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A first-principles study on the bond characteristics in carbon containing Mo, Ag, or Al impurity atoms

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ABSTRACT

The atomic bond characteristics between carbon and metal atoms are investigated by the first-principles calculation using a tetrahedron bond model. Both the charge density distribution of the highest occupied molecular orbital and the partial density of states were examined to reveal the bond characteristics. The chemical bond characteristics between Mo and carbon are nonbonding, which would reduce the bond directionality. On the other hand, noble metals such as Ag show antibonding characteristic with carbon. The bond between Al and carbon has ionic characteristics and was found to prefer a two-dimensional configuration. The effect of metallic impurities in carbon materials could be explained from the difference in the atomic bond characteristics.

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1. Introduction

The addition of a third element to carbon materials such as amorphous carbon films and carbon nanotubes provides another degree of freedom to control their atomic bond structure and corresponding physical and chemical properties [1–8]. For example, alloying amorphous carbon films with metals such as Ti, Mo, Cr, Al, or W, have been one of the most common strategies to reduce the high residual compressive stress and to improve the electrical conductivity or the chemical affinity to the substrate materials [1–6]. It is widely known that the physical properties of the films are strongly dependent on the metal elements. The addition of a small amount of W reduces the residual stress dramatically without a noticeable deterioration of the hardness of the film [6], whereas the addition of Al significantly diminishes both the residual stress and the hardness [2]. To date, most of researches have been limited to the phenomenological explanation but the fundamental understanding based on atomic bond characteristics has been seldom studied. In order to understand the role of the metal elements added in the car-

bon materials, however, a comprehensive understanding of the bond characteristics between the metal element and carbon is required.

Recently, we reported the total energy of a system with changes in the bond angles between the metal (Ti, Mo, Cr, W, Ag, Au, Al, Si, etc) and carbon atoms by the first-principles calculations in order to understand the effect of metal atoms added in an amorphous carbon network on the residual compressive stress [9]. In a pure carbon system, the total energy increased substantially as the bond angle deviated from the equilibrium angle of the tetrahedral sp^3 bonds, which would be one of the reasons for the high residual compressive stress of amorphous carbon films. However, the increase in the total energy was significantly reduced by the addition of metal elements.

Although the previous work provided a general tendency of the metal addition, the atomic bond characteristics between metal and carbon were not investigated completely. In the present work, we focus on the electronic structure of the atomic bonds between various metals and carbon atoms. The hybridization of the electronic states is evaluated by the spatial

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charge density distribution of the highest occupied molecular orbital (HOMO) and the partial density of states (PDOS). Mo, Ag, and Al atoms are selected as the representative elements of transition, noble, and simple metals, respectively. As a simplified model system, we investigated the situation when the metal atom replaces the central carbon of tetrahedron. Even if this tetrahedron bond model represents a limited situation of the metal atoms in a carbon network, it is expected that this model is satisfactory to provide an important insight of the bonds characteristics between the metal and the carbon atoms. The present work shows that the bond characteristics are strongly dependent on the metal elements, which would explain the changes in the physical and chemical properties of carbon materials containing metal atoms observed in the experiments.

2. Calculation methods

Schematics of the tetrahedron bond model used in the present work are shown in the insets of Fig. 1. The four carbon atoms are arranged as a tetrahedron, with a carbon or a metal atom located at the center of the tetrahedron. Each carbon atom at the corner is passivated by three hydrogen atoms. From the relaxed structure (inset A in Fig. 1) which is chosen as a reference state, the C(Me)–C bond angles are changed to generate the distorted structure (inset B in Fig. 1). Three of the C(Me)–C bond angles are varied from the equilibrium angle of the tetrahedral bond, 109.5° , to 90° with respect to the z-axis. The C(Me)–C distance is then completely relaxed for a given distorted angle in order to consider the effect of the bond angle distortion only. In the case of Al at the center, the relaxed structure is obtained by fixing the angles between the central atom and the four carbon atoms, otherwise the calculation does not converge. The changes in the total energy and the electronic structure of the bonds are calculated for various central atoms.

