

Modeling Liquid Surfaces



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- Motivation
- Approach
- Early results
- Summary

Surface-induced ordering of liquid surfaces



- Predictions have been known since the late 70's and 80's
- Advances in synchrotron sources in last 10 years have allowed measurements to be made of the near surface
 - High accuracy positioning
 - Spectrally pure beam
 - In-situ oxide removal
 - Capillary effects accounted for
- Observations from many systems imply that surface ordering is a general result for liquid surfaces
- The effect of surface density stratification and coordination number need to be introduced into sputtering calculations for liquid metals

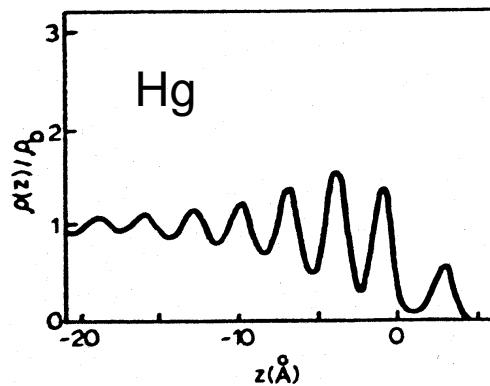
Review article

J. Penfold, Rep. Prog. Phys. 64 (2001) 777.

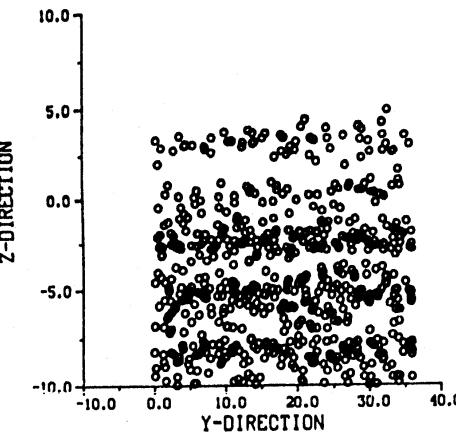
Early liquid surface models showed effect on self sputtering yield



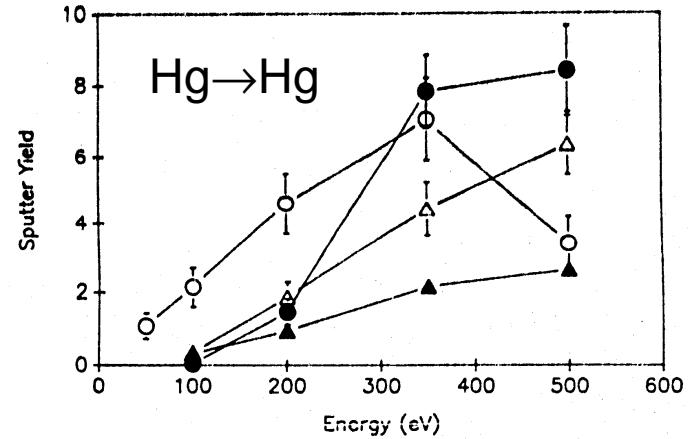
- Stratified layer predicted by D'Evelyn and Rice (1982)



M. P. D'Evelyn and
S. A. Rice,
J. Chem. Phys. 78
(1983) 5081.



- Sputtering calculations using MD calculation and model density from above were performed by Morgan (1988)

