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Design, construction, and operation of a laboratory scale reactor for the production of high-purity, isotopically enriched bulk silicon

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Materials Sciences Division

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1 Abstract

The design and operation of a recirculating flow reactor designed to convert isotopically enriched silane to polycrystalline Si with high efficiency and chemical purity is described. The starting material is SiF_4 , which is enriched in the desired isotope by a centrifuge method and subsequently converted to silane. In the reactor, the silane is decomposed to silicon on the surface of a graphite starter rod (3 mm diameter) heated to 700 – 750 °C. Flow and gas composition (0.3 – 0.5% silane in hydrogen) are chosen to minimize the generation of particles by homogeneous nucleation of silane and to attain uniform deposition along the length of the rod. Growth rates are 5 $\mu\text{m}/\text{min}$, and the conversion efficiency is greater than 95%. A typical run produces 35 gm of polycrystalline Si deposited along a 150 mm length of the rod. After removal of the starter rod, dislocation-free single crystals are formed by the floating zone method. Crystals enriched in all 3 stable isotopes of Si have been made: ^{28}Si (99.92%), ^{29}Si (91.37%), and ^{30}Si (88.25%). Concentrations of electrically active impurities (P and B) are as low as mid- 10^{13} cm^{-3} . Concentrations of C and O lie below 10^{16} and 10^{15} cm^{-3} , respectively.

2 Introduction

There is increasing interest in the properties of materials enriched in the stable isotopes of Si (natural abundance = 92.2% ^{28}Si , 4.7% ^{29}Si , and 3.1% ^{30}Si). For example, some measurements of the thermal conductivity κ of highly enriched ^{28}Si in both thin film [1,2] and bulk [3] form reported increases exceeding 50% at room temperature. This is of interest to manufacturers of high-performance integrated circuits; the higher thermal conductivity of Si could be utilized to transport heat more effectively in a densely packed device, allowing higher operating clock rates. However, the consensus of more recent measurements is that the room temperature enhancement is actually in the range of 10-15% [4,5]. It has also been found that photoluminescence (PL) and impurity absorption lines in isotopically enriched ^{28}Si are extraordinarily sharp [6,7,8]. Finally, a number of proposed quantum computing schemes involve the use of stable Si isotopes either as a spin free matrix of highly enriched ^{28}Si [9,10], or directly as the qubits using the ^{29}Si nuclear spin ($I = 1/2$) [11]. In this context, it has been reported recently that decoherence times of electrons bound to ^{31}P in enriched ^{28}Si can be greater than 10 ms at low temperature [12] and that there is an unexpectedly long persistence of ^{29}Si spin echoes in natural Si [13].

Full exploration of the effects of isotopic composition on the properties of Si will require material enriched in all three stable isotopes with higher chemical purity than in the past. For example, the PL line widths measured in refs. 6 and 8 are still 10x larger than the lifetime limit. It is also clear that practical demonstrations of Si-based quantum computing are likely to require highly enriched ^{28}Si and/or ^{29}Si sources. We are aware of a number of previous reports of isotopically enriched ^{28}Si [14,15,16] and ^{29}Si and ^{30}Si crystal growth [17]. While enrichments >99% have been achieved for each isotope and some crystals have low concentrations of electrically active impurities (e.g. $<10^{15} \text{ cm}^{-3}$), the combination of high chemical purity and dislocation-free crystal growth has not been achieved in every case. A production methodology that can achieve this and that is

compatible with the relatively small quantities of enriched precursors is clearly needed. We describe here a laboratory-scale reactor designed to convert isotopically enriched silane to poly-Si with high conversion efficiency and chemical and isotopic purity. Single crystals produced from the poly-Si by the floating zone process have excellent electronic characteristics. Such material will be valuable in performing definitive thermal conductivity studies and in exploring the scientific and technical applications of the stable isotopes of Si.

3 Experimental Design

3.1 *Silicon precursors*

Enriched Si in the form of SiF_4 was obtained from the Electrochemical Plant (ECP), Zelenogorsk, Russia. The stated isotope enrichments are summarized in Table 1. All three precursor gases had 50-100 ppm of CF_4 , C_2F_6 , CO_2 , O_2 , HF , and H_2O . SiF_4 was converted to SiH_4 by Voltaix, Inc (North Branch, NJ). Gas chromatography/mass spectrometry (GC/MS) was used to measure major impurity species. CH_4 was the major measurable contaminant and ranged from 7 ppm in the $^{28}\text{SiH}_4$ to 70 and 100 ppm in the $^{30}\text{SiH}_4$ and $^{29}\text{SiH}_4$, respectively. The concentrations CF_4 , CO_2 , Si_2H_6 , and siloxanes were less than the 5 ppm detection limit.

Table 1. Summary of isotopic composition measurement in the precursor gas (SiF_4). The gas measurements were provided by the vendor and performed by GC-MS

isotope at. %	nat. Si	^{28}Si enriched SiF_4	^{29}Si enriched SiF_4	^{30}Si enriched SiF_4
^{28}Si	92.23	99.93	4.26	2.00
^{29}Si	4.67	0.065	91.37	7.35
^{30}Si	3.10	0.005	4.37	90.65

3.2 *Poly-Si deposition considerations*

The established industrial method for synthesizing the highest purity natural Si is deposition of polycrystalline Si (poly-Si) by the decomposition of silane in the so-called “Komatsu process” or by decomposition of trichlorosilane (“Siemens process”) followed by growth of single crystals by the floating zone technique [18,19,20]. Crystals of up to 200 mm in diameter with a room temperature resistivities in excess of 30,000 $\Omega\text{-cm}$ are made by this process [21,22]. Both of these industrial processes are operated in a batch mode and a typical deposition run involves several hundred kilograms of poly-Si; this currently exceeds the present manufacturing capability for isotopically enriched precursors.

A number of different deposition schemes were considered here for converting the isotopically enriched SiF_4 to high purity Si single crystals. A crucial constraint was the total amount of enriched precursors available; in the case of the minority ^{29}Si and ^{30}Si isotopes, the amount that could be obtained did not exceed 500 gm. Given the scale of the industrial processes discussed above, it was by no means clear that they could be adapted to function with high efficiency with relatively small amounts of the Si precursor. For example, the fluidized bed method [23,24,25,26] now used commercially by MEMC was considered. However, the granular poly-Si produced by this method is not suitable for subsequent float-zone (FZ) growth of single crystal Si (it was desirable here to use FZ as opposed to Czochralski growth to reduce oxygen incorporation in the

crystal and to eliminate any possibility of isotope exchange with the silica crucible). Ultimately, a silane process ($\text{SiH}_4 \rightarrow \text{Si} + 2\text{H}_2$) was chosen over a trichlorosilane process based on its lower operating temperature (700 – 900 °C vs. 1100 °C), higher potential conversion efficiency, and non-corrosive nature of the precursor [20]. As discussed below, the reactor was designed with full consideration of the disadvantages of the silane process, which are primarily homogeneous nucleation and particle generation and the pyrophoric nature of silane.