We employ a well-tested plane-wave DFT code, Vienna Ab initio Simulation Package (VASP) [10] with a cutoff energy of 550 eV, Gaussian smearing factor of 0.05 eV, a projector augmented-wave (PAW) potential [11], and the generalized gradient approximation (GGA) for the exchange-correlation

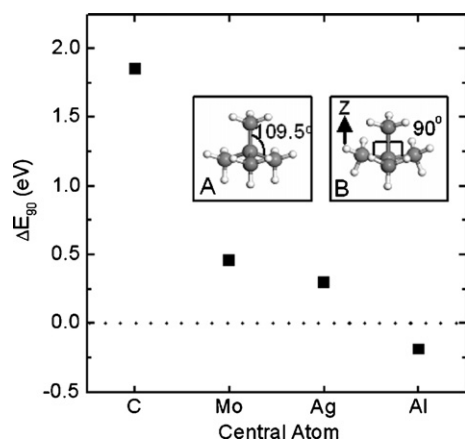


Fig. 1 – Total energy change by a bond angle distortion from 109.5° to 90° for different central atoms in the tetrahedron bond model.

potential, specifically parametrized by Perdew, Burke, and Ernzerhof (PBE) [12]. Spin-polarized calculations are done. The self-consistent loop is iterated until the total energy difference of the system between the consecutive iterating steps becomes less than 10^{-5} eV. The ionic relaxation based on the conjugate gradient method [13] is carried out until the Hellmann-Feynman forces are below 0.01 eV/Å. A gamma point calculation is performed on the periodic supercell having a size of $15 \times 15 \times 15$ Å³ to avoid the interaction with adjacent images of the tetrahedron bond model. To visualize the spatial distribution of the charge density in the HOMO, *vaspview*¹ is used. The partial density of states (PDOS) are calculated by the projection on the s, p, and d spherical harmonics within the spheres given by the C, H, Mo, Ag, and Al covalent radii of 0.863, 0.370, 1.455, 1.503, and 1.402 Å, respectively.

3. Results and discussion

Fig. 1 shows the change in total energy ΔE_{90} by the bond angle distortion of the C(Me)–C tetrahedron from the reference structure (state A) to the 90° distorted structure (state B) for different central atoms. With a carbon atom at the center, the total energy increases drastically as the bond angle deviates from the equilibrium value of the tetrahedral bond. However, with a metal atom at the center of the tetrahedron, the increase in the total energy by the distortion is significantly reduced and Ag appears to be more significant than Mo. When an Al atom is placed at the center, a contrasting behavior is observed: the total energy decreases by the bond angle distortion, which shows that the 90° distorted structure is energetically more favorable. The Al addition may induce a structural change, as will be discussed later. All the present calculations are quantitatively in good agreement with those obtained by an all-electron calculation using DMol³ [9].

The charge density distribution of the HOMO is obtained to understand the atomic bond characteristics. Fig. 2 shows the distribution of the charge density of the HOMO passing through the central atom and two carbon atoms at the corner of the tetrahedron in the reference state. The density values at the top of the figure are the maximum values of the charge density of the HOMO, ρ_{\max} , in the unit of number of electrons/Å³. The charge density of the HOMO is logarithmically scaled in the color spectrum from red for the maximum density to blue for a minimum value approaching zero. The distance between two carbon atoms, d shown in Fig. 2a is 1.54 Å, which agrees well with the interatomic distance of the diamond structure. The replacement of the central carbon atom by the larger metal atom increases the interatomic distance of the relaxed tetrahedron.

For a C–C bond as shown in Fig. 2a, the region with a high charge density is restricted to the line joining two carbon atoms, which is a typical characteristic of covalent bond having high bond strength and directionality. PDOS also confirms the covalent characteristic of this bond. Fig. 3 shows the spin-dependent PDOS in the reference state. For ease of visibility, the PDOS of corner carbon atom is plotted separately and the Fermi level is shown as dotted lines. Fig. 3a shows the PDOS when a carbon atom is located at the center. The HOMO

¹ <http://vaspview.sourceforge.net>.