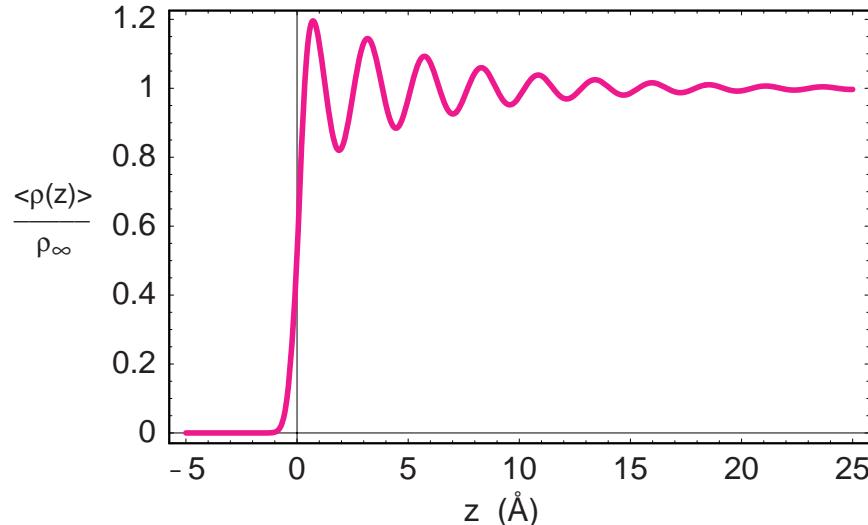


W. L. Morgan, J. Appl. Phys. 65 (1989) 1265.

Model for stratified density fit to X-ray diffraction data of liquids



- Recent experimental surface data is for Ga and Hg
- Surface density model includes layering and capillary wave broadening
- No lithium surface data



$$\frac{\langle \rho(z) \rangle}{\rho(\infty)} = \operatorname{erf} \left[\frac{z - z_0}{\sigma} \right] + \theta(z) A \sin \left(\frac{2\pi z}{d} \right) e^{-z/\zeta}$$

