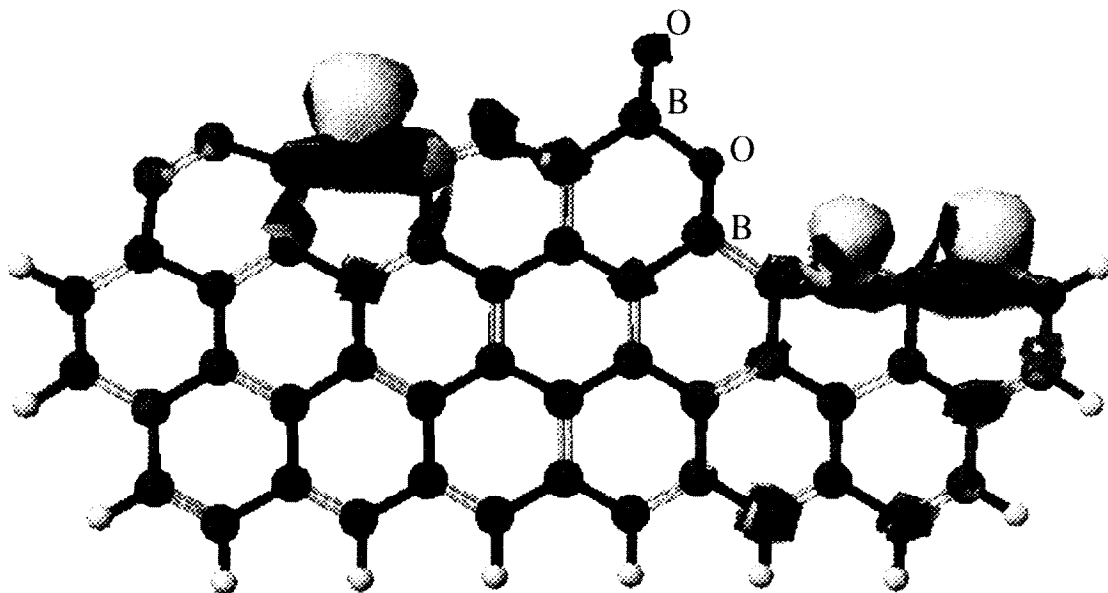


Fig. 8. The electron density distribution of the carbon cluster with the formation of boron oxide on the surface area.

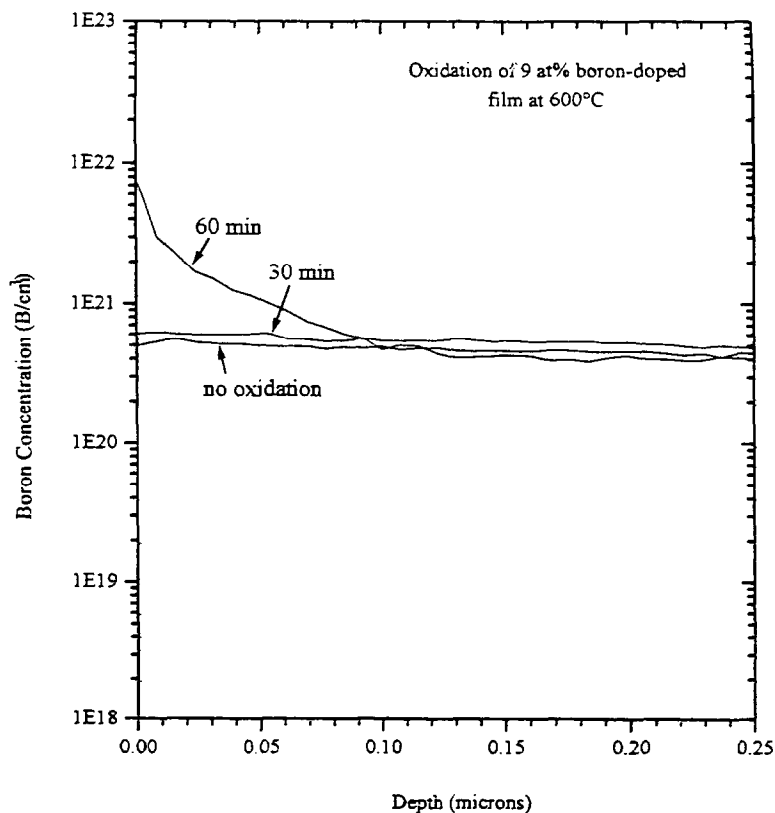


Fig. 9. SIMS profile of the $^{11}\text{B}^+$ in the 9 at% boron doped film showing the effect of oxidation on the surface boron concentration. The oxidation took place at 600°C under 5 mL min^{-1} flowing air.

