Thin Solid Films 607 (2016) 67–72

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Effect of metal doping on structural characteristics of amorphous carbon system: A first-principles study

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ARTICLE INFO

Article history:
Received 7 April 2015
Received in revised form 1 April 2016
Accepted 2 April 2016
Available online 7 April 2016

Keywords:
Transition metals
Amorphous carbon
Bonding
Residual stress
First-principles calculation

ABSTRACT

First-principles calculation was performed to investigate the effect of metal doping on the structural characteristics of amorphous carbon system, and the 3*d* transition metals (TM) were particularly selected as representative case. Results showed that the total energy in TM–C systems caused by distorting the bond angles was reduced distinctly for comparison with that in C–C system. Further electronic structure revealed that as the 3*d* electrons of doped TM increased, the bond characteristic of highest occupied molecular orbital changed from bonding (Sc, Ti) to nonbonding (V, Cr, Mn, Fe) and finally to antibonding (Co, Ni, Cu) between the TM and C atoms. Meanwhile, the TM–C bond presented a mixture of the covalent and ionic characters. The decrease of strength and directionality of TM–C bonds resulted in the total energy change upon bond angle distortion, which demonstrated that the bond characteristics played an important role in reducing residual stress of TM-doped amorphous carbon systems.

1. Introduction

Diamond-like carbon films (DLC) have attracted extensive interests from scientific disciplines and industrial societies due to their unique structures and excellent mechanical, electronic, optical as well as magnetic properties [1–4], which are widely used as protective coatings in the fields of automobile engine components, solar cells, data storages, biomedical implants, etc. [5–7]. More recently, from the technical performance, DLC films are functionalized by the addition of third transition metals (TM), such as Ti, W, Cr, Fe, Ni, Cu, and Ag, to overcome their high residual stress and improve other properties [8–13]. Note that, however, the strong dependence of structures on the variety and content of doped metal atoms and the diversity of deposition techniques lead to the disputable understanding for the effect of doped metal on the film structure and physical and chemical properties. In particular, the stress reduction mechanism of TM–C system caused by the metal doping is still in its infancy. For example, doping Ti, W, or Cr into amorphous carbon matrix decreased the stress without seriously deteriorating the hardness because of the partly formed hard carbide nano-particulates, increased sp^2 graphitization, C-sp^3 substitution by doped TM atoms as well as the proposed pivot relaxation role [8,14]. While the alloying of DLC with Cu, Ag or Al generally led to the formation of soft and ductile phase, and thus both the stress and hardness decreased significantly [15–17]. To distinctly address the reason for the reduced residual stress caused by the metal doping, understanding the structural characteristics of TM-doped amorphous carbon system from the atomic scale is necessary.

Recently, Wang et al. found that due to the reduced directionality of the W–C bonds, the doped W atoms could play a pivotal action to decrease the strain energy arising from the distortion of the bond angles, resulting in a significant reduction of residual stress [9]. Choi et al. [18] also performed the first-principles calculation using the same simplified tetrahedral model and revealed the bond characteristics of TM–C system by the doping of Mo, Ag, or Al, respectively, from which the effect of metallic impurities in carbon materials could be explained. Nevertheless, the previous works paid no attention to the strong correlation between the structural characteristics and the valence electrons of the doped TM atoms. A more systematic study of TM–sp^3–carbon interactions in TM–C system, such as their electronic structure and electron transfer behaviors, is needed to fully understand the general behavior of these TM–C structures and explore the dependence of bond characteristics on *d* electrons.

In this paper, the structural characteristics and bond interactions of TM–C system were investigated by the first-principles calculation. In order to elucidate the role of valence electrons on the bond structures, we selected all 3*d* TMs from Sc to Cu as the representative TM elements. It is well known that the mechanical properties of DLC films are related with the tetra-coordinated C atoms content, and the previous study also revealed the high residual stress mainly attributed to both the bond angle and bond length distortions [19], so the tetrahedral model was used for C(TM)–C systems, and the structural evolutions with the

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http://dx.doi.org/10.1016/j.tsf.2016.04.004
0040-6090/

bond angles were evaluated by the partial density of states (PDOS), charge density distributions and molecular orbital (MO) diagrams. The obtained distinct changes in TM–C bond characteristics by comparing with that in C–C system were discussed to understand the general experimental phenomena, in which the significant reduction of residual stress was visible due to the doping of TM into amorphous carbon matrix.

2. Computational details

Fig. 1 shows the schematics of employed tetrahedral bond model, in which four carbon atoms are arranged as a tetrahedron with either a carbon or TM in the center and each peripheral carbon atom is terminated by hydrogen atoms for the sake of simplicity. This model had been proved to be satisfactory to provide a reasonable explanation for the experiments in amorphous carbon system [9,18]. All 3*d* TMs from Sc to Cu were selected particularly as the representative substitution of the central carbon atom in the tetrahedral TM-C system. The structure with a bond angle of 109.471° was chosen as a reference state (Fig. 1(a)). When the bond angle was distorted in a range of 90–130° (Fig. 1(b)), the structural relaxation could be characterized from the electronic structure and the change of total energy in TM–C system. Details of calculation model can be found in elsewhere [18], which has proved that this model is appropriate for investigating metal incorporation (or adsorption) into a carbon network even when the distorted structure is generated using a constrained relaxation.