$$z_0 = 0$$

$$\sigma = 0.5 \text{ \AA}$$

$$A = 0.5$$

$$d = 2.56 \text{ \AA}$$

$$\zeta = 5.8 \text{ \AA}$$

M. J. Regan, et. al., Phys. Rev. Lett. 75 (1995) 2498.

Guide to surface values for Li can be made from other materials



■ Ga

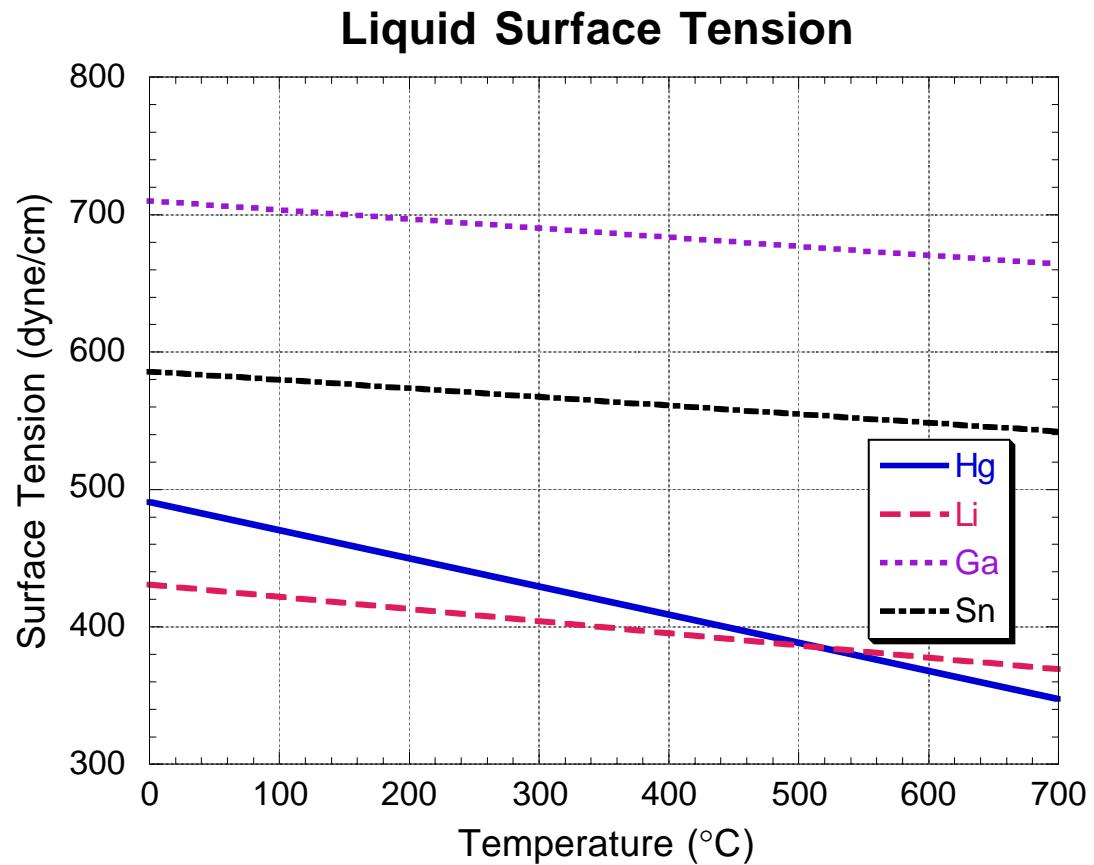
- Layering decay length of 5.8 Å

■ Hg

- Layering decay length of 3.5 Å

■ Li

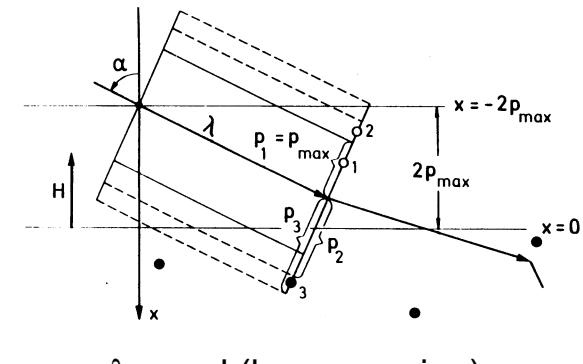
- Temperature scaling of decay length for Ga agrees with capillary wave broadening
- Li has similar surface tension to Hg
- $K_{80}Na_{20}$ shows no layering (≈ 110 dyne/cm)



Liquid sputtering model development