noticeable change in the density distribution of high energy electrons on the active sites 4 and 8 (Fig. 6). The corresponding reactivities, R , on these two active sites are reduced from 0.820 and 1.100 to 0.534 and 0.261, respectively (column (c) of Table 1). This indicates that boron substitution on the near-surface sites may also enhance the oxidation resistance of graphite by reducing the reactivity of active sites on the surface, although the degree of reduction is not as high as in the case of direct substitution of boron atoms for carbons on the active sites.

The density distribution of high energy electrons is shown in Fig. 7 for the case of boron substitution on the deep internal sites 35 and 37. The resulting oxidation reactivities for the four surface active sites are listed in the last column (d) of Table 1. By comparing the values in column (a) of Table 1, it can be clearly seen that boron substitution in the deep internal lattice sites produces little changes in the reactivities of the active sites, indicating that the substitutional boron atoms on the deep internal lattice sites do not improve the oxidation resistance of the graphene layer.

In summary, boron substitution for carbon on the surface or near-surface sites will significantly reduce the density of high energy electrons on some of the surface active sites; whereas, boron substitution on the deep internal lattice sites does not have a significant effect on the electron distribution at the surface.

3.5 Surface oxidation

It must be pointed out that substitutional boron atoms on the surface could have possibility to be further oxidized and form boron oxide on the surface of the boron-doped graphene layer [19]. The boron in the boron oxide can still chemically bond together with the surface of the graphene layer. It has been suggested that the formation of the boron oxide may reduce the oxidation rate of the graphene layer by providing a physical diffusion barrier [3,19]. Our simulations indicate that the oxidized boron can also reduce the electron density with high energy at its neighboring active sites, as shown in Fig. 8, and hence play a role in the oxidation inhibition.

Therefore, the following is a proposed physical picture for describing the oxidation processes in boron-doped graphite. During the initial stage of oxidation, some of the surface sites will be occupied by carbon, and they will react with oxygen and be removed. As a result, new surface active sites will be created. If the new surface sites are again occupied by carbon atoms, the oxidation will most likely continue. The oxidation will be significantly slowed down when all the surface active sites, or their neighbors, are occupied by boron atoms or boron oxide. It is quite reasonable to expect, therefore, that boron atoms can accumulate on the graphite surface during the oxidation process. Figure 9 shows the SIMS profile of the ^{11}B ion in the 9 at% boron-doped chemical vapor deposition (CVD) film before and

after oxidation at 600°C under 5 mL min^{-1} flowing air for 30 and 60 minutes. It can be seen that there is little change in the boron profile after 30 minutes of oxidation. However, a large buildup of boron is observed at the surface of the sample oxidized for 60 minutes. According to the SIMS analysis, the surface concentration of boron increases about one order of magnitude as a result of oxidation. Therefore, our proposed oxidation picture seems to agree with the experimental measurement. Of course, at higher temperature, the volatilization of boron oxide can compete with this accumulation of boron oxide at the surface.

4. CONCLUSION

The electronic structures of various carbon clusters have been simulated by MOPAC with AM1 parameters to investigate the oxidation behavior of graphene layers and the oxidation-inhibition in boron-doped graphite. The results show that 1) substitutional boron atoms on the surface play very significant roles in oxidation inhibition of the boron-doped graphene layer by changing the density distribution of high energy electrons along the edges of the layer; 2) substitutional boron atoms on the deep internal lattice sites do not produce any significant effect on the electron density distribution along the edges of the graphene layer; 3) a model is proposed for describing the oxidation process in boron-doped graphite. It is concluded that the mechanism of oxidation inhibition due to boron-doping of a graphene layer is chemical inhibition via the reduction of electron density at surface sites, and consequently, a reduction in the total number of active sites for gasification of carbon.

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