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Ab initio molecular dynamics simulation on stress reduction mechanism of Ti-doped diamond-like carbon films

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ABSTRACT

Structural properties of Ti-doped diamond-like carbon (DLC) films as a function of Ti concentrations (1.56–7.81 at.%) were investigated by ab initio molecular dynamics simulation to clarify the stress reduction mechanism. Results showed that with introducing Ti into DLC films, the residual compressive stress decreased firstly and then increased, which was consistent with the previous experimental results. Structural analysis revealed that the addition of Ti efficiently relaxed both the highly distorted bond angles and bond lengths, which led to the reduction of residual stress; the increase of residual stress at the high Ti concentration was attributed to the existence of distorted Ti–C structures and the increased fraction of distorted C – C bond lengths.

1. Introduction

Diamond-like carbon (DLC) films have attracted extensive interests both from scientific disciplines and industrial societies due to their unique structures and excellent mechanical, electronic, optical, as well as the magnetic properties [1–4], which make them not only used as a protective coating in various industrial applications, but also considered in the fields of solar cells, data storages, biomedical implants etc. [5–7]. However, high level of residual compressive stress formed in the deposition limits the films thickness to a few tens of nanometers and is the major drawback for their technological applications. Recently, it has been shown experimentally that an effective way to decrease the high residual stress of DLC films is the addition of a certain amount of metal elements such as Ti, Cr, W, Ni, Cu, or Ag during the growth process [8–13]. For example, doping Ti, W, or Cr into amorphous carbon matrix decreased the stress without serious deterioration of hardness because of the partly formed hard carbide nano-particulates, increased sp^2 graphitization, C-sp^3 substitution by doped transition metal atoms as well as the proposed pivot relaxation role [8,9]. It is well known that the residual stress strongly depends on the distorted atomic bonds of amorphous carbon systems. However, the addition of metal atoms brings the complexity of film structure. Especially, due to the limited experimental characterization of the atomic bond structure, the effect of doped metal atoms on the atomic bond structure from the viewpoint of atomic scale is yet to be clarified, leading to the phenomenological explanation of stress reduction mechanism.

In the present work, ab initio molecular dynamics (AIMD) simulation based on the density functional theory (DFT) was carried out to study the structure and properties of Ti-doped DLC (Ti-DLC) films. The Ti concentration was changed from 1.56 to 7.81 at.%. The radial distribution function (RDF), properties including the residual compressive stress and bulk modulus, and both the bond angle and bond length distributions were evaluated to reveal the dependence of structural properties on Ti concentrations and finally to elucidate the stress reduction mechanism. Results showed that the structural evolution was strongly dominated by the concentrations of the doped Ti atoms, which provided the explanations for the changes in the physicochemical properties of Ti-DLC films.

2. Computational details

The structural models for Ti-DLC films were generated from liquid quench by AIMD simulation, which has been demonstrated to give a good description of DLC materials and reveal the intrinsic relation between the structure and properties [14–17]. The Vienna ab initio simulation package [18,19] based on the DFT was employed for the spin-polarized calculations with a cutoff energy of 500 eV, a generalized gradient approximation with the Perdew–Burke–Ernzerhof parameterization [20], a Gaussian smearing factor of 0.05 eV and a gamma point. The periodic boundary conditions were imposed on the supercell. In this work, the initial configuration contained 64 atoms in a simple cubic supercell with constant volume throughout the simulation. To obtain Ti-doped amorphous structures, the systems were firstly equilibrated at 8000 K for 1 ps using a canonical ensemble with a Nose thermostat to become completely liquid and eliminate their correlation to the initial configurations. Then the samples were cooled down to 1 K within 0.5 ps, corresponding to a cooling rate of 1.6×10^{16} K/s. After that, geometric optimization was performed using conjugated gradient method [21], in which a self-consistent field was created using an

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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.

Five samples were obtained at each density (2.03 or 2.87 g/cm^3) with various Ti concentrations (1.56–7.81 at.%, corresponding to 1, 2, 3, 4 and 5 Ti atoms in 64-atom systems, respectively). In order to provide more representative models of the real Ti-DLC system than the direct substitution of carbon by Ti atoms in previously generated pure DLC networks, Ti atoms were introduced by substituting carbon atoms in the liquid carbon system [16]. Pure DLC films were also involved for comparison with Ti-doped ones. Before characterizing the structure and coordination number of Ti-DLC films, the RDF, g(r), in the Ti-DLC system with high Ti concentration (39 at.%) was analyzed firstly to define the Ti and C atoms being bonded or non-bonded with each other. The distance to the first minimum in RDF was set as the cutoff distance, R_{cut}, for C–C of 1.85 Å, C–Ti of 2.56 Å, or Ti–Ti of 3.51 Å [22,23].