- Use liquid surface density model from the literature
- Use Monte Carlo TRIM code (TRVMC98) for calculating incident and recoil trajectories and calculating collision cascade
 - Stationary surface layering
- Work with Eckstein to extend TRIM to accommodate liquid surface effects
 - Increase number of layers (presently 3)
 - Revise collision bookkeeping to correctly handle density variations in very thin layers
 - Incorporate improved binding energy model
- Upgrade computing power
 - 6 x 6 matrix of results requires 5 - 8 hours
 - New computer will run $\approx 6\times$ faster



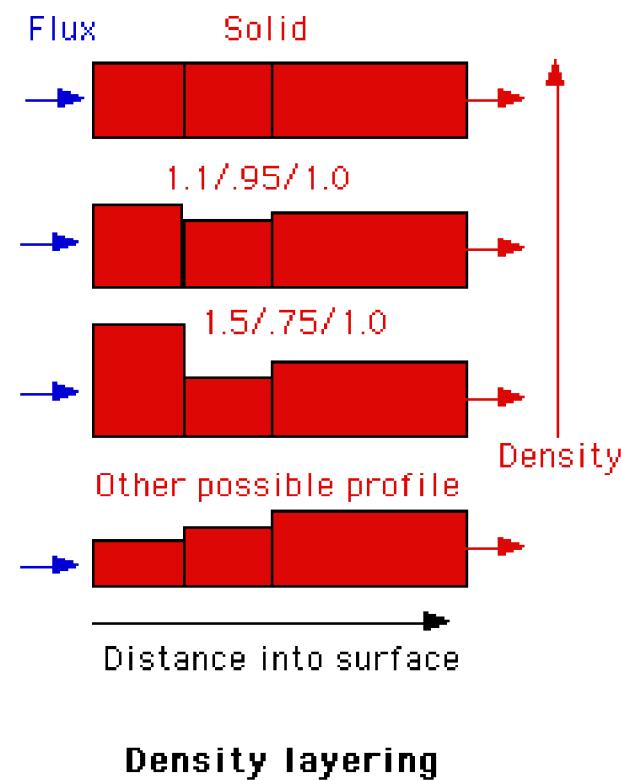
$\lambda, p_i \approx d$ (layer spacing)