3.3 Reactor overview

The reactor design was based on a one-pass flow reactor that had been used previously to measure the growth rate of poly-Si from silane [27]. In that study, the decomposition of silane along a 300 mm long rod in the center of a 15 mm diameter flow tube was studied under various flow conditions at rod temperatures between 700 and 900 °C; the amount of Si deposited in a typical run was less than 1 mm. Constructing a flow reactor for bulk poly-Si production requires the addition of process gas recirculation to increase the overall conversion efficiency and careful design of the flow and reactor conditions to attain uniform deposition and minimum particle generation. Additional design considerations for the processing of isotopically enriched gases are the prevention of any sort of isotope exchange with the reactor materials and the avoidance of possible sources of chemical contamination.

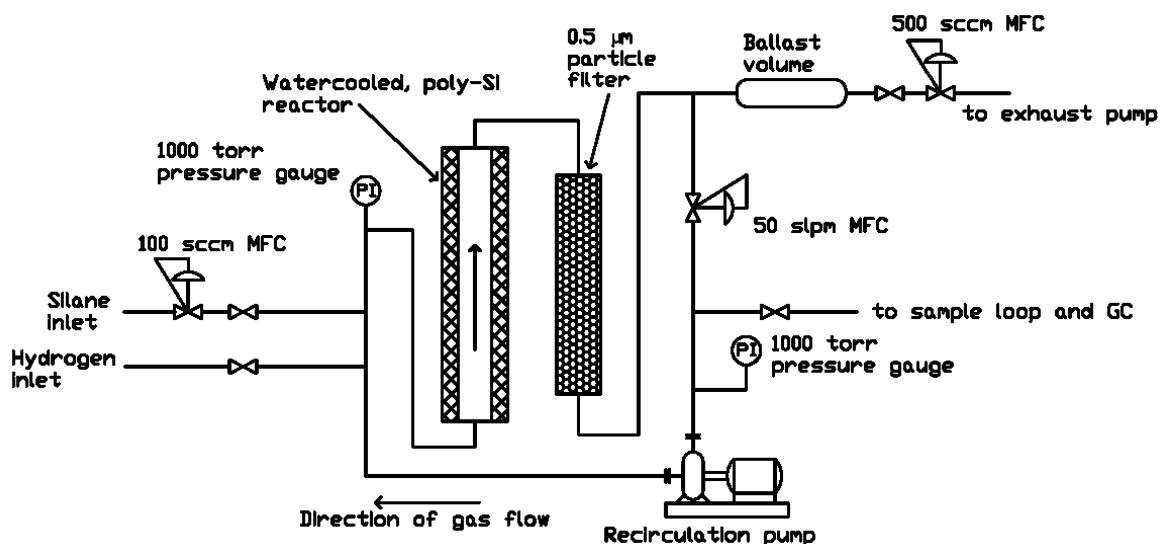


Fig. 1. Polysilicon reactor: overview of process loop.

An overview of the process loop and a detailed drawing of the double tube reactor are shown in Figs. 1 and 2. Silane cylinders were installed in a vented gas cabinet equipped with a 7-valve gas purge panel (Scott Omnigas 58PA200SVA) which allows gas cylinders to be changed without cross contamination. Some initial deposition runs were done with natural UHP silane from Voltaix (99.999%). Nitrogen (>99.9995%) was used as the gas panel purge gas. The initial carrier gas was UHP hydrogen (>99.9999%). An oil-free diaphragm pump (Senior Flexonics MB-302) was used to recirculate the

process gas. As discussed below, a dilute mixture of silane in H_2 at slightly above atmospheric pressure was used as the process gas. The inner tube in the reactor was a 25 mm diameter fused silica and was surrounded by a 2" OD Lexan tube. The reaction zone was defined by the distance (150 mm) between two water cooled high-current electrodes (Insulated Seal Inc.) in the reactor. Cooling water was supplied to the electrodes and to the space between the Lexan and fused silica tube by a closed cycle chiller (Neslabs CFT-75).

Poly-Si growth was initiated on 3 mm diameter graphite rods (>99.997%, Goodfellow) which were cut to the appropriate length. The rod was resistively heated by two high current power supplies wired in parallel (EMI SCR 120-40 and EMI TCR 40S70). The upper electrode contact was designed to have some axial freedom of movement to compensate for thermal expansion of the rod. A Ga-Sn eutectic solution was used to form a sliding contact with low electrical resistance. The rod temperature was measured before silicon deposition with an optical pyrometer (Pyro-Werk "Optix"). The temperature was measured subsequently imaging light from the rod through a bandpass filter (880 nm, 70 nm BW) onto a Si photodiode. It was necessary to continuously increase the power to the rod as its diameter increased due to increased rates of radiative and convective cooling; typical power settings were 440 W at the beginning of a run and 1.4 kW at the end of a run with a 12 mm diameter rod. The recirculation flow rate was controlled by a high capacity mass flow controller (MFC, Unit 2000 series). The pressure was measured upstream and downstream of the recirculation with 1000 torr capacitance manometers (MKS 722A); a typical pressure drop across the pump during operation at 15 slpm was 70 torr.

All tubing used was 1/4" diameter stainless with welded VCR fittings. All valves were pneumatically actuated (Nupro B Series) and computer controlled. The silane flow into the process loop was controlled with a 100 sccm MFC (Unit 1200). In order to maintain a constant process loop pressure, the loop had to be exhausted at rate approximately equal to twice the silane feed. Exhaust vacuum was provided by an oil-free diaphragm pump (Edwards D-Lab 20-100) and controlled with an 500 sccm MFC

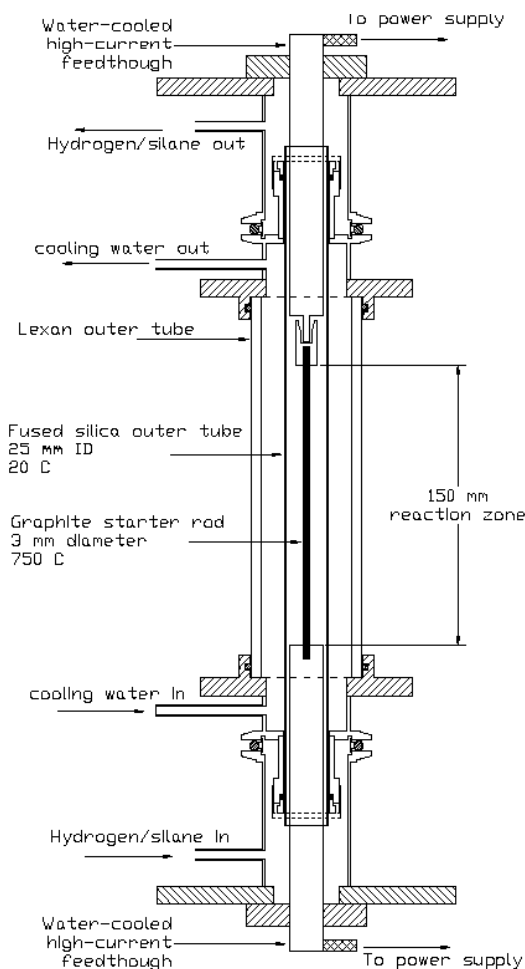


Fig. 2. Polysilicon reactor: reaction zone detail.

(Unit 1200). It was necessary to place a 1 liter ballast volume in front of the exhaust MFC to achieve a stable exhaust flow.

