

# Thermochemical and Kinetic Databases Designed for the Solar Grade Silicon Materials

Kai Tang  
SINTEF Materials and Chemistry  
Norway

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# Motivation

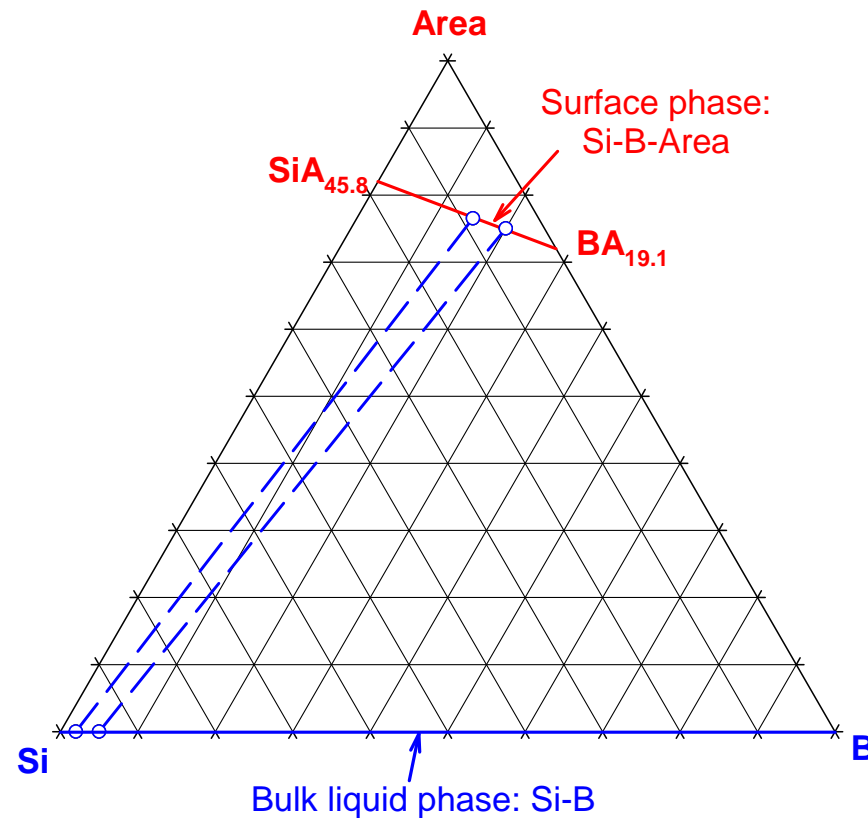
- Thermochemical properties of the impurities in pure Si are essential for the controlling and optimization of the SoG-Si feedstock production.
- The distribution of impurity in the sc- and mc-silicon, precipitation of impurity clusters/particles and doping process are all related to the diffusivity of impurity
- Coupling of the impurity diffusivities with their thermochemical properties may enhance our understanding and controlling of the impurities in SoG-Si ingot and wafer:
  - simulate the time-temperature-transformation relations of impurities in solid silicon. This may further be used to the defect engineering of SoG-Si (gettering, annealing, ...)
  - predict the grain boundary segregation of the impurities in mc-Si

# Motivation

- The Si-based thermochemical databank has recently been updated by implementation of the surface tension property. Surface tensions of the Si-based multicomponent melts are now able to determine directly from the equilibrium calculation.
- Other thermophysical properties, e.g. viscosity, conductivity, ...etc. will be implemented using the new developed physical based models.
- The thermophysical properties implemented databases are expected to
  - provide reliable basic data for other simulation tools (CFD for instance)
  - estimate the wettability between liquid silicon and different solid materials
  - evaluate the effect of nano-size particle on the phase equilibria in the Si-based system

# Basic principle for the surface tension calculation

- Equilibria between the bulk phase and a monolayer thickness surface phase is assumed
- An imaginary component, *Area*, is then introduced to the surface phase
- The constituents of surface phase are the “fictitious” components,  $SiA_m$ ,  $BA_n$ , ...



# Basic principle for the surface tension calculation

- The stoichiometry of the “surface area contained” component can be determined by the molar surface area of pure element
- Chemical potentials of the components in surface phase can be described by  $\mu_{i(\text{surf})} = \mu_{i(\text{bulk})} + A_i \sigma_i$
- The molar surface areas and surface tensions of the metastable liquid B, C, O and N have been estimated from the experimental values available in the literature. A special code has been written for this purpose.
- The chemical potential of the fictitious component,  $\mu_{\text{Area}}$ , is equivalent to the surface tension of liquid melt,  $\sigma$ , in the unit of mN/m.
- In this way the surface tension of the multicomponent melt can be directly determined using the commercial thermodynamic software, e.g. ChemSheet<sup>®</sup>.

# Information of the surface tension implemented thermochemical database

```
System Si-Ag-Al-Au-B-Bi-C-Ca-Co-Cr-Cu-Fe-Mg-Mn-Mo-N-Ni-O-P-S-Sb-Sn-Ti-W-Zr-Area
```

System Components:

1: Al	2: Area	3: Au
4: B	5: C	6: Ca
7: Co	8: Cu	9: Fe
10: Mg	11: Mn	12: Mo
13: N	14: Ni	15: O
16: P	17: S	18: Sb
19: Si	20: Sn	21: Ti
22: W	23: Zr	

Mixture Phases:

1: BULK	2: SURFACE	3: Solid
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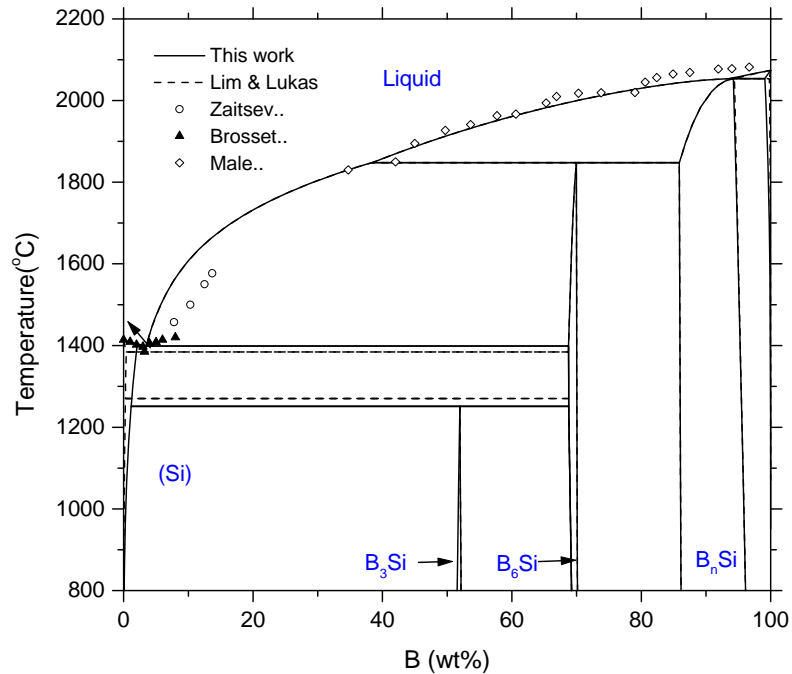
Stoichiometric Condensed Phases:

1: SiB3	2: SiB6	3: SiC_csi
4: SiO2_cristobalite	5: SiO2_quartz	6: SiP2
.....		
64: Al_fcc	65: Area	66: B2O3
.....		

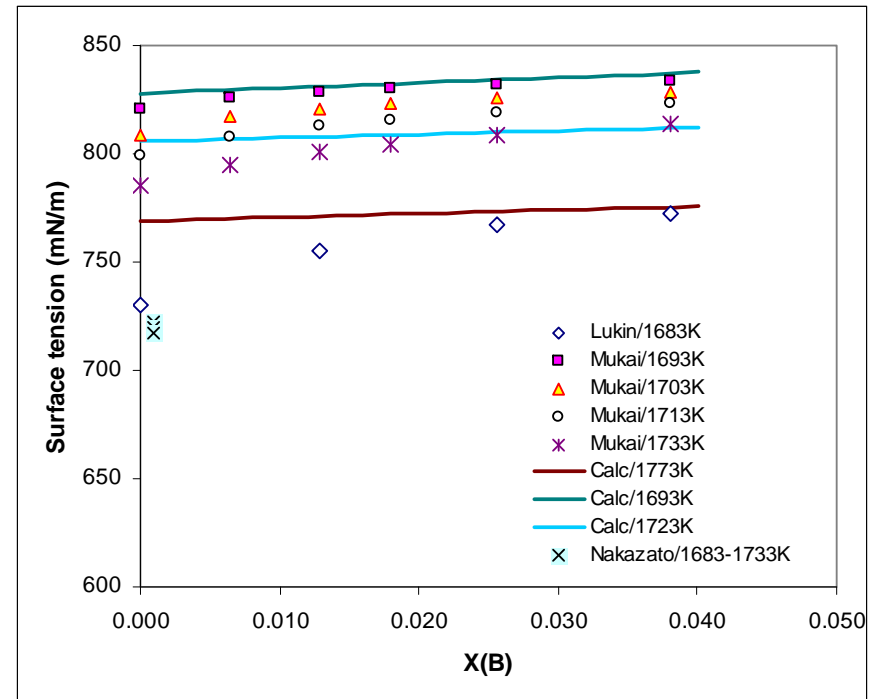
Fictitious component "Area" and artificial "surface" phase are added for the determination of the surface tension of liquid alloy