Progress to date

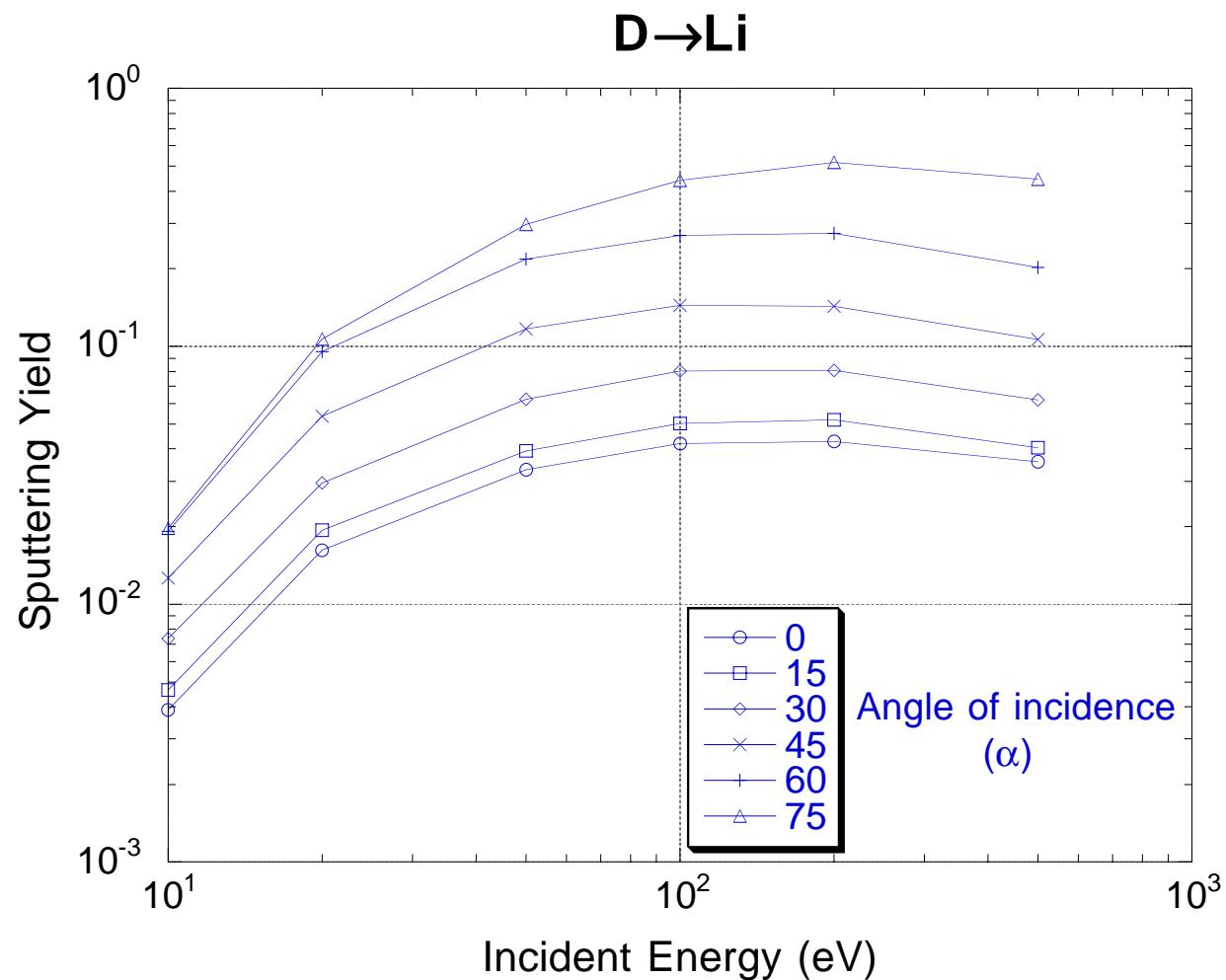


■ Initial calculations

- Validate multi-layer code results with previous TRIM calculations (Eckstein's survey from 1993)
- Initial look at effect of one period of the surface layer structure (on semi-infinite bulk density)
- Check variation of surface binding energy



