Surface Freezing and quasi-2D phase transitions in Binary Metallic Liquids

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Do Surfaces Always Melt before Bulk does?

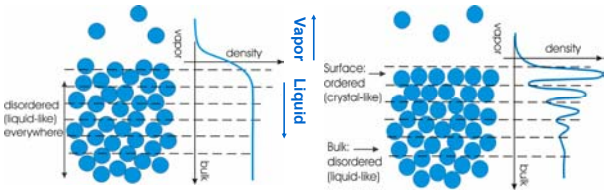
Structural phase transitions at surfaces and interfaces are of great interest to a variety of disciplines, ranging from environmental phenomena (formation of ice, glacier movements, heaving) to properties of nanoscale objects that are governed primarily by interfacial science. Contrary to well-accepted paradigm of pre-melting behavior – formation of liquid-like wetting layer at the facet of a crystal tens degrees below bulk melting point – we report a unique discovery of a reverse phenomenon ("surface freezing") in eutectic AuSi alloy – a coexistence of crystalline surface monolayer and underlying liquid bulk well above bulk melting temperature.

Publication: O. G. Shpyrko et al., (2005)

Surface-normal quasi-crystalline structure (layering) in liquids:

• Classical Van-der Vaals treatment predicts a disordered liquid-vapor interface (dielectric fluids)

•However, interactions between Fermi sea of delocalized electrons and ions result in surface-induced ordered atomic layers in liquid metals. Layering correlation length is less than 1 nm, same as the bulk correlation length.

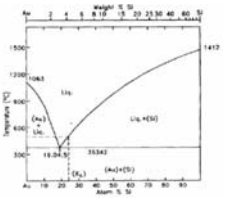


Liquid-Vapor interface in Van-der-Vaals liquids (true for dielectrics such as water, Shpyrko et al., PRB 2004)

Surface-normal profile for metallic liquids: ordered structure intrudes between two disordered phases (liquid and vapor)

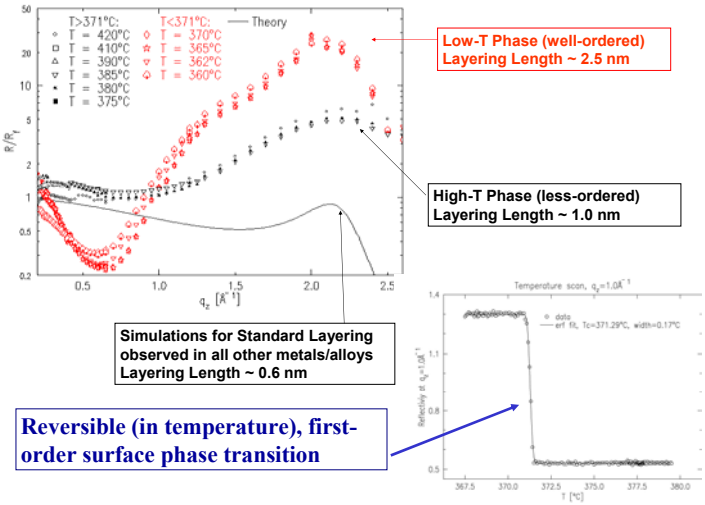
Do atoms also order along the surface plane?

While long-range in-plane ordering in liquid may form as a trivial result of phase-separation and crystallization of surface monolayer in dilute *immiscible* mixtures, until now it was NOT observed in pure liquids or *homogeneous* miscible mixtures, such as eutectic alloys



X-ray reflectivity measurements

• Layering structure cannot be currently resolved with any surface technique other than x-ray scattering (penetrating ability of x-rays, atomic-scale resolution, high flux 10^{12} ph/s)
• Reflectivity is enhanced by Bragg-like peak due to constructive interference between atomic surface layers, but reduced due to thermal capillary fluctuations (Debye-Waller-like factor)
• Surface Structure Factor enhances signal by a factor of ~100 (less for binary mixtures) in ALL of the metals measured so far: Ga, Hg, In, Sn, Bi, K, GaIn, BiIn, GaBi, GaPb, BiSn etc.
• AuSi shows enhancement by a factor of 2,000, nearly 20 times that of other liquid metals!
• At T=371 degC (12 degrees above eutectic bulk melting point) surface undergoes a phase transition to a less-ordered system.