# The Si-B system & surface tension

## The Si-B system

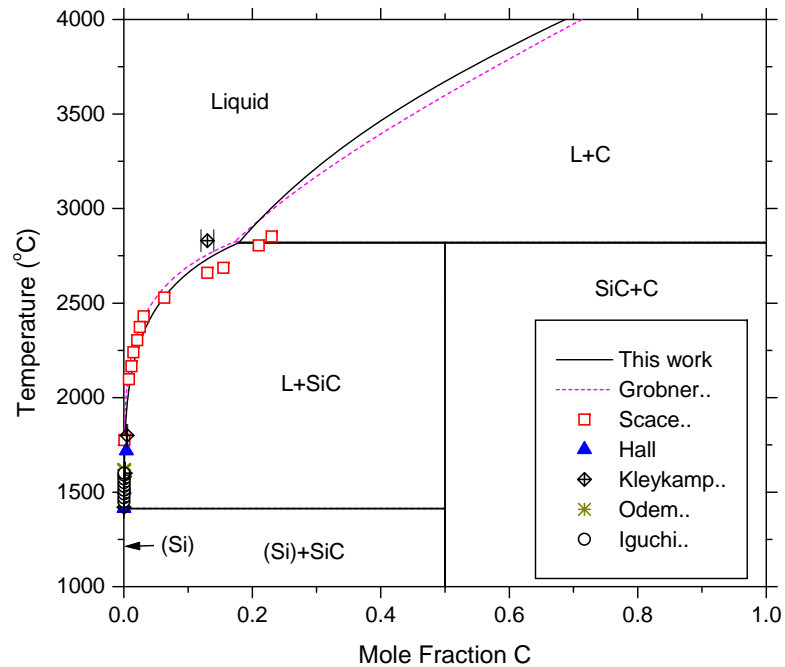


## Surface tension of Si-B melt

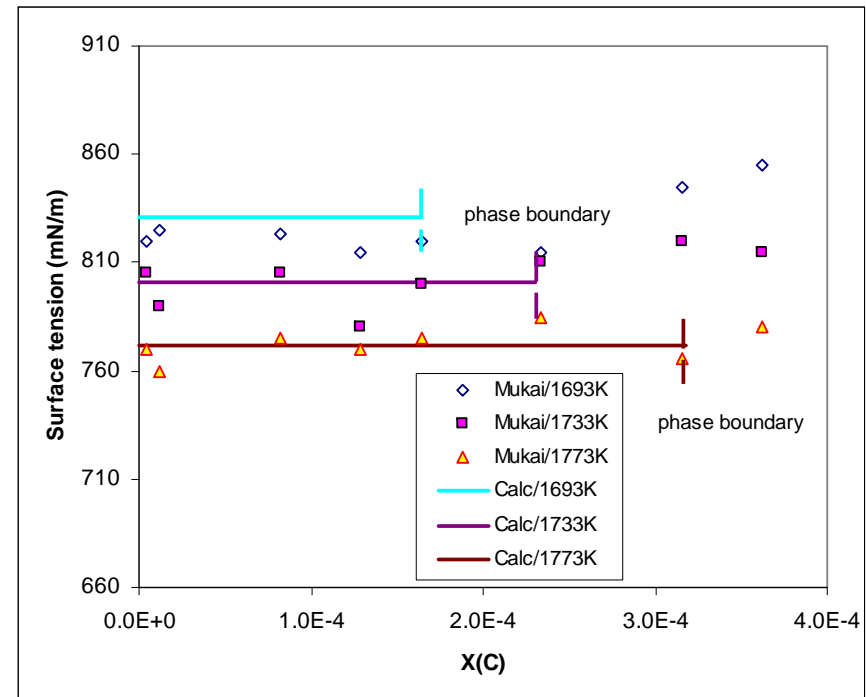


# The Si-C system & surface tension

## The Si-C system

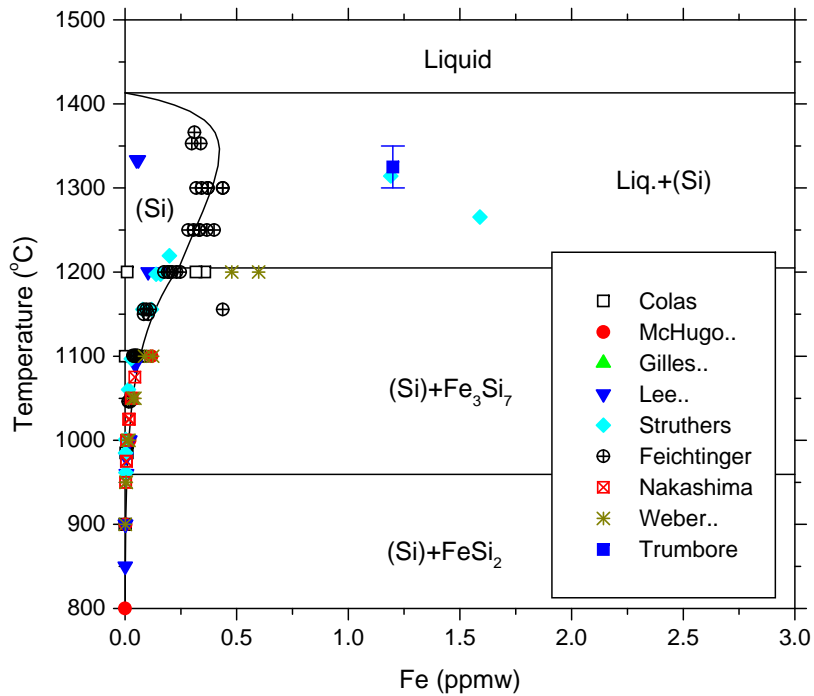


## Surface tension of Si-C melt

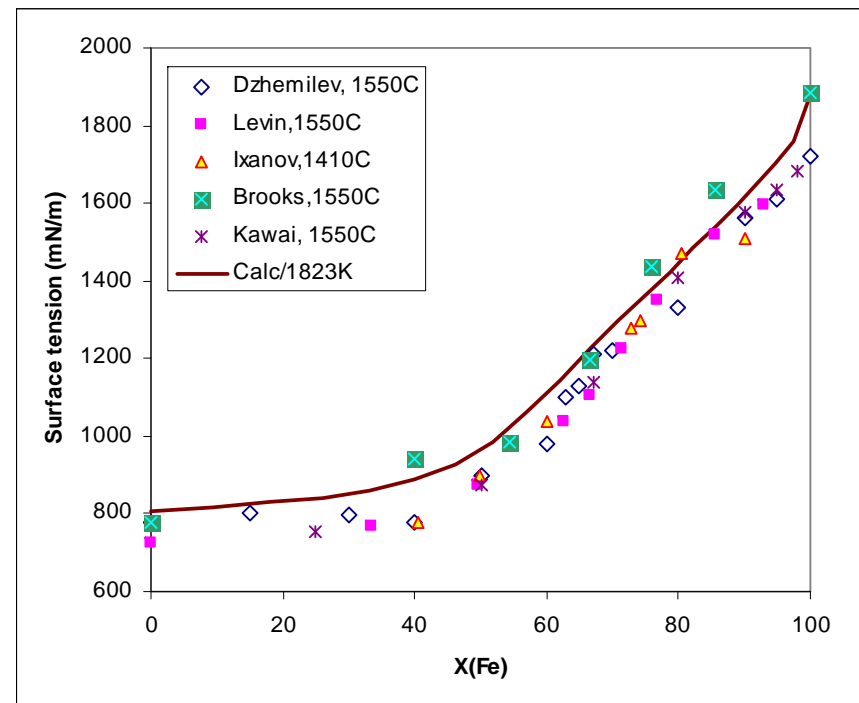


