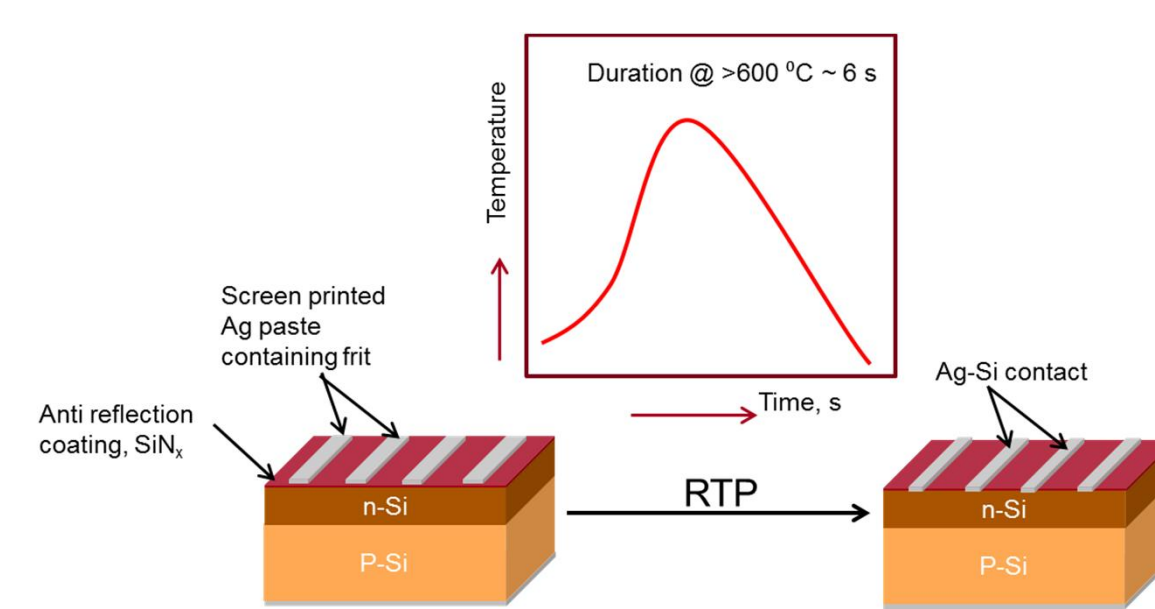


In situ rapid thermal processing / X-ray diffraction for materials forensics

Introduction

- Rapid thermal processing (RTP) : Widely used for processing materials in the photovoltaic (PV) industry, most notably for metal contact formation in Si solar cells
- Ag-Si contact processing time : ~10 seconds
- RTP parameters have evolved empirically over time
 - Lack of in-situ time resolved characterization facility with time resolution <1 sec.
- Several alternative mechanisms/reaction pathways proposed mainly based on ex-situ studies
- Precise mechanism/ reaction pathways uncertain



Contact processing

- Screen printing silver paste over anti-reflection coating
- Firing @ ~ 750-800 °C
 - Ramp rates > 50 °C/s