3.4 Particle filtration

Based on reported data from industrial users of the Komatsu process, particle generation on the order of 1 wt. % of the deposited poly-Si might be expected. Therefore, efficient particle filtration downstream of the reactor and upstream of the process loop MFC and pump was required. It was also important to select a filtration method with relatively high gas conductance. The anticipated particle generation integrated over several process runs greatly exceeds the capacity of most standard in-line filters sold for semiconductor manufacturing applications. A suitable filter was fabricated from a porous 316 SS “filter/sparger” (Mott 6400 series, 0.5 μm pore size, 1” diameter x 12” long) which was mounted inside a welded 316 SS tube with VCR fittings. This filter contributed a less than 10 torr pressure drop to the process loop. No evidence of particles downstream of the filter was observed.

3.5 Silane concentration measurement

The silane concentration in the process loop was monitored by sampling the process gas at 6 minute intervals by a gas chromatograph (HP 5790A) equipped with a thermal conductivity detector operated at 225 °C. A 1/8” x 6’ Porapak N column was used at 30 °C. The carrier gas was UHP He at a flow rate of 30 cc/min. The steps in the sampling sequence were evacuation of the 10 cc sample loop with an oil-free pump (Alcatel Drytel 31), opening of a pneumatically actuated valve to introduce the process gas to the evacuated volume, and then of switching a two-way valve (Valco A4SD6MWE) to direct the gas to the GC. As shown in

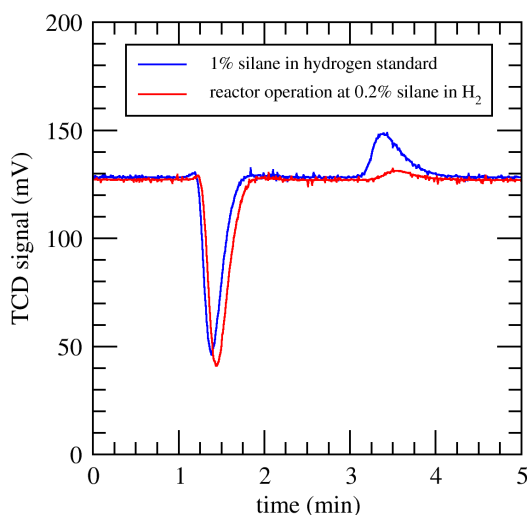


Fig. 3. Typical GC data during reactor operation.

Fig. 3, under these conditions a negative H_2 peak was observed at 1.3 minutes and a positive silane peak was observed at 3.7 minutes. Calibration runs were performed frequently with a 1% silane in hydrogen standard. The estimated minimum detectable silane concentration was 0.02%.

3.6 Gas flow selection

The kinetics of the decomposition of silane to poly-Si on a heated surface are well studied. In nearly all industrial processes, hydrogen is used as the carrier gas due in part to its high thermal conductivity. The reaction has an activation energy of 1.4 eV above 650 °C and 2.2 eV below 650 °C; the increased activation energy at lower temperatures is attributed to hydrogen termination of the growth surface [28]. Growth of crystalline Si is observed above 600 °C [29]. At a given concentration of silane, there is a temperature above which the reaction is mass-transport-limited; atmospheric pressure reactors for

depositing thin poly-Si films are often operated in this regime (ca. 1000 °C) in order to reduce the sensitivity of the growth rate to surface temperature [30]. An overview of observed Si deposition rates as a function of temperature is shown in Fig. 4.

In a flow tube reactor, if the effective deposition rate is too high, the silane concentration will decrease as the process gas transits the reactor and the resultant poly-Si rod will not be uniform in thickness (this effect was observed by Hashimoto *et al.* [27] for many of the flow conditions used in a one-pass tube reactor). The effective deposition rate can be reduced by reducing the rod temperature and/or increasing flow rate. In a one-pass reactor, this would decrease the overall conversion efficiency. However, the addition of gas recirculation in the present reactor allows the gas velocity to be increased while maintaining high conversion efficiency (see Appendix).

It was desirable to operate the reactor in such a way as to minimize the generation of particles (also known as “snow” or “soot”) that form as a result of the homogeneous nucleation of silane which occurs when gas temperature exceeds 400 °C. A number of studies [31,32,33,34] have investigated the critical silane concentration for homogeneous nucleation as a function of gas temperature and silane concentration. Data from these studies are graphed in Fig. 5. For example, at 800°C, it appears that particle formation can be observed for silane concentrations (in hydrogen) exceeding 0.2%. It thus

desirable to decrease the volume of the reactor in which the temperature is >400 °C; this can also be accomplished by increasing the process gas flow to prevent heated inner rod from completely heating the process gas as it flows through the reactor. In the present

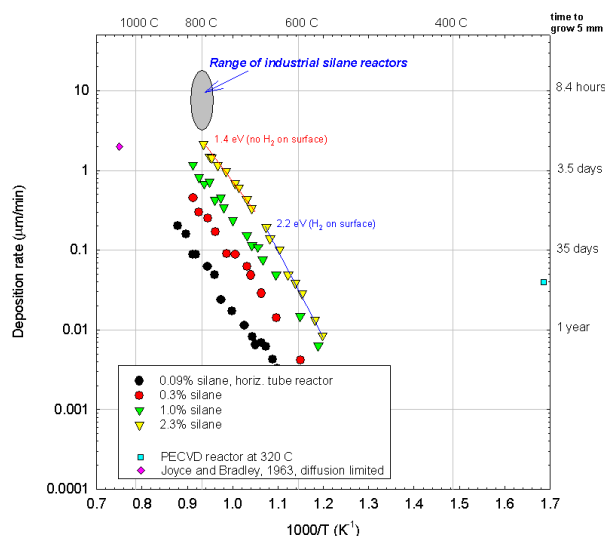


Fig. 4. Summary of literature data for Si deposition rate during the growth of poly-Si by decomposition of silane.

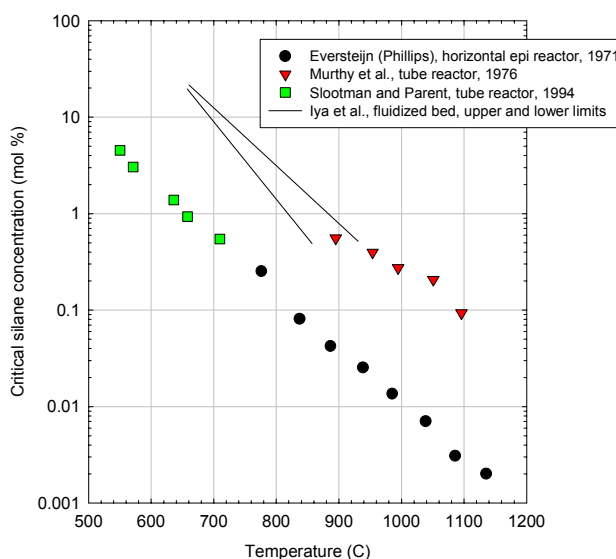


Fig. 5. Literature data for the critical silane concentration in hydrogen that leads to observable particle formation. Actual operation parameters (0.5% silane, 730 °C) were chosen to minimize particle formation.

case, a practical upper limit was set by the maximum flow rate (ca. 20 slpm) that the recirculation pump could achieve in the process loop.