# The Si-Fe system & surface tension

## The Fe-Si system

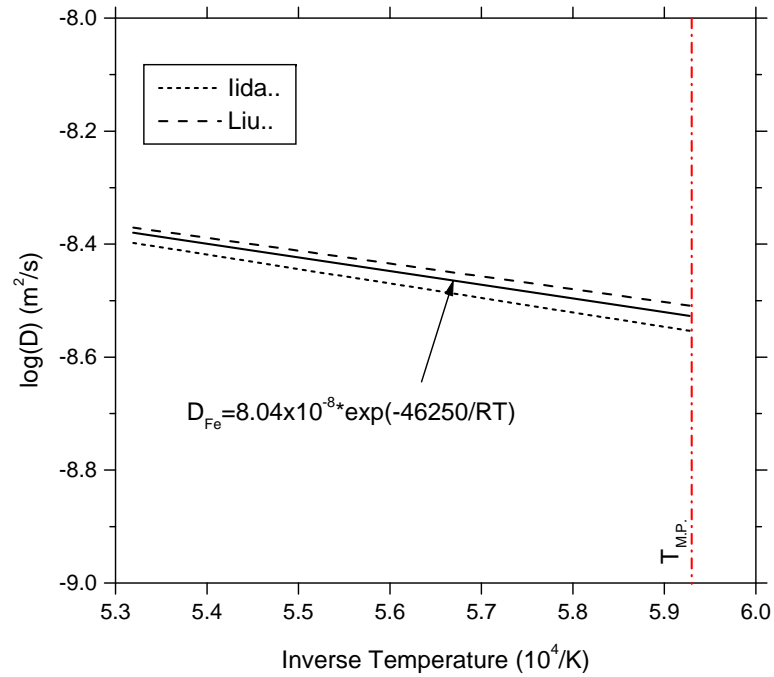


## Surface tension of Si-Fe melt

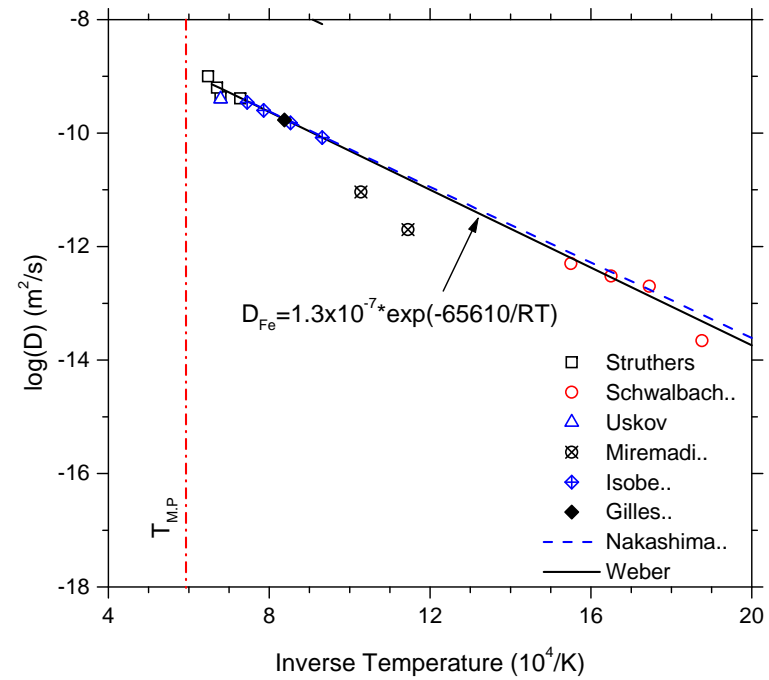


# Diffusivity of Fe

■ The diffusivity of Fe in Si

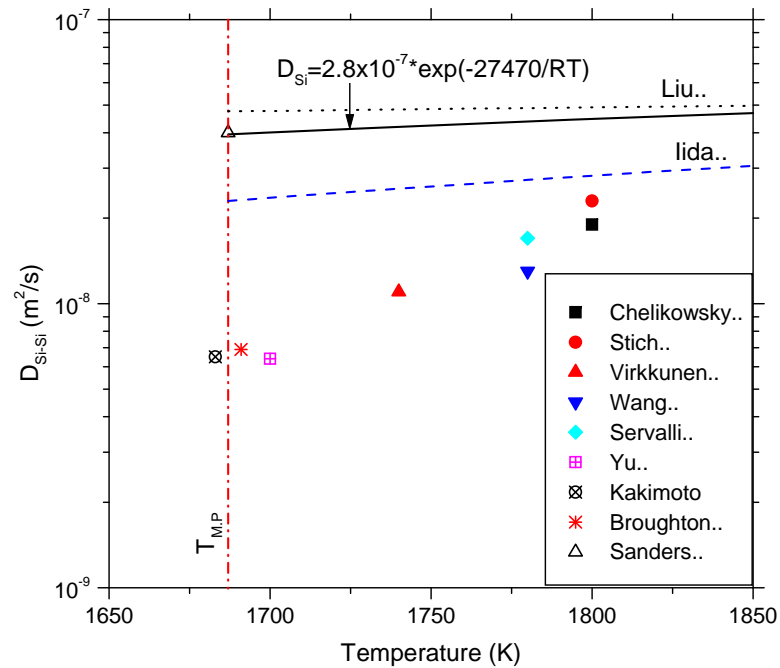


■ The diffusivity of Fe in (Si)

