Harvard
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Anomalies of the Surfaces of Au-Si-Ge Liquid Alloys*

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Introduction:

The atomic structure of the surface of liquid metals is a crucial property in numerous applications like soldering, brazing as well as growth of Si-Ge nanowires. Within the last decade our group has used synchrotron radiation to demonstrate the atomic layering that was predicted by Rice et al. in the early 80's for metallic liquids like Ga and In. In addition layering in alloys such as Bi-In, Sn-Bi and Au-Sn were observed to exhibit chemical segratation. Typically, the layering persists for about 3-4 atomic distances into the bulk liquid.

Surprisingly the surface of liquid eutectic Au-Si exhibited an unusual high x-ray-reflectivity (XRR) that indicated an anomalous strong layering effect normal to the surface. Grazing incidence x-ray diffraction (GID) revealed the presence of a 2-dimensional crystalline surface layer at the surface.

In an attempt to understand the unexplained surface anomaly of Au-Si we have carried out, and are continuing the following:

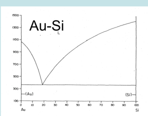
1.) Measurement of "truncation rods" that better characterize the Au-Si surface phase.

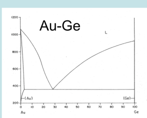
2.) Asked how the effect of replacing Si by Ge influences the surface structure.

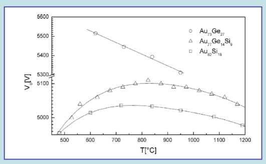
3.) Examined the temperature dependence of Au-Si surface phase formation.

4.) Plan to search for surface phases in other alloys. Is this effect more universal?

5.) Correlate with structure of the bulk liquid. Relate to properties like glass forming ability.



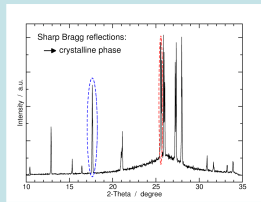




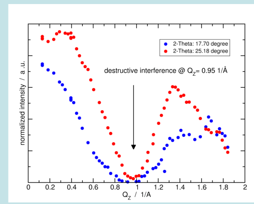
Ion extraction voltages V_0 vs. T (Bischoff et al. Ultramicroscopy 2004) suggest similar surface structure of $Au_{82}Si_{18}$ and $Au_{73}Si_9Ge_{14}$,but different structure for Au-Ge although the phase diagrams of Au-Si and Au-Ge are similar.

Surface structure of liquid $Au_{82}Si_{18}$ eutectic: low temperature phase (LT)

High Resolution Grazing Incidence Diffraction of $Au_{82}Si_{18}$



Truncation-Rods for two Bragg reflections (New Measurements)

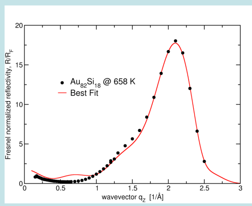


Vanishing intensity at Q_z=0.95Å^{-1} for all Bragg reflections

⇒ Crystalline phase is a bilayer with spacing of 3.31 Å.

Unit cell of the 2-dim phase: orthorhombic, a=7.39Å, b=9.39Å c=3.31Å.(c normal to the surface)

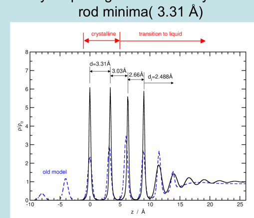
New Best Fit Model for Surface Structure Factor



Reflectivity data taken from: Shpyrko et al. Science 2006

New Best Fit Model for electron density

Identical first and second layers
1st layer spacing constrained by truncation rod minima(3.31 Å)



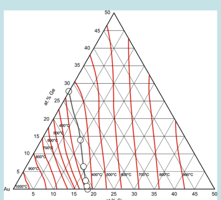
Is the new model of electron density physically more realistic ?

Surface structure in liquid Au-Si-Ge alloys ("low-temperature" region))

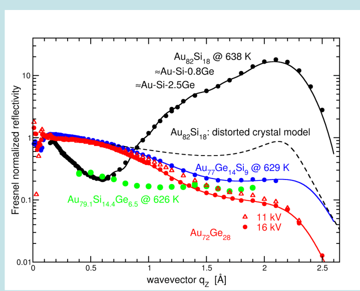
Effects attributed to Gibbs surface adsorption of Si and Ge (Ge displaces Si).

