Quantifying the protective properties and adhesion to the substrate of ultra-thin multi-layer diamond-like carbon coatings using molecular dynamics simulation

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Introduction: DLC coatings

- Diamond-like carbon (DLC) coatings protect substrate materials from contact with other bodies to avoid
  - Damage
  - Wear
  - Corrosion

- DLC has excellent protective properties:
  - High hardness
  - Low coefficient of friction with many materials
  - Chemical stability in many environments
Introduction: Applications and challenges

- DLC coatings are used as a protective coating in a variety of applications
  - Hard disk drives (HDDs)
  - Razors
  - Automotive engine pistons
  - MEMS/NEMS devices
  - Medical implants

Challenges:
- DLC coatings display poor adhesion to many substrate materials
- Difficult to quantify deformation and delamination when coatings are less than several nanometers thick

Research objective

• Lack of knowledge about deformation of ultra-thin coatings inhibits improving adhesion of DLC coatings to substrates within given design constraints.

The research objective is to test the hypothesis that the protective properties of ultra-thin DLC coatings, including their ability to prevent plastic deformation of the substrate and their adhesion to the substrate, can be improved by tuning the design parameters of a multi-layer DLC coating.

• DLC coating design parameters:
  – Thickness
  – Composition
  – Number of layers
  – $sp^3$ fraction of DLC layer

• To achieve our research objective, we will:
  – Quantify mechanical properties of the coating
  – Quantify plastic deformation during combined normal and tangential loading of the coating
  – Quantify adhesion of the coating to the substrate

As a function of coating design parameters
Outline

• Introduction
• Objective
• Background
  – DLC and DLC coatings
  – DLC coatings in hard disk drives
  – Previous work to improve adhesion of DLC coatings
  – Molecular dynamics
• Simulation model
  – MD model
  – Overview of simulation procedures
• Results
  – Nanoindentation simulations
  – Combined loading simulations
  – Nanoscratch, simple shear, and simple tension simulations
• Conclusions
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Background: Diamond-like carbon (DLC)

- Amorphous form of carbon
- Atomic structure primarily $sp^3$- and $sp^2$-bonded carbon atoms

- Properties depend on fraction of $sp^3$- and $sp^2$-bonded carbon atoms
- $sp^3$ and $sp^2$ fraction controlled through coating deposition process parameters
- Properties range between those of diamond ($sp^3$) and graphite ($sp^2$)
  - Both have mechanical properties desirable for protective coatings
  - Tunable values for hardness, friction coefficient, chemical resistance
Poor adhesion between DLC and many substrates
  - Amorphous structure leads to high residual compressive stress
  - Diamond-like chemical resistance prevents bonding to substrate materials

These challenges can be overcome by:

Use of multi-layer coatings:
  - Does not change the intrinsic mechanical properties of DLC itself
  - Does not damage nanostructures on/in the substrate
Background: DLC coatings in HDDs

- Multi-layer DLC coatings in hard disk drives (HDDs)
  - Protect against accidental contact between the recording head and magnetic disk
  - Protect magnetic materials from corrosion
  - a-Si layer improves adhesion between DLC and substrate

- To increase data storage density of HDDs, the magnetic spacing is decreased
  - Requires a decrease in thickness of the DLC coatings
  - DLC coatings in current HDDs are less than 2 nm thick

Source: [1] https://commons.wikimedia.org/wiki/File:01b-hard-drive-cover-removed.JPG
Nanoindentation measures micro- and nanoscale hardness \((H)\) and Young’s modulus \((E)\) of DLC coatings

- Without substrate deformation: \(H\) and \(E\) of DLC coating
- With substrate deformation: \(H\) and \(E\) affected by substrate and change as a function of indentation depth

It is difficult to prevent substrate deformation when DLC coatings are on the order of several nm thick

Understanding how deformation of both coating and substrate affects \(H\) and \(E\) is critical to the design of ultra-thin, multi-layer DLC coatings
Background: Measuring adhesion of DLC