All the spin-polarized first-principles calculations were performed by the DMol^3 software package (Accelrys Inc.) based on the density functional theory. The exchange-correlation was handled in the generalized gradient approximation with the Perdew–Burke–Ernzerhof parameterization [20], and all electrons double-numerical polarization basis was used. A self-consistent field was created using an energy convergence criterion of 10^{-5} eV, and atomic relaxation was repeated until the forces acting on the atoms were below 0.01 eV/Å. The Kohn–Sham wave functions were expanded to an orbital cutoff of 9 Å to guarantee convergence. A cubic supercell with a lateral size of 15 Å was used to avoid interactions between the adjacent images of the model.

3. Results and discussion

Fig. 2 shows the values of electron density, ρ_{max}, in the unit of electrons/Å^3 right before its isosurfaces between the central TM and the peripheral carbon atoms are spatially separated. For comparison, the characteristic of C–C system was also performed. The isosurfaces of

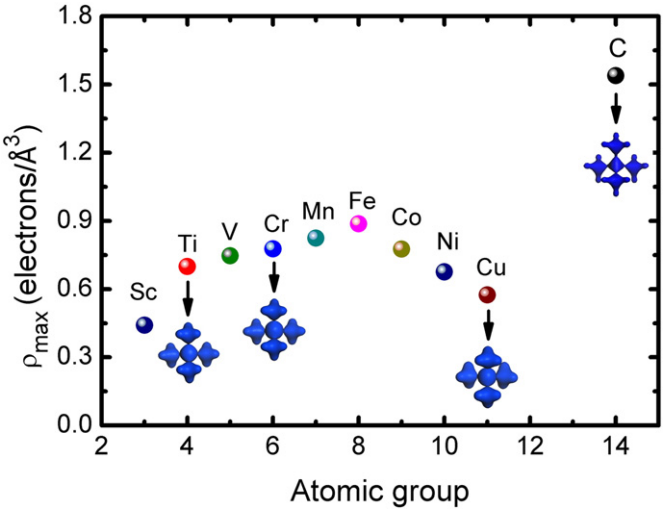

Fig. 2. Electron density before its isosurface is separated; the insets are the isosurfaces of electron density for C–C, Ti–C, Cr–C, and Cu–C systems right before the isosurfaces between the central atom and peripheral C atoms are separated.

electron density for C–C, Ti–C, Cr–C, and Cu–C systems are presented as insets of Fig.2, respectively. For C–C case, the maximal ρ_{max} of 1.5391 electrons/Å^3 and the strongest angular shape of isosurface imply the highest strength and directionality of C–C bonds. This is because the repulsive force between two carbon atoms can be counteracted by the higher electron density, which in turn drives the formation of more stable structure. On the contrary, when TM (Sc–Cu) replaces the central carbon atom in the unit, the ρ_{max} decreases significantly for each case following the increased isotropic characteristics of isosurface, indicating that both the strength and directionality of TM–C bonds are reduced. Since the structural distortion mainly arises from the distortion of both the bond angles and bond lengths, the different change of ρ_{max} with increasing the valence electrons of TMs may be one of the dominate factors for reducing the residual stress. Nevertheless, if one keeps in mind the disputed existence of stress reduction mechanism caused by various doped TM atoms in literatures [8–10, 14–17], as well as the changes, further insight into the bond characteristics and hybridization among atoms must be executed distinctly.

The bond characteristics in the system were analyzed using the PDOS for the model, the charge distribution of the highest occupied molecular orbital (HOMO) in the plane composed of the central atom and

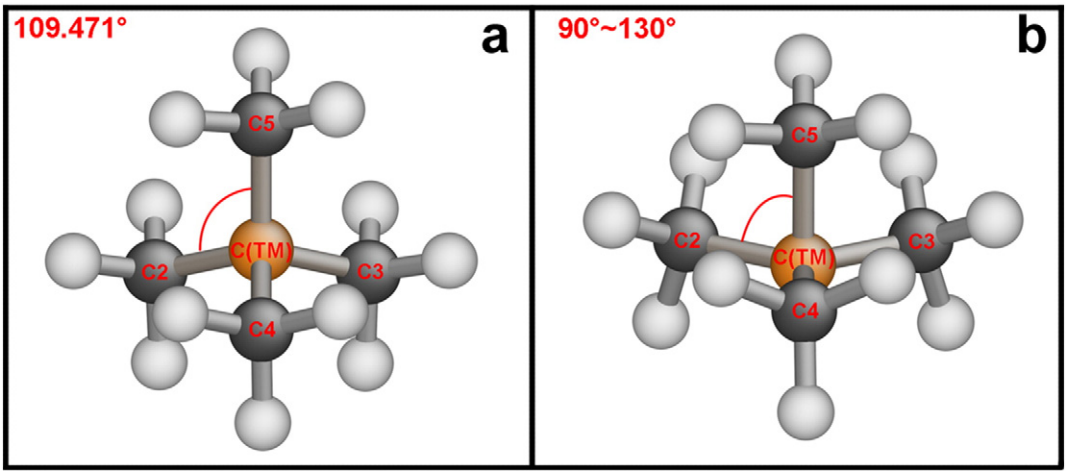

Fig. 1. (a) Reference state for the tetrahedral model with a carbon or TM atom (Sc–Cu) in the center with bond angles of 109.471°. (b) Distorted tetrahedral model where the three bond angles containing the central atom and peripheral carbon C5 were changed over the range from 90 to 130°. Black, yellow and white balls correspond to peripheral carbon, doped C(TM), and hydrogen atoms, respectively.