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Study of Nickel Silicide as a Copper Diffusion Barrier in Monocrystalline Silicon Solar Cells

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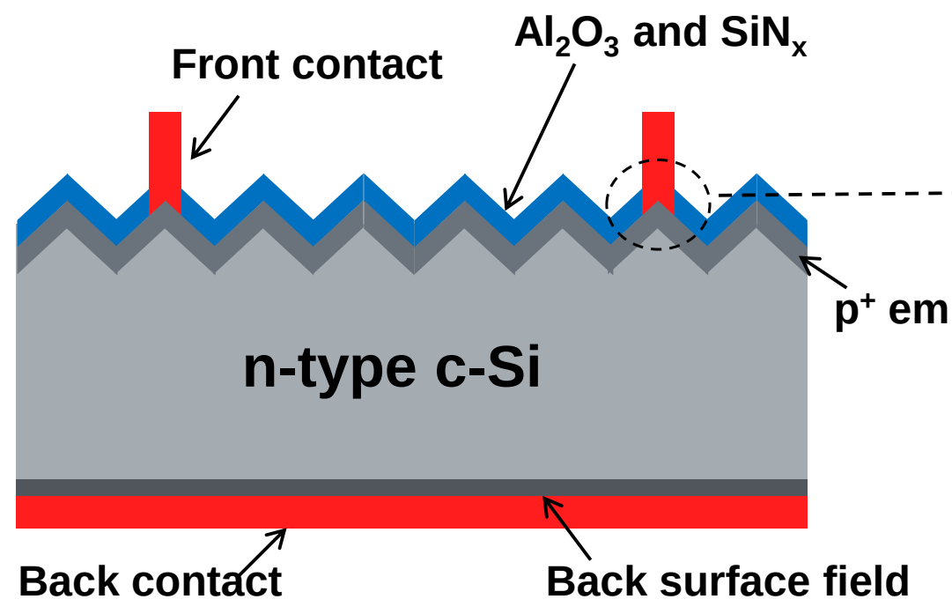
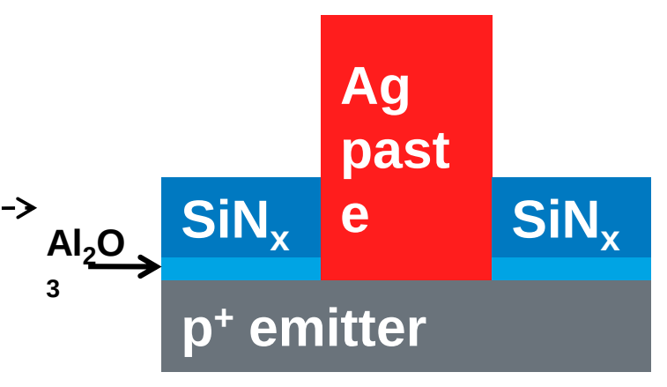
Motivation – Replace Ag with Cu