- Nanoscratch experiment measures adhesion between ultra-thin DLC coatings and the substrate

- Coating degradation or failure:
  - Wear of the coating
  - Cracking or fracture of the coating
  - Delamination of the coating from the substrate

Understanding how deformation of each material layer affects delamination is critical to the design of ultra-thin multi-layer DLC coatings
Background: Molecular dynamics (MD)

• Molecular dynamics (MD) supplements experiments of ultra-thin coatings
  – Describe deformation of the coating and substrate due to external loading
  – Simulate separation of a coating from the substrate

• MD approach
  – Atoms modeled as rigid particles
  – Atomic interactions modeled using potential energy functions

  Atomic interactions

  Each atomic interaction is calculated using the potential energy function

  Potential energy, $U$ [eV]

  Interatomic distance, $r$ [Å]

  – Forces on each atom determined from the derivative of the potential energy functions
  – Dynamics obtained by numerically integrating Newton’s equations of motion, yielding the trajectory of each particle as a function of time, taking into account boundary conditions
Background: MD nanoindentation of DLC

• Previous studies that model nanoindentation of DLC or multi-layer coatings:

  Mechanical properties of single-layer DLC coatings

  Change in atomic structure of single-layer DLC coatings

  Deformation of multi-layer metallic coatings

  Limitations:
  - Single-layer DLC coating
  - No substrate deformation

  Limitations:
  - Single-layer DLC coating
  - No substrate deformation
  - Do not model effect of coating thickness

  Limitations:
  - Crystalline materials, not DLC
  - Small hardness mismatch between layers

• No MD simulations that quantify plastic deformation of multi-layer DLC coatings

• Critical for understanding effect of DLC coating design parameters on $H$ and $E$

Previous studies that model combined normal and tangential loading of DLC

Limitations:
- No substrate deformation
- Single-layer DLC coatings only

Limitations:
- Focus on friction or graphitization, not delamination
- Adhesion with counterface, not substrate

No MD simulations that quantify adhesion of multi-layer DLC coatings

Critical for understanding the effect of substrate deformation on adhesion of the coating when designing ultra-thin multi-layer DLC coatings

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MD model of recording head

- We use MD to create an atomistic model of an HDD recording head
- We model only a portion of the recording head
  - Wear is observed experimentally at the top pole of the recording head [1]
  - Soft magnetic (NiFe) substrate susceptible to plastic deformation, corrosion

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Simulation procedures

- **Nanoindentation**
  - Mechanical properties of coating
  - Plastic deformation of coating and substrate

- **Combined loading**
  - Plastic deformation of coating and substrate

- **Nanoscratch**
  - Plastic deformation of coating and substrate
  - Adhesion of coating to substrate

- **Simple tension**
  - Adhesion of coating to substrate

- **Simple shear**
  - Adhesion of coating to substrate

Effect of coating design parameters
- Coating layer thickness
- Coating layer composition
- Number of layers
- $sp^3$ fraction of DLC layer
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MD nanoindentation simulations

• MD nanoindentation simulations of multi-layer DLC coatings with different coating design parameters:

  - Indenter tip
  - HDD recording head

• Anticipated outcomes:
  - Understand how mechanical properties of multi-layer DLC coatings change as a function of coating design parameters
  - Understand how resistance to plastic deformation of the coating and substrate due to normal loading changes as a function of coating design parameters
Nanoindentation: Procedure

- Nanoindentation procedure described by Oliver and Pharr [1]
  - Repeated loading and unloading of a hard indenter tip into the DLC coating
  - Monitor the force as a function of indentation depth
  - Modified to decrease computational requirements [2]

- Simulations with constant:
  - Indentation depth
  - Indentation energy

Nanoindentation: Determining $H$ and $E$

- Determine $H$ and $E$ using force $P$ versus indentation depth $h$ curves

- From the $P-h$ curves:
  - Maximum load $P_{\text{max}}$
  - Unloading stiffness $S$
  - Contact depth $h_c$ [1]
  - Contact area $A$