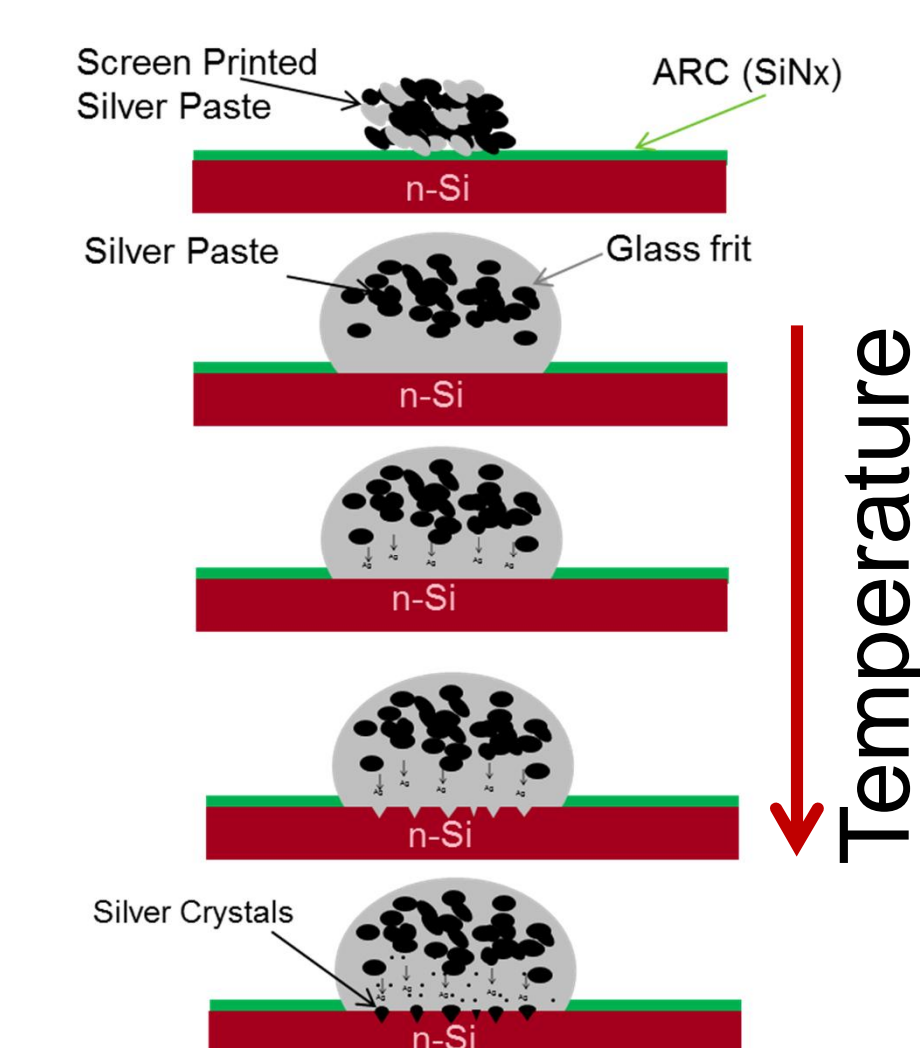
Proposed Mechanisms

SiNx etching

- PbO based Frit: $\text{SiO}_2, \text{PbO}, \text{B}_2\text{O}_3, \text{ZnO}, \text{NiO}$
 $\text{SiNx} + 2\text{PbO} \rightarrow \text{SiO}_2 + 2\text{Pb} + x/2\text{N}_2$ (1)
- Silver can dissolve in glass frit
 $\text{SiNx} + 2\text{Ag}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{Ag} + x/2\text{N}_2$ (2)

