Adhesion and Thermo-Mechanical Reliability in Emerging Thin-Film Device and Energy Technologies

Organosilicate Films
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Polymers and Hybrid Nanomaterials
Jeffery Yang, Ruiliang Jia, Marta Giachino, Chaohui Wang, Linying Cui

Ultra-Thin Barrier Films
Ryan Birringer and Tissa Mirfakhrai

Chip Package Interactions
Alex Hsing and Ryan Brock

Photovoltaic and Flexible Electronic Materials
Fernando Novoa, Chris Bruner, Stephanie Dupont, Warren Cui

Biological Hybrids
Krysta Biniek, Olgaby Martinez, Mai Bui, Kemal Levi

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Molecular Hybrid Films in Device Technologies

…but hybrid films can be fragile and exposed to harsh environments!

Bioscience

1. skin science
2. sensing and drug delivery
3. environmental diffusion and fracture

solar UV

hybrid film

substrate
Outline

• Molecular Modeling and Design of Hybrids
  • molecular structure and mechanical properties

• High-Toughness Ceramic-Like SiC:H Films
  • toughening devices with plastic a-SiC:H layers

• Hybrid Materials in Plastic Electronics and OPV
  • cohesion and adhesion, kinetics and lifetimes

• Biological Hybrid Films and Treatments
  • biomechanics of human skin, UV exposure and treatment
Quantitative Adhesion/Cohesion and Debond Kinetics

Cohesion Energy, G (J/m²)

Solar Cells

Adhesion/Cohesion

Degradation Kinetics (temp/environment/UV effects)

UV intensity

1.2 mW/cm²

0 mW/cm²

0.6 mW/cm²

Threshold crucial for reliability

Al (100 nm)
Ca (7 nm)
P3HT/PCBM (~150 nm)
PEDOT:PSS (50-100 nm)
ITO (150 nm)
Functionally-Graded Hybrid Layers for High-Performance Adhesion

- combination of organic and inorganic components from molecular to macro length scales enables materials with multifunctional property sets
- opportunity to tailor mechanical, thermal, electrical, and optical properties

**Molecular Hybrids**
- epoxy-functionalized silane (GPTMS)
- metal alkoxide (Zr, Al, Ti, Si)

**Functionally Graded Hybrids**
- toughened epoxy

**High Performance Adhesion**

**Bottom-Up Design of Multifunctional Hybrid Materials**

Source: www.wikipedia.org
Reliability Challenges with Packages and 3D Structures

...environmental degradation of toughened UF epoxy, causing continued growth of interfacial defects even at very low loads
Hybrid Layers for High-Performance Adhesion

Performance Bonding
- multiple substrates, 3D structures, embedded sensors, ...
- hybrid layer optimization
- single-step dual bonding/barrier layer

Debonding and Fracture
- moisture, temperature and fatigue
- kinetic mechanisms and long-term reliability

Computational Modeling
- molecular structure and properties
- new materials discovery
Hybrid Layers for High-Performance Adhesion

### Critical Fracture Energy, $G_c$ (J m$^{-2}$)

<table>
<thead>
<tr>
<th>Substrate</th>
<th>IEP</th>
<th>Max Gc (J/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WO$_3$</td>
<td>0.2-0.5</td>
<td>---</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>1.7-3.5</td>
<td>57.4 ± 7.4</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>4.5-5</td>
<td>33.6 ± 4.4</td>
</tr>
<tr>
<td>BMG</td>
<td>4.7</td>
<td>25.4 ± 2.4</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>6</td>
<td>27.9 ± 3.6</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>7-8</td>
<td>21.9 ± 1.3</td>
</tr>
<tr>
<td>ITO</td>
<td>8.3</td>
<td>18.8 ± 1.1</td>
</tr>
<tr>
<td>NiO</td>
<td>10-11</td>
<td>11.4 ± 2.2</td>
</tr>
</tbody>
</table>

**tune parameters:**
- sol-gel pH
- composition
- metal atoms
- surface catalysis

**Sol pH**

**Isoelectric Point (IEP)**

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**Critical Fracture Energy, $G_c$ (J m$^{-2}$)**

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- **ITO**
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Hydrogenated Amorphous Silicon Carbide (a-SiC:H)

- network backbone: Si-C, C=C
- terminal groups: -H, -CH$_3$
- crystalline SiC
- a-SiC:H

- fully connected
- reduced connectivity

- chemical and thermal stability
- unique opt-electrical properties

Si-O-Si bond free...

