



Chemical Bond Structure of Metal-Incorporated Carbon System

Xiaowei Li^{1,2}, Kwang-Ryeol Lee^{2,*}, and Aiyang Wang^{1,*}

¹Ningbo Key Laboratory of Marine Protection Materials, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, P. R. China

²Computational Science Center, Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea

The interactions between incorporated metal atoms (Me) and carbon atom were investigated by the first-principles calculations based on the density functional theory. The simplified tetrahedral cluster model was used. The electronic structure analysis revealed that the ionic bond was generated between I A~III A metal atom (Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Al, Ga, In, Tl) and C atoms except Be case; for all transition metals, the characteristic of highest occupied molecular orbital changed from bonding (Sc, Y, Lu, Ti, Zr, Hf) to nonbonding (V, Nb, Ta, Cr, Mo, W, Mn, Tc, Re, Fe, Ru, Os) and to antibonding (Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg) as *d* electrons increased. The different bond characteristics and the partial ionic contribution caused by the electronegative difference between Me and C atoms reduced the strength and directionality of bond which explained the smaller energy changes of Me-(CH₃)₄ systems to the external distortion of the structure. These results also implied that the compressive stress in carbon-based systems could be reduced by the incorporation of these metals.

Keywords: First-Principles Calculations, Bond Characteristics, Metal Incorporation, Stress Reduction.

1. INTRODUCTION

Diamond-like carbon films (DLC) have attracted extensive research interests due to their unique structures and electrical, optical and magnetic properties.¹ But the high residual compressive stress, deteriorating the adhesion between the film and the substrate and leading to the failure of the coated surface, prohibits the potential applications of DLC films. The incorporation of metal element into DLC films has been shown to be an attractive approach which can not only reduce the stress, but also improve other tribological or biological performance.²⁻⁴

But the incorporated metal elements (Me) have different effects on the physical properties resulting in the complexity of stress reduction mechanism. For example, the addition of Cr or W into amorphous carbon matrix led to the stress reduction significantly without serious change of the hardness,^{5,6} while the addition of Al reduced both the stress and hardness drastically.⁷ This attributes to the limited analytical tools for characterizing the atomic bond structure which is closely related with the high level of residual stress. In order to clarify the mechanism of stress

reduction in metal-incorporated carbon systems, the further insight of the bond characteristics between Me and carbon atoms is still required.

Recently, we reported the interactions between Si, Ge or Sn and C atoms by a first-principles study,⁸ and Choi et al.⁹ revealed the bond characteristics in carbon containing Mo, Ag or Al impurity atoms, which provided reasonable explanations for the experiment phenomenon.^{7,10,11} However, the previous works only focused on a few elements. More systematic study for the evolutions of Me—C bond structures is yet to be clarified. So in the present work, we performed first-principles calculations to investigate the electronic structure of various Me—C systems using the tetrahedral cluster model. For a comprehensive understanding, all transition metals (TMs, I B~VIII B), alkali metals (I A), alkaline earth metals (II A) and poor metals (III A) were treated as incorporated metal elements, respectively. The present results indicated that the bond characteristics strongly depended on the incorporated metal atoms. Especially for the TM incorporation, the characteristics of highest occupied molecular orbitals (HOMO) evolved from bonding to antibonding. This could be used to account for the physical properties change in Me-DLC system.

*Authors to whom correspondence should be addressed.

2. COMPUTATIONAL METHODS

The tetrahedral cluster model was used in the present work for the calculation simplicity, as shown in Figure 1.⁹ The four carbon atoms were arranged as a tetrahedron, with a carbon or a Me atom located at the center of the tetrahedron. Each carbon atom at the corner was passivated by three hydrogen atoms. Hereafter, we designated the present tetrahedral model as C-(CH₃)₄ or Me-(CH₃)₄. The structure with the bond angle of 109.471° was chosen as a reference state for all Me substitutions as seen in Figure 1(a). Distorted structure was generated by changing three bond angles commonly containing the bond between central atom and carbon 5 (Fig. 1(b)) in the range from 90° to 130°. The system energy was calculated with the fully relaxed bond distances while keeping the bond angles fixed. Although this constrained structure shows a limited situation, it is still available to predict the characteristics of bond structures in the metal-incorporated carbon systems.