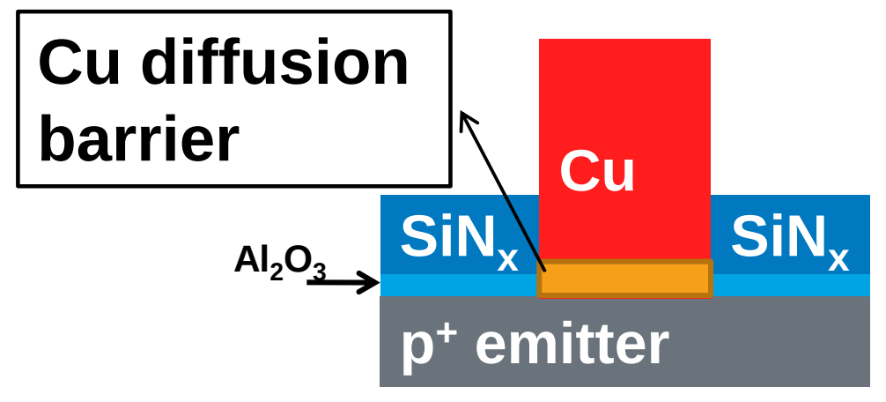


n-type c-Si solar cell structure



Screen printed Ag paste firing process

Cu precipitates in Si reduce lifetime



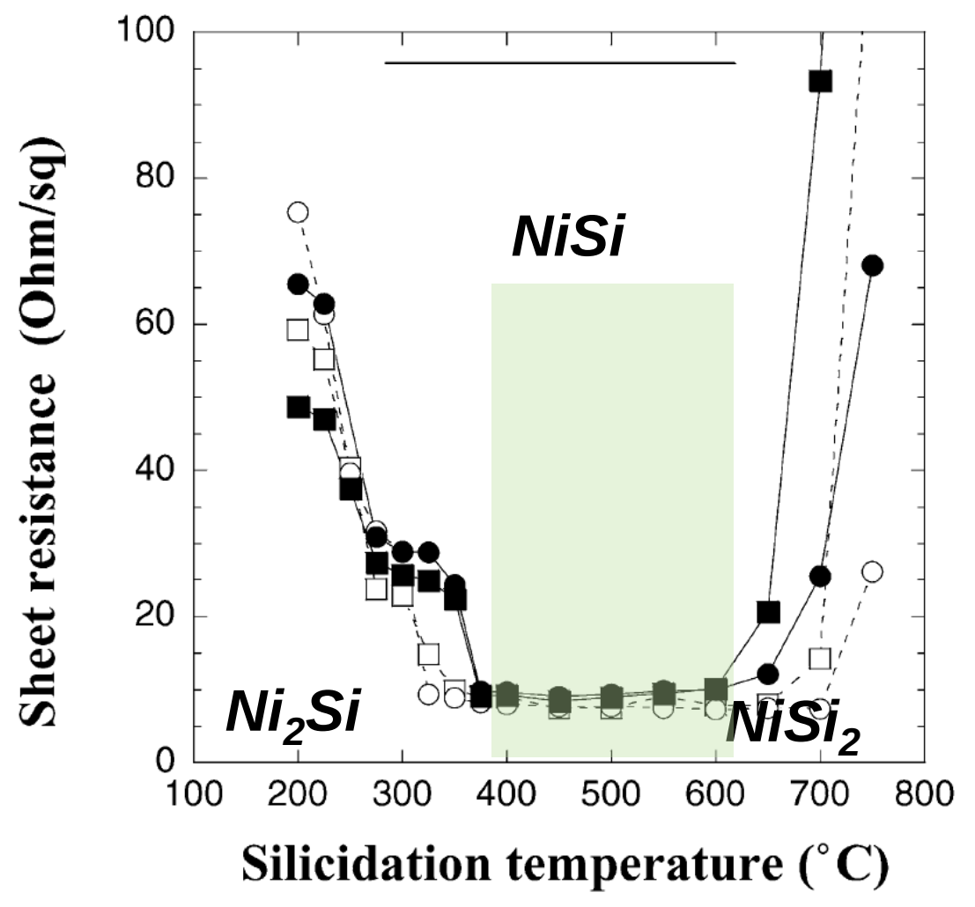
Electroplated Cu contact

- Ag is expensive
- Glass frit, organic binder, solvents
- High contact resistance
- Shading losses

Why study NiSi as Cu diffusion barrier?

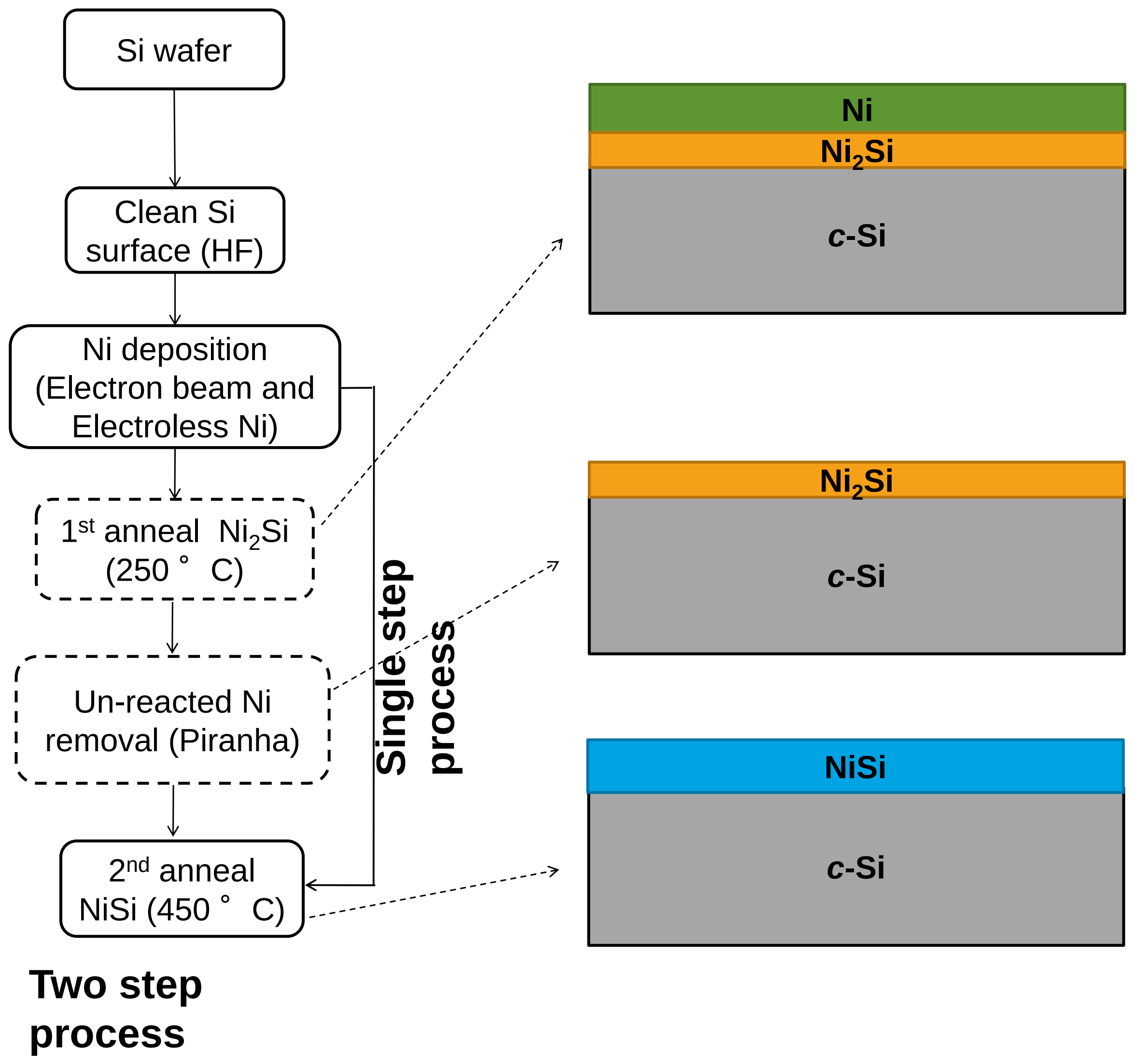
- Metal silicides in microelectronics
  - Ohmic and Schottky barrier contacts.
  - Gate electrodes and Interconnects.
  - Diffusion barriers.
  - **NiSi** and $CoSi_2$ are commonly used.