- low sensitivity to moisture cracking
- can exhibit high fracture resistance

PE-CVD at 400$^\circ$C

- precursors: methylsilane, phenylsilane, He, H$_2$
- stoichiometric (C/Si $\sim$ 1)
- non-stoichiometric (C/Si $\sim$ 5)
- phenyl organic porogen

Hydrogenated Amorphous Silicon Carbide (a-SiC:H)

- network backbone: Si-C, C=C
- terminal groups: -H, -CH₃

• chemical and thermal stability
• unique opt-electrical properties

Si-O-Si bond free ...(trace amounts)
• low sensitivity to moisture cracking
• can exhibit high fracture resistance

Cohesive Fracture Energy and Connectivity

Fracture Energy, $G_c$ (J/m$^2$) vs. Average Coordination Number, $m$

- SiC-I (C/Si~5)
- SiC-H (C/Si~5)
- non-stoichiometric
- stoichiometric
- single crystal
- plasticity?

C$^{13}$ NMR
- CH$_x$ (-C-C-C-C-)
- C-Si
- C=C

Plasticity in Non-Stoichiometric a-SiC:H Films

\[ G_c (\text{J/m}^2) \]

sp\(^3\) CH\(_x\)/Network Si-C bonds were characterized by FTIR, XRR, and RBS.
Plasticity in Non-Stoichiometric a-SiC:H Films

- **SiC-H (brittle)**: phenyl, C=C
  
  \[ \text{SiC-H} \rightarrow \text{crack tip} \]

- **SiC-I (plasticity)**: porogen $\rightarrow$ sp$_3$ C chain $\rightarrow$ plasticity

Fracture Energy, $G_c$ (J/m$^2$) vs. Film Thickness, $h$ (nm)

- SiC-I
  - load=3mg
  - $\sigma_{YS}=153$MPa
- SiC-H
  - load=5mg
  - $\sigma_{YS}=792$MPa

Nanoindentation

- pileup

Vertical Displacement, $z$ (nm) vs. Horizontal Displacement, $x$ ($\mu$m)

- SiC-I
  - $2r_p$ of 215nm
- SiC-H
  - $2r_p$ of 3nm
Toughening with Ceramic-Like a-SiC:H Films

\[ G_C = G_0 + G_{\text{plasticity}} \]

- SiCN (25 nm)
- nanoporous hybrid glass
- SiCN (25 nm)
- silicon substrate

Cu layer thickness 300 Å - 16.4 μm
(Lane, Dauskardt, 2000)

\[ \text{thickness limit} \sim 300 \text{ nm} \]

limited metal plasticity at nanoscale
- low dislocation \( \rho \) and mobility
- small grain size (Hall-Petch)

Matsuda, Dauskardt et al., Small, 2012 in review.
Toughening with Ceramic-Like a-SiC:H Films

\[ G_C = G_0 + G_{\text{plasticity}} \]

- SiCN (25 nm)
- Nanoporous hybrid glass
- SiCN (25 nm)
- Silicon substrate

Fracture Energy, \( G_c (\text{J.m}^2) \)

Film Thickness, \( h (\text{nm}) \)

- SiCN
- SiO\textsubscript{2}

(Kearney, Dauskardt, 2004)

- Dense polymer PAE/SiO\textsubscript{2}

**Polymer plasticity at nanoscale**
- Limited thermal stability
- Incompatible deposition

Matsuda, Dauskardt et al., Small, 2012 in review.
Toughening with Ceramic-Like a-SiC:H Films

much more effective toughening than metal films, more thermally stable than polymers

$$G_C = G_0 + G_{\text{plasticity}}$$

a-SiC:H (25-250 nm) nanoporous OSG (100 nm) SiCN

a-SiC:H (250 nm) nanoporous OSG (20 - 1000 nm) SiCN

a-SiC:H yield strength 71 - 995 MPa

Matsuda, Dauskardt et al., Small, 2012 in review.
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Degradation and Reliability of PV Devices and Modules

Severe operating environments:

Thermal cycling, mechanical stress, moisture, chemically active environmental species, and solar UV.

