Gibbs Adsorption in Binary Liquid Mixtures: Concentration Variations Beyond Surface Monolayer in BiSn alloy

Oleg Shpyrko[1], Alexei Grigoriev[1], Diego Pontoni[1], Reinhard Streitel[1], Peter Pershan[1], Ben Ocko[2], Moshe Deutsch[3], Binhua Lin[4], Mati Meron[4], Tim Graber[4]

[1]Department of Physics, Harvard University, Cambridge, MA; [2]Brookhaven National Lab, Upton, NY; [3]Bar-Ilan University, Israel, [4]Argonne National Lab, Argonne, IL

Abstract

•Lead-Free Solders:
- -Technological importance
- -Basic understanding of surface structure and thermodynamics of two-component liquid alloy

• Experiment & Theory:
- -Resonant X-ray measurements
- -Probing surface layering & composition
- -Comparison of results with Gibbs theorem and Defay-Prigogine model

MOTIVATION

Practical:

• Ban of Pb-based solders in industrial production due to health risks

➡ Need to replace PbSn solders by Pb-free alternatives

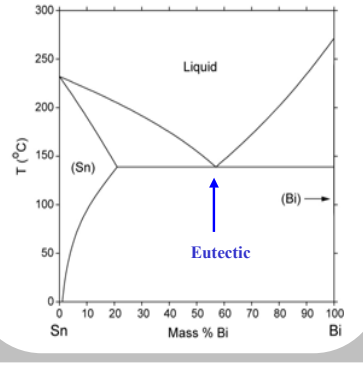
• Appealing candidate – BiSn:
- ★ Low melting temperature
- ★ No health hazards
- ★ Inexpensive

Fundamental:

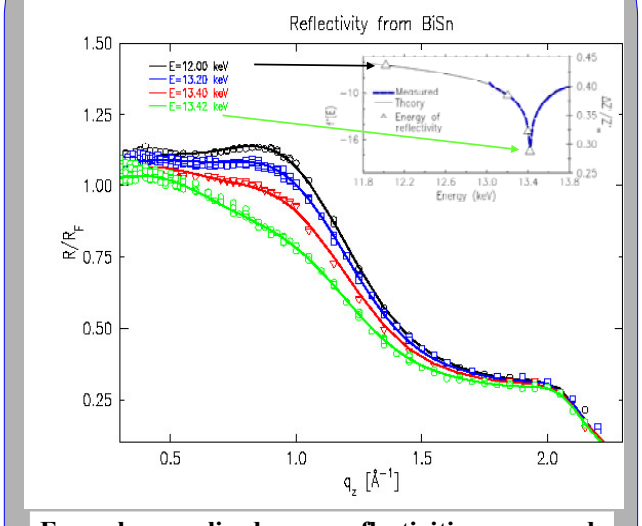
• Lack of understanding of surface thermodynamics of binary alloys: studied so far - BiIn, GaIn, GaBi, AuSi, AuGe, HgAu - behave differently!

• How do the properties of the two components define the surface of the binary alloy?

BiSn Phase Diagram:



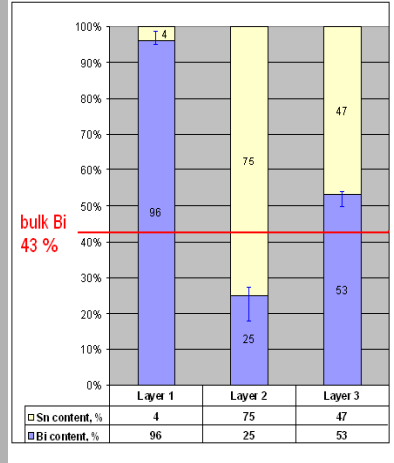
Resonant X-Ray Reflectivity



Fresnel normalized x-ray reflectivities measured at four different energies, the lines show the best fit obtained using a three layer surface model.

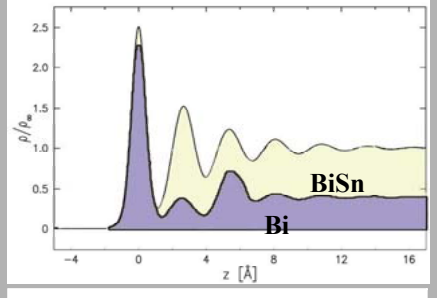
Inset ("Δ" energies used for measurements):
- Bi L3 absorption edge @ E = 13.418 keV
- Right scale shows electron density contrast

BiSn composition at the surface



	Layer 1	Layer 2	Layer 3
Sn content, %	4	75	47
Bi content, %	96	25	53

Bi & BiSn electron density profiles



-Bi and BiSn (total) electron density
Bi excess is observed in the first and the third layer
-approaching bulk composition beyond the third layer

-Gibbs absorption theorem (assumes ideal solution) predicts a monolayer excess of Bi to reduce surface tension and surface energy
(γ(Bi) = 378 mN/m, γ(Sn) = 560mN/m*)

-extended Defay-Prigogine model (assumes regular solution) provides corrections for the oversimplified Gibbs absorption theorem

-BiSn data shows good agreement with Defay-Prigogine model and explains surface demixing within the first three layers

* surface tension @ melting temperature

Summary

•Studies of Pb-free solders such as BiSn are of great importance for industry and fundamental science

•BiSn shows well-defined layering and composition variations at the topmost three layers

•BiSn is the first system that shows atomic scale demixing proven by X-ray reflectivity measurements

•Surface segregation and surface demixing can be explained within the Defay-Prigogine approach

O.G. Shpyrko et al., submitted to PRL (2005)

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