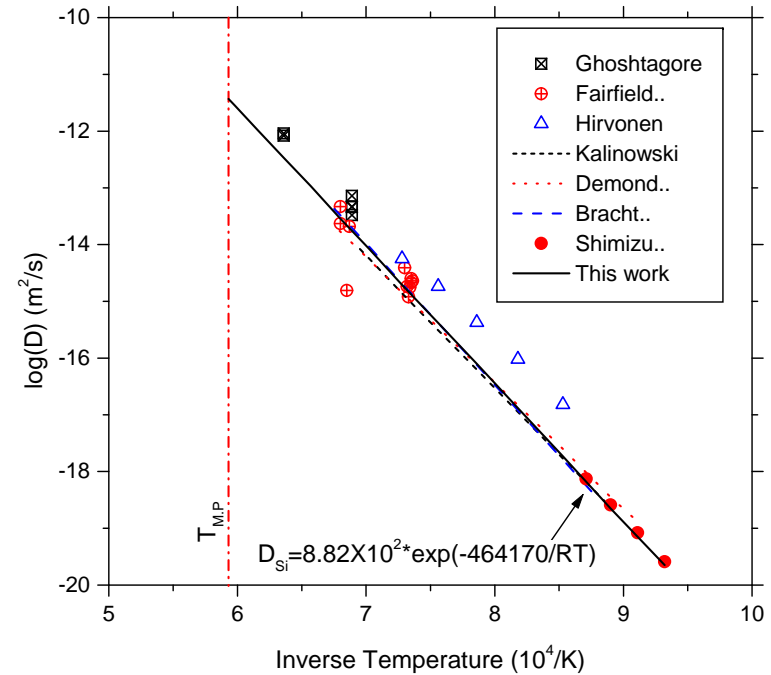


# Si self-diffusivity

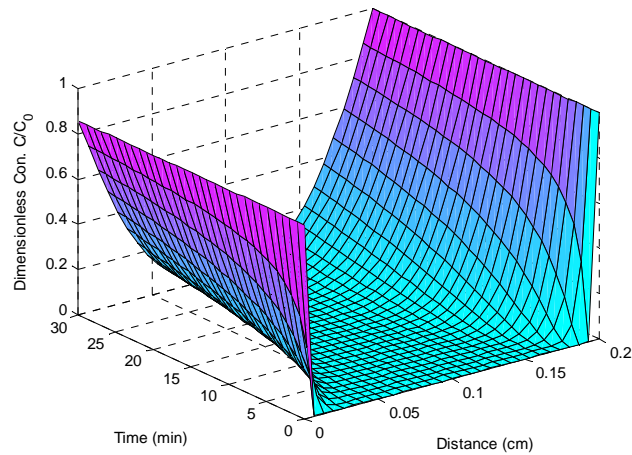
## Si self-diffusivity in $\underline{\text{Si}}$



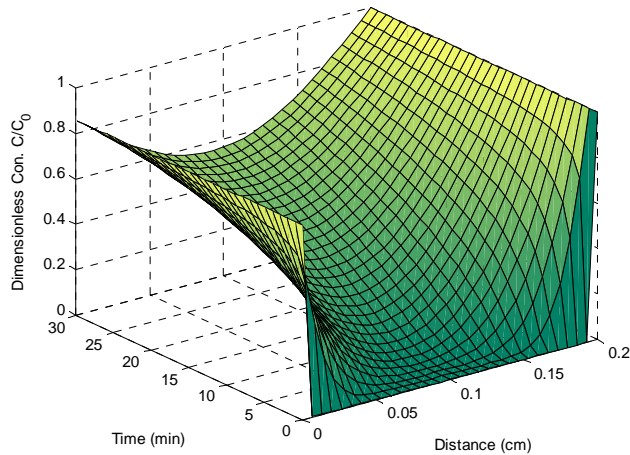
## Si self-diffusivity in (Si)



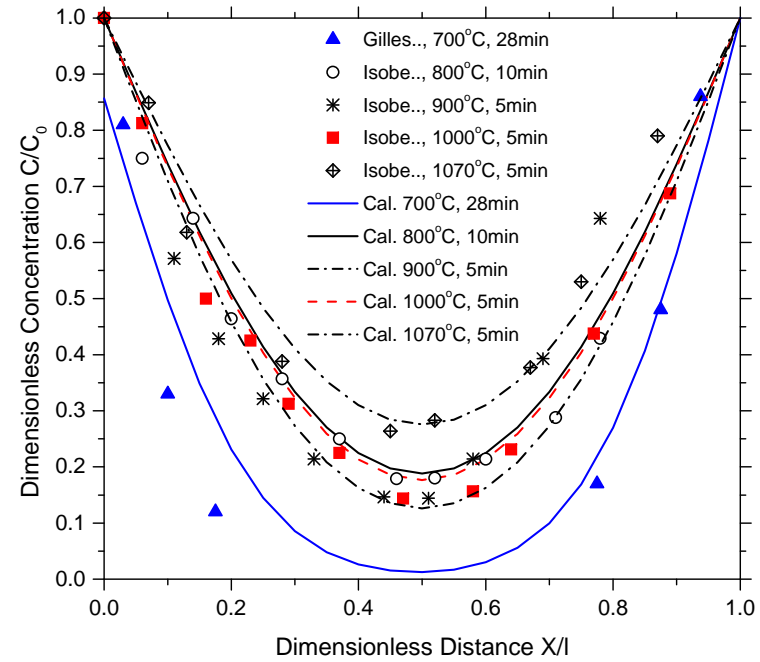
# Fe distribution profile in Si wafer & 3D-simulation of Fe distribution profile