Uncertain degradation kinetics and reliability models.
Roll-to-Roll Flexible Inverted Polymer Solar Cell

- Manufacturing: automated R2R
  - high throughput
  - large area
- Materials
  - abundant
  - cheap
  - light weight
- Flexible Substrates

Typical Inverted Polymer Solar Cell

P3HT:PCBM $\rightarrow$ hydrophobic

PEDOT:PSS $\rightarrow$ hydrophilic

poor cohesion

poor adhesion

poor

flexible PET

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MATERIALS SCIENCE AND ENGINEERING
Effect of BHJ Composition on Adhesion

Adhesion Energy, $G_C$ (J/m$^2$)

Efficiency, $E$ (%)

Fraction PCBM in P3HT:PCBM (wt%)

Fullerene rich layers lead to very poor adhesion

Dupont, Oliver, Krebs, Dauskardt, Sol. Eng. Mat., 2011
Factors Effecting Cohesion of BHJ Layers

- **Heterojunction layer thickness**
  - is cohesion in organic layers sensitive to layer thickness?

- **Composition of the heterojunction layer**
  - limited bonding to fullerene
  - polymer/PCBM ratio makes stronger layer

- **Molecular intercalation**
  - manipulating the types of intermolecular interactions

- **Annealing**
  - morphology of the BHJ layer changes with annealing
Effect of Molecular Intercalation on Cohesion

Fracture Energy, $G_c$ (J/m$^2$)

- PQT-12
- PC$_{71}$BM intercalated cell
- pBT TT-C14
- PC$_{71}$BM intercalated cell
- bis-PC$_{71}$BM non-intercalated cell
- bis-PC$_{71}$BM non-intercalated cell

1:1 polymer to fullerene mass ratio

Failure in BHJ layer

Glass Substrate

BHJ Layer

ITO

Al
Barrier Films in Solar Modules

Source: Vitex Systems
Assessing UV and Environment on Debonding Kinetics

Simulated UV Exposure

- Glass Substrate
- ITO
- Polysiloxane Barrier
- ITO
- Glass Substrate

Test data

**DTS Delaminator v8.2**

- Automated load relaxation debond growth analysis
- Compliance analysis

**sensitivity to** \( < 10^{-10} \text{ m/s} \)

Debonding Kinetics

- UV flux
- Humidity, \( \text{O}_2 \), OH, ...
- Temperature
- Mechanical loading
UV Effects on Molecular Bond Rupture

UV Exposure (3.4 eV)

Crack Growth Rate, $\frac{da}{dt}$ (m/s)

Strain Energy Release Rate, $G$ (J/m$^2$)

UV intensity
1.2 mW/cm$^2$
$G_{hv} \sim 1.3$ J/m$^2$

No UV
0 mW/cm$^2$

0.6 mW/cm$^2$
$G_{hv} \sim 0.8$ J/m$^2$

$\frac{da}{dt} = K_T [a_{H2O}]^n \sinh \left[ \frac{G + (C_{hv} \times N \times I)}{2NkT} \right]$
Backsheet and Encapsulant Debonding in Solar Modules
New Portable Full Panel Adhesion

Square Cantilever Beam Adhesion
Adhesion energy, \( G_c \), depends on:

- \( P \) (delamination force)
- \( E \) (young modulus of the square)
- \( h \) (thickness of the square)

\[
G = \frac{3}{2} \frac{P^2}{Eh^3}
\]