Reversible (in temperature), first-order surface phase transition

Surface-parallel Structure (X-ray Grazing Incidence Diffraction):

• Penetration depth of x-rays is approx. 3nm (or about 10 atomic layers)

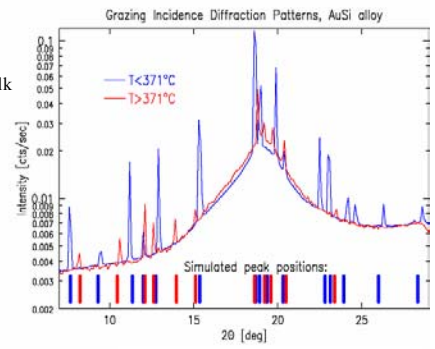
• Normally liquids only exhibit a broad bulk structure peak (due to short-range packing)

• We observe a number of sharp diffraction peaks, indicating the long-range crystalline structure in near-surface region

• Long-range in-plane ordering is present in both low-T AND high-T surface phases!

• Peaks are present in coexistence with a broad liquid bulk structure peak – underlying phase is liquid (no long-range in-plane order)

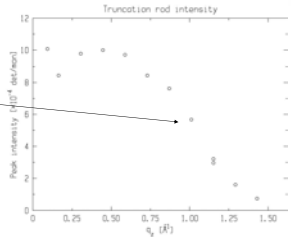
• Rotation of the sample does not change the diffraction pattern – indicates isotropic "2D powder" distribution of crystallites oriented parallel to the surface



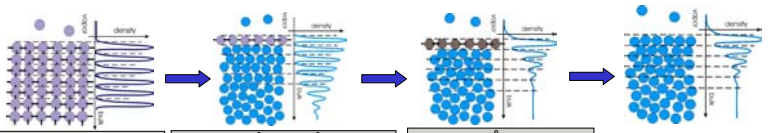
Crystal Truncation Rod

• Intensity distribution along the truncation rod of diffraction peaks indicates that only the surface monolayer is crystalline, while the underlying bulk has a liquid-like in-plane structure

Slow intensity fall-off indicates width of solid-like structure w < 0.4 nm (single monolayer)

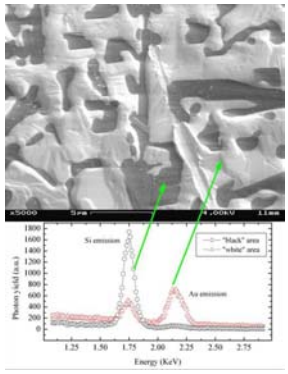


Structural Evolution of the AuSi Liquid-Vapor Interface



T<Tm=359°C	359°C < T < 371°C	371°C < T	High T configuration
3D Solid (Polycrystalline, Sinodally Separated into Au and Si regions)	2D-Crystalline Surface Monolayer (Low-T Phase) Induces enhanced surface-normal layering ~3 nm	2D-Crystalline Monolayer (High-T Phase) Layering length ~1nm	Standard Liquid Layering profile

Conclusions



• Eutectic AuSi alloy exhibits a unique melting behavior: a coexistence of crystalline surface monolayer and liquid bulk above eutectic temperature, in striking contrast to surface melting behavior found in most crystals

• The quasi-2D crystalline monolayer undergoes a solid-solid phase transition 12 K above eutectic point.

• Low-temperature monolayer phase induces surface-normal ordering of underlying liquid bulk atoms with correlation length of ~2.5 nm, while the high-temperature phase is associated with layering length of only about 1 nm. Reduction in order parameter is possibly due to structural and compositional differences between the two quasi-2D monolayer phases.

•Discovery of crystalline surface phases is remarkable as bulk AuSi has no known stable intermetallic crystalline compounds. The stability of the surface phases is attributed to surface potential, and underscores the different requirements for formation of stable atomic configuration in 3D vs. 2D

• Despite somewhat similar chemical properties and phase diagram, AuGe eutectic does not exhibit surface freezing behavior reported here

• Unexpectedly rich and exotic phase diagram of AuSi surface phase is of great importance to semiconductor industry which commonly uses a combination of gold interconnects and silicon substrates in computer chip manufacturing. As the size of the components rapidly approaches nanometer scale, the structure and function of these objects are governed primarily by interfacial effects, rather than bulk physics we are accustomed to

Acknowledgments

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