Stress Control of Diamond-like Carbon Films by Metal Incorporation


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Diamond-like Carbon Film

- Amorphous Solid Carbon Film
- Mixture of (sp$^1$), sp$^2$ and sp$^3$ Hybridized Bonds
- High Content of Hydrogen (20-60%)

Properties
- High Hardness and Excellent Tribological Properties
- Smooth Surface with Optical Transparency
- Chemical Inertness and Hemo-compatibility

Heart valve
Hard disk
Major Obstacle

✓ High residual compressive stress and poor adhesion.
Hardness and Residual Stress

![Graph showing the relationship between hardness, sp³ fraction, and stress (GPa). The graph includes data points for Fallon, Weiler, Xu, and Chhowalla.](image)
Hardness and Residual Stress
Structure and Mechanical Properties

- **Hardness**
  - 3-D interlink of the atomic bond network

- **Residual Stress**
  - Distortion of bond angle and length

- Both are dependent on the degree of 3-D interlinks.

2-D Analogy of the Structure
Si/ ta-C

Si atoms substitute the carbon atoms of sp³ site.

Ti-/ a-C:H

Percolation structure transition from a-C:H like to TiC like occurs.

Me/ a-C:H

Increase in sp² site and fraction release stress.

References:
Me-DLC nanocomposite films

Refractory phases: nc-TiN, TiC, WC ...

Primary phases: a-C, C:H, Si₃N₄...

Hardness, thermal stability, friction behavior, no grain boundary sliding, no dislocations activity, strong interface, strong segregation (immiscibility).

Origin of stress reduction with Me incorporation is still disputable due to the difference in the deposition parameter and used metal.
W incorporated DLC

Deposition parameters

- **Working gas:** $\text{Ar} + \text{C}_6\text{H}_6$ (total: 12sccm)
- **Base pressure:** $2.0 \times 10^{-6}$ Torr
- **Substrate bias:** -200 V
- **Power density of target:** 4.2~7.3 W/cm$^2$
- **Deposition Pressure:** $0.6 \sim 1 \times 10^{-4}$ Torr
- **Thickness:** 350±50nm
- **Substrate:** P-type Si(100), 500µm, 100µm
- **Deposition temperature:** < 200°C
Composition of the Deposited Film

![Graphs showing the variation of W and H concentrations with Ar fraction in gas mixture.](image)

- **Energy (MeV)**
  - Si in substrate
  - C
  - Ar
  - W

- **W concentration (at. %)**
  - 0.55 0.60 0.65 0.70 0.75 0.80 0.85 0.90 0.95
  - 0 1 2 3 4 5

- **H concentration (at. %)**
  - 38.2 33.7 32.8 31.4 30.2
  - -0.1 0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9

- **Ar fraction in gas mixture**
  - 0.55 0.60 0.65 0.70 0.75 0.80 0.85 0.90 0.95
  - 0 5 10 15 20 25 30 35 40

- **Normalized Yield**
  - Channel
Stress & Mechanical properties

(a) Residual stress (GPa) vs. W concentration (at.%) plot showing a minimum at around 4 at.%. The error bars indicate the variability in the measurements.

(b) Hardness (GPa) and Elastic modulus (GPa) vs. W concentration (at.%) plot. The hardness reaches a peak at about 3 at.%, with a value of 21 ± 3 GPa. The elastic modulus peak is at around 10 at.%, with a value of 170 ± 15 GPa.
TEM Microstructures

W atoms are dissolved in a-C:H matrix.

Amorphous to crystalline WC\textsubscript{1-x} transition occurs.

Nano-crystalline α-W\textsubscript{2}C phases evolve.

Residual stress (GPa) vs. W concentration (at.%) graph.
TEM Microstructures

(a) α-W2C (101) 1.9 at.%
(b) α-W2C (102) 2.8 at.%
(c) α-W2C (101) 3.6 at.%
(d) α-W2C (101) 8.6 at.%
GI XRD

Intensity (a.u.)

\(\alpha\)-W\(_2\)C

Residual stress (GPa)

W concentration (at.%)
Raman & EELS Spectra

(a) Intensity (a.u.) vs. Wave number (cm$^{-1}$)

(b) Normalized Intensity (a.u.) vs. Energy (eV)

$W_{1.9 \text{ at.\%}}$

$W_{2.8 \text{ at.\%}}$

$W_{3.6 \text{ at.\%}}$

$W_{4.7 \text{ at.\%}}$

$W_{6.0 \text{ at.\%}}$

$W_{8.6 \text{ at.\%}}$

$\pi^*$

$\sigma^*$

$I_{\pi}/I_{\sigma} = 0.55 \pm 0.1$
W atoms are dissolved in a-C:H matrix. Amorphous to crystalline WC$_{1-x}$ transition occurs. Nano-crystalline α-W$_2$C phases evolve.
Role of W atoms - ab initio calculation
Iso-\(e^\text{-}\) density surface