	$CoSi_2$	NiSi
Resistivity (μΩ-cm)	14-20	14-20
Formation temperature (° C)	600-800	400-600
Si consumption (nm per nm of metal)	3.6	2.2
Controlling mechanism	Kinetics	Ni Diffusion



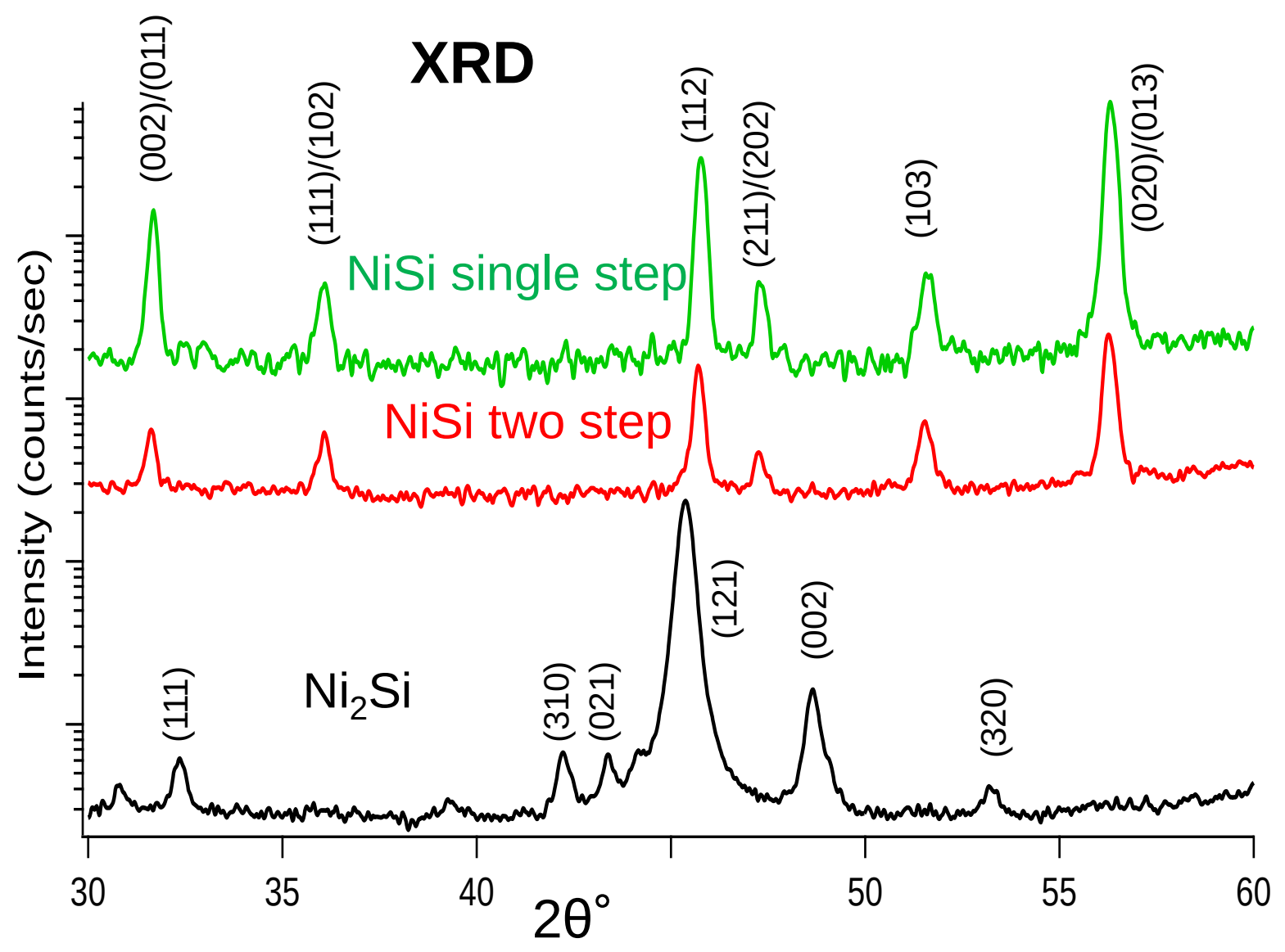
Chen, *JOM*. **57**(9), 24-31 (2005)
Lauwers, *Mat. Sci. Eng. B*. **114-115**, 29-41 (2004)