We employed spin-polarized first-principles calculations based on the density functional theory as implemented in DMol³ package. The exchange-correlation was treated in the generalized gradient approximation with the Perdew–Burke–Ernzerhof parameterization¹² and all electrons double-numerical polarization basis set was used. Self-consistent field was converged when the total energy difference between two continuous iterating steps was below 10⁻⁵ eV and the atomic relaxation was carried out until the forces acting on atoms were lower than 0.01 eV/Å. A cubic supercell with a lateral size of 15 Å

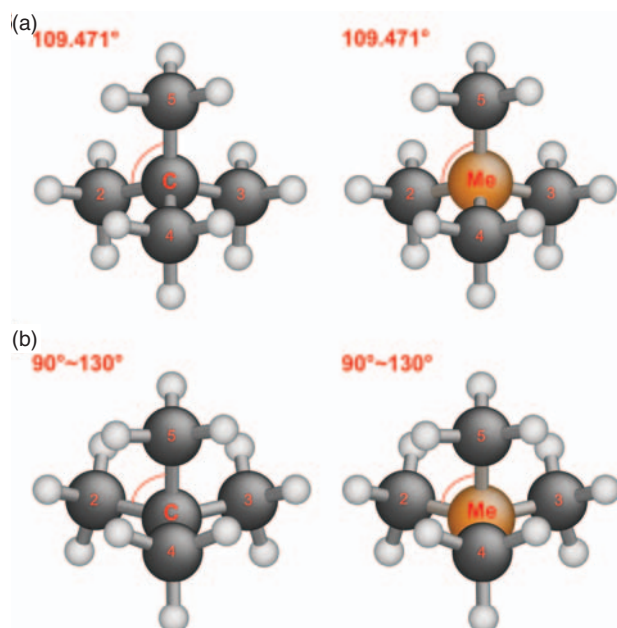


Fig. 1. (a) Tetrahedral cluster model with carbon atom or Me atoms at the center of the reference state with the bond angle 109.471°. (b) Distorted tetrahedral cluster model, in which three bond angles containing the bond between the central atom and carbon 5 were changed in the range from 90° to 130°.

was used to avoid the interaction with adjacent images of the model.

3. RESULTS AND DISCUSSION

Atomic bonding characteristics in the model systems were analyzed by the projected density of states (PDOS) and the charge distribution of HOMO. For C-(CH₃)₄ tetrahedron, the bond characteristic has been explained in previous publications,^{8,9} in which the results showed that HOMO was a strongly hybridized state between 2*p* orbitals of carbon atoms and was a bonding state according to the molecular orbital (MO) theory which enhanced the stability of system.

3.1. I A~III A Metal-Incorporated Carbon System

With I A (Li, Na, K, Rb, Cs), II A (Mg, Ca, Sr, Ba) or III A (Al, Ga, In, Tl) atom in the center of cluster, the character of ionic bond can be observed. Taking Li-(CH₃)₄ case for an example. Figure 2 shows the calculation results of Li-(CH₃)₄ system in the reference state: spin resolved PDOS and spatial charge density distribution of HOMO. Although the PDOS shows that HOMO is composed by C 2*p* and Li 2*s* orbitals, the charge density of HOMO is concentrated around the more electronegative atom, carbon, suggesting that the bond characteristic between Li and C atoms is an ionic bond. The quantitative value for charge transfer, which is determined by integrating the density of states (DOS) of the central atom, is given in Table I. In Li-(CH₃)₄ system, the transferred charge from Li to peripheral C atoms is 0.69*e*.