800°C

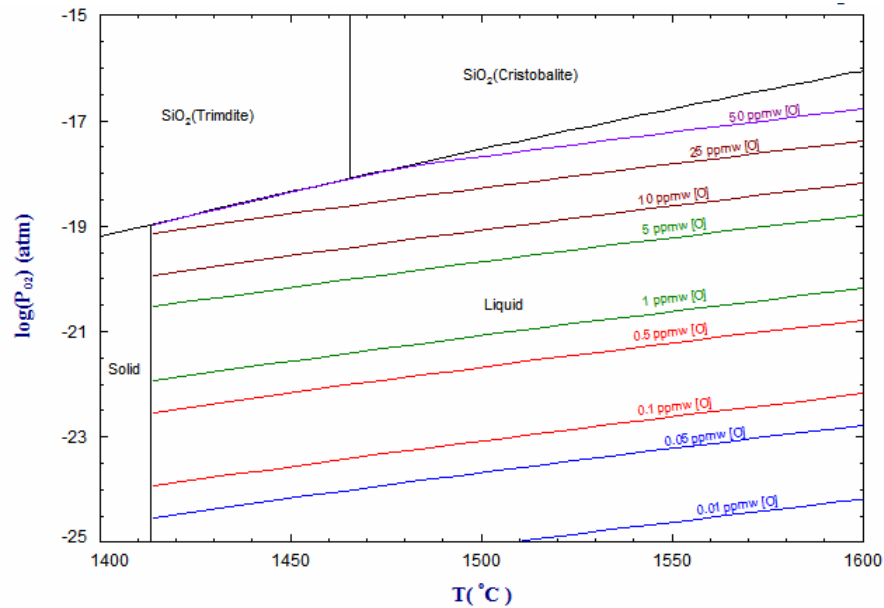


1000°C

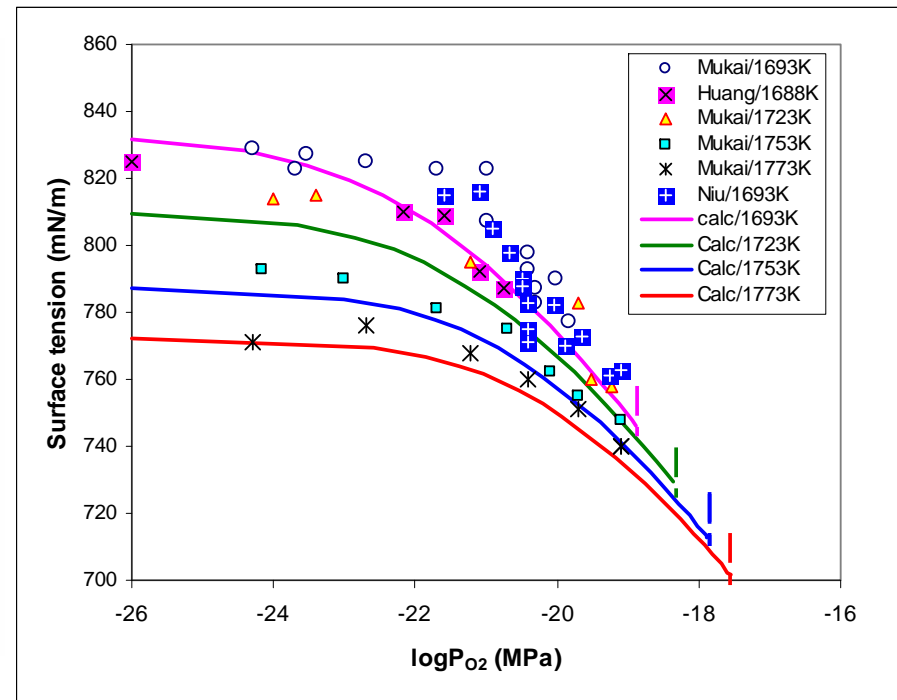


# Phase equilibria in the Si-O system & surface tension of Si-O melt

■ The Si-O system



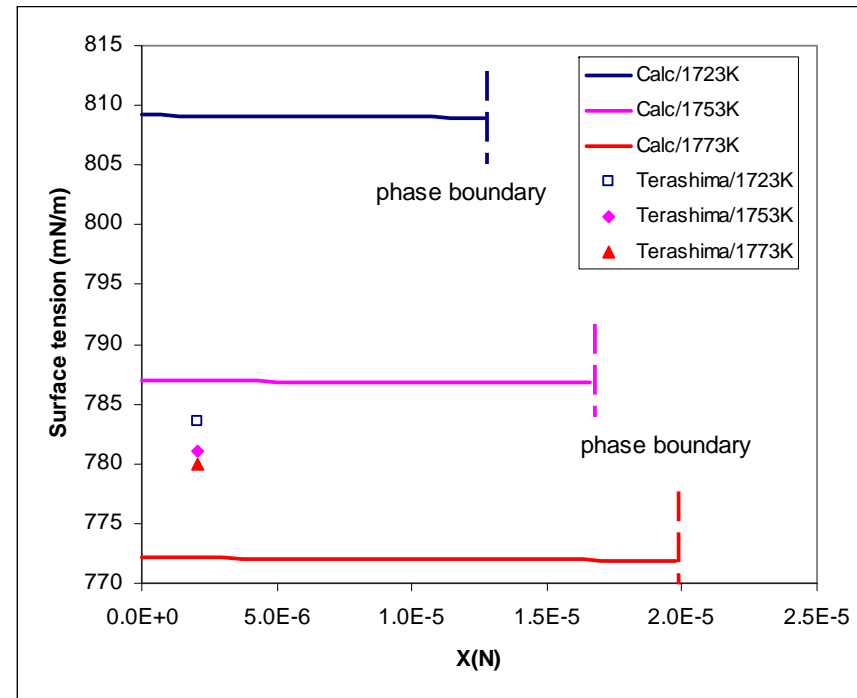
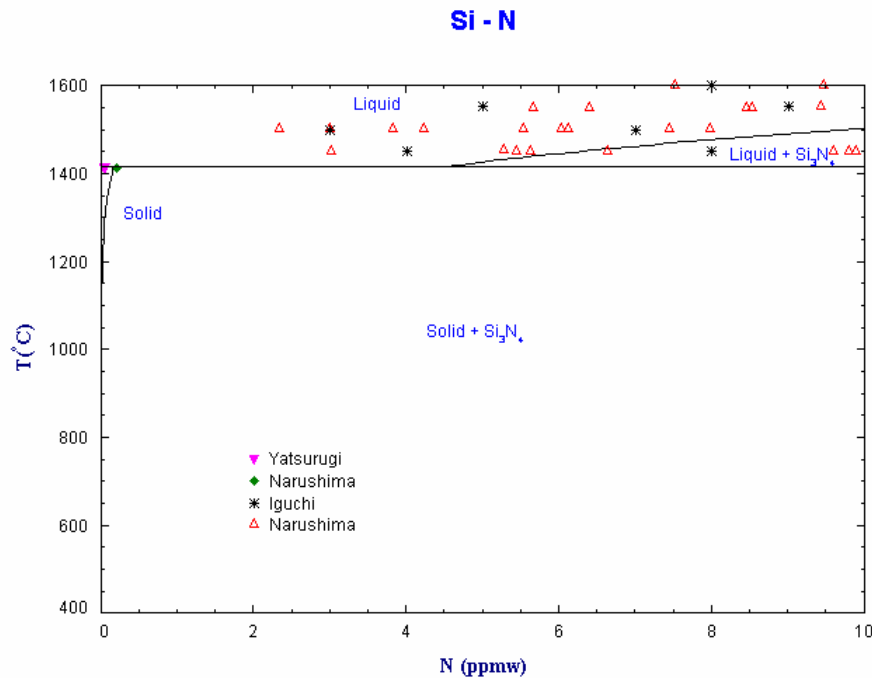
■ Surface tension of Si-O melt