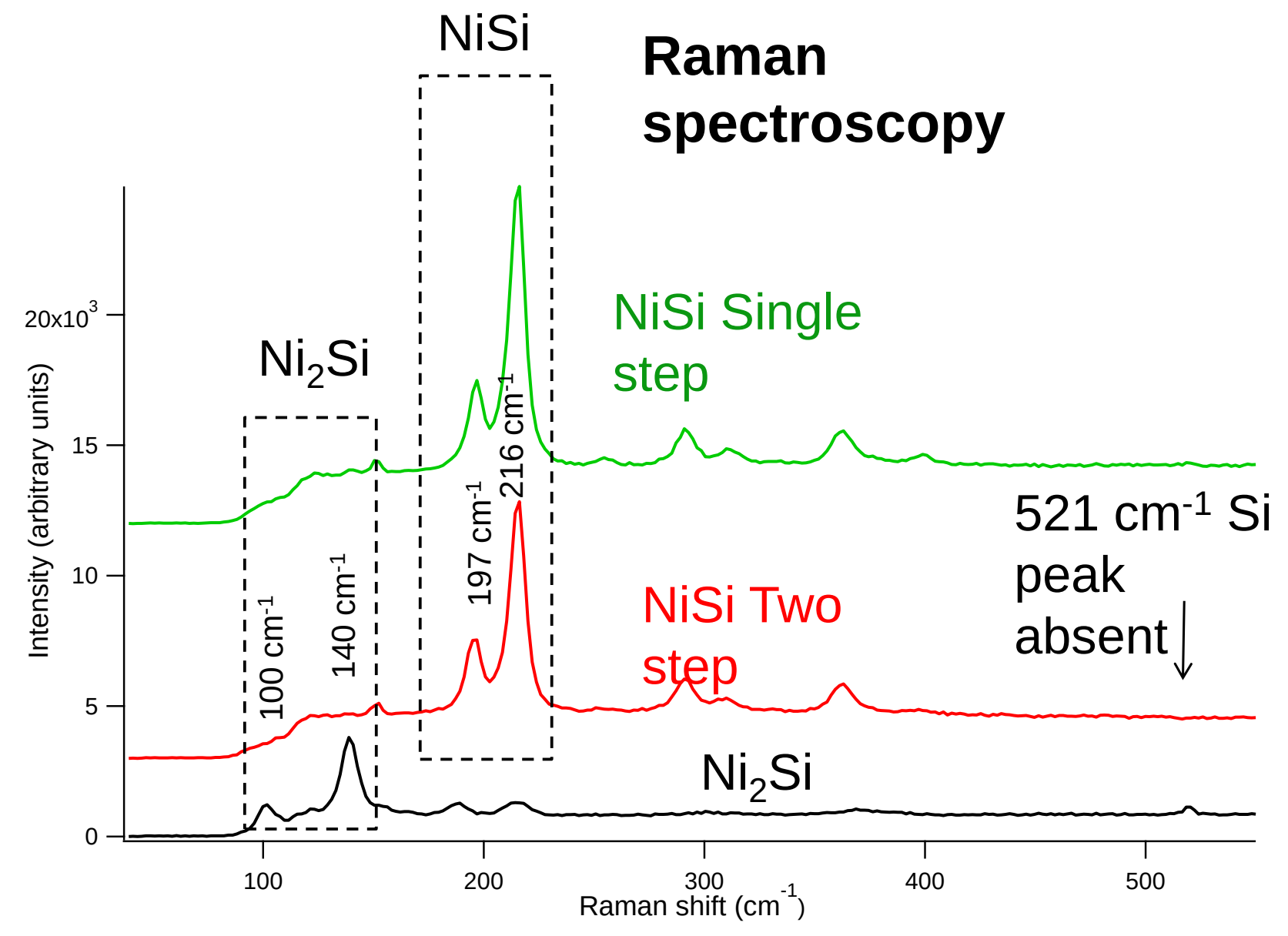
Formation of NiSi



Single step process eliminates need of Piranha etch and 1st anneal.

