Nanomechanical testing of renewable and sustainable energy related materials for improved performance

Nadimul H. Faisal\textsuperscript{1}, Saurav Goel\textsuperscript{2}, Ben D. Beake\textsuperscript{3}
\textsuperscript{1}School of Engineering, Robert Gordon University, Aberdeen
\textsuperscript{2}School of Aerospace, Transport and Manufacturing, Cranfield University, Cranfield
\textsuperscript{3}Micro Materials Ltd, Wrexham & University of Leeds

In photo: Honorable Prime Minister of India highlighting the potential of solar energy in India, especially Gujarat

No part of this slide pack should be used or distributed without prior consent
Renewable Energy News feed in past 24 hours (31 July 2016)

Potential work: Radioactive ionizing radiation and structural health of photovoltaic solar cells
Presentation Scheme

1. Renewable & Sustainable Energy Related Materials
2. Manufacturability & Tribology
3. Contact Mechanics
4. Nanomechanical Measurements
5. Measurements in DLC and Si
6. Summary

Renewable & Sustainable Energy Related Materials

a. MATERIALS for renewable energy storage and conversion
   Batteries
   Supercapacitors
   **Fuel cells** (one example on SOFC)
   Hydrogen storage
   **Photovoltaics and solar cells** (examples on Si, DLC/Si)

b. MATERIALS for renewable and sustainable fuel production
   Hydrogen production and fuel generation from renewables (catalysis)
   Solar-driven reactions to hydrogen and fuels from renewables (photocatalysis)
   Biofuels
   Carbon dioxide sequestration and conversion

c. MATERIALS for energy saving
   Thermoelectrics
   Novel illumination sources for efficient lighting
   Energy saving in buildings

Ref: Materials for Renewable and Sustainable Energy [Journal, Springer]
Solar Power

Photovoltaic
- Thin Film
- Flat Panel
- Concentrated
  - Lenses
  - Mirrors

Solar Power

Courtesy: Dr Saurav Goel, Cranfield University
Silicon is the basic material in the micro- and nanoelectronics, and photovoltaic industry.

Because of the high refractive index of a single crystal silicon (n = 3.5), a significant portion of a solar radiation is reflected from the surface of the photovoltaic converter (reflectance value may be greater than 35 %) and, as a consequence, this does not contribute to the carrier pair generation process.

Therefore, the creation of the anti-reflective coatings is important.

One of these materials is the porous silicon (por-S), formed on the surface of a monocrystalline silicon (c-Si).

Seeing that the porous silicon is degradable, it is reasonable to use the protective films and coatings that do not negate the effectiveness of the solar energy conversion.
Silicon: micro- and nanoelectronics, and photovoltaic industry

- The SiO2, TiO2, silicon nitride (SiNx) and boron nitride (BNx) films which are good anti-reflective coatings for solar cells because of their spectral stability, high strength and sufficiently wide bandgap are used as the materials with low reflection.
- The promising protective materials are diamond-like carbon films (DLC).
- DLC effectively absorb the ultraviolet radiation, have a low infrared (IR) absorption, they are transparent to visible light and have the chemical inertness.
- Provide hardening of the functional layers of the porous silicon, significantly increasing the limit of fragility and fracture of toughness at the contact effects, and increase the radiation resistance of silicon also.
- Usage of the porous silicon structures with the diamond-like coatings (DLC) can be one of the methods to increase the efficiency and protection of the silicon solar cells.

Diamond-like Carbon (DLC) films as protective and anti-reflecting coating for silicon solar cells

- **DLC films**: high hardness, chemical and radiation stability, and the possibility to change their optical properties under the variation of deposition conditions.

- **Variation of deposition conditions**: Allows formation of multi-layer anti-reflection and protective coatings for solar cells just during the same technological process.

- It enables to avoid deposition of different antireflection layers, such as, for example, \( \text{SiO}_2, \text{Si}_3\text{N}_4, \text{SiN:}H, \text{ZnO}, \text{ZnS}, \text{MgF}_2 \), etc.
Manufacturability (Silicon surface)

(a) analytical model (2D representation of the 3D condition showing nose radius of the tool)

Chip thickness = R - \sqrt{R^2 + f^2 - 2fRd - d^2}

W: Width of cut, W_d: ductile width of the chip, f: feed rate, R: tool nose radius and y_c: critical damage depth, a_0: Depth of cut

Ref: (a) Scattergood et al. (b) Kovalchenko et al. (c) Goel et al.