However, when Be atom is located at the center of tetrahedron in the reference state, the long interatomic distance of C2-Be (2.23 Å) and C3-Be (2.38 Å) shown in Figure 3 suggests that Be atom only interacts with C4 and

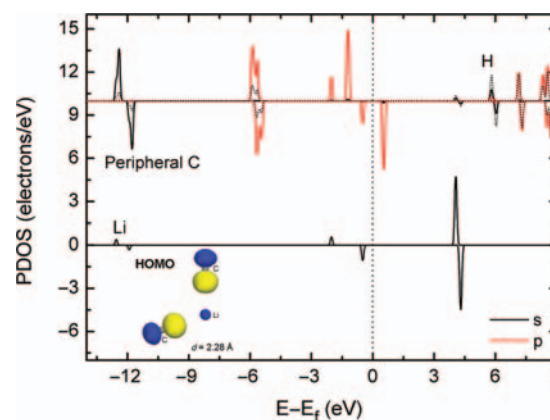


Fig. 2. PDOS of Li-(CH₃)₄ system in the reference state. The inset shows the charge density of HOMO on one of the planes composed of central Li atom and peripheral carbon atoms, in which blue and yellow colors indicate the positive and negative sign of wavefunctions, respectively and *d* is the interatomic distance between the central Li and peripheral C atoms.

Table I. Transferred charge from different central atom to peripheral C atoms.

Central atom	Li	Na	k	Rb	Cs	Mg	Ca	Sr	Ba	Al	Ga	In	Tl
$\Delta q_{\text{DOS}} (e)$	0.69	0.69	0.77	0.79	0.90	1.43	1.68	1.72	1.81	0.75	0.51	0.74	0.77

C5 atoms. PDOS of Figure 3 also shows that only C4 $2p$ and C5 $2p$ orbitals hybridize with Be $2p$ orbital in the HOMO state; the charge density of HOMO (inset of Fig. 3) connects the C4, C5 and Be atoms together, implying the obvious characteristic of covalent bond. By comparing the energy of HOMO with that of C $2p$ and Be $2p$ atomic orbitals, the HOMO is proved to be a bonding state according to the MO theory. But it should be noted that the charge density shifts toward the peripheral C atoms and both the strength and directionality of bond decrease. The effect of charge transfer behavior, induced by the electronegative difference between Be and C atoms, can be described by ionicity which is determined by Pauling theory.¹³ The value of ionicity is 0.21 for the Be—C bond, indicating the contribution from the partial ionic characteristics of the bond.

3.2. TM-Incorporated Carbon System

For all TM—(CH₃)₄ systems, HOMO states showed from bonding, nonbonding to antibonding characteristics as the electrons in d shell of the central TM atom increased. In addition, for the same subgroup elements there was no change of the characteristics of HOMO following the increase of the number of electronic shells. Representative three cases of Zr, W and Au were illustrated in Figures 4–6.

Figure 4 shows the calculation results of Zr—(CH₃)₄ system in the reference state. PDOS reveals that the hybridization occurs between Zr $4d$ and C $2p$ orbitals in the HOMO state which is a bonding state according to the MO theory, but the significant charge transfer can also be observed

due to the large difference of electronegativity between Zr and C atoms (inset of Fig. 4). The ionicity value is 0.31 for the Zr—C bond. So the contribution of ionic characteristic to the bond results in the decrease of both strength and directionality of bond. For other III B (Sc, Y, Lu) and IV B (Ti, Hf) metal atoms, they have the same HOMO characteristic, bonding.

For the incorporation of V B (V, Nb, Ta), VI B (Cr, Mo, W), VII B (Mn, Tc, Re) or VIII B (Fe, Ru, Os) metal atoms, the nonbonding characteristic was observed for all HOMO levels, which was composed of only TM's d orbitals. Figure 5 shows the calculation results of W—(CH₃)₄ system as an example. PDOS demonstrates that only the W $5d$ orbital contributes to the HOMO and no hybridization occurs between W $5d$ and C $2p$ orbitals; the charge density of HOMO is isolated around the central W atom as illustrated in the inset of Figure 5. These results evidently reveal the nonbonding characteristic between W and C atoms in the cluster.

Following the increase of the number of d electrons in TM—(CH₃)₄ systems, some of them occupied the higher energy states such as antibonding states. Results on the incorporation of VIII B (Co, Rh, Ir, Ni, Pd, Pt), I B (Cu, Ag, Au) or II B (Zn, Cd, Hg) atoms showed typical antibonding characteristics. For example, Figure 6 shows the PDOS and the charge density of HOMO of Au—(CH₃)₄ cluster in the reference state. It is obvious that the hybridization behavior occurs between Au $5d$ and C $2p$ orbitals. The charge density of HOMO shows the nodal structure, where antibonding behavior exhibits between Au and peripheral C atoms. It is also confirmed by the MO theory.