# Phase equilibria in the Si-N system & surface tension of Si-N melts

■ phase equilibria in the Si-N system

■ surface tension of Si-N melt

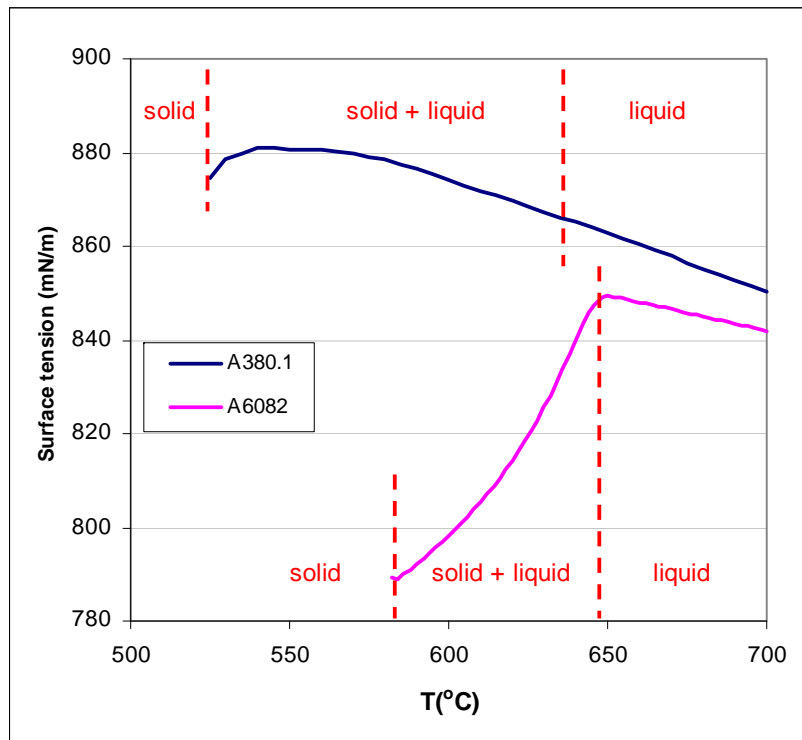


# Discussion

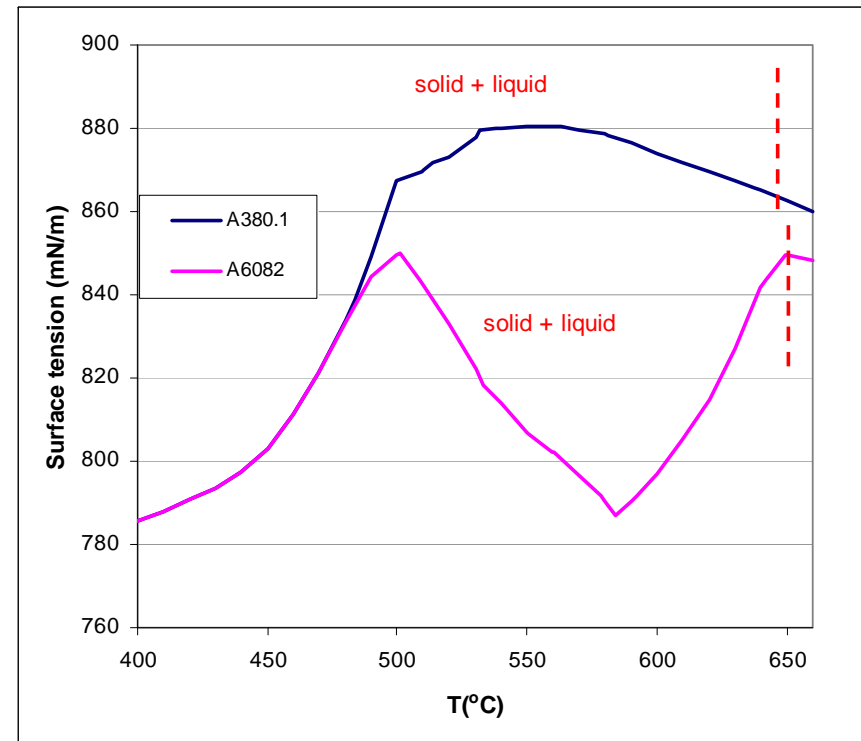
- Effect of impurity on the surface tensions of liquid silicon can be reliably calculated using the special designed thermochemical database. The surface-related properties, e.g. temperature coefficient and composition gradient of surface tension, surface excess quantity, even the driving force due to the surface segregation are readily obtained from the database.
- In addition to the surface tension, phase equilibria and thermochemical properties of the corresponding system can simultaneously be obtained in the calculation. This may provide more efficient and accurate way to simulate the practical problems.
  - Example 1: the surface tension changes of commercial Al-alloys, A380 and A6082, along with the equilibrium/non-equilibrium solidification paths can now be simulated using the special thermochemical database.
  - Example 2: the surface tension variations along with the liquidus boundary of Pb-Sn solder alloy can also be simulated