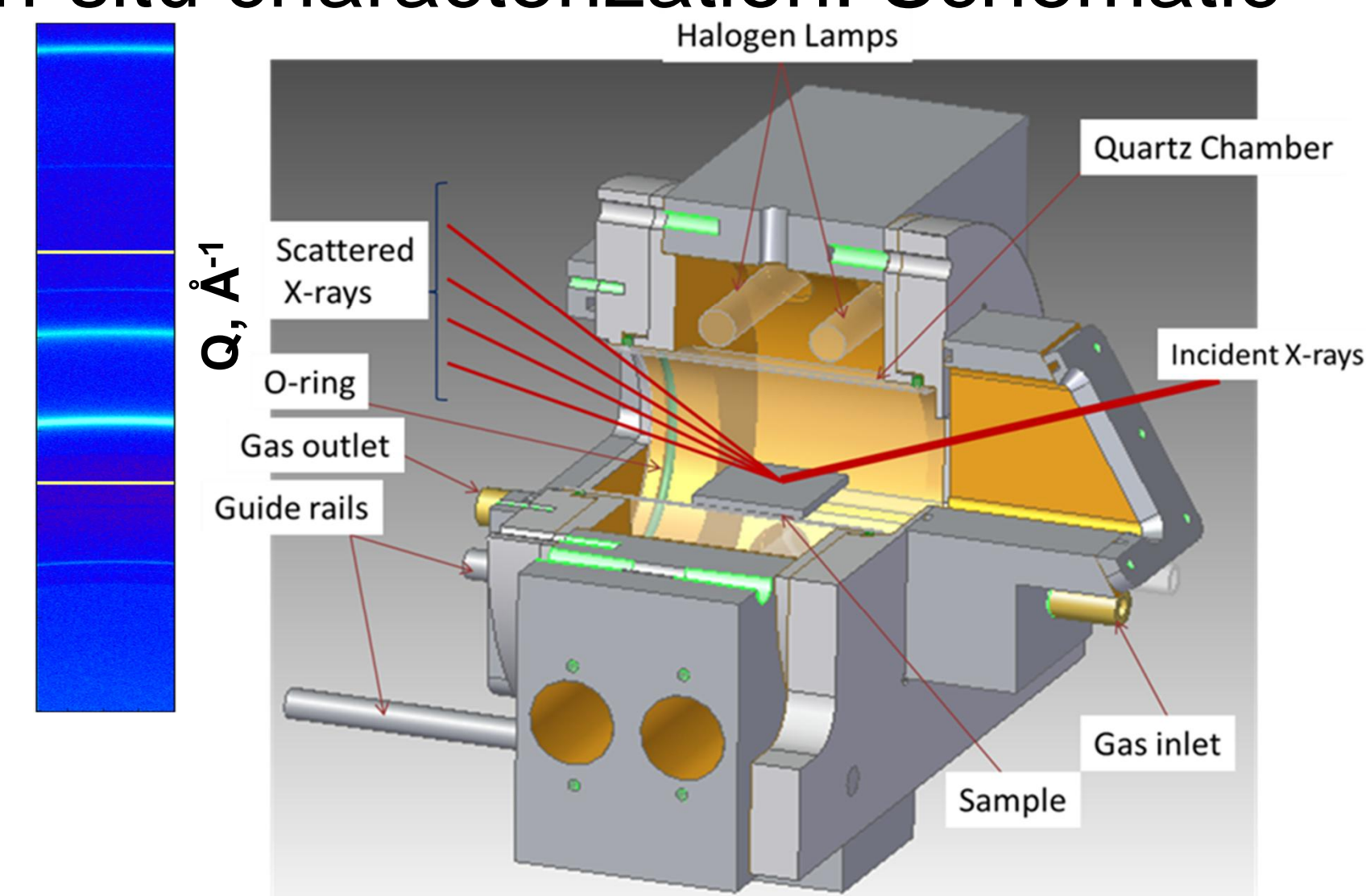
Ag deposition

- Ag dissolved in glass can deoxidize at the Si surface:
 $2\text{Ag}_2\text{O} + \text{Si} \rightarrow 4\text{Ag} + \text{SiO}_2$ (3)
- Ag forms ternary liquid alloys with Pb and Si which separate out on cooling