C–C

W–C
Total energy vs. the bond angle distortion

\[ \Delta E_{90^\circ} \text{ (eV)} \]

atomic group (# of valence e\(^{-}\))

- 2nd period
- 3rd period
- 4th period
- 5th period
- 6th period
Total energy vs. the bond angle distortion

\[ \Delta E_{90^\circ} (\text{eV}) \]

atomic group (# of valence e\(^-\))
<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Al</th>
<th>Mo</th>
<th>Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>atomic #</td>
<td>6</td>
<td>13</td>
<td>42</td>
<td>47</td>
</tr>
<tr>
<td>e- configuration</td>
<td>$2s^2 \ 2p^2$</td>
<td>$3s^2 \ 3p^1$</td>
<td>$4d^5 \ 5s^1$</td>
<td>$4d^{10} \ 5s^1$</td>
</tr>
<tr>
<td>$\Delta E_{90^{\circ}}$ (VASP) (eV)</td>
<td>1.85</td>
<td>-0.19</td>
<td>0.46</td>
<td>0.30</td>
</tr>
<tr>
<td>$\Delta E_{90^{\circ}}$ (DMol$^3$) (eV)</td>
<td>1.88</td>
<td>-0.20</td>
<td>0.64</td>
<td>0.20</td>
</tr>
</tbody>
</table>
Charge density of HOMO & PDOS

C
\[ \rho_{\text{Max}} = 1.05 \]

Al
\[ \rho_{\text{Max}} = 0.69 \]

Mo
\[ \rho_{\text{Max}} = 0.69 \]

Ag
\[ \rho_{\text{Max}} = 0.63 \]

- \( \rho_{\text{Max}} \) values indicate the maximum charge density.
- \( d \) values represent distances in Å.
- PDOS ( states/eV/atom ) graphs show the energy levels and states per atom.
- Labels such as covalent, ionic, nonbonding, antibonding provide insight into electronic configurations.

PDOS (states/eV/atom)

Energy (eV)

Corner

Center
Charge density of HOMO & PDOS

**C**
- $\rho_{\text{Max}}=1.05$
- $d=1.54$
- $p_x, p_y, p_z$

**Al**
- $\rho_{\text{Max}}=0.69$
- $d=2.05$
- $p_x, p_y, p_z$

**Mo**
- $\rho_{\text{Max}}=0.69$
- $d=2.10$
- $d_{xy}, d_{yz}, d_{xz}$

**Ag**
- $\rho_{\text{Max}}=0.63$
- $d=2.27$
- All $p$ & all $d$

**PDOS (states/eV/atom)**

**Energy (eV)**

Covalent

Ionic

Nonbonding

Antibonding
**Charge density of HOMO & PDOS**

- **C**(\(\rho_{\text{Max}}=1.05\))
  - \(\rho_{\text{Max}}=0.69\)
  - \(d=1.54\)
- **Al**(\(\rho_{\text{Max}}=0.69\))
  - \(\rho_{\text{Max}}=0.69\)
  - \(d=2.05\)
- **Mo**(\(\rho_{\text{Max}}=0.69\))
  - \(d=2.10\)
- **Ag**(\(\rho_{\text{Max}}=0.63\))
  - \(d=2.27\)

- \(p_x, p_y, p_z\)
- \(\rho_{\text{Max}}\)
- \(\rho_{\text{Max}}\)

- **PDOS (states/eV/atom)**
  - **Energy (eV)**
  - **PDOS (states/eV/atom)**
  - **PDOS (states/eV/atom)**
  - **PDOS (states/eV/atom)**

- **Corner**
- **Center**

- **Covalent**
- **Ionic**
- **Nonbonding**
- **Antibonding**
Charge density of HOMO

C
Max: 1.05
Z: 4
p_x, p_y, p_z

Al
Max: 0.69
p_x, p_y, p_z

Mo
Max: 0.69
d_{xy}, d_{yz}, d_{xz}

Ag
Max: 0.63
all p & all d

px, py

HOMO
Max: 0.62
d = 2.59

Max: 0.63
d = 1.99

Max: 1.05
d = 1.54

Max: 0.69
d = 2.05

Max: 0.69
d = 2.10

Max: 0.63
d = 2.27
Experimental Results: Al

Ag Incorporated DLC

![Graph showing compressive stress vs. Ag concentration (at.%)](image)

- Compressive Stress (GPa) vs. Ag Conc. (at.%)
Conclusions

• Incorporation of small amount of metal (<2 at.%) in amorphous carbon network is effective to control the residual stress of DLC films.
  – Pivotal action of the metal atoms due to the reduction in the directionality of the metal-carbon bond.

• *Ab initio* calculations revealed the characteristics of the metal-carbon bonds, which enables us to predict the changes in the residual stress and the mechanical properties with metal incorporation.