- Hardness and Young’s modulus calculated as:
  - $H = P_{\text{max}} / A$
  - $E = (S/2) \cdot (\pi/A)^{1/2}$

Nanoindentation: Quantify plastic deformation

- Quantify plastic deformation using following metrics:
  - Atomic displacement
  - Potential energy per atom
  - Change in volume per atom
  - Change in number of bonds
  - Change in bond length and bond angle

- Reduce uncertainty due to thermal vibration of atoms
  - Time averaging: mean deformation over sequential simulation time steps
  - Spatial averaging: discretize the simulation box into grid elements
Nanoindentation results: $H$ and $E$

- Coatings of constant thickness $t_1 + t_2 = 21$ Å:
  - $H$ and $E$ increase with increasing $t_C$ and decreasing $t_{Si}$
    - DLC hardest of the three materials comprising coating and substrate
    - Si softest of the three materials comprising coating and substrate
  - $H$ and $E$ approach that of Ni with increasing indentation depth
Nanoindentation results: DLC layer deformation

- Plastic deformation of each coating layer
  - Effect of $t_1$ and $t_2$ on plastic deformation of coating layers
  - Fraction of each material layer permanently displaced: $f_C, f_{Si},$ and $f_{Ni}$

  \[
  f_C \text{ increases with increasing indentation depth}
  \]
  \[
  f_C \text{ increases with decreasing } t_1 \text{ because } H \text{ decreases with decreasing } t_1
  \]
Nanoindentation results: Ni and Si layer deformation

- $f_{Si}$ and $f_{Ni}$ are independent of $t_I$ over range of parameters investigated
- $t_I$ affects deformation of DLC layer but not substrate

For constant total coating thickness budget, increasing the fraction of the coating comprised of DLC will decrease plastic deformation of the coating
Effect of coating composition on \( H \) and \( E \) of the multi-layer coating
- Vary the \( sp^3 \) fraction of the DLC layer
- Constant indentation energy \( e_{ind} = 2700 \text{ eV} \) and coating thickness \( t_1 + t_2 = 21 \text{ Å} \)

\[ \begin{align*}
\text{Hardness, } H \ [\text{GPa}] & \quad \begin{array}{c}
\text{30} \\
\text{40} \\
\text{50} \\
\text{60}
\end{array} \\
\text{Youngs modulus, } E \ [\text{GPa}] & \quad \begin{array}{c}
\text{30} \\
\text{100} \\
\text{200} \\
\text{300}
\end{array}
\end{align*} \]

- \( H \) and \( E \) of the multi-layer coating increase then decrease with increasing DLC \( sp^3 \) fraction
- \( H \) and \( E \) of bulk DLC increase monotonically with increasing \( sp^3 \) fraction [1]

Nanoindentation results: Hardness mismatch

- Mismatch between $H$ and $E$ of DLC layer and the Si and Ni layers
  - Mismatch increases with increasing DLC $sp^3$ fraction
  - Plastic deformation is increasingly preferential to the Si and Ni layers
- The hard DLC layer bends into the plastically-deformed substrate

### Local plastic strain after indentation

<table>
<thead>
<tr>
<th>Strain [Å/Å]</th>
<th>$t_1 = 12$ Å, $t_2 = 9$ Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.015</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>0.0075</td>
</tr>
<tr>
<td>0.015</td>
<td>0.015</td>
</tr>
</tbody>
</table>

-0.015 to 0.015

- Bending of DLC layer indicated by regions of tensile and compressive strain
- Plastic strain in DLC and Si layers concentrated under the indenter
- Increase in plastic strain in the Si layer and Ni substrate

**Hardness mismatch between coating layers, and not coating hardness alone, must be considered when designing multi-layer DLC coatings**
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MD combined loading simulations