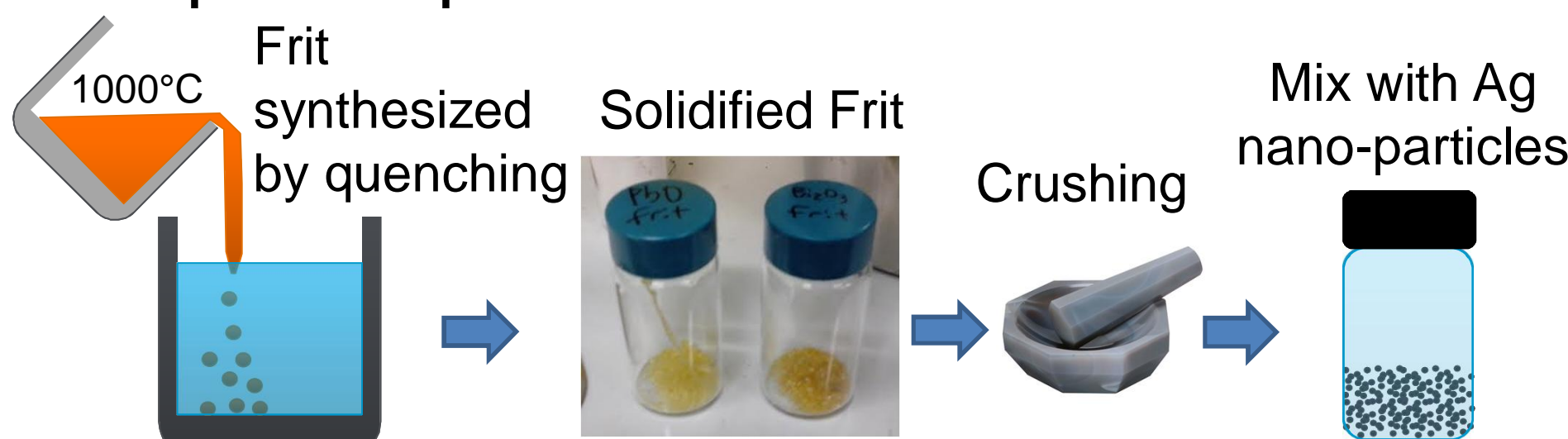


RTP Setup

In-situ characterization: Schematic



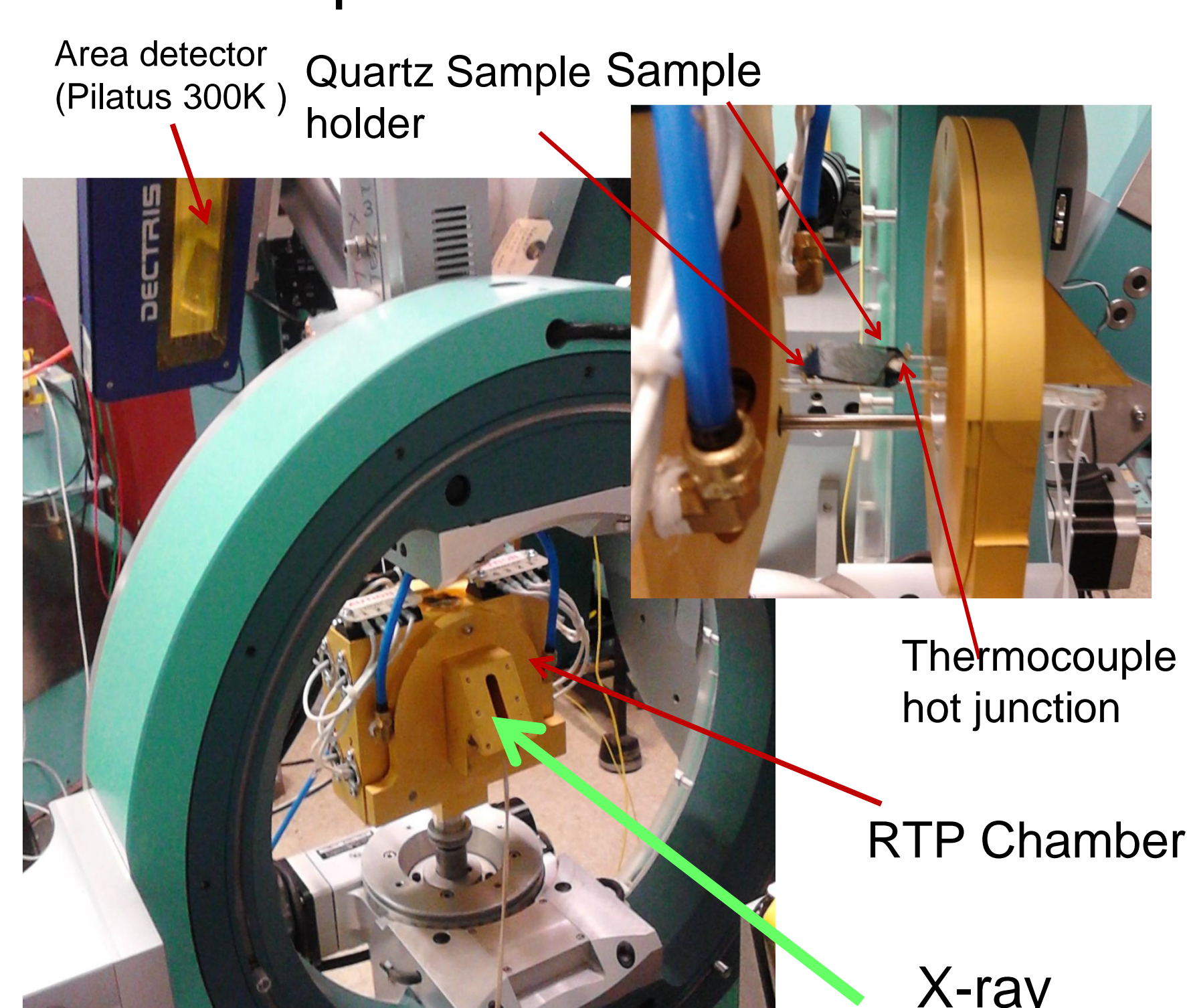
Sample Preparation



- PbO frit mixed with all combinations of Si, SiNx, Ag nanoparticles
- Equal parts by mole ratio in all combinations

Ahmad, Van Campen, Fields, Yu, Pool, Parilla, Ginley, Van Hest, Toney. "Rapid thermal processing chamber for in-situ x-ray diffraction." *Review of Scientific Instruments* 86, no. 1 (2015): 013902.