$D \rightarrow Li$ (solid)



D → Li (liquid) [Y/Y_s]



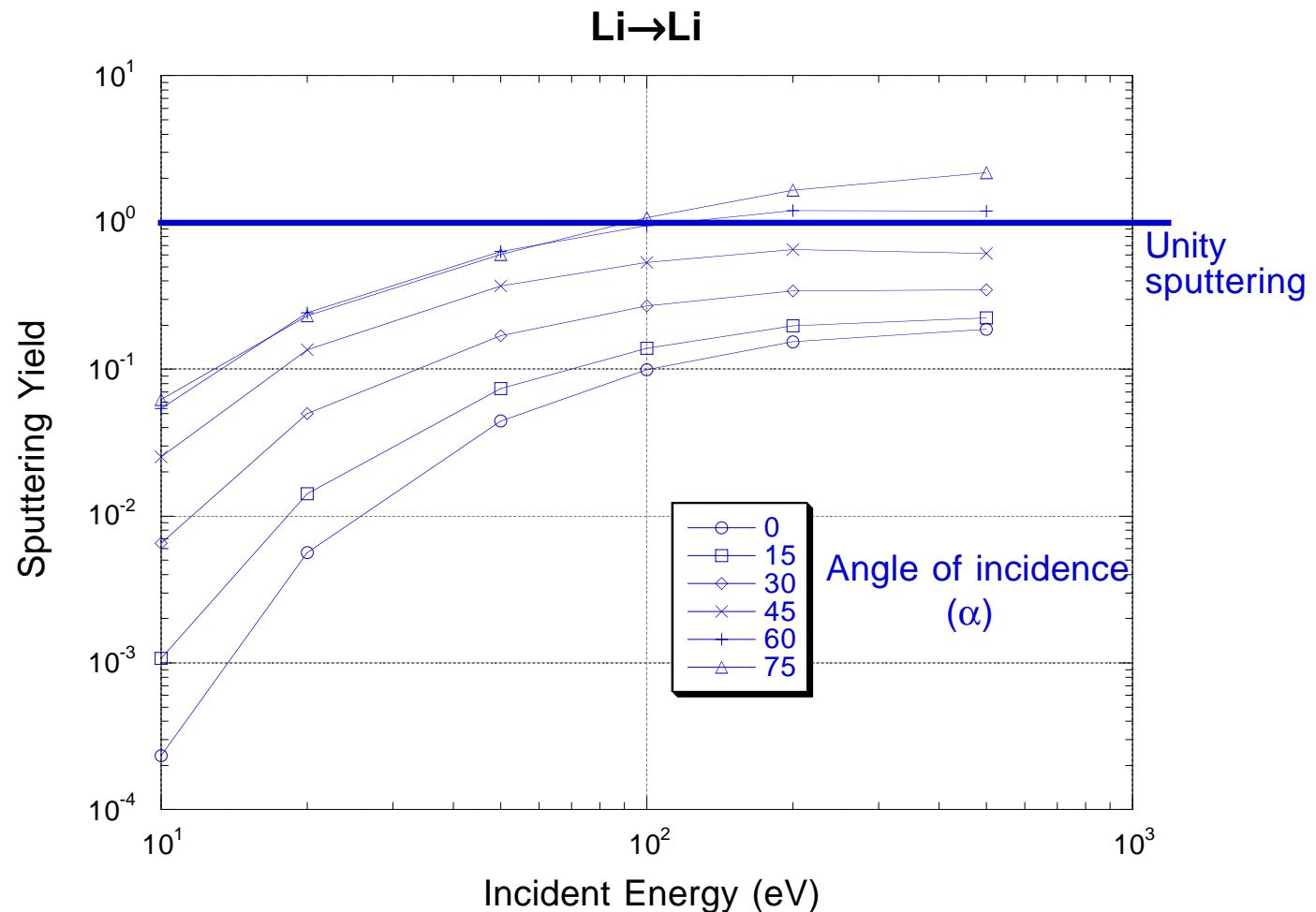
Energy (eV)	0°	15°	30°	45°	60°	75°
10	0.97	0.94	1.09	1.01	1.03	0.99
	1.10	1.06	1.08	1.14	0.98	0.80
20	1.03	0.98	1.02	1.04	1.01	0.98
	1.16	1.15	1.15	1.16	1.09	0.87
50	1.05	1.08	1.06	1.05	1.03	1.00
	1.15	1.22	1.20	1.17	1.13	0.95
100	0.99	1.02	1.04	1.04	1.05	1.01
	1.17	1.14	1.16	1.16	1.14	1.02
200	1.04	1.01	1.02	1.02	1.02	1.00
	1.20	1.17	1.15	1.13	1.10	1.05
500	1.01	1.01	1.01	1.02	1.00	1.02
	1.12	1.22	1.13	1.11	1.06	1.06

