Molecular Dynamics simulation of C/H/O polymers and Ohnishi parameter

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AVS 56th International Symposium San Jose, CA
November 8-13, 2009
Motivation and Focus

- Ion interaction with polymers is important.
  - Understand Ion beam sputtering of Photoresist.
- Molecular Dynamics (MD) Simulation
  - Polymers with H, C and O
- Chapter 1:
  - MD Simulation of different polymers:
- Chapter 2:
  - Ohnishi Parameter (Sputter yield for different polymers)
- Conclusion
What is Molecular Dynamics Simulation?
Molecular Dynamics Simulation - Introduction

- Simulation of atoms using MD

Potential V for every pair of atoms.
- Code developed by Dr. Humbird, Dr. Vegh
MD Setup for polymers

- C-H-O REBO Potential*
- Ar+ at 100 eV (normal incidence) from top
- Sample polymer simulation cell (~20 Å in x and y)
  - 9 chains of 20 monomers each
  - Bottom two fixed
- Periodic boundary conditions in X and Y
- Additional material added to the bottom
- Minimum # of atoms maintained
- Cell cooled back to 300K

**Polymers simulated (C/H/O)**
1. PS, PMMA, PVN, PBN, P4MS, PMAMA
2. HDPE, Teflon

Periodic boundary conditions

- Mimics an infinite surface
Chapter 1: MD Simulation of polymers
PMMA sputtering

- Crust formation (22 nm of material etched)

Ar$^+$ Fluence ($10^{16} \text{ cm}^{-2}$)

Fluence:

0 1 2 3 6
PMMA (C₅H₈O₂) simulation

- PMMA- sample polymer
- Ar ion fluence of 10¹⁷ Ar cm⁻² (4000 Ar impacts)
- Black –C White-O Grey-H
- Dehydrogenated
- Deoxygenated Layer
- H/C ratio in Top Layer
  - Drops from 1.6 to <0.3
- Initial polymer structure is lost in the top crust part.
Sputter yield vs fluence (Movie)
Depth Profile

- High amount of C in top layer
- Hydrogen conc. Increases slowly from top to bottom
- Oxygen buildup just below the Crust
- Ar Ions pushes atoms downwards
  - H being small can escape
  - O Cant through Crust
  - Hence a buildup
PMMA sputter yield

- Drastic drop in Sputter yield.
- Sputter yield for two different sets.
- Small variation.
- Final S.S. sputter yield if let run for long time is same within +/- 0.01
- Sharp sputter yield drop as seen in experiment.
- SS Sputter yield = 0.05
- Similar observation for most polymers.

MD captures the sharp sputter yield drop very well for all polymers.
How does it compare to experiments?
Quantitative comparison

- QCM Data from Ion beam system in our lab
- Initial sputter yield matches very well.
- Sharp drop is observed
- Initial sputter yield
  - MD ~14 C/Ar
  - Experiment ~ 12 C/Ar

Experimental data by Dustin Nest
Chapter 2: Ohnishi Parameter
Experiments: Ar Ion beam at 300 eV

They expected
- E. Rate $\propto \frac{(N=N_C+N_H+N_O)}{N_C}$
- $C_5H_8O_2 \frac{(5+8+2)}{(5-2)}$

However it was observed
- $N/N_C$ is fairly good but
- $N/(N_C-N_O)$ is better

No explanation other than oxygen is playing some role.

Ref: Ohnishi et al. 1983
Sputter yield comparison

- Experimental results scaled
- Using square root dependence of etch yield with ion energy
- We are comparing only the slope.

![Graph showing sputter yield comparison](image)
Sputter yield comparison

- Steady State Values from MD
- Reproducing Linear trend with Ohnishi parameter
  - They fall on a straight line.
  - Very good correlation.
- Experimental results scaled
- Using square root dependence of etch yield with ion energy

MD captures the linear trend with Ohnishi parameter very well.
Why linear trend with Ohnishi Parameter?
Why the linear trend with $N/(N_C-N_O)$

- Why Etch yield follows the trend $N/(N_C-N_O)$
- To explain this we gather data from MD and propose a Model.
- Observation from MD:
  - All O leave as CO and all H leave as $H_2$.

![Diagram](image)

![Graph](image)
Model

- $J_C, J_O, J_H$ are flux of C, O and H
- $J_{C'} = J_C - J_O$ and $J_{CO} = J_O$
- At steady state
  - Flux of $C'$ $\propto$ $C'$ mole fraction in bulk
- Sputter rate $\propto$ $(1/C'$ mole fraction) $\sim (N_T/(N_C - N_O))$
- Exact solution

$$Y_T = Y_C' \frac{(N_C + N_O + N_H)}{N_C - N_O}$$

$Y$ is sputter yield (# of atoms removed/Ar ion), $\nu$ is atomic volume,

$$J_{C'} = Y_T \nu$$

$J_{C'} = Y_{C'} \square Ohnishi\ Parameter$
Model

- $Y_c'$ is a constant
  - $Y_c' = 0.016$ from MD
  - $Y_c' \sim F$ (Ions, Energy)
  - Yield of pure C under 100 eV Ar ion bombardment 0.013 (close to $Y_c'$)

- Damaged layer formation is necessary for ion bombardment to follow the linear trend with Ohnishi parameter.

It’s the C that doesn’t leave with CO controls the sputter rate
Do all polymers follow the linear trend with Ohnishi Parameter?
Polyethylene and Teflon

- After 4000 impacts:
  - Doesn’t converge
  - Polymer structure doesn’t change much
  - No sharp etch yield drop
  - No crust formation
  - Does not follow model:
    - Assumptions are not met.
- Zekonyte et al. observed very high etch yields for Teflon compared to other polymers

Conclusions

- A carbon rich damaged layer is observed in MD simulations for many O containing polymers
  - Sharp drop in sputter yield
- Reproduced sputter yield correlation with Ohnishi parameter in MD
- Why the linear trend with Ohnishi parameter.
  - A model to explain
- **C rich damaged layer formation is necessary to follow the linear trend with Ohnishi parameter**
- Polymers with high F/H content deviate
Acknowledgements

- We gratefully acknowledge the following for funding
  - NIRT (CTS-0506988)
  - NSF DMR 0705953
- Prof. David B. Graves (Advisor)
- Dr. Joe Vegh (Lam research)
- Group - Ting, Monica, Yuki, Dustin, Kohei, Ning, Joe, Tomai
- Software
  - VMD
    - www.ks.uiuc.edu/Research/vmd/
  - POVRay
    - www.povray.org