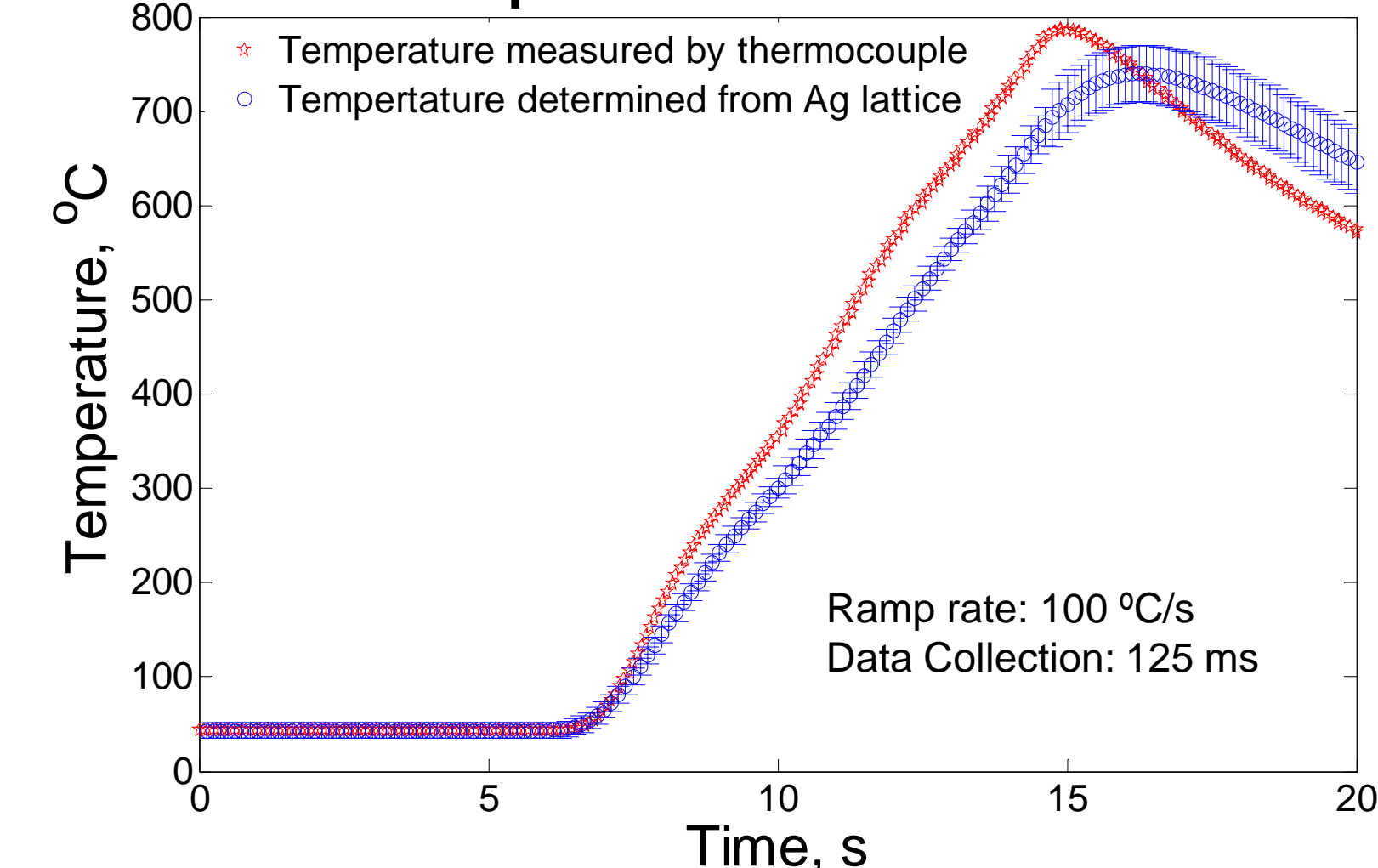
RTP Setup in Beamline 7-2 @ SSRL



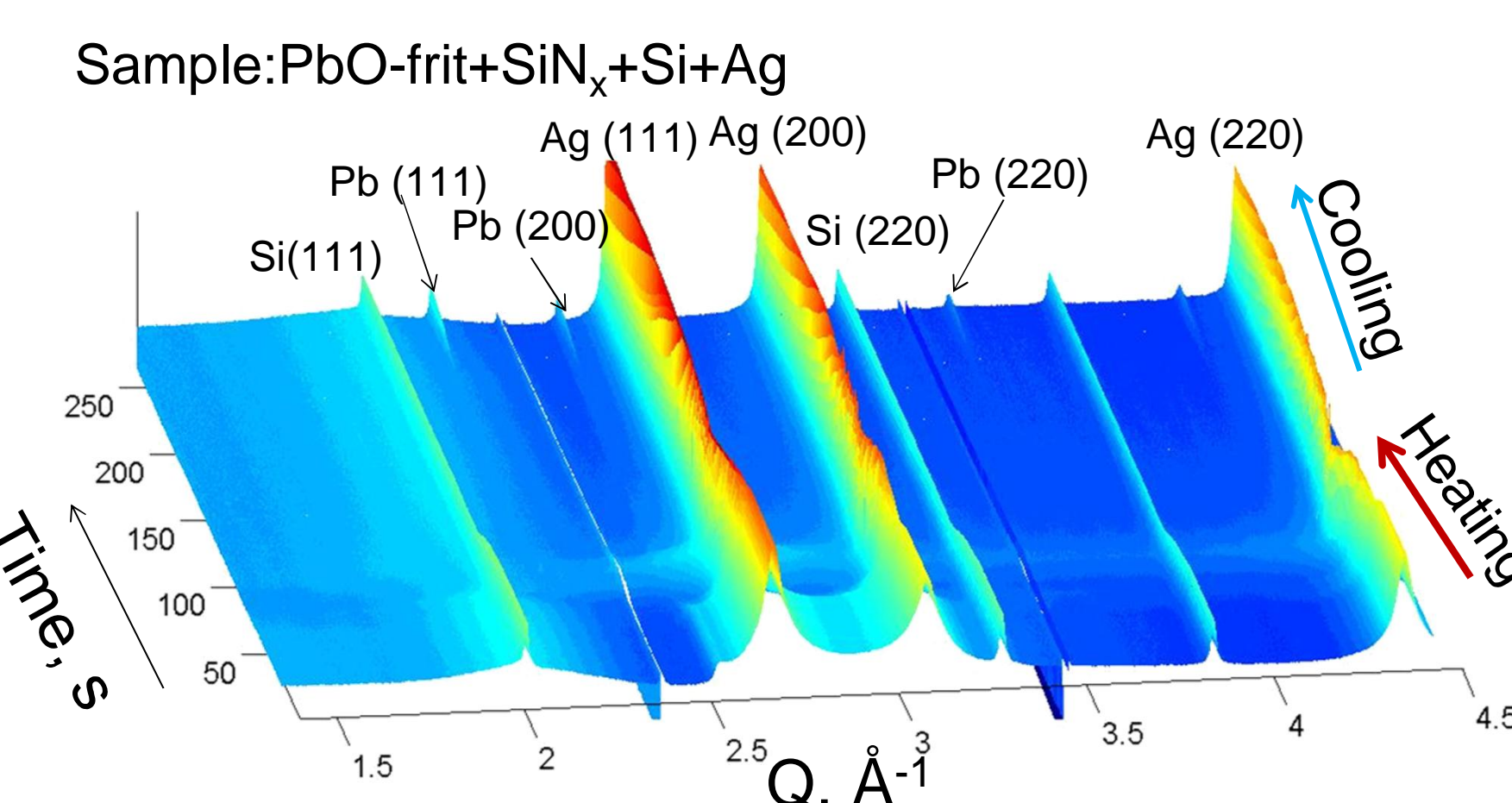
Frit Composition

Frit	Active Component	Glass Network Components	
1	PbO	SiO ₂	B ₂ O ₃
	mol %	mol %	mol %
	60	30	10