Ternary Au-Si-Ge phasediagram

Open circles indicate investigated eutectic compositions



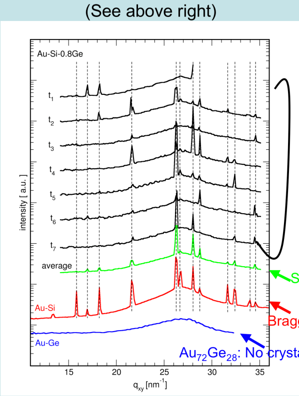
Reflectivity



Anomalous R/R_F for Au-Si-Ge (atm% Ge ≤2.5%). Normal R/R_F: (1) broken line is distorted crystal model (2) $Au_{72}Ge_{28}$ and (3) $Au_{77}Si_9Ge_{14}$. Energy dependence of data for $Au_{72}Ge_{28}$ proves Ge surface adsorption.

Grazing Incidence Diffraction

(See above right)

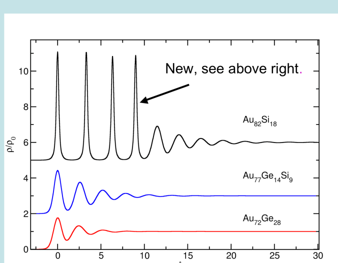


Trace amounts of Ge (0.8 atm%)

➔ Fluctuating GID

➔ large grain size.

Compare models for electron densities



- Ge ≤ 2.5 at-%: Anomalous reflectivity and crystalline surface phase formation in liquid phase.
- Ge ≥ 14 at-%: "Standard" surface similar to the distorted crystal mode.
- Ge = 28 at-%: Surface enrichment of Ge detected, in accordance with Gibbs adsorption rule.

➔ Deep eutectic alone is not responsible for surface phase formation in liquid.

➔ Influence of chemical interactions between the constituents ?

Mixing enthalpy of Au-Ge (-20 kJ/mol) less than of Au-Si (-30 kJ/mol)

➔ Correlation to bulk liquid structure and to glass forming ability? Au-Si forms a glass but Au-Ge does not.

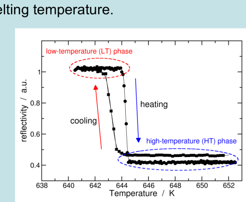
➔ Plan: investigate Pd-based alloys: Pd-Si, Pd-Ge, Pd-P: deep eutectics + even larger negative mixing enthalpy than Au-Si + high glass forming ability and prototypes for technological bulk metallic glasses.

Temperature dependence of surface phase formation

Previously:

1.) 1st order transformation from rigid 2D-surface low-temperature (LT) phase) to high-temperature (HT) phase at ~ 12°C above melting temperature.

2.) Similar effects observed in the alloys with Ge-content up to 2.5 at-%



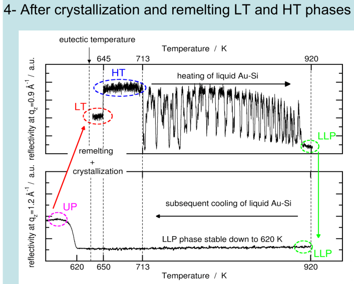
New: preliminary results!

1- Giant fluctuations in reflectivity set in at ~713 K and persist to ~920 K.

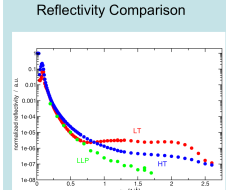
2- Above 920K there is a new surface (LLP).

3- Cooling from above 920K neither HT or LT phases form, but instead a new "unknown" phase (UP) forms at 620K. (I.e. below eutectic temperature)

4- After crystallization and remelting LT and HT phases are observed again.



Reflectivity Comparison



➔ Structure of liquid not uniquely described by temperature.

➔ Surface configurations depend on thermal history.

➔ Origin of this effect correlated to structure of bulk liquid ?

➔ Is this part of explanation for high overheating of melt necessary to form glass? Crystalline nuclei in the liquid directly after melting?

➔ Do liquid metal alloys have memory ?