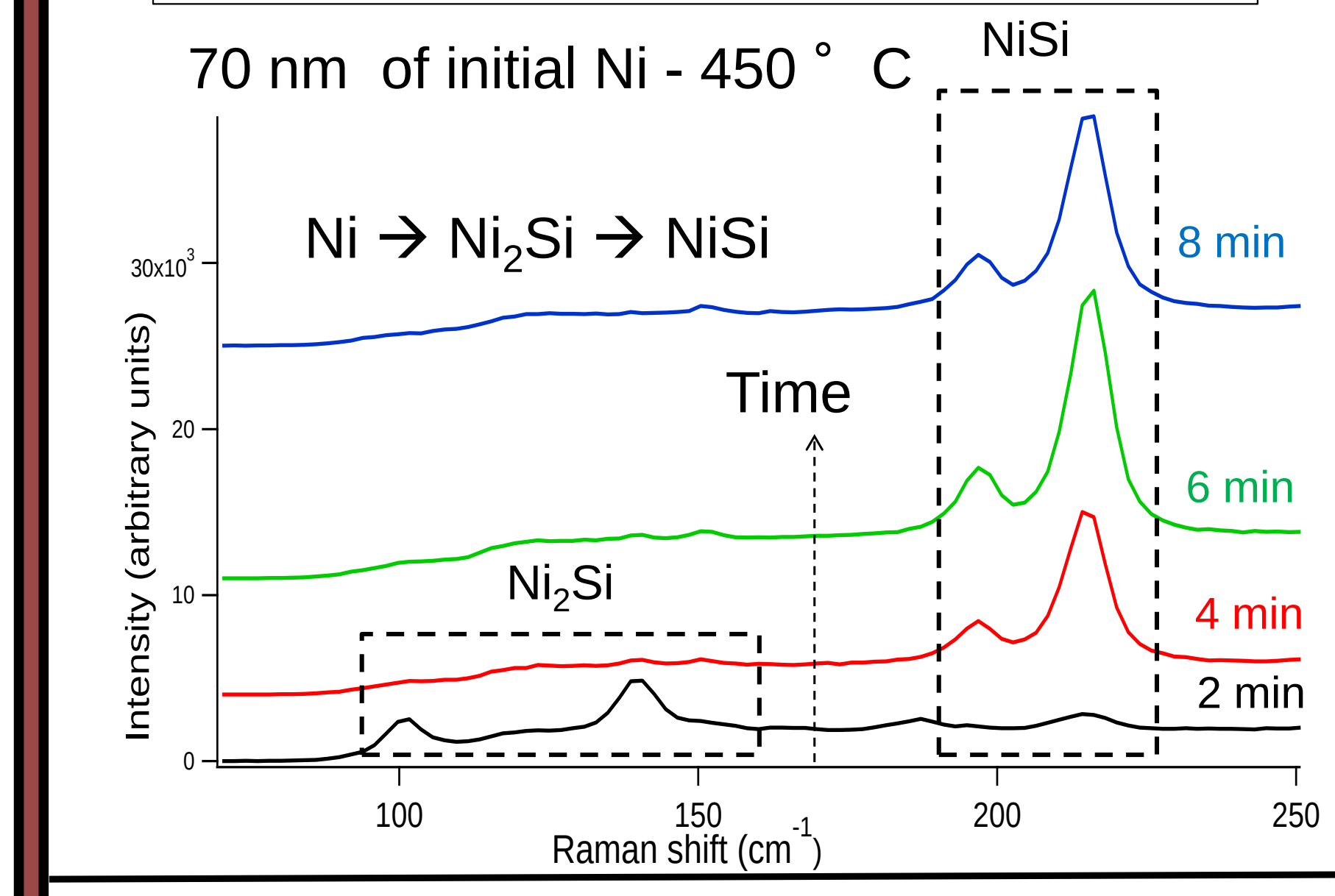
Conversion of *e*-beam Ni to NiSi





Single step – Ni/*c*-Si to NiSi conversion via formation of Ni_2Si

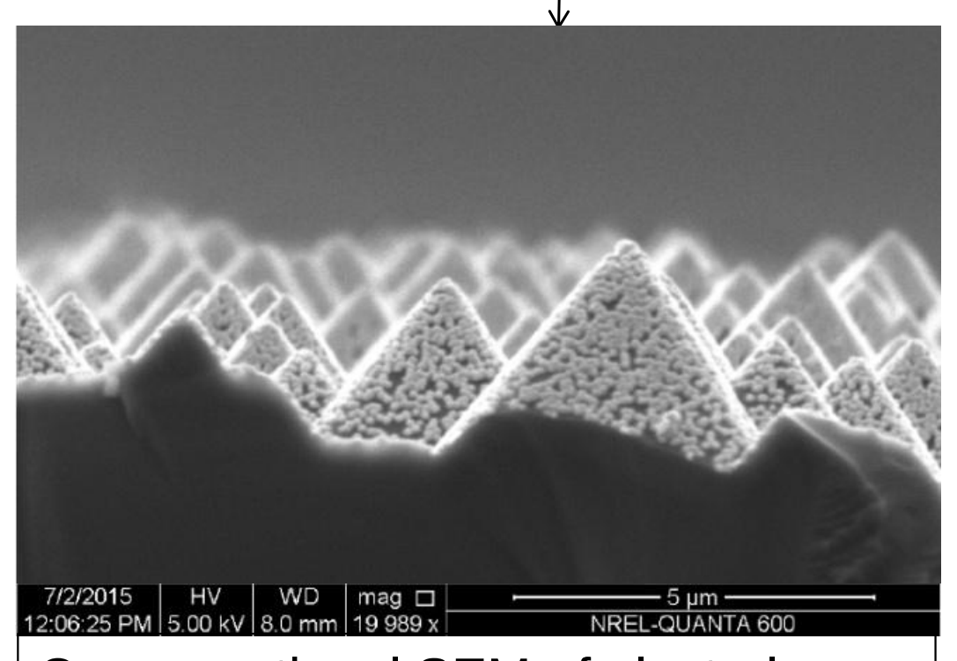
70 nm of initial Ni - 450 ° C



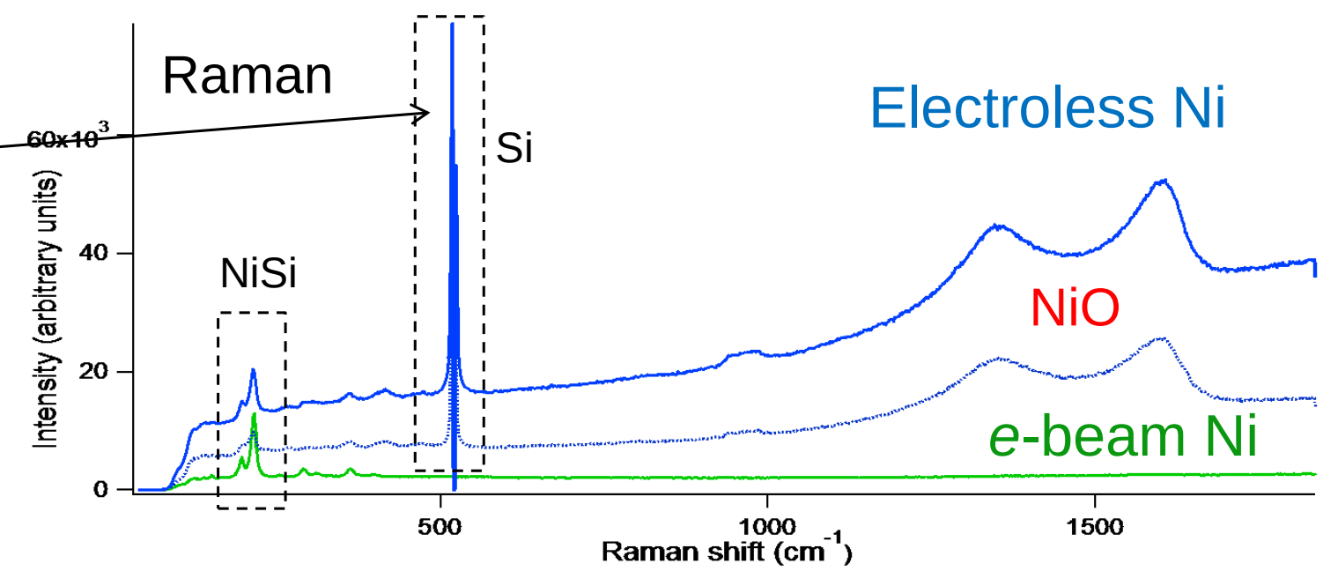
- NiSi from single step as good as from two step process.
- Complete surface coverage using *e*-beam Ni.
- Formation of NiSi occurs through formation of Ni_2Si