Temperature Calibration

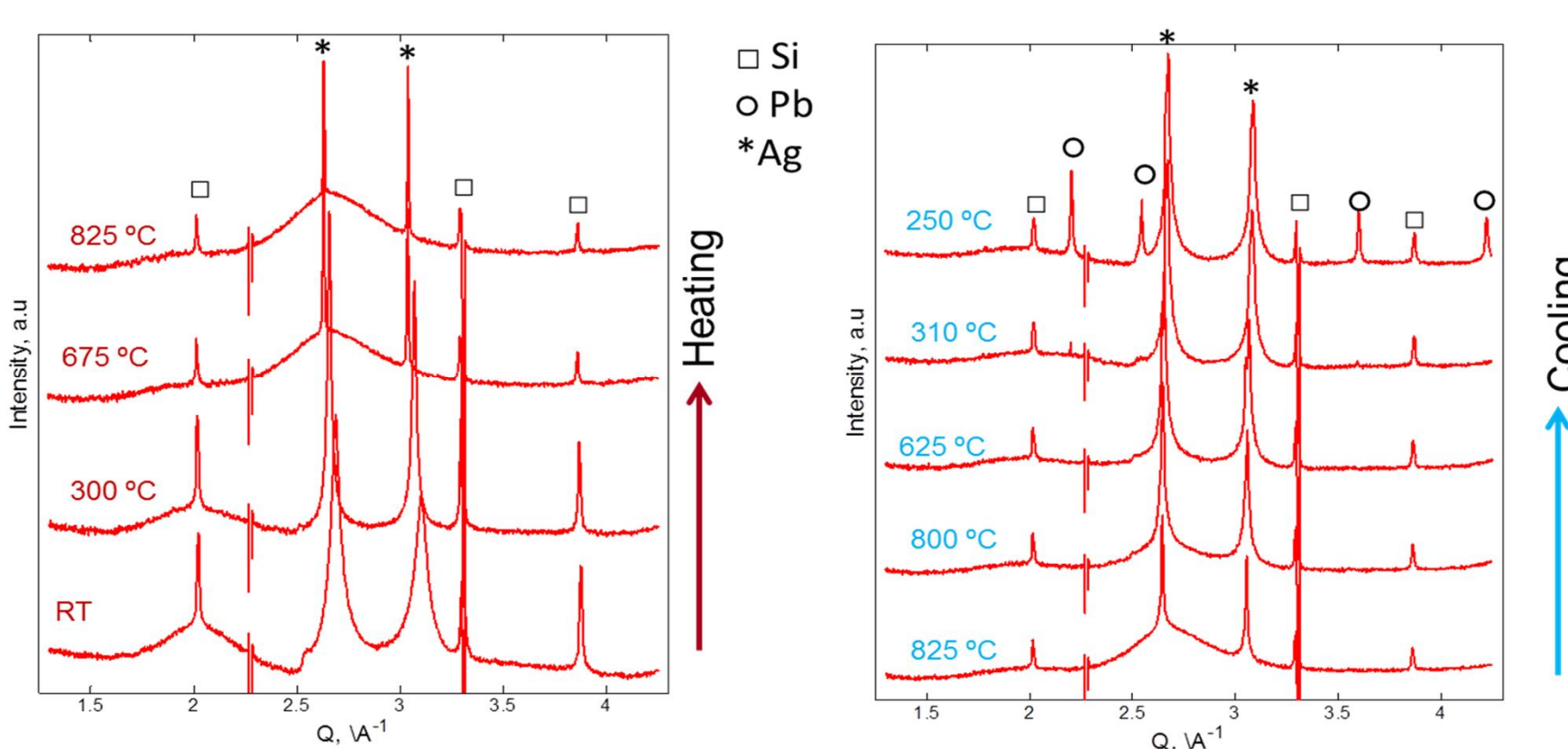


Temperature obtained from Ag lattice agrees well with thermocouple



Processed in Air: Heating rate 100 °C/s

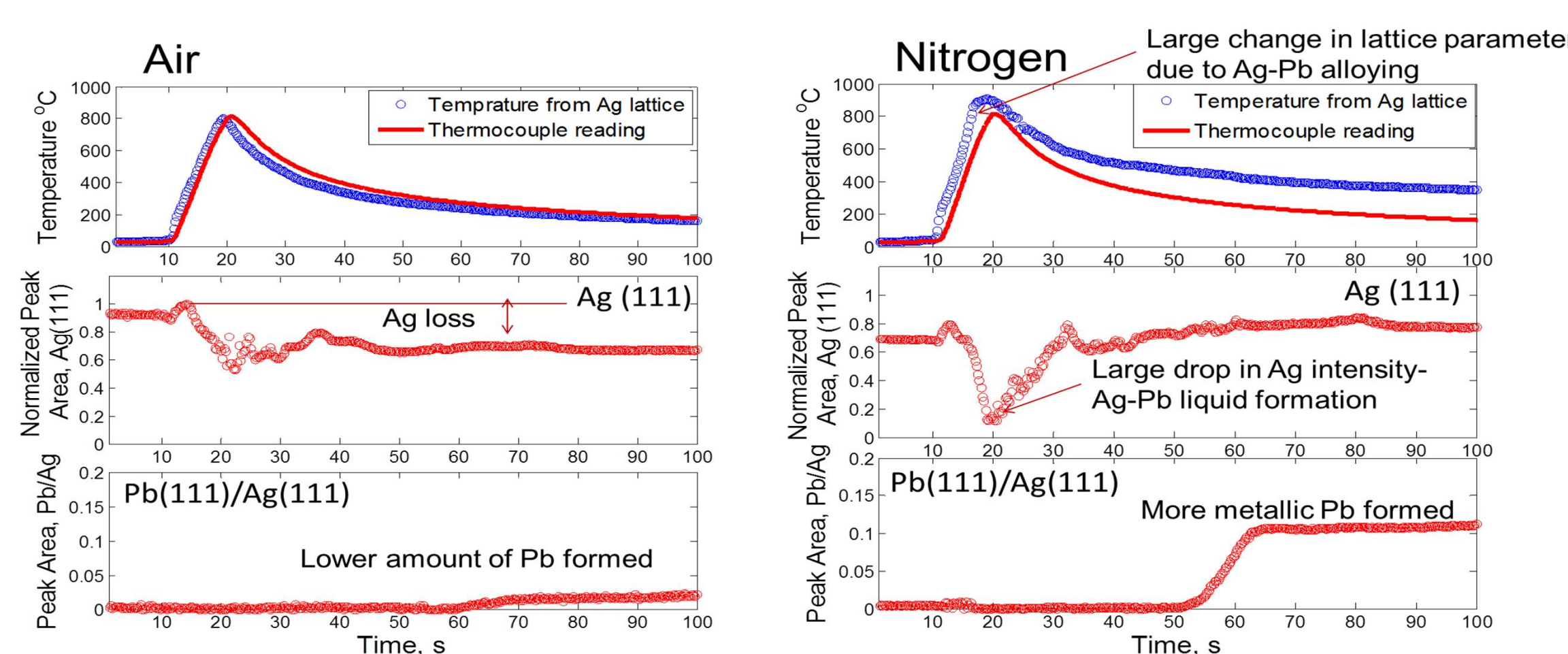
PbO-frit+Si+SiNx+Ag powder mixture (1:1:1:1)



- Grain growth of Ag on heating
- Appearance of diffused scattered peak below Ag(111): Ag-Pb liquid formation
- Ag(111) peak intensity increases on cooling with slight broadening (due to Ag nano-crystal formation).

Ag-Si cell contact formation mechanism

Effect of Processing environment: Air Vs Nitrogen



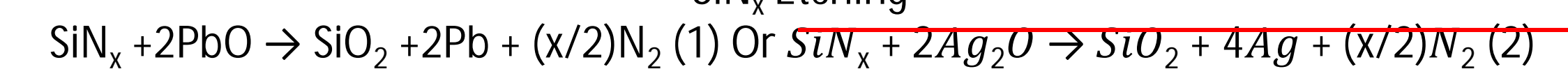
- Ag loss in Air: Ag dissolution in frit followed by precipitation of tiny particles on cooling
- Ag deposition on Si surface and etching should be coupled for contact formation: Ag⁺ dissolved in frit attacks the Si surface and Ag is deposited according to reaction.