Back Side of Full Panel

Delaminator (v8.2) Adhesion Test System

DTS system and support: dauskardt@stanford.edu
Ageing Temperature Effect on Debond Energy

Debond Energy, \( G_c \) (J/m\(^2\))

Ageing Temperature (°C)

Unaged

Ageing time = 1000 hrs

Backsheet

Polyvinyl fluoride
Polyester
EVA Seed
EVA Encapsulant
Tempered Glass

Mechanical load

PMMA Beam
PET
EVA Seed
EVA Encapsulant
Tempered Glass
Temperature Effect on Debond Kinetics

Debond Growth Rate, $da/dt$ (m/s)

Debond-Driving Force, $G$ (J/m$^2$)

Debond Kinetics Model

Arrhenius

$$\frac{da}{dt} = \frac{\pi}{8} \frac{\delta_c}{\varepsilon_y (\delta_c \varepsilon_y)^{1/n}} \left( \frac{G}{E_0(RH)} \right)^{1/n} \frac{e^{-\frac{E_a}{RT}}}{RT - T_r}$$

Williams-Landel-Ferry (1955)

$$\frac{da}{dt} = \frac{\pi}{8} \frac{\delta_c}{\varepsilon_y (\delta_c \varepsilon_y)^{1/n}} \left( \frac{G}{E_0(RH)} \right)^{1/n} \frac{c_a(T - T_g)}{10^c_b + (T - T_g)}$$

Polyvinyl fluoride

Viscoelastic relaxation

Polyester

RH=40%
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Biological Hybrid Films and Treatments

http://www.npr.org/blogs/health/2012/10/02/162159367/how-sunlight-weakens-your-skin

Mechanical Function of Human Skin

mechanical behavior effects

mechanical function and solar UV exposure, wound care, biosensing, drug delivery, and scar formation...
Climate change increases incidence of UV exposure.
Biomechanical Model for SC Damage

SC in tension

SC in compression

Cracking and Chapping

Buckling Instability

natural skin stress
Solar UV Effects on Biomechanical Function

**Delamination**

- (Corneocyte adhesion)

**Fracture Strain, \( \varepsilon_{SC} \)**

- Broadband UVB Dosage (J/cm\(^2\))
  - Control: 1.8
  - 6.7
  - 43
  - 160

**Micro Tension**

- (Strain to failure)

- Broadband UVB Dosage (J/cm\(^2\))
  - Control
  - 160
  - 800
Solar UV Effects on Biomechanical Function

UVB Sunscreen
Carrier (Phenethyl Benzoate) + Sunscreen (8% Padimate O)

UVB absorber
Ethylhexyl Dimethyl PABA

UV Exposure

Delamination Energy, $G_c$ (J/m$^2$)

<table>
<thead>
<tr>
<th>Delamination Energy, $G_c$ (J/m$^2$)</th>
<th>Broadband UVB Dosage (J/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>Control</td>
</tr>
<tr>
<td>1.8</td>
<td>1.8</td>
</tr>
<tr>
<td>6.7</td>
<td>6.7</td>
</tr>
<tr>
<td>43</td>
<td>43</td>
</tr>
<tr>
<td>160</td>
<td>160</td>
</tr>
</tbody>
</table>

Delamination (corneocyte adhesion)

Delamination Energy, $G_c$ (J/m$^2$)

- Carrier + Sunscreen no UV
- Carrier + Sunscreen 20 J/cm$^2$ NB UVB
- Carrier Only 20 J/cm$^2$ NB UVB

UVB absorber chemical structure: $(CH_3)_2N-CO-O-C-H-C_4H_9$
Skin Stresses and the Driving Force for Damage

- wafer curvature technique for SC stresses
- effects of treatment on stresses

In-Plane Bi-Axial Stress State

\[ G = \frac{Z \sigma_{SC}^2 h_{SC}}{E_{SC}} \]

Predicted UVB Effects on SC Damage

\[ G = \frac{Z \sigma_{SC}^2 h_{SC}}{E_{SC}} \]

- no damage
- damage
- channeling
- surface cracking

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