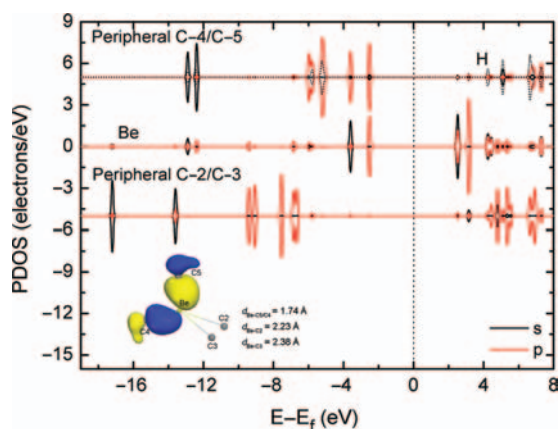


Fig. 3. PDOS of Be—(CH₃)₄ system in the reference state. The inset shows the charge density of HOMO between the central Be atom and the peripheral C atoms, in which blue and yellow colors indicate the positive and negative sign of wavefunctions, respectively and d is the interatomic distance between the central Be and peripheral C atoms.

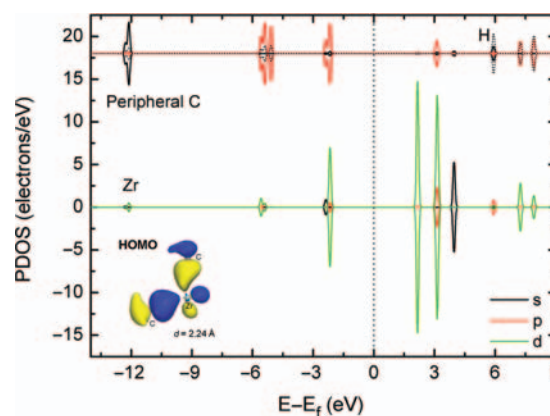


Fig. 4. PDOS of Zr—(CH₃)₄ system in the reference state. The inset shows the charge density of HOMO on one of the planes composed of central Zr atom and peripheral carbon atoms, in which blue and yellow colors indicate the positive and negative sign of wavefunctions, respectively and d is the interatomic distance between the central Zr and peripheral C atoms.

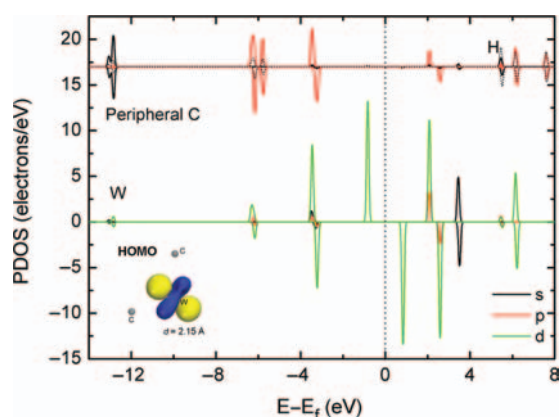


Fig. 5. PDOS of $W-(CH_3)_4$ system in the reference state. The inset shows the charge density of HOMO on one of the planes composed of central W atom and peripheral carbon atoms, in which blue and yellow colors indicate the positive and negative sign of wavefunctions, respectively and d is the interatomic distance between the central W and peripheral C atoms.

It is well known that incorporating metal atoms into carbon-based systems can lower the high residual compressive stress which is related with the distortion of bond angle and bond length.⁵⁻⁷ So in order to evaluate the effect of bond characteristics on stress reduction behavior, we calculated the total energy change of $C-(CH_3)_4$ and $Me(Li, Zr, W, Au)-(CH_3)_4$ clusters when the bond angles were deviated from the reference state of 109.471° to 90° , 100° , 120° and 130° (Fig. 1(b)). Comparing with the reference state, the energy change (ΔE) with various bond angles in each case is shown in Figure 7. For $C-(CH_3)_4$, ΔE increases drastically due to the stable and pure covalent bond with high strength and directionality. However, with the substitution of central atom by Li, Zr, W or Au, the increase of ΔE induced by the