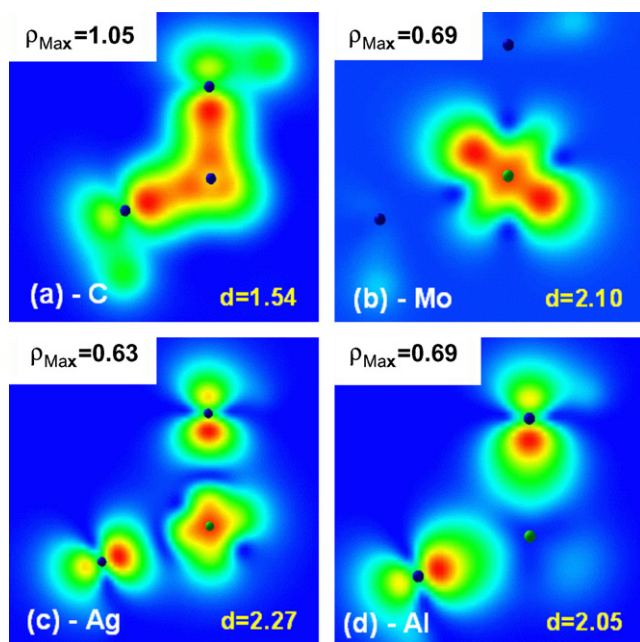


Fig. 2 – Charge density of the HOMO passing through the central atom and two corner carbon atoms of the tetrahedron bond model when a: (a) C, (b) Mo, (c) Ag, or (d) Al atom is located at the center. The green and blue dots indicate the location of the metal and carbon atoms, respectively.

is composed of strongly hybridized states between the 2p orbitals of the C atoms, resulting in strong covalent bonds be-

tween two carbon atoms. By comparing the PDOS of each atom in the tetrahedron bond model with that in its atomic state, the HOMO turns out to be a bonding state according to the molecular orbital theory. The molecular orbital theory explains that the atomic orbitals start to overlap to form molecular orbitals (MO) as atoms get closer [14]. If electrons fill the bonding state, then they strengthen the bond, whereas they rather weaken the bond by filling up the antibonding state. Meanwhile, electrons in the nonbonding state hardly affect the bond strength. For the C–C bond, electrons fill up to the bonding states and the antibonding states are located above the Fermi level of the hybridized state. Therefore, the high strength and directionality of the covalent bonds account for the large energy increase by bond angle distortion. The states denoted by H appear due to the corner C-2p orbitals interacting with the H-1s orbital, which is not hybridized with states of the central atom.

On the contrary, the replacement of the central carbon by other metal elements induces diverse aspects. When the central carbon atom is replaced by Mo, the charge distribution in the HOMO is isolated around the central Mo atom (Fig. 2b). In addition, the PDOS clearly shows that only the Mo-4d orbital contributes to the HOMO and no hybridization occurs between the Mo and C orbitals. (Fig. 3b), implying the nonbonding character between a Mo and C atom. The lower energy increase by the bond angle distortion in Mo–C compared to C–C would be attributed to the decrease in both strength and directionality, which generally occurs by the addition of transition metals.

When a Ag atom substitutes the central carbon atom, the charge distribution in the HOMO shows a nodal structure