3.7 Reactor operation

The reactor modeling approach developed by Hashimoto *et al.* [27] was used to select the process conditions for the reactor (see Appendix). In order to maximize the poly-silicon growth rate (which is proportional to the silane concentration), the industrial process operates at ca. 800°C with silane concentrations in H₂ in the range of 1.5 – 5% [35,36]. Here, it was advantageous to operate at a somewhat lower temperature (730 °C) and silane concentration range (0.3 – 0.5%) to decrease particulate formation. Photographs of reactor operation are shown in Fig. 6. As the poly-Si rod increased in

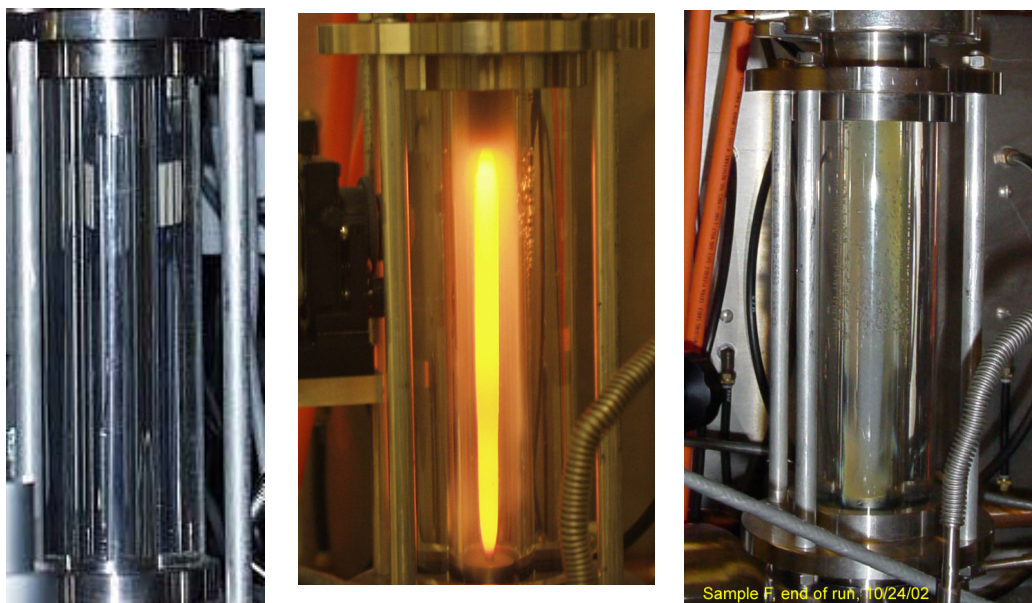


Fig. 6. Reactor operation: (left), reactor with graphite starter rod visible; (center), during operation at 730°C with a process gas flow of 15 slpm; (right) at the end of a run. Some particulate formation is observed.

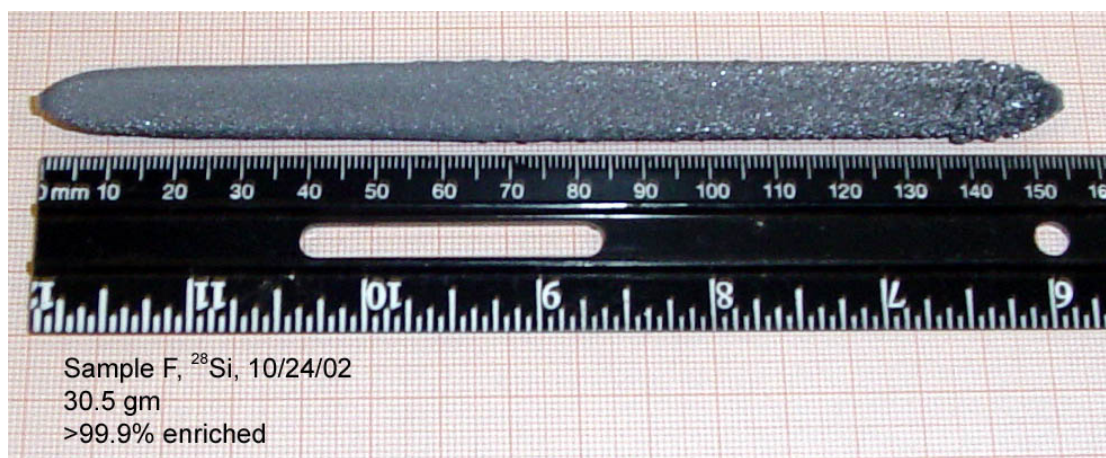


Fig. 7. Polycrystalline rod enriched in ²⁸Si grown with the LBNL reactor. The right hand side of the rod was at the top of the reactor during growth.

size, the silane feed was increased from 0.8 gm/hour (Si equivalent) to 4 gm/hour at the end of the run when the rod had grown to rod diameter of 12 mm. Particulate formation was observed on the walls of the reactor near the outlet after a few hours of operation but did not seem to affect the quality of the poly-Si or the observed yield (>95%). The typical deposition time was 16 hours to grow a rod of mass of 33 – 36 gm. A typical poly-Si rod is shown in Fig. 7. Larger crystallites are observed at the top of the rod; this is attributed to a slightly higher temperature generated there by the convective action of the flowing H_2 (this can also be seen in Fig. 6). The average deposition rate was 5 $\mu\text{m}/\text{min}$ which is comparable to that of industrial reactors. As shown in Fig. 8, the growth rate was uniform along the length of the rod.

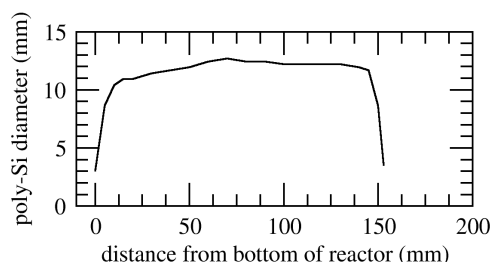


Fig. 8. Diameter of poly-Si rod as a function of distance in the reactor. Growth rate is uniform throughout the reaction zone.

3.8 Floating zone crystal growth

In order to perform detailed tests of impurity content, isotopically enriched poly-Si rods were converted to single crystals using the floating zone method. The graphite starter rod was removed from the poly-Si by a combination of drilling and lapping. Thorough etching with HF and HNO_3 was used to remove mechanical damage and residual graphite or SiC grains. Sections of the poly rods were converted to dislocation-free single crystal Si in a floating zone (FZ) crystal puller. In the case of ^{28}Si and ^{29}Si isotopically enriched seeds were used. A natural seed was used for ^{30}Si . Photographs of enriched Si crystals are shown in Fig. 9.

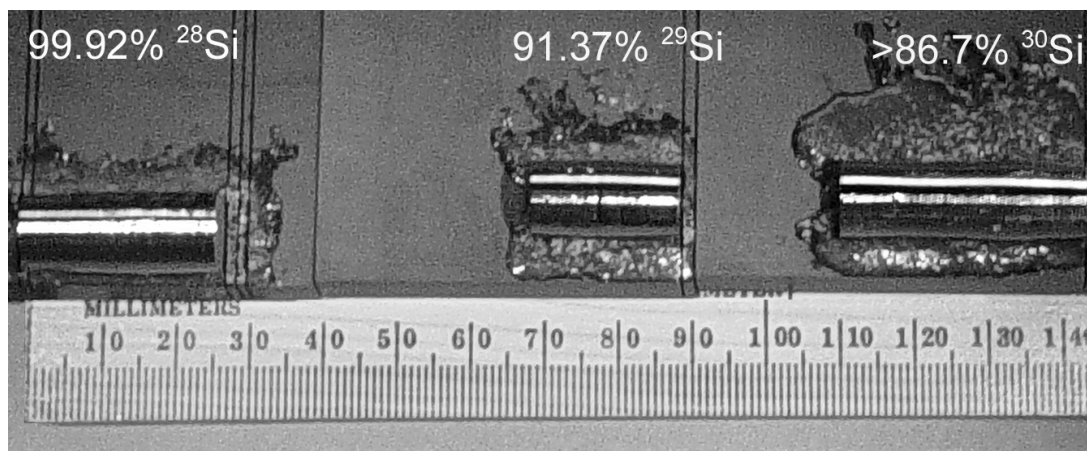


Fig. 9. Dislocation-free single crystals of isotopically enriched Si.