(c) MD model (2D model showing cutting edge radius)

Ref: Blake and Scattergood, Faisal et al., International Materials Reviews, 2011

Courtesy: Dr Saurav Goel, Cranfield University
The mechanism of nanoindentation film failure for **conical indenter** can be summarised in three stages:

- **Stage 1:** Forward depth increase leading to plastic deformation in the thin film and substrate
- **Stage 2:** Mismatch in the interfacial strain leading to thin film delamination from the substrate
- **Stage 3:** Depth decreases due to backward depth deviation in the delaminated thin film

Nanomechanical Measurement

Instrumented Indentation Testing?

- **COMMERCIALY AVAILABLE (Nanoindentation)**
  An indentation machine which can measure
  - Indentation Load \( P \) & Depth \( h \) during loading, holding & unloading stage
  - Hardness, Elastic Modulus

\[
S(\delta) = \frac{2}{\pi} E_r \sqrt{A(\delta)}
\]

\[
\frac{1}{E_r} = \left(1 - \nu_r^2\right) + \left(1 - \nu_i^2\right) E_i
\]

\[
A(\delta) = C_1 \delta^2 + C_2 \delta^3 + C_3 \delta^4 + \ldots
\]

- Nanoindentation
- Nanoimpact
- Nanoscratch

One of the most cited paper in Materials Science

Indicative of the stiffness \( S \) of contact (Oliver-Pharr method, JMR, 1992, 7, pp. 1564-1583)
Understanding material response using $P-h$ curve

Nanoindentation

(a) Elastic solid

(b) Fused silica

(c) Steel

(d) Crystalline silicon

(e) Sapphire

(f) Polymer

Faisal et al., Materials Science and Technology, 28(9-10), 2012, p. 1186-1197

Faisal et al., WIT Transactions on Engineering Sciences, Tribology and Design II, 76, 2012

Faisal and Ahmed, Recent Patents on Mechanical Engineering, 4(2), 2011, p. 138-152

Source: Anthony C. Fischer-Cripps, Nanoindentation, 2002, Springer
The loading and unloading cycles for nanoindentation tests involved linearly loading the specimen to full load in 10 sec, holding at full load for 5 sec, and then releasing to 30% of the test load in 10 sec.

Source: www.micromaterials.co.uk
Nanoscratch

Conventional wear testing
• ex situ analysis
• multi-asperity contact
• No direct access to real contact pressure

Benefits of nano/microtribology:
• Single asperity contact – to simulate single abrasive machining events
• More control and direct access to mean contact pressure

Possible to directly study:
• Onset of wear
• Fundamentals of friction
• Evolution of contact pressure and friction in a wear test
• Surface roughness effects
• Correlation with micro-structure

Courtesy: Prof Ben Beake, Micro Materials Ltd.

Ref: Kathy Wahl and Greg Sawyer, MRS Bull.
Measurements in DLC thin film on Si wafer

**SPECIMEN DETAILS**
- DLC film of 100 nm thickness deposited on Si wafer using sputtering of graphite target in pure argon (Ar) atmosphere without intentional substrate heating.
- Substrate-to-target distance = 100 mm,
- Argon gas flow rate = 15 sccm, pressure = 5 mTorr.
- Base pressure of the chamber = $2 \times 10^{-3}$ mTorr.
- RF plasma power = 150 W.
- Deposition rate = 12.5 nm/min

---

**Pre-existing residual stress** -874±120 MPa
Curvature method (Stoney’s equation)

DLC films range from -500 MPa to -12.5 GPa.


**Nanoindentation results:**
- Film hardness 12.5±0.3 GPa
- Elastic modulus 153±4 GPa

---

DLC Coating

-- Causes the instability of the film
-- Affects the physical properties

Jin-Won Chung, Comparison of Elastic Modulus of Very Thin DLC Films Deposited by r.f.-PACVD and FVA, KIST
Measurements in DLC thin film on Si wafer

Table 2. Summary of P-h profile (Berkovich indenter)

<table>
<thead>
<tr>
<th>Sl. no.</th>
<th>Indentation load range</th>
<th>Total no. of cycles at each load range</th>
<th>Total no. of repeats</th>
<th>Forward depth deviation repeats (FD)</th>
<th>Backward depth deviation repeats (BD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1-1.0 mN</td>
<td>10</td>
<td>3</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>1-10 mN</td>
<td>10</td>
<td>3</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>10-100 mN</td>
<td>10</td>
<td>3</td>
<td>3</td>
<td>0</td>
</tr>
</tbody>
</table>
Measurements in DLC thin film on Si wafer