Key Observations

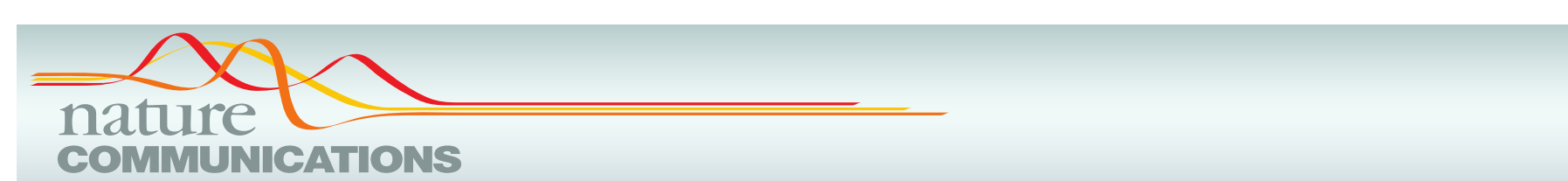
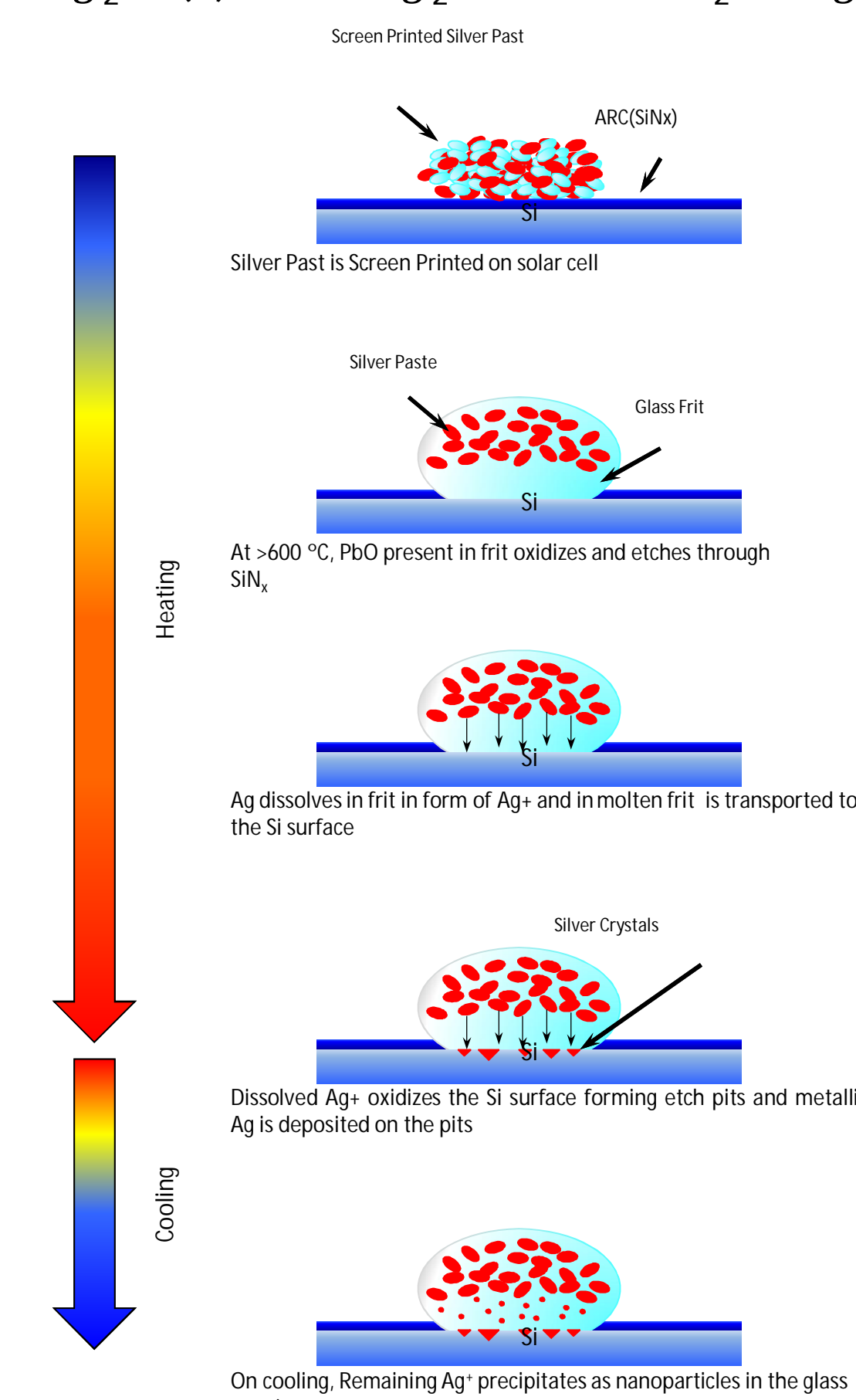
- More metallic Pb upon processing in nitrogen atmosphere -reaction (1)
- Grater reduction in Ag peak intensity upon firing in nitrogen : More Ag-Pb liquid formation
- Ag loss upon processing in Air : Ag dissolution in frit followed by precipitation on cooling to form very small particles.
- Ag deposition on Si surface and etching of Si should be coupled for contact formation: Ag dissolved in frit can preferentially attacks Si surface and get deposited – reaction (3)
- Si does not form ternary liquid with Pb and Ag. Binary Ag-Pb liquid observed.

Summary

SiNx Etching



Ag deposition:



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The formation mechanism for printed silver-contacts for silicon solar cells

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