4 Results and Discussion

Initial tests of the full synthesis process were performed with natural silane with a stated purity of 99.999%. Typical room temperature resistivities of the natural FZ crystals were in the 3-10 $k\Omega$ range (p-type), corresponding to a room temperature carrier

concentration of less than 10^{13} cm^{-3} . This demonstrates that the process is capable of making Si whose purity is only limited by that of the precursor silane.

Table 2. Summary of isotopic composition measurement in the precursor gas and in the enriched single crystals. The gas measurements were performed by GC-MS and the crystal measurements were performed with SIMS. Due to the use of a natural Si seed, the ^{30}Si enriched crystal has an isotopic gradient.

isotope at. %	nat. Si	^{28}Si enriched		^{29}Si enriched		^{30}Si enriched	
		SiF_4	crystal	SiF_4	crystal	SiF_4	crystal
^{28}Si	92.23	99.93	99.92	4.26	4.3	2.00	2.5-5.7
^{29}Si	4.67	0.065	0.075	91.37	91.37	7.35	7.5-7.7
^{30}Si	3.10	0.005	.005	4.37	4.3	90.65	86.7-89.8

SIMS measurements of the isotopic composition are summarized in Table 2. With the exception of the ^{30}Si crystal, which has an enrichment gradient from the seed to the tail due to partial melting of the natural seed isotopic enrichments of the crystals are the same as those of the precursor gas. Temperature dependent Hall effect data is shown in Fig. 10. All enriched crystals were n-type. In the ^{28}Si crystal, the net-carrier

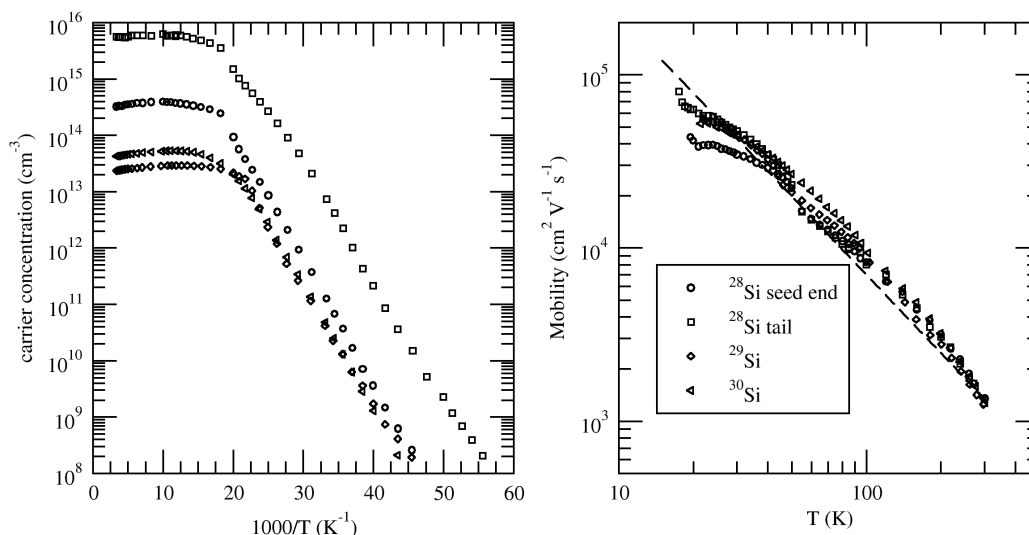


Fig. 10. Variable temperature Hall effect data for isotopically enriched Si crystals: 99.92% ^{28}Si , 91.37% ^{29}Si , and 86.7% ^{30}Si . All crystals are n-type. The net carrier concentration is higher in the tail end of the ^{28}Si crystal compared to the seed end due to P segregation during the float zone growth. A dashed line indicates the $T^{-3/2}$ dependence for the mobility data. Data courtesy I. Sharp and C. Liao, LBNL.

concentration was $3 \times 10^{14} \text{ cm}^{-3}$ at the seed end and $5 \times 10^{15} \text{ cm}^{-3}$ at the tail; this effect is attributed to the expected segregation of the P to the tail region during FZ growth. For the ^{29}Si and ^{30}Si enriched crystals, the net carrier concentration was in the mid 10^{13} cm^{-3} range. Room temperature mobilities for n-type material were between 1220 and 1360 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and increased monotonically down with $T^{-3/2}$ to 20 K. This shows that the crystals have a very low acceptor compensation resulting in negligible ionized impurity scattering.

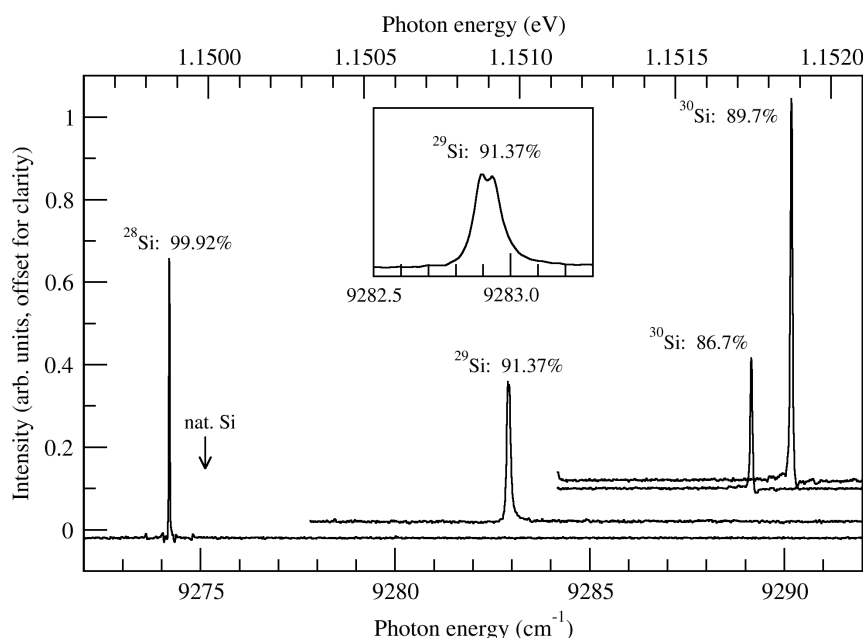


Fig. 11. Photoluminescence spectra obtained at 4 K of the P_{NP} transition in enriched Si single crystals. Positions and linewidths are: ^{28}Si : 9274.18 cm^{-1} , 0.022 cm^{-1} ; ^{29}Si : 9282.9, 0.013 cm^{-1} (line is split due to substitutional carbon incorporation, see inset and text); ^{30}Si with two different enrichments due to natural Si incorporation during FZ growth: 9289.15 and 9290.18 cm^{-1} , 0.064 cm^{-1} , respectively. The location of the transition in natural Si is indicated with an arrow. Data courtesy M. Thewalt, Simon Fraser University.