- MD simulations of combined normal and tangential loading of multi-layer DLC coatings with different coating design parameters:

- **Anticipated outcome:** Understand how coating design parameters affect resistance to plastic deformation of the coating and substrate due to combined normal and tangential loading.
Combined loading procedure

- 5-step combined loading simulation procedure:
  - Monitor the number of bonds throughout the simulation
    - Atomic bonds implicitly modeled by many-body potentials
    - Two atoms bonded when distance between them is less than cutoff
  - Bond cutoff values:
    - C-C: 1.91 Å
    - Si-C: 2.31 Å
    - Si-Si: 2.91 Å
    - Ni-Si: 2.75 Å
    - Ni-Ni: 2.97 Å
  - Combined normal (N) and tangential (T) loading

Rigid, hydrogen-terminated diamond counterface

Red: hydrogen atom
Black: carbon atom (diamond)
Combined loading results: Number of atomic bonds

- Number of bonds of each type throughout the simulation:

![Graph showing the normalized number of bonds over time for different bond types](image)

Simulation parameters:
- \( t_1 = 9 \) Å, 70% \( sp^3 \) ta-C
- \( t_2 = 3 \) Å, \( p_c = 48 \) GPa
- \( T = 25^\circ C \), \( v_x = 75 \) m/s

- Deformation during loading
  - Deformation of all bond types
  - Negligible in the DLC layer

- Plastic deformation
  - In Si layer, at Ni-Si and Si-C interfaces
  - Negligible plastic deformation in Ni and DLC layers
Combined loading results: Atomic bond types

- **Resistance to plastic deformation**
  - The strength of a bond decreases with decreasing cohesive energy
  - Crystal lattices more resistant to permanent deformation than amorphous structures [1]

<table>
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<tr>
<th>Bond type</th>
<th>Cohesive energy [eV]</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Ni</td>
<td>4.44</td>
<td>fcc</td>
</tr>
<tr>
<td>Ni-Si</td>
<td>5.51</td>
<td>amorphous</td>
</tr>
<tr>
<td>Si-Si</td>
<td>4.63</td>
<td>amorphous</td>
</tr>
<tr>
<td>Si-C</td>
<td>6.47</td>
<td>amorphous</td>
</tr>
<tr>
<td>C-C</td>
<td>7.84</td>
<td>amorphous</td>
</tr>
</tbody>
</table>

Combined loading results: Plastic deformation

- No effect of $t_1$ or $t_2$ for range of parameters investigated
- Net increase in Ni-Si and Si-Si bonds due to combined normal and tangential loading
- Net decrease of Si-C bonds in some cases
- Confinement of coating atoms under compressions prevents large loss of bonds or separation of material layers
- Difficult to draw conclusions about delamination

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MD nanoscratch simulations

- MD nanoscratch simulations of multi-layer DLC coatings with different coating design parameters:

  * Anticipated outcomes:
    - Understand how resistance to plastic deformation of the coating and substrate due to combined normal and tangential loading changes as a function of coating design parameters
    - Understand how coating adhesion to the substrate changes as a function of coating design parameters
MD simple shear and tension simulations

- Delamination of coating from substrate does not occur after a single scratch
- MD simulations of simple shear and tension of multi-layer DLC coatings with different coating design parameters:

  - **Anticipated outcome:** Understand how coating adhesion to the substrate changes as a function of coating design parameters by modeling separation of coating from substrate
Quantifying adhesion: Procedures

- Nanoscratch procedure consists of the following steps:

- Simple shear and tension procedures each consist of one step:
Different combinations of coating and substrate materials used for:

- Nanoscratch simulations
- Simple shear and tension simulations

We quantify adhesion using the following sequence of simulations:

- Create coating
- Scratch
- Simple shear
- Simple tension

Different combinations of coating and substrate materials include:

- ta-C
- a-Si
- Ni
- ta-C
- a-C
- Ni
- ta-C
- a-C
- Si

ta-C: 70% $sp^3$ fraction DLC
a-C: 30% $sp^3$ fraction DLC
We quantify adhesion as the force to separate the coating from the substrate. Force required to separate the coating is higher in tension than in shear. Negligible effect of DLC layer $sp^3$ fraction. Coatings without a-Si layer are much weaker than coatings with a-Si layer. Optimum a-Si layer thickness $t_2 = 3$ Å over range of parameters investigated.
Quantifying adhesion: Effect of a-Si layer

- The presence of a-Si prevents distortion of the Ni lattice
- Energy, volume, and bond length near interface closer to equilibrium values when a-Si is present
- Ni and Si form Ni$_3$Si, a FCC material with similar lattice constant to Ni
Quantifying adhesion: Optimum a-Si thickness

- An optimum a-Si layer thickness exists
  - For thinnest a-Si coatings, the region of shear failure is thicker than the a-Si layer
  - Failure occurs partially in the Ni substrate

- When $t_{Si} \geq 6$ Å, critical shear region is entirely in a-Si layer
- When $t_{Si} = 3$ Å, critical shear region occurs in a-Si layer and Ni substrate
- When $t_{Si} = 0$ Å, critical shear region occurs in distorted Ni lattice
Quantifying adhesion: ta-C/a-C coatings

- Previous experimental results: a-C improves adhesion of ta-C coatings to Si substrates [1,2]
- We replace a-Si layer with a-C to evaluate adhesion of ta-C/a-C coatings on Ni and Si substrates:

  - We observe improved adhesion to Si but not Ni substrates in shear
  - Negligible effect on adhesion in tension

Quantifying adhesion: Effect of atomic structure

• **Bond density indication of local atomic structure**
  – Less mismatch between Ni and ta-C than between Ni and a-C
  – Less mismatch between Si and a-C than between Si and ta-C

• **Bond length indication of local strain**
  – Ni-Ni and Ni-C bond length deviation increases with increasing a-C layer thickness
  – Si-Si and Si-C bond length deviation decreases with increasing a-C layer thickness

• Use of intermediate a-C layer improves adhesion to Si but not Ni substrates
Quantifying adhesion: Weakening due to scratch

- Intermediate layer protects substrate from plastic deformation
  - ta-C/a-Si coatings and ta-C/a-C coatings
  - Ni and Si substrates

- Plastic deformation of coating prevents damage that leads to delamination
  - Weakening due to scratch decreases with increasing intermediate layer thickness
  - Softest coating (a-C/a-Si) shows no weakening over the range of parameters investigated

- To reduce delamination, coating design should account for intrinsic adhesion between material layers and the protective properties of the coating
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• *H* and *E* of ultra-thin multi-layer DLC coatings:
  – Increase with increasing \( t_1 \)
  – Increase with decreasing \( t_2 \)
  – Approach *H* and *E* of the substrate with increasing indentation depth
  – Depend on the hardness mismatch between the layers

• Prevent plastic deformation of substrate:
  – Decreasing plastic deformation of substrate with increasing \( t_2 \), decreasing \( t_1 \)
  – Increasing plastic deformation of multi-layer DLC coating with increasing \( t_2 \), decreasing \( t_1 \)

• Improve adhesion of coating to substrate:
  – Intermediate a-Si layer critical for adhesion of ta-C to Ni substrates
  – Optimum a-Si layer forces failure region into undistorted Ni substrate
  – Intermediate a-C layer improves adhesion of ta-C to Si but not Ni substrates
  – Damage that leads to delamination decreases with increasing \( t_2 \), independent of coating and substrate composition for the materials investigated
List of publications

• Journal publications (2 published, 1 under review):

• Conference proceedings (4 published):

• Awards:
  – ASME Information storage and processing systems (ISPS) conference: Tribology, Head/Media Interface Track Best Paper Award, 2014
Questions?

Tan: 2 nearest neighbors

176 Å

C (amorphous)
Si (amorphous)
Ni (fcc)