Composite Dendrimer Materials

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Motivations

• Model system for exploring organic/inorganic hybrid structures
• Host/template for nanoparticles
• Adhesion/Lubrication/Tribology
• Functionalization of surfaces
• Molecular electronics
• Ultraflat films
• Biochemical sensors
• Catalytic Arrays

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PAMAM Dendrimer

- PAMAM dendrimers are hyper-branched macromolecules
- **EXAMPLE:** G4 has an EDA core with 4 iterative branch repeat units
- 64 NH$_2$-endgroups
- Repeat Unit \( \rightarrow (\text{CH}_2)_2\text{-CO-NH-}(\text{CH}_2)_2 \)
- 4.5 nm diam. in solution
- 2.3 nm height as monolayer
Research Projects

• **Patterning and Templating**
  • Dendrimer adlayer patterning
  • Metals electrodeposition
  • Nanoparticle formation and characterization

• **Dendrimer-metal Nanocomposites**
  • Tribology of dendrimer-based composites
  • Grain size effects
Patterning Surfaces using Microcontact Printing

- Microcontact printing (µCP) is a means of forming chemical patterns on surfaces.
- A polydimethylsiloxane (PDMS) stamp is used. The stamp is treated with the chemical “ink” which is subsequently transferred to the substrate.
Dendrimer Multilayer Patterning

AFM Image of Patterned G4 Dendrimer Multilayer

Unusually stable dendrimer multilayers can be patterned using microcontact printing techniques.


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Dendrimer Aerosol Patterning

Dendrimer solution/Sprayer → 10 µm droplets → Mica substrate

AFM Images: 10 µm x 10 µm

Increasing dendrimer solution concentration

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Dendrimer Bilayer Formation

New morphologies upon aerosol deposition and dewetting. Strong tendency for formation of 2 ML structures.

Electrochemical Deposition of Copper

- Electroplating solution: 0.2M CuSO$_4$; 0.25M Na$_2$SO$_4$; 0.42M H$_3$BO$_3$; distilled water
- Substrate: doped Si (n-type, 0.01 $\Omega$/cm)

The dendrimer monolayer can be used to promote adhesion of copper electroplated from an acidic copper bath onto the native oxide of doped Si.
Optical Microscopy Images

-1.2V for 15 seconds  -1.2V for 300 seconds

Arrington et al. manuscript in preparation
Formation of Metal Nanoparticles within PAMAM dendrimers

The dendrimer monolayer can attract copper ions to its interior. The electrons supplied during electrodeposition could simply allow reduction of Cu$^{2+}$ to Cu$^{0}$ (metal).

UV Irradiation of Co(II)/G4-OH System

\[
\text{CoCl}_2 \text{ aqueous} + \text{Dendrimer aqueous} \rightarrow \text{Mixed Amine-coordinated Co}^{2+}
\]
TEM image of Acicular Co Nanoparticles

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The Co particles produced are relatively monodisperse, acicular, magnetic, and apparently metallic.

Zhang et al. manuscript in preparation

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Dendrimer Monolayers

Dendrimers self-assemble into molecular monolayers using extremely simple spontaneous assembly methods.

In the ‘condensed phase’ the formerly spherical molecules tend to ‘collapse’ and become laterally confined.

~ Spherical in solution

Collapsed and confined on a surface

clean, dip, rinse

Substrate

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Tribology of Metal/dendrimer Nanocomposites

(a) native silicon

(b) G8 monolayer

c) metal layer w/out G8

d) metal layer with G8
AFM Images: 12.5 nm Au Films

Without Dendrimer Interlayer
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With Dendrimer Interlayer
TEM Plan View of Sputtered Au Films

J. Yang
U. Pitt.

10 nm Au/Si
10 nm Au/D8/Si

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Molecular Interlayers and Abrasive Wear

- AFM image of residual impression left by diamond scratch tip
- Impression made in thick Cu film
- Blunted Berkovitch shape
- Scratches carried out in face-forward mode
- Velocity: 1 micron/second

Constant load (4 mN) nanoscratches, 100 µm long.
SEM Images of Nanoscratch Events

4 mN constant load, Berkovitch tip (face forward)

15 nm Cu/Si

Plowing

15 nm Cu/G8/Si

Irregular cutting


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Ramped Load Scratch Tests

Li et al. Submitted

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**Sputtered deposition**

- Formation of nitride layer at the interface for Cr and Co.
- Low binding feature apparently indicates bond-breaking in dendrimer adlayer.
- Consumption of dendrimer nitrogen exceeds that associated with the amine shell: ~ 50% of internal amide nitrogen involved.
- Degree of metal reaction (penetration) decreases as the generation number increases.

Conclusions

Dendrimer-metal Nanocomposites

• The presence of the dendrimer monolayer influences the morphology, nanomechanical properties and chemical composition of overlayer metal ultrathin films
• The reactivity of the overlayer metal and the deposition kinetics play roles in the nature of the nanocomposite (growth modes, grain size, chemical composition of the interface, resistivity of the thin film)
Some Future Directions

• Detailed TEM studies of films and wear phenomena using SiN window TEM grids as the substrate – better understanding of dendrimer mediated growth, grain structure, and deformation

• Studies of the viscoelastic behavior of the dendrimer monolayers and composites; more detailed nanoindentation and nanoscratch optimized for ‘soft’ and ‘soft/hard’ composite materials systems; reactive metal overlayers

• Grain size effects: control of grain size, influence on resistivity of metallic thin films