Low temperature PL was performed using techniques described in detail elsewhere [37]. Analysis of the TO-assisted transitions showed that P was the majority donor in all cases and that the concentration of B was typically 10x lower, consistent with the Hall data. Spectra showing the no-phonon phosphorus-bound exciton (P_{NP}) transition are shown in Fig. 11. The effect of the isotopic composition in renormalizing the

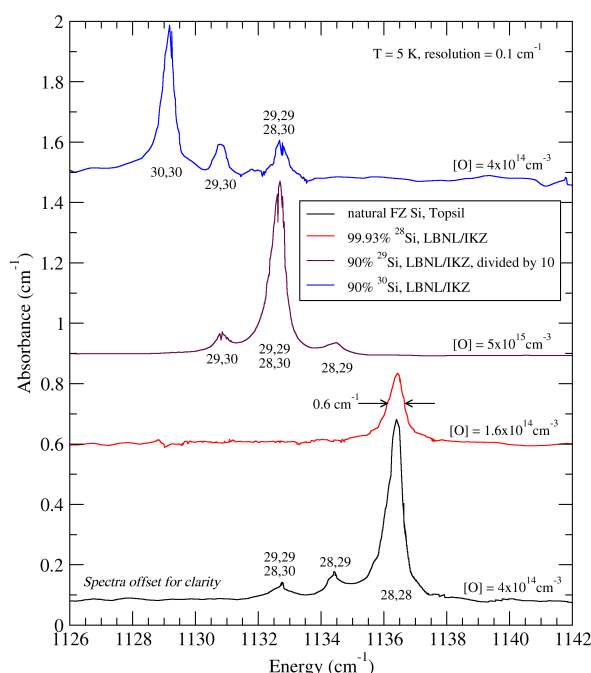


Fig. 12. Evaluation of oxygen content using the O local vibration mode absorption. Data courtesy A. Ramdas, Purdue University.

bandgap is seen clearly. It is interesting to compare the spectra to prior measurements of enriched Si crystals. For the ^{28}Si crystals, the observed FWHM is near-instrument-limited at 0.022 cm^{-1} . More detailed analysis by PLE [38] showed that the linewidth is just slightly wider than the narrowest reported in ^{28}Si to date [6]. For ^{29}Si , the line was slightly split (inset of Fig. 11). Assigning the splitting to strains caused by the presence of substitutional carbon, a concentration of $2 \times 10^{17}\text{ cm}^{-3}$ was estimated [39]. This is in reasonable agreement with subsequent SIMS and FTIR measurements which found carbon concentrations of $6 \times 10^{16}\text{ cm}^{-3}$ and $1 \times 10^{17}\text{ cm}^{-3}$, respectively. It should be noted that this crystal was grown from silane that had the highest level of methane contamination. Based on the absence of splitting of the P_{NP} PL line carbon concentrations were below 10^{16} cm^{-3} (200 ppb) in both the ^{28}Si and ^{30}Si enriched crystals. This is notable given the ppm levels of CH_4 in the silane used for their growth. In the case of ^{29}Si and ^{30}Si , the PL linewidths were much narrower than previously reported for crystals enriched in these two isotopes [37]. The oxygen content was evaluated by FTIR, as shown in Fig. 12. With the exception of the ^{29}Si -enriched crystal, the samples had equivalent or lower oxygen contents compared to commercial FZ material (i.e. $< 4 \times 10^{14}\text{ cm}^{-3}$). The characterization results are summarized in Table 3.

Table 3. Summary of characterization results for isotopically enriched Si crystals.

Crystal	Enrichment %	ρ $\Omega\text{-cm}$	net carriers cm^{-3}	μ $\text{cm}^2\text{ V}^{-1}\text{ s}^{-1}$	Electrically Active impurities from FTIR and PL			Other impurities	
					B	P	As	O	C
^{28}Si seed	99.92	14	3.2×10^{14}	1350	2×10^{14}	$\sim 3 \times 10^{14}$		1.6×10^{14}	$< 10^{16}$
^{28}Si tail		0.9	5.6×10^{15}	1270					
^{29}Si seed	91.37	210	2.3×10^{13}	1250	2×10^{13}	high 10^{13}	3×10^{12}	5×10^{15}	2×10^{17}
^{29}Si tail		275	2×10^{13}	1220	2×10^{13}	high 10^{13}			
^{30}Si seed	86.7	110	4.3×10^{13}	1360	2×10^{13}	6×10^{13}	2×10^{12}	4×10^{14}	$< 10^{16}$
^{30}Si tail	89.8	180	2.4×10^{13}						

5 Conclusions

A process consisting of high-yield production of isotopically enriched bulk polycrystalline Si in a laboratory scale reactor followed by float zone crystallization has been demonstrated to produce dislocation-free single crystals enriched in all three stable isotopes of Si (^{28}Si , ^{29}Si , and ^{30}Si). The 99.9+% ^{28}Si , 91% ^{29}Si , and 88% ^{30}Si crystals described in this report are among the highest quality isotopically enriched Si made to date with electrically active impurities at 10^{15} cm^{-3} and below, low oxygen and carbon concentrations, and minimal amounts of inhomogeneous lattice strain. These crystals will be used for high resolution optical spectroscopy and, potentially, for measurements of the coherence lifetime limits of the ^{31}P ESR spin and the ^{29}Si nuclear spin. Isotopically enriched crystals of still higher purity can be grown when high purity precursor gases become available.

6 Appendix. Reactor modeling

As discussed in Section 3.6 above, it is desirable to operate the reactor in such a way as to (1) reduce the volume of the reactor above 400 °C, the homogeneous nucleation threshold for silane, (2) maintain a constant Si deposition rate along the length of the rod, and (3) deposit Si at a sufficiently fast rate ($> 1 \mu\text{m}/\text{minute}$). A quantitative modeling procedure was developed by Hashimoto *et al.* [27] in the context of measuring the reaction kinetics of poly-Si formation from silane in a one-pass tube reactor similar in design to the one used here. The Navier-Stokes equations for reacting gas flow in the positive z direction (neglecting buoyancy) in a symmetric annulus with inner diameter $2r_i$ and outer diameter $2r_o$ are

$$\frac{1}{r} \frac{\partial}{\partial r} (r \rho v_r) + \frac{\partial}{\partial z} (\rho v_z) = 0 \quad (\text{A1})$$

$$\rho \left(v_r \frac{\partial v_z}{\partial r} + v_z \frac{\partial v_z}{\partial z} \right) = \frac{1}{r} \frac{\partial}{\partial r} \left(r \mu \frac{\partial v_z}{\partial r} \right) - \frac{\partial P}{\partial z} \quad (\text{A2})$$

$$\rho C_p \left(v_r \frac{\partial T}{\partial r} + v_z \frac{\partial T}{\partial z} \right) = \frac{1}{r} \frac{\partial}{\partial r} \left(r \lambda \frac{\partial T}{\partial r} \right) \quad (\text{A3})$$

$$\rho \left(v_r \frac{\partial w_A}{\partial r} + v_z \frac{\partial w_A}{\partial z} \right) = \frac{1}{r} \frac{\partial}{\partial r} \left(r \rho D_A \frac{\partial w_A}{\partial r} \right) \quad (\text{A4})$$

where the independent variables are v_r and v_z , the radial and axial velocities, w_A , the mass fraction of the reacting species A, and T , the gas temperature. Equation (A1) is a continuity equation for momentum. The gas properties which are, in general, temperature dependent are C_p (heat capacity), ρ (density), and λ (thermal conductivity) and P (pressure). D_A is the diffusion coefficient of A in the carrier gas. For the present reactor the temperature is fixed at the inner and outer walls at T_i and T_o , respectively. The mass fraction of A is related to the molar concentration C by

$$C_A = \rho w_A / M_A \quad (\text{A5})$$

where M_A is the molecular weight of A (32 amu for silane).