# Surface tension changes of commercial Al-alloys along with the solidification paths

## Equilibrium cooling

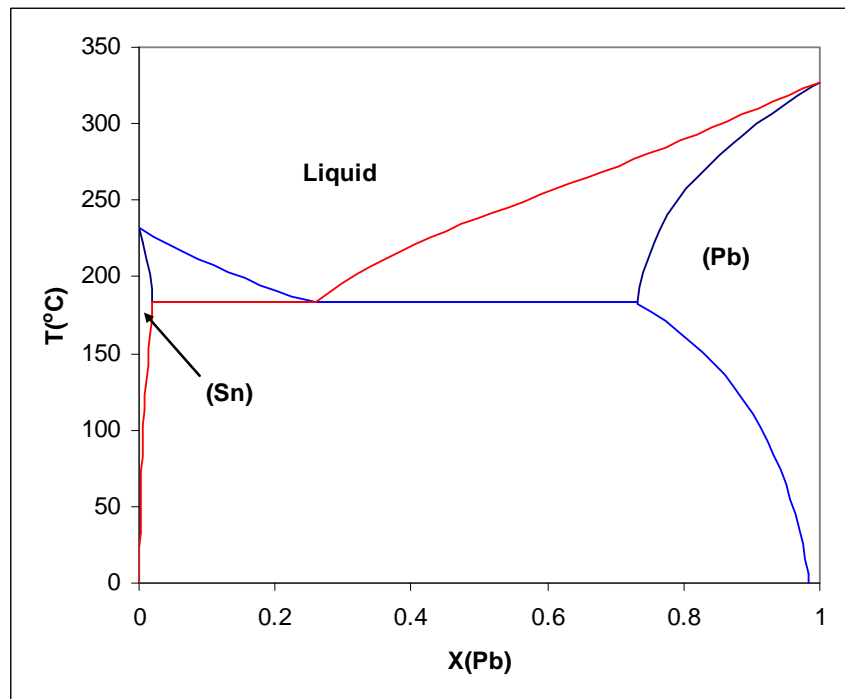


## Scheil cooling

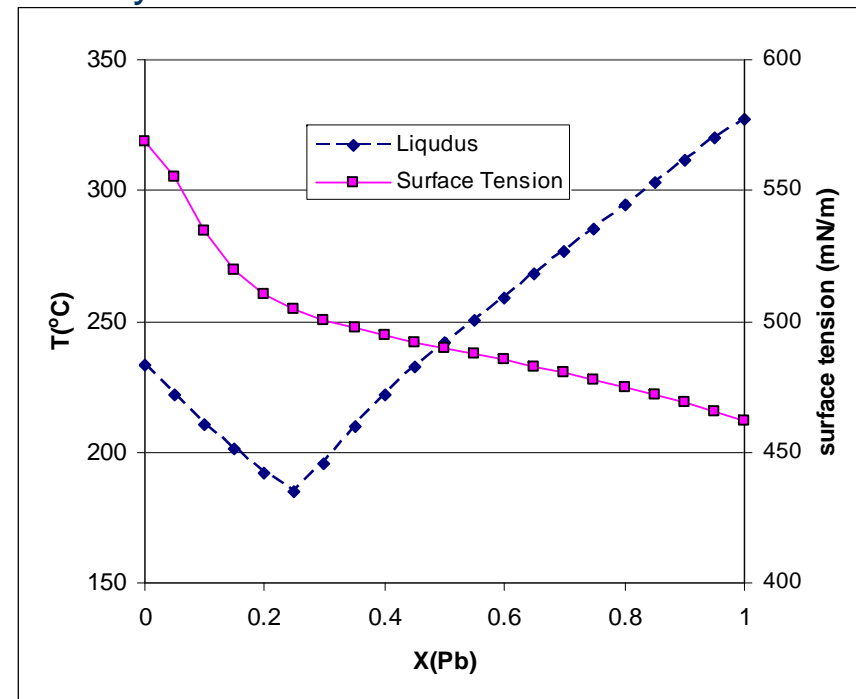


# Surface tension changes along with the liquidus boundary of micro-solder alloys

## ■ The Pb-Sn system



## ■ Surface tension variations along with the liquidus boundary in the Pb-Sn system



# Conclusion

- Thermochemical properties of the Si-based [Al-As-B-C-Fe-N-O-P-S-Sb](#) system have been reevaluated at SINTEF MK. By appending the existing assessments for the Si-X binary and ternary systems, a thermochemical database covers the Si-Ag-Al-As-Au-B-Bi-C-Ca-Co-Cr-Cu-Fe-Ga-In-Li-Mg-Mn-Mo-N-Na-Ni-O-P-S-Sb-Te-Ti-V-W-Zn-Zr system has been developed.
- The Si-based thermochemical database has recently been updated by implementing the liquid surface properties. Effect of impurity on the surface tensions of liquid silicon can be reliably evaluated using the special thermochemical database.
- In addition to the surface tension, phase equilibria and thermo-chemical properties of the corresponding system can simultaneously be obtained in the calculation. This may provide more efficient and accurate way to simulate the practical problems. ( e.g. The surface tension/viscosity implemented micro-solder alloy thermochemical database is expected to work more efficiently for the design/optimization of the lead-free solder alloys).

# Suggestion

- Thermo-Calc Software AB has high reputation worldwide on thermochemical and kinetic simulation. Cooperation between Thermo-Calc and SINTEF MK will be fruitful:  $1+1>2$  !
- The following cooperation areas are suggested by the present author:
  - modeling the substitutional & interstitial species in solid Si phase –  $\text{Si}_s$ ,  $\text{Si}_i$ ,  $\text{Fe}_s$ ,  $\text{Fe}_i$ , ...
  - modeling the metastable cluster/phases appear in the Si-based materials – “B-Fe”, “B-O”, ... pairs
  - modeling the behavior of metastable precipitators (TTT diagram, annealing, ...)
  - ...