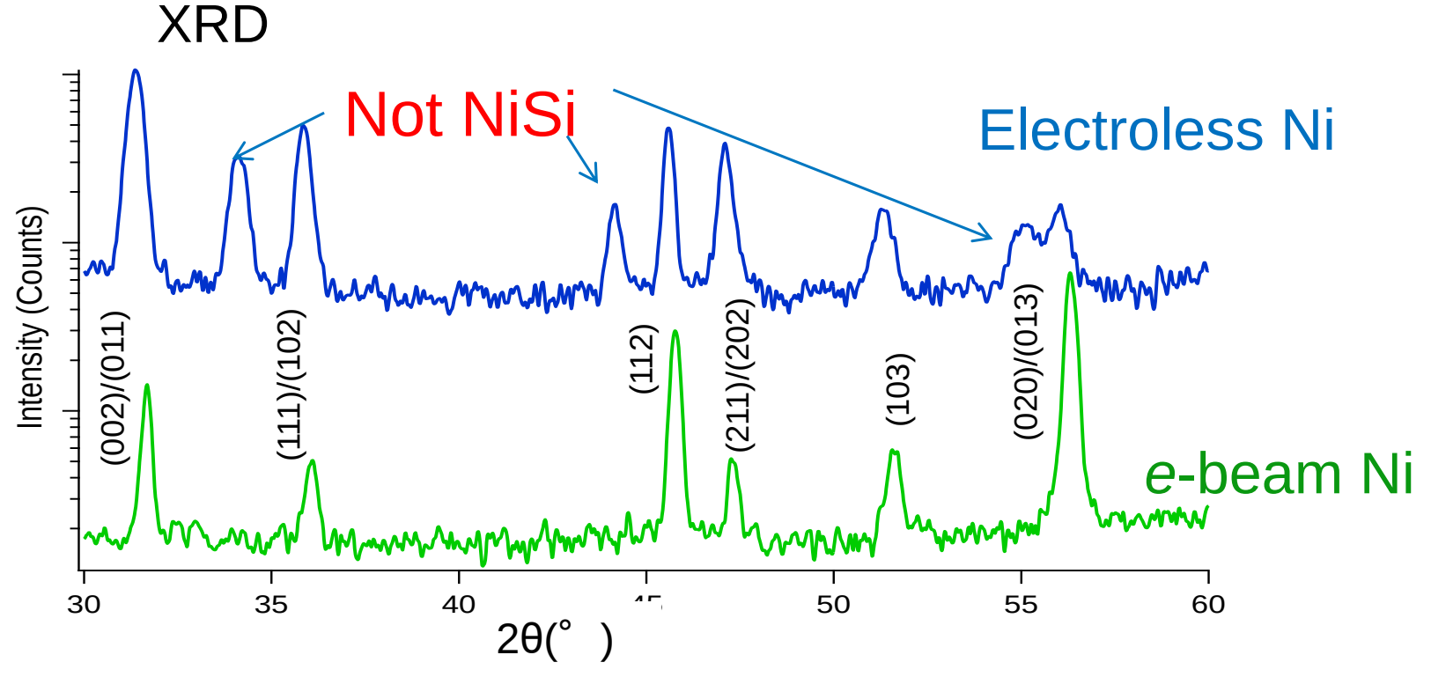
Conversion of electroless Ni to NiSi

Incomplete coverage of Si



Cross sectional SEM of electroless Ni on textured Si surface





- Oxygen and phosphorus are know contaminants in electroless Ni process

Tous et al., *Energy Procedia* **21**, 39-46 (2012)

Diffusivity and solubility of Cu in Si

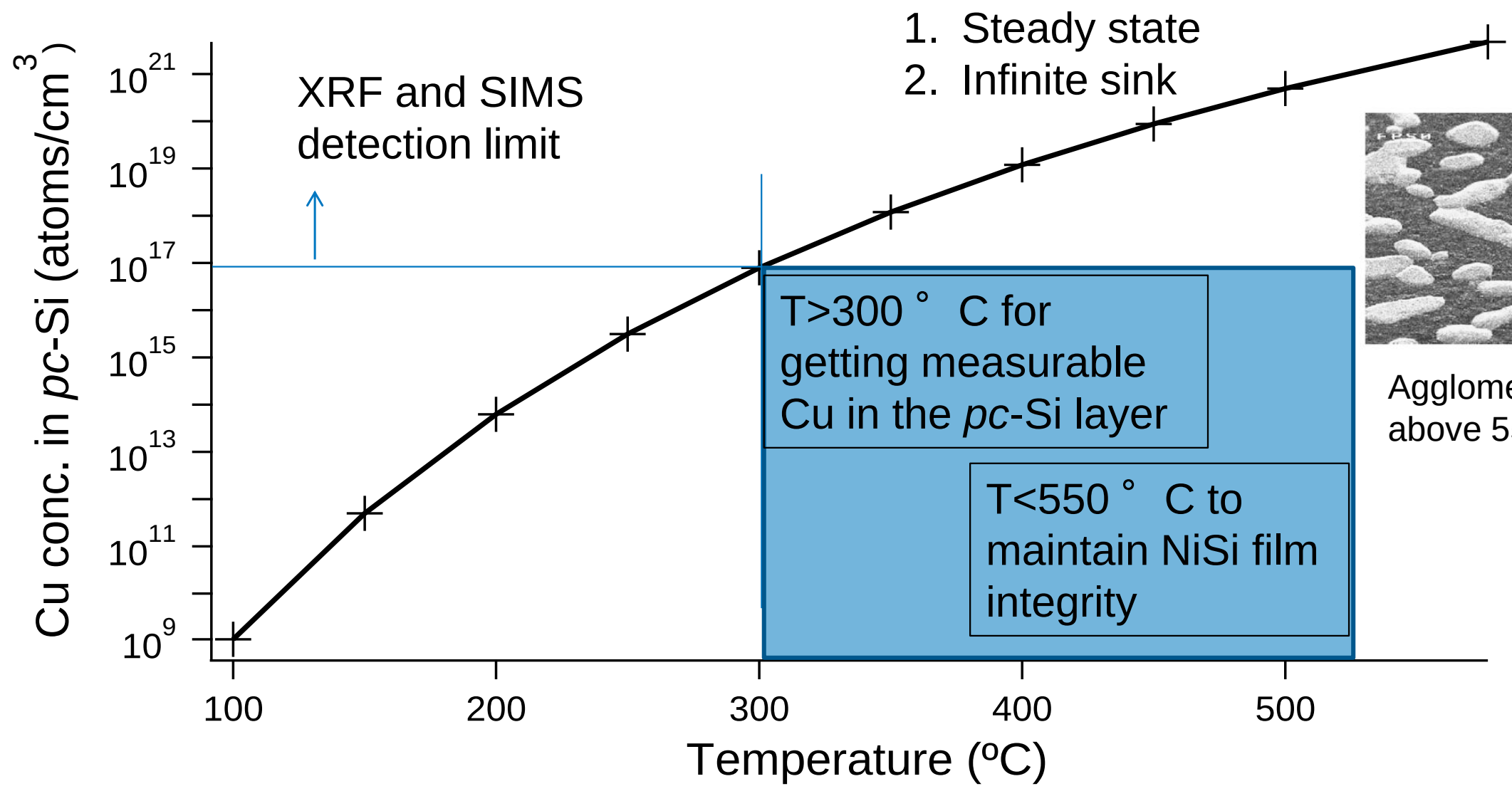
$$D_{int} = 3\times10^{-4}\times\exp\left(-\frac{0.18\,eV}{k_BT}\right)cm^2/sec$$