It is convenient to introduce a number of reduced variables and other terms:

$$r^* = r_i / r_o, \text{ reduced radius} \quad (\text{A6})$$

$$r_m = \left(\frac{r_o^2 - r_i^2}{2 \ln(r_o / r_i)} \right)^{1/2}, \text{ mean radius} \quad (\text{A7})$$

$$D_h = 2(r_o - r_i), \text{ hydraulic diameter} \quad (\text{A8})$$

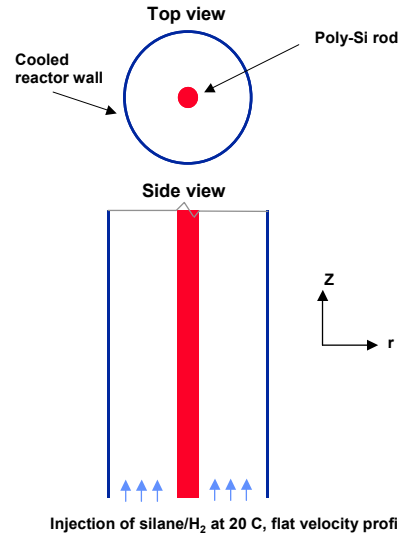


Fig. A1. Reactor geometry and coordinate system: 3 mm diameter starter rod heated to 730°C, 25 mm diameter flow tube with its walls maintained at 20 °C, 150 mm reaction zone.

$$\text{Re} = \frac{\bar{v}}{\nu} \frac{\rho D_h}{\mu}, \text{ Reynolds number} \quad (\text{A9})$$

$$\text{Pr} = \frac{C_p \mu}{\lambda}, \text{ Prandtl number} \quad (\text{A10})$$

$$\bar{z} = \frac{z}{D_h} \frac{1}{\text{RePr}}, \text{ unitless axial distance} \quad (\text{A11})$$

Appropriate boundary conditions at $z = 0$ (entrance to the reaction zone) are

$$v_z = Q_0 / \pi(r_o^2 - r_i^2) \quad (\text{A12})$$

$$T = T_o \quad (\text{A13})$$

$$w_A = w_{A0} \quad (\text{A14})$$

and represent a cool entrance gas flow with a flat radial velocity profile determined by the volume flow rate Q_0 with an initial mass fraction of silane w_{A0} . As the gas flows down the tube, it will be heated at the inner wall ($T_i > T_o$) and silane will react and deposit at $r = r_i$. Boundary conditions at the inner and outer walls are

$$v_z = 0, \quad T = T_i, \quad \partial W_A / \partial r = k_s w_A / D_A \text{ at } r = r_i \quad (\text{A15})$$

$$v_z = 0, \quad T = T_o, \quad \partial W_A / \partial r = 0 \text{ at } r = r_o \quad (\text{A16})$$

where

$$r_s = k_s C_A(r = r_i) \quad (\text{A17})$$

and the surface reaction rate r_s has units of moles $\text{m}^{-2} \text{s}^{-1}$.

Before addressing the full, coupled, non-linear set of partial differential equations (A1)-(A4), some simpler limiting cases are discussed [40]. Neglecting reaction for the moment, at sufficiently large z , “fully developed” profiles are attained. For a given average velocity $\bar{v}$ the fully developed velocity profile is

$$v(r) = 2\bar{v} \left(\frac{r_o^2 - r^2 - 2r_m^2 \ln(r_o/r)}{r_o^2 - r^2 - 2r_m^2} \right), \quad (\text{A18})$$

where $\bar{v}$ is obtained from the gas flow by

$$\bar{v} = Q_0 / \pi(r_o^2 - r_i^2). \quad (\text{A19})$$

The fully developed temperature profile is obtained by setting $\frac{\partial T}{\partial z} = 0$ and $\frac{\partial v}{\partial r} = 0$ and reducing (A3) to

$$\frac{1}{r} \frac{dT}{dr} \left(r \lambda \frac{dT}{dr} \right) = 0 \quad (\text{A20})$$

which, for constant thermal conductivity λ can be expressed as

$$\frac{d^2 T}{dr^2} + \frac{1}{r} \frac{dT}{dr} = 0. \quad (\text{A21})$$

There is an exact solution for (A21):

$$T_{FD}(r) = \left(\frac{\ln(r/r_o)}{\ln(r_i/r_o)} (T_i - T_o) \right) + T_o \quad (\text{A22})$$

Neglecting reaction for the moment, the problem reduces to calculating v and T in the “entrance length” of the reactor (that is, for the volume before the fully developed profiles are attained). Hashimoto *et al.* [27] made some additional assumptions, which also use here, to aid in the solution of coupled Eqs. (A1) – (A4): $v_r = 0$, neglect radial velocity; assume gas transport properties independent of w_A . With these simplifications,

it is possible to convert (A1)-(A4) to finite difference (FD) equations and solve them numerically. We used the implicit method with a tridiagonal solver [41]. It should be noted that the neglect of radial velocity in (A1) would lead to momentum non-conservation in the solution. A related issue is the treatment of dP/dz , the pressure gradient in Eq. (A2). In the present approach, dP/dz was determined by Newton's method at each z step in order to maintain constant mass flow (in general, the pressure drop falls as the fully developed T and v profiles evolve). This was more exact than the methodology used by Hashimoto *et al.* [42].

A number of tests were performed to validate the present numerical approach. The evolution of the temperature profile in annular flow for constant fluid properties and fully developed velocity flow at $z = 0$ (thermal entrance length) was solved exactly for a number of values of r^* by Lundberg *et al.* [43]. In the nomenclature of that work, the present geometry is a problem of the "first kind with a temperature step at the inner wall." Solutions are expressed in terms of the bulk temperature

$$T_{bulk} = \frac{\int_{r_i}^{r_o} T(r)v(R)2\pi r dr}{\int_{r_i}^{r_o} v(R)2\pi r dr} \quad (A23)$$

and the reduced mean temperature

$$\vartheta_m = \frac{T_{bulk} - T_o}{T_i - T_o}. \quad (A24)$$

The equation to be solved is (A3) with $v_r = 0$ and v_z given by (A19). T_i was set to 730°C and T_o to 20°C. 500 evenly spaced radial points were used and 2000 variable z steps (shorter near $z = 0$). A geometry close to that of the actual reactor ($r_i = 2$ mm, $r_o = 8$ mm) was used to compare to an exact solution at $r^* = 0.25$. As shown in Fig. A2, agreement of the numerical solver with the exact solution was excellent.

