

Raman studies of the reversible nanoscale Si–SiP transition in phosphorus vapor

Katherina S. Shavelkina, Sergei S. Bubenov, Vadim M. Popelensky, Kirill A. Cherednichenko, Alexander A. Vinokurov, Valeriya V. Rybina and Sergey G. Dorofeev

Materials and Methods

For two-zone anneals we employed a modified “SUOL-0.15.1.4/12 MR-I3” portable tube furnace with K-type thermocouples and PID temperature controllers. The temperature of the “cold” zone had an upper limit of 400 °C, while the second heating zone was employed to maintain temperatures in the region from 500 to 900 °C.

FTIR spectra were recorded on a Frontier (Perkin Elmer) spectrometer in a wavenumber range of 400 – 8000 cm⁻¹ after the NC samples were ground with KBr and pressed into pellets inside a glovebox. Raman spectra were obtained for powders inside the ampoules with the use of a iRamanPlus (BWTech) portable Raman spectrometer. TEM studies were carried out on a JEM-2100 (JEOL) microscope equipped with a LaB₆ gun and Quemesa 11 megapixel (Olympus) CCD camera. The accelerating voltage was set to 200 kV. NC-containing sols were drop-cast on carbon-coated copper grids and dried.

Section S1. Formulae and constants for thermodynamic calculation:

$$H^{\circ} - H^{\circ}_{298.15} = A \cdot t + B \cdot t^2/2 + C \cdot t^3/3 + D \cdot t^4/4 - E/t + F - H$$

$$S^{\circ} = A \cdot \ln(t) + B \cdot t + C \cdot t^2/2 + D \cdot t^3/3 - E/(2 \cdot t^2) + G$$

where H° = standard enthalpy (kJ/mol), S° = standard entropy (J/mol*K), t = temperature (K) / 1000.

Constants	A	B	C	D	E	F	G	H
for red phosphorus	24.32214	-1.809807	7.486431	3.147950	-0.296815	-25.70876	50.77995	-17.46004
for Si	22.81719	3.899510	-0.082885	0.042111	-0.354063	-8.163946	43.27846	0.000000

$$\text{For SiP: } G^{\circ, \text{SiP}}_{\text{P-Si}} = -77110.5 + 228.49 \cdot T - 38.34 \cdot T \cdot \ln(T) - 0.00544 \cdot T^2 + 2.825 \cdot 10^5 \cdot T^{-1}$$

where $G^{\circ, \text{SiP}}_{\text{P-Si}}$ = standard Gibbs energy (kJ/mol).

Table S1 Calculated values of Gibbs free energy.

Temperature, °C	ΔG^0 , kJ/mol	$\Delta G^0(\text{adjusted})$, kJ/mol	Temperature, °C	ΔG^0 , kJ/mol	$\Delta G^0(\text{adjusted})$, kJ/mol
850	-10.2	-1.4	805	-20.1	-11.3
845	-11.3	-2.5	800	-21.2	-12.4
840	-12.4	-3.6	795	-22.3	-13.5
835	-13.5	-4.7	790	-23.4	-14.6
830	-14.6	-5.8	785	-24.5	-15.7
825	-15.7	-6.9	780	-25.6	-16.8
820	-16.8	-8.0	775	-26.7	-17.9
815	-17.9	-9.1	770	-27.8	-19.0
810	-19.0	-10.2			

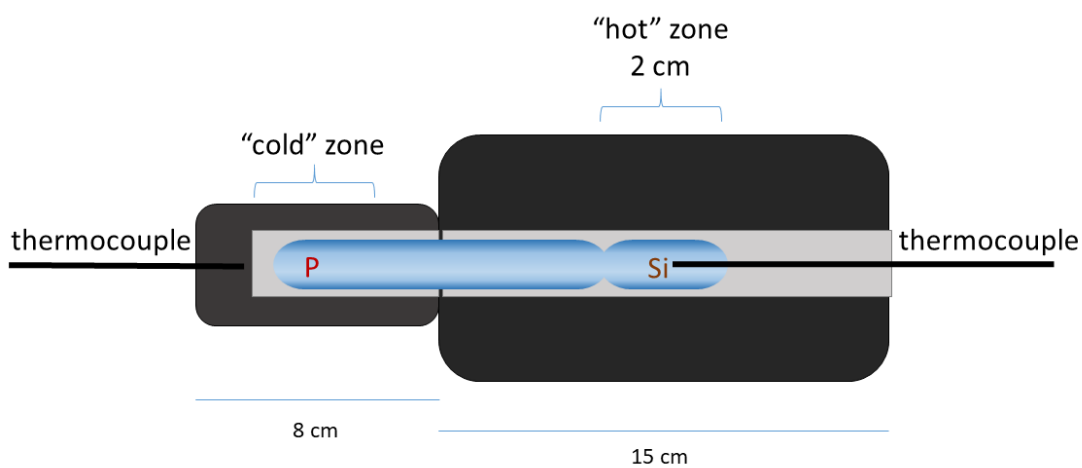


Figure S1 Scheme of the two-zone annealings.

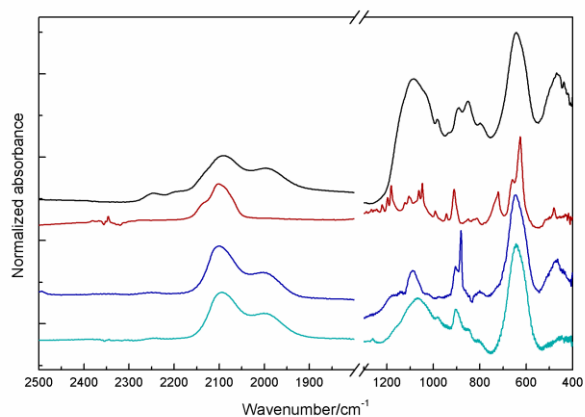


Figure S2 IR spectra of Si nanocrystals: black – initial particles; red – after wet etching; blue – after 1 day of glovebox storage; cyan – after 3 days of glovebox storage. The spectra are normalized for the intensity of Si-H vibrations and offset vertically for clarity.



Figure S3 HR TEM image of a crystallite in the sample, cycled through Si/SiP transition 10 times.