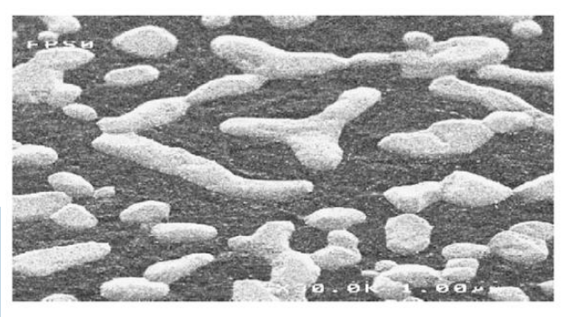
$$S = 5.51\times10^{23}\times\exp\left(-\frac{1.49\,eV}{k_BT}\right)cm^{-3}$$

$$N_{Cu} \propto \frac{D}{L}\times S\times t$$

N_{Cu} gives the amount of Cu that accumulates in the infinite sink after time 't' here, 11 hrs

Assumptions:
1. Steady state
2. Infinite sink



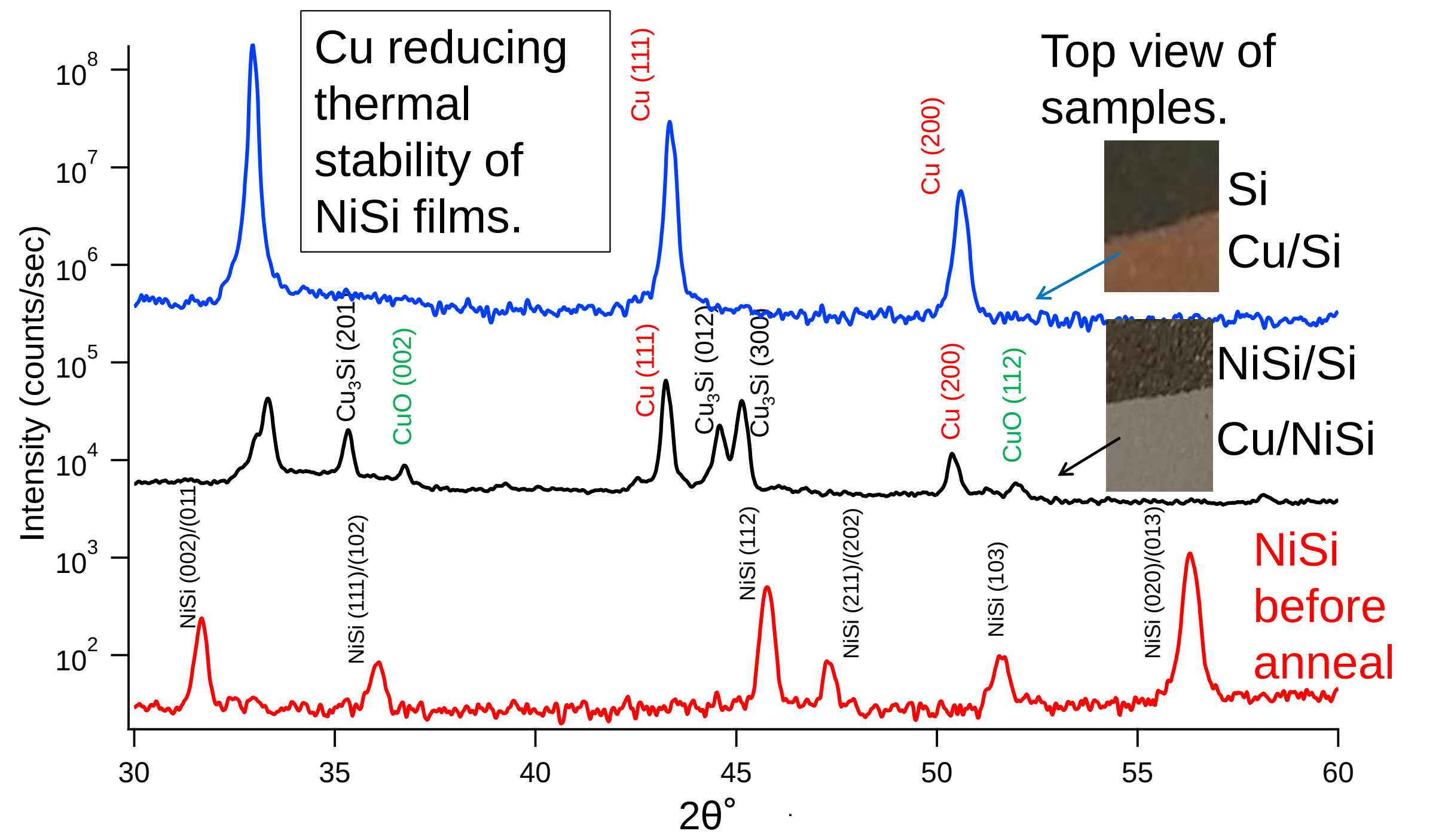


Agglomeration of NiSi above 550 ° C

Istratov et al., J. *Electrochem. Soc*. **149** (1), G21-G30 (2002)
Foggiato et al. *Mat. Sci. Eng. B* **114–115**, 56–60 (2004)