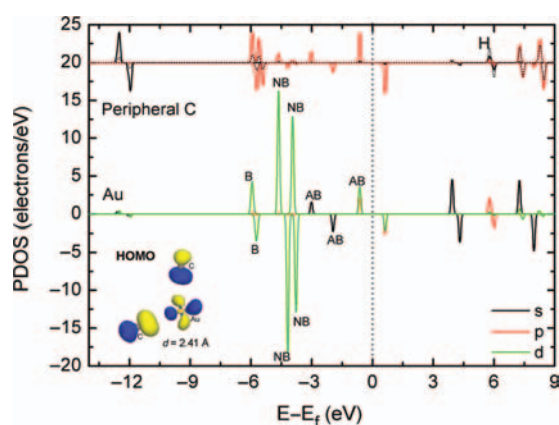


Fig. 6. PDOS of $Au-(CH_3)_4$ system in the reference state. The inset shows the charge density of HOMO on one of the planes composed of central Au atom and peripheral carbon atoms, in which blue and yellow colors indicate the positive and negative sign of wavefunctions, respectively and d is the interatomic distance between the central Au and peripheral C atoms.

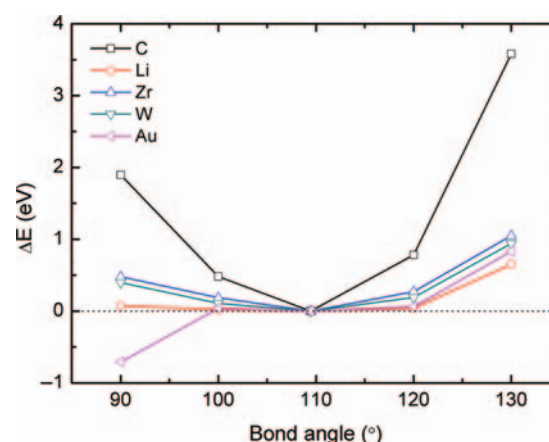


Fig. 7. Total energy changes of the $Me-(CH_3)_4$ and $C-(CH_3)_4$ systems as a function of bond angles variation.

bond angles distortion is decreased significantly, implying the reduction of residual stress. The small distortion energy change, on the one hand, attributes to the formation of ionic bond such as $Li-C$ bond or the contribution from partial ionic characteristic caused by the electronegative difference between Me and C atoms such as $Zr-C$ and $W-C$ bond, weakening the directionality of the bond and resulting in less sensitivity to the bond angles distortion than that of $C-(CH_3)_4$. On the other hand, the characteristic of HOMO also affects the strength of system. Peculiarly, the antibonding characteristic such as $Au-C$ bond deteriorates the bond strength and the system stability seriously, leading to the negative energy change.

4. CONCLUSION

First-principles calculations were undertaken to study the evolutions of bond structures between incorporated metal atoms and carbon atoms in metal-carbon system using the simplified tetrahedral cluster model. The effect of bond characteristics on the energy change caused by the bond angles distortion was also considered. The PDOS and HOMO results indicate that when the I A, II A or III A metal atom is incorporated, the ionic bond is generated except for $Be-C$ case with a covalent bond. For all transition metals, the characteristics of HOMO change from bonding (Sc, Y, Lu, Ti, Zr, Hf), nonbonding (V, Nb, Ta, Cr, Mo, W, Mn, Tc, Re, Fe, Ru, Os) to antibonding (Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg). This attributes to the increased d electrons which could occupy the higher energy states such as antibonding. However, for the same main group or subgroup metal atoms there is no change of HOMO characteristics with the increase of the number of electronic shells. Comparing with the $C-C$ bond, both the strength and directionality of $Me-C$ bond are decreased due to the different bond characteristics and the contribution from partial ionic characteristic originated

from electronegative difference, by which the small distortion energy change of Me-(CH₃)₄ system resulted from the deviation of bond angles could be explained. These calculation results found in the present work open up new opportunities for the future nanostructured carbon materials with high performance, such as DLC films with high hardness and low stress.

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