Top line = 1.1/.95/1.0 profile

Bottom line = 1.5/.75/1.0 profile

Blue ⇒ > 15% Yield change

Li → Li (solid)



Li → Li (liquid) [Y_f/Y_s]



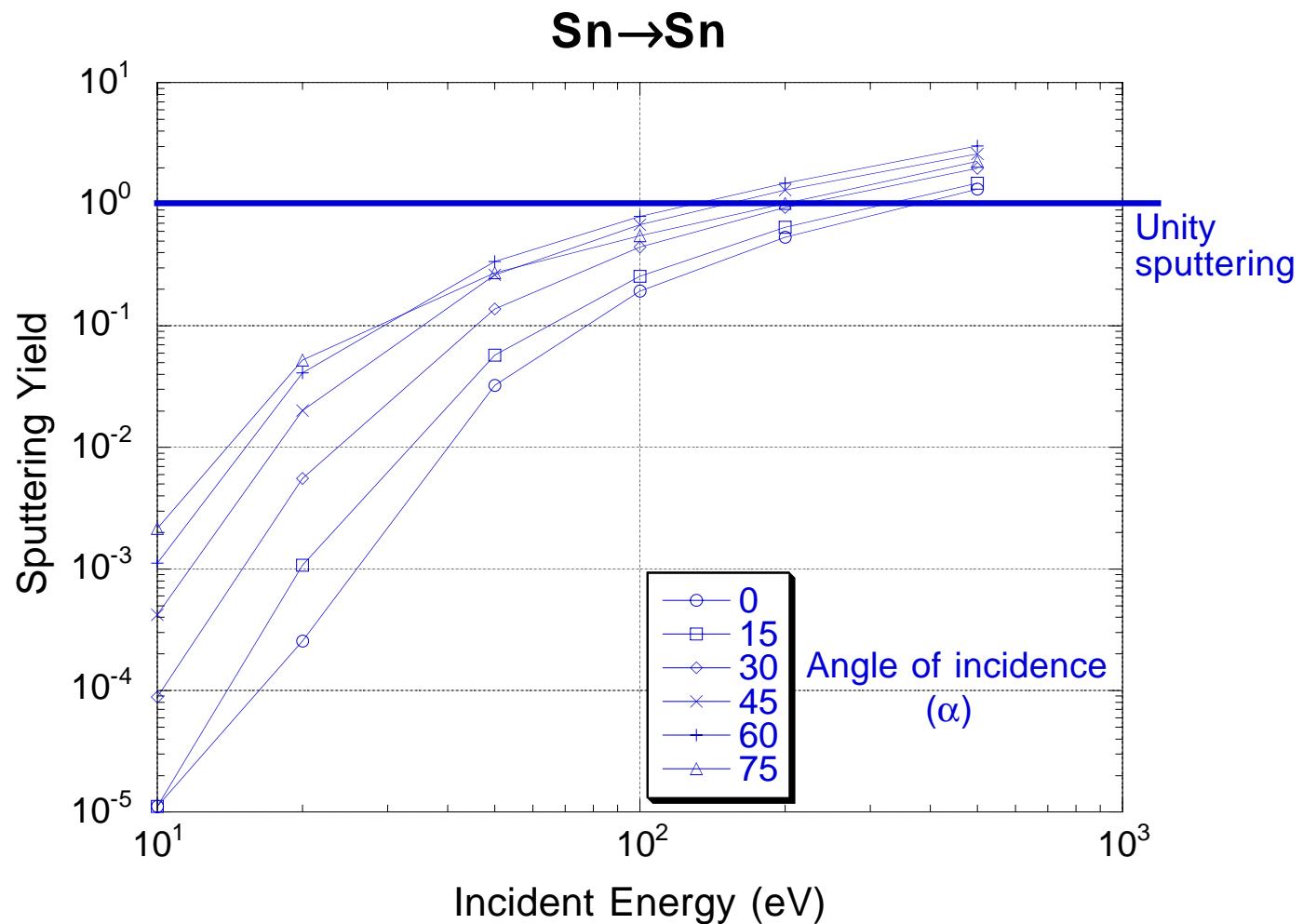
Energy (eV)	0°	15°	30°	45°	60°	75°
10	1.19	1.10	1.07	1.02	1.00	0.99
	2.10	1.29	1.23	1.10	0.98	0.88
20	1.07	1.01	1.06	1.07	1.02	0.97
	1.64	1.35	1.28	1.21	1.03	0.82
50	1.10	1.08	1.06	1.03	1.01	0.96
	1.45	1.33	1.25	1.18	1.07	0.82
100	1.07	1.07	1.04	1.05	1.02	0.98
	1.34	1.30	1.23	1.17	1.08	0.87
200	1.06	1.06	1.05	1.02	1.02	0.99
	1.30	1.26	1.21	1.14	1.08	0.96
500	1.04	1.05	1.03	1.02	1.02	1.00
	1.26	1.22	1.16	1.13	1.08	1.02