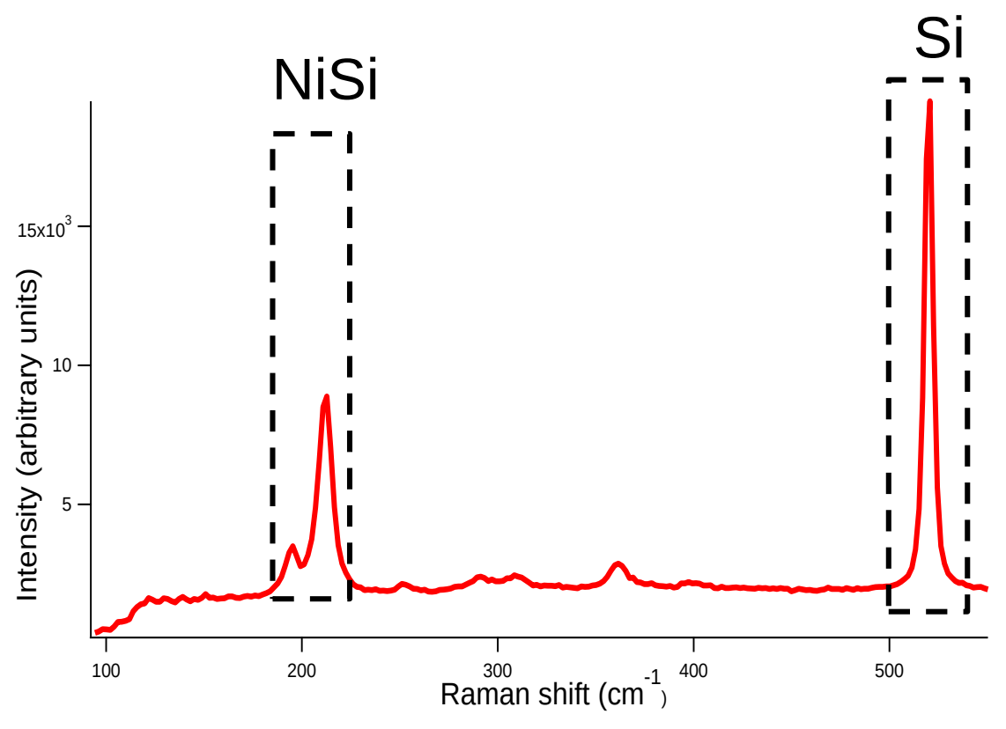
Degradation of NiSi due to Cu

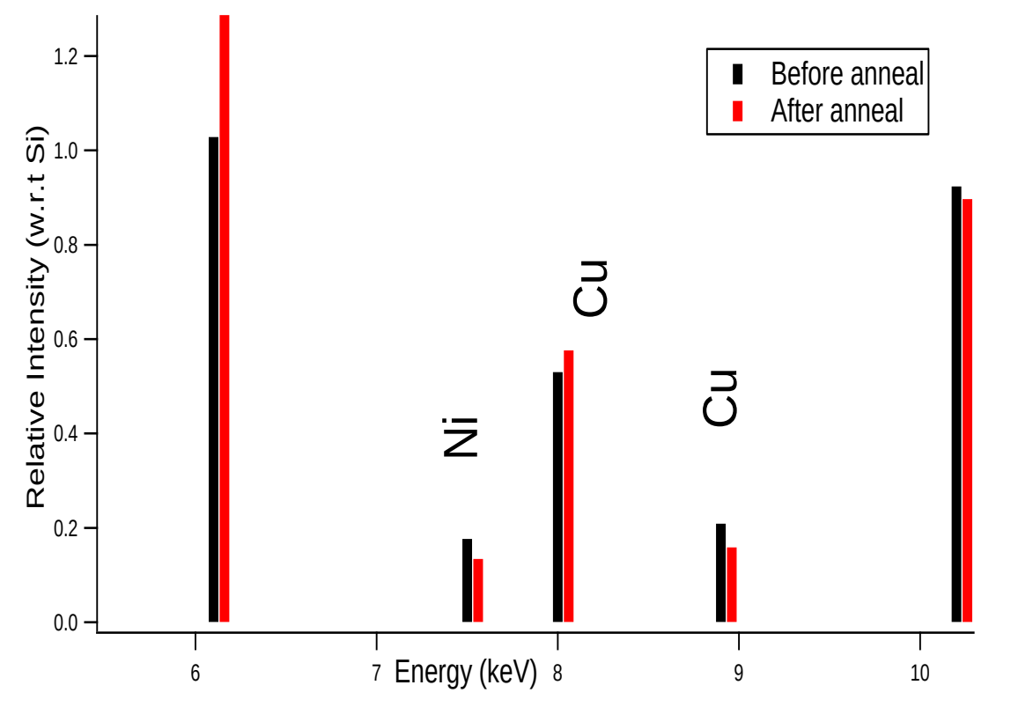
Cu reducing thermal stability of NiSi films.



- NiSi with no Cu on it does not undergo degradation

- XRF detects Cu on opposite side.
- Either XRF not suitable or *pc*-Si is not a good sink for Cu.





Cu diffusion test structures

Measure Cu conc. in *pc*-Si layer

- Make test structures with and without NiSi barrier and anneal them.
- Cu has low solubility in *c*-Si making detection difficult and hence, use a sink/gettering layer.
- Cu present in *pc*-Si as Cu_3Si at defect locations and grain boundaries.

Istratov et al., J. *Electrochem. Soc*. **149** (1), G21-G30 (2002)

Conclusions

- Single and two step process for NiSi formation give similar films.
- Electroless Ni process needs optimization – Impurities and Surface coverage.
- Cu enhances the degradation of NiSi.
- Temperature limitations makes this study difficult.
- Use cell I-V characteristics, Suns-V_{oc}, Photoluminescence Imaging for monitoring cell degradation due to Cu diffusion.

Chaudhari et al., *Sol. Energ. Mat. Sol. Cells*. **94**, 2094-2101 (2010).
Bartsch et al., *J. Electrochem. Soc*. **157** (10), H942-H46 (2010).
Trupke et al., *Appl. Phys. Lett*. **89**, 044107 (2006).

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