Table 3. Summary of $P-h$ profile (Conical indenter)

<table>
<thead>
<tr>
<th>Sl. no</th>
<th>Indentation load range</th>
<th>Total no. of cycles at each load range</th>
<th>Total no. of repeats</th>
<th>Forward depth deviation repeats (FD)</th>
<th>Backward depth deviation repeats (BD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1-1 mN</td>
<td>10</td>
<td>3</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>1-10 mN</td>
<td>10</td>
<td>3</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>10-100 mN</td>
<td>10</td>
<td>3</td>
<td>3</td>
<td>0</td>
</tr>
</tbody>
</table>

Measurements in DLC thin film on Si wafer

Figures: Multiple-cycle repeating nano-indentation (conical indenter):
(i) $P-h$ profile, (ii) corresponding AFM image after final cycle.

Source: Jin-Won Chung, KIST
Measurements on Si at room and high temperature

- $R = 5$ mm
- 20 indents over 50-500 mN
- Elastic at <40 mN
- Load-dependent phase transformations
- Lateral cracking

Si hardness controlled by phase transformation during loading
- Unloading transitions are complex function of temperature and unloading rate


Courtesy: Prof Ben Beake, Micro Materials Ltd.
Measurements in DLC thin film on Si wafer

<table>
<thead>
<tr>
<th>Indenter type</th>
<th>Impact load (µN)</th>
<th>No. of impacts</th>
<th>Total test time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Berkovich</td>
<td>100</td>
<td>1000</td>
<td>2000</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>1000</td>
<td>2000</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>1000</td>
<td>2000</td>
</tr>
<tr>
<td>Conical</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(10 µm tip radius, 60° included angle)</td>
<td>250</td>
<td>1000</td>
<td>2000</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>1000</td>
<td>2000</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>1000</td>
<td>2000</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>1000</td>
<td>2000</td>
</tr>
</tbody>
</table>
Measurements in DLC thin film on Si wafer

250 μN

1000 μN

Conical indenter

Backward depth deviation

Nanoimpact (Conical)
Progressive load nano-scratch testing of a-C films on Si

- Changing substrate bias from -20V to -80V doesn’t alter the critical load
- In all cases max VM stress is in substrate - multi-pass nano-scratch tests to improve sensitivity to interfacial stress

*Courtesy: Prof Ben Beake, Micro Materials Ltd.*
Sub-critical load multi-pass nano-scratch

- 5 passes over the same track at sub-critical load (150 mN)
- Load selected so that max VM stress is very close to the interface assuming no compression of coating (hard aC on softer Si)
- Substrate bias during deposition influences the interfacial strength with higher bias coatings failing rapidly

*Courtesy: Prof Ben Beake, Micro Materials Ltd.*

Marked influence of thickness on behaviour of CVD DLC

Analysis shows max VM stress is closer to the interface for the 1 µm DLC

Courtesy: Prof Ben Beake, Micro Materials Ltd.
Measurements in Solid Oxide Fuel Cell (SOFC)/Anode layer

(c) Mo-Mo$_2$C/TiO$_2$

(i): H (9.6 GPa), Er (218 GPa)
(ii): H (8.6 GPa), Er (190 GPa)
(iii): H (6.7 GPa), Er (218 GPa)
(iv): H (2.1 GPa), Er (42 GPa)
(v): H (7.6 GPa), Er (128 GPa)

Faisal et al., 6th Asian Thermal Spray Conference, ATSC-2014, 24-26 Nov 2014, Hyderabad, India, p.139-140
Measurements in Solid Oxide Fuel Cell (SOFC)/Anode layer

Neutron beam direction

Neutron beam direction

Vanadium tubes filled with anode powder materials

Neutron strain measurement, ENGIN-X, ISIS/STFC (experiment number RB1510238, Faisal et al., 2015)
Key Summary

- Nanomechanical testing important to characterise renewable and sustainable energy related materials for improved TRIBOLOGICAL performance.
- Selections of indenter shape and loads provide a new approach to the investigation of cohesive and adhesive failure of thin films.
- Opportunities to investigate several properties in variety of ENERGY related materials.

Reading material (Examples: DLC on Silicon, Silicon, SOFC applications)
Thank you

Any Questions, Comments or Suggestions!!!