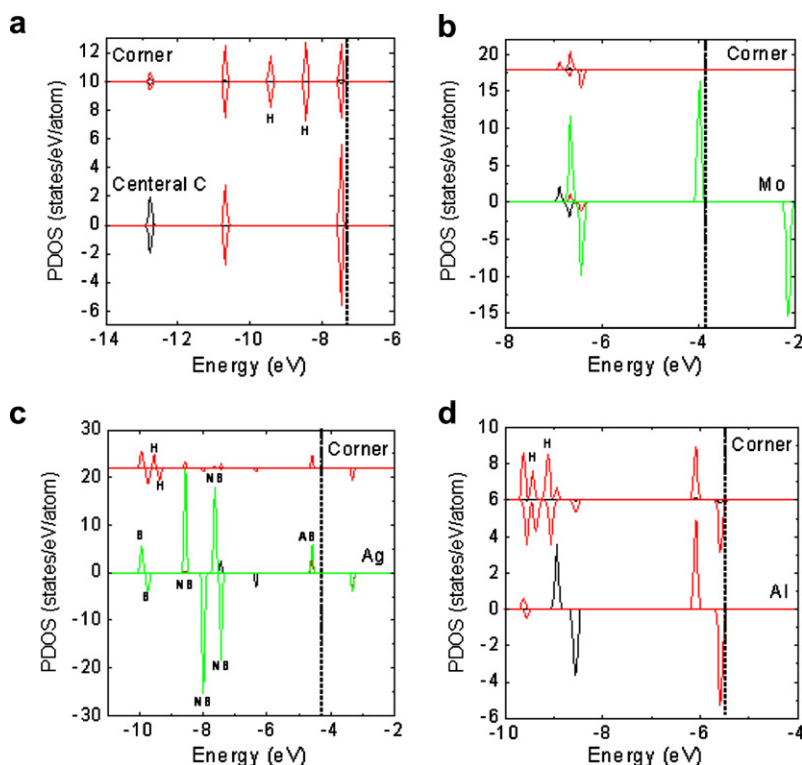


Fig. 3 – PDOS of the central atom and the corner carbon atom when a: (a) C, (b) Mo, (c) Ag, or (d) Al atom is located at the center. The Fermi level is shown as dotted line and the s, p, and d orbitals are illustrated in black, red, and green, respectively.

between the central Ag atom and the corner atoms (Fig. 2c), whereas the HOMO consists of Ag-4d and C-2p atomic orbitals as shown in Fig. 3c. This HOMO is supposed to be the antibonding state because the states in the deeper level indicated by B and NB correspond to the bonding and nonbonding states formed by the hybridization between the same Ag-4d and C-2p atomic orbitals. The nonbonding states between Ag and C can be inferred from the negligible contribution from the carbon atom to the NB states. All bond characteristics described above are also confirmed by comparing the energy level of each atom in the hybridized state of the tetrahedron bond model with that in its atomic state. Note that the noble metal Ag with filled d-orbitals, has five more d-electrons than the transition metal Mo with unfilled d-orbitals. Therefore their electrons may fill the upper part of the MO formed with carbon, the antibonding state, resulting in a weaker bond between Ag and C. This weaker bonding is believed to be one reason for the lower directionality of the bonding and consequently the lower energy increase by the bond angle distortion in Ag–C compared to Mo–C. In addition, the equilibrium distance of Ag–C is longer than that of Mo–C, which would be accompanied by the weaker electron-pair repulsion, resulting in the less directionality [15].

When Al is located at the center (Fig. 2d), the charges of the HOMO are concentrated around the more electronegative atom, carbon. This suggests that the bond character between Al and C is ionic although the HOMO consists of Al-3p and C-2p atomic orbitals as shown in Fig. 3d. Therefore, the three valence electrons of Al are expected to favor the configuration with a coordination number three. This is supposed to account for the negative ΔE_{90} in the case of Al at the center, as shown in Fig. 1, which indicates that the sp^2 -like two-dimensional configuration is energetically more favorable. In fact, the interatomic distance between the Al and the C atom along the z-axis in the 90° distorted tetrahedron is not only much longer (2.59 Å) than that perpendicular to the z-axis (1.99 Å) but it is also much longer than the equilibrium distance of Al–C in the reference tetrahedron (2.05 Å). In addition, the electrons from the C atom along the z-axis in the distorted tetrahedron do not contribute to the HOMO (not shown here), which implies that this C atom and the central Al do not bond. The preference of a two-dimensional atomic configuration would infer the experimental observations that the Al addition in amorphous carbon films resulted in both the relaxation of the residual stress and the pronounced deterioration of the hardness [2].

4. Conclusion

The electronic structure calculations using the tetrahedron bond model reveals that the bond characteristics between metal and carbon strongly depend on the metal elements. A transition metal with unfilled d-orbitals, such as Mo, shows nonbonding characteristics and reduces the directionality of the chemical bond with carbon atoms. When a noble metal with filled d-orbitals, such as Ag makes bond with carbon, the antibonding states are occupied, which would reduce both the strength and the directionality of the bonds more significantly compared to the transition metal. On the other

hand, the bond characteristics between Al and carbon prefer the formation of a two-dimensional configuration.

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