3. Results and discussion

Fig. 1 shows the final morphologies for pure-DLC and Ti-DLC films with the Ti concentrations of 1.56, 3.13 and 7.81 at.% at 2.87 and 2.03 g/cm^3, respectively. Red spheres represent the carbon atoms while purple ones are Ti atoms. All the films are amorphous as will be described later by RDF. It is noted that comparing with the pure-DLC film at 2.87 g/cm^3, the low-density structure of pure-DLC film (2.03 g/cm^3) is looser and contains many planar chains which are weakly cross-linked; as the density changes to 2.87 from 2.03 g/cm^3, the sp^3C content increases to 56.25% from 15.62%. After the addition of Ti, the sp^3 hybridized structure with the Ti concentration increases gradually and then decreases for each case. Taking the Ti-DLC films at 2.87 g/cm^3 for example (Fig. 1a), when the Ti concentration is 3.13 at.%, the maximal sp^3C content reaches to 71.88%. This is attributed to the doped Ti atoms that could easily bond with the sp^2C atoms with low bonding energy, which agrees well with the experimental results [8]. With further increasing Ti concentration to 7.81 at.%, many highly distorted five-coordinated C atoms with the content of 14.06% are generated, causing the decrease of sp^3C content and also the existence of many distorted C–C and C–Ti atomic bond structures which would produce the high residual compressive stress.

Fig. 2 shows the RDF spectra of pure-DLC and Ti-DLC films with different Ti concentrations, in which the vertical dotted lines represent the 1st and 2nd nearest peak positions of crystalline diamond. It reveals that for each case the film exhibits the typical amorphous character that is long-range disorder and short-range order. Firstly, for pure-DLC films, the 1st C–C nearest neighbor peak with increasing the density is displaced from 1.46 Å at 2.03 g/cm^3 to 1.50 Å at 2.87 g/cm^3, which is

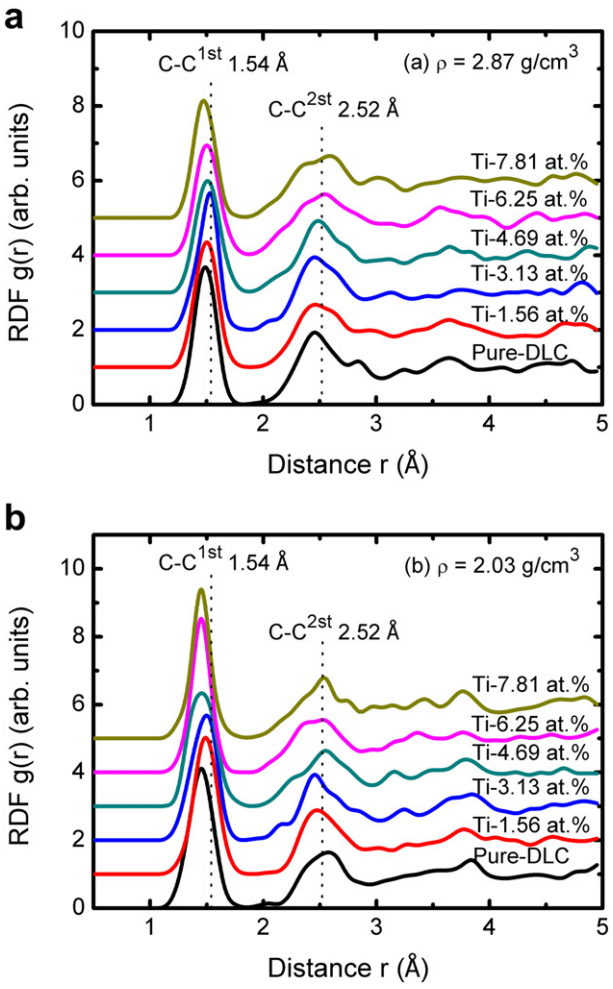

Fig. 2. RDF spectra of pure-DLC and Ti-DLC films with different Ti concentrations at densities of (a) 2.87 or (b) 2.03 g/cm^3, respectively. The vertical dotted lines represent the 1st and 2nd nearest peak positions of crystalline diamond.

well consistent with the previous experimental [24,25] and theoretical results [16], suggesting that the simulated results represent the nature of real system. In general, the 1st peak is related with the atomic bond lengths, and the 2nd peak has correlation with both the bond angles and bond lengths. However, after the addition of Ti into DLC films, the

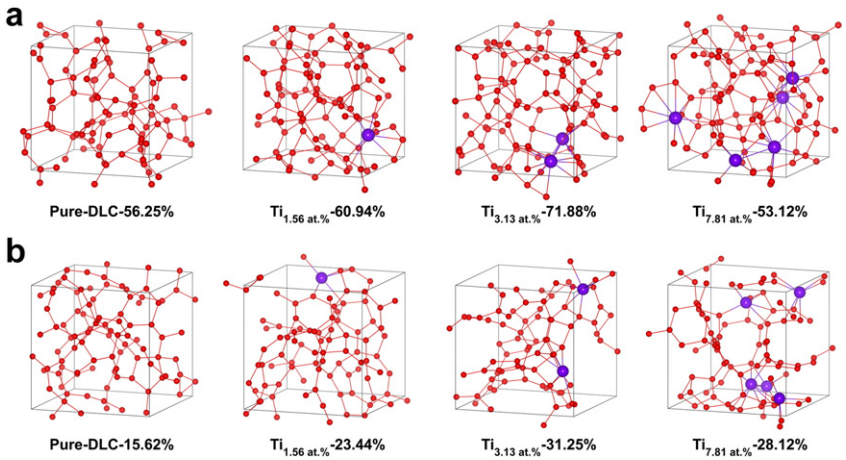

Fig. 1. Atomic structure of pure-DLC and Ti-DLC films with Ti concentrations of 1.56, 3.13, and 7.81 at.% at densities of (a) 2.87 g/cm^3 and (b) 2.03 g/cm^3, where the numbers are the sp^3C contents in each film, and red, purple colors indicate the C and Ti atoms, respectively.