Top line = 1.1/.95/1.0 profile

Bottom line = 1.5/.75/1.0 profile

Blue ⇒ > 15% Yield change

Sn → Sn (solid)



Sn → Sn (liquid) [Y_f/Y_s]



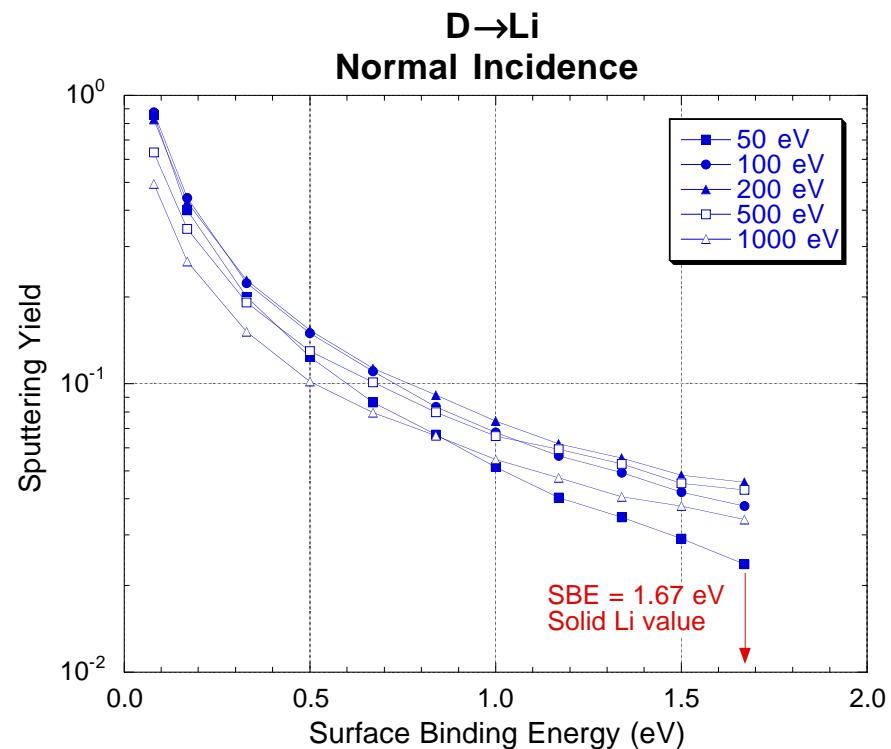
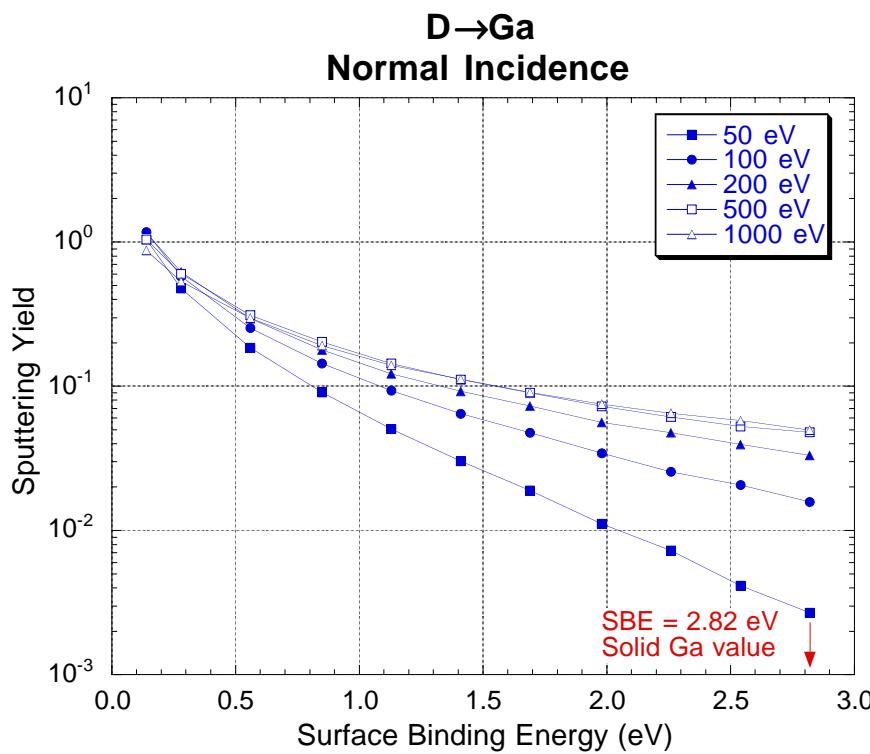
Energy (eV)	0°	15°	30°	45°	60°	75°
10	-	-	-	0.95	0.91	0.96
	-	-	-	1.05	0.96	1.00
20	1.04	0.94	1.05	0.99	1.05	0.94
	1.00	1.13	1.10	1.03	0.98	0.78
50	1.11	1.05	1.04	1.04	0.99	0.95
	1.23	1.20	1.10	1.01	0.92	0.76
100	1.05	1.05	1.03	1.02	0.99	0.94
	1.22	1.18	1.12	1.03	0.91	0.77
200	1.05	1.04	1.02	1.01	0.99	0.95
	1.19	1.16	1.10	1.05	0.95	0.79
500	1.04	1.04	1.03	1.02	1.00	0.98
	1.16	1.15	1.10	1.06	0.98	0.83

Top line = 1.1/.95/1.0 profile

Bottom line = 1.5/.75/1.0 profile

Blue ⇒ > 15% Yield change

Varying the surface binding energy can strongly affect yields



Summary



- Surface density layering can result in modest increases in the sputtering yield (largest for self-sputtering)
- Extrapolation of surface structure parameters may be needed for Li
- Further model development is needed to accurately represent surface layering and coordination number effects
 - Add additional layers to and improve collision bookkeeping in TRIM98
 - Improve surface binding energy model
 - Consider additional energy transport effects