The analogous problem of the development of the velocity profile (hydrodynamic entrance length) in an annulus $T_i = T_o$ and a flat velocity profile at $z = 0$ was considered by Heaton *et al.* [44] and by Shah and Farnia [45]. Solutions are described in terms of the evolution of the normalized critical velocity $v_{max}/\bar{v}$ and normalized critical radius (r at which $v = v_{max}$ divided by r_o). Comparison of the present solver to these two more exact solutions for $r^* = 0.1$ is shown in Fig. A3. The agreement is not as good as that obtained for the evolution of the temperature profile; the finite difference solution evolves somewhat

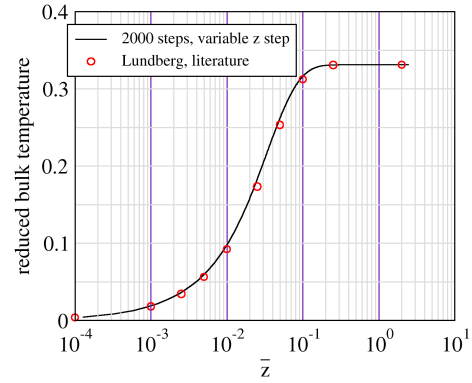


Fig. A2. Comparison of numerical (line) and exact (points) for development of the radial temperature profile in an annulus with $r^* = 0.25$ and a fully developed velocity profile.

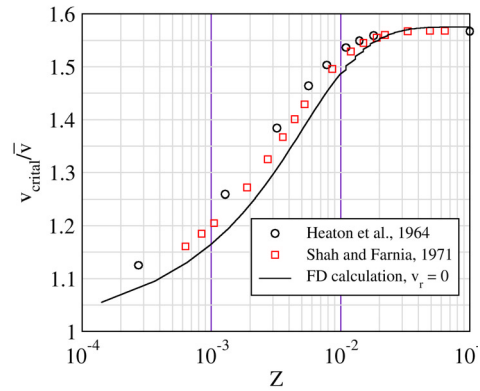


Fig. A3. Comparison of numerical (line) and literature (points) for development of velocity profile in an annulus with $r^* = 0.1$ and a constant temperature profile.

more slowly to the fully developed solution. This is attributed to the neglect of the radial velocity.

The coupled problem of the simultaneous development of T and v in an annulus was considered by Shumway and McEligot [46] for a number of reactor geometries and values of Pr . It is interesting to note that for $Pr \ll 1$ (low pressure gases), the thermal entrance length will be less than the hydrodynamic entry length while for $Pr \gg 1$ (fluids like water, oil, etc.), the thermal entrance length is greater than the hydrodynamic entry length. Here, the outer wall temperature was adjusted to obtain a value of Pr that corresponded to one of the published solutions. There are some additional reduced variables associated with this solution:

$$z^+ = \frac{z}{D_h} \frac{1}{RePr}, \text{ unitless axial distance with Re and Pr evaluated at } z = 0, \quad (A25)$$

$$P^+ = \frac{P - P_e}{\rho \bar{v}}, \text{ "pressure defect," where } p_e \text{ and } \bar{v} \text{ are evaluated at } z = 0. \quad (A26)$$

Heat fluxes at the inner and outer walls are computed from the temperature gradient. A comparison of the present solver to Shumway and McEligot is shown in Fig. A4. As with the previous two validations, agreement is better for the thermal (left and right) than for the hydrodynamic (center) aspects of the solution. This was expected given the

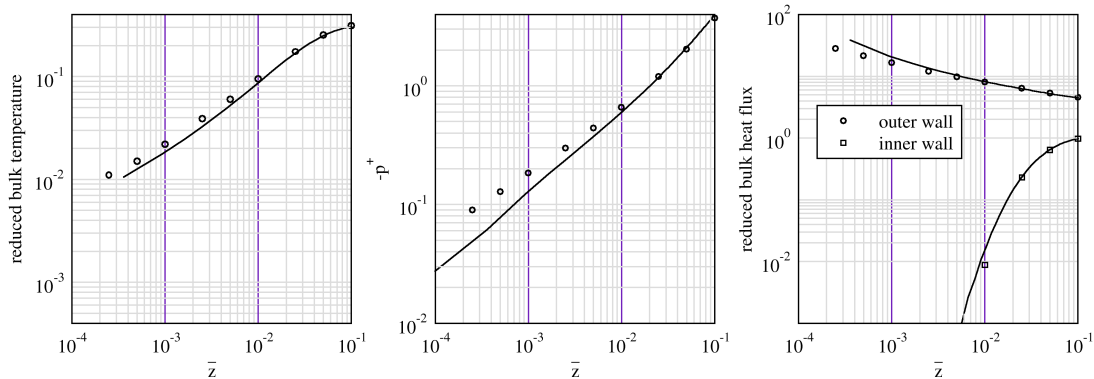


Fig. A4. Simultaneous temperature and velocity profile development in an annulus. Points are from Shumway and McEligot and lines are from finite difference solver. Plots are (left to right) bulk gas temperature, pressure defect, and reduced heat flux.

neglect of v_r discussed above. Nevertheless, it is concluded that the present approach is sufficiently accurate for modeling the present reactor and that the pressure drop down the reactor is being treated realistically.

The reactor was modeled given the geometry shown in Fig. A1 for three different carrier gas flows (5, 15, and 25 slpm). Temperature contours as a function of z are shown in Fig. A5. It is seen that for the slowest flow, the fully developed T profile is reached at $z = 50$ mm while for the faster flows the fully developed profile is not reached within the reactor. Figure A6 shows the fraction of the reactor volume above 400°C , the homogeneous nucleation threshold for silane, as a function of carrier gas flow. For the fully developed T profile (that is, for very slow flow rates), 9% of the reactor is above 400°C . Faster flow rates reduce this value. At a flow of 15 slpm, the volume of the reactor above 400°C is only 6%, which is a 50% reduction compared to slower flows. Figure A7 shows the evolution of the evolution of the pressure drop (left) and

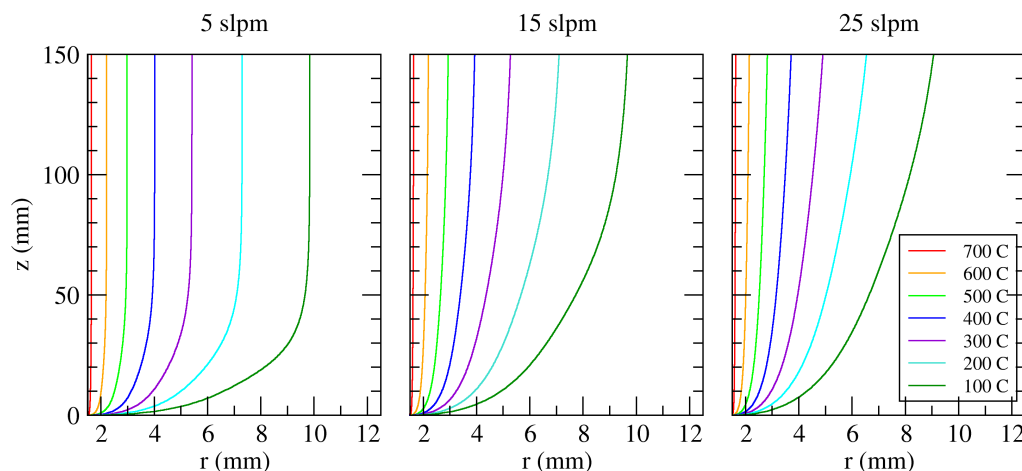


Fig A5. Calculated temperature profiles in the poly-Si reactor for different carrier gas flow. The inner surface of the annulus is heated to 730°C while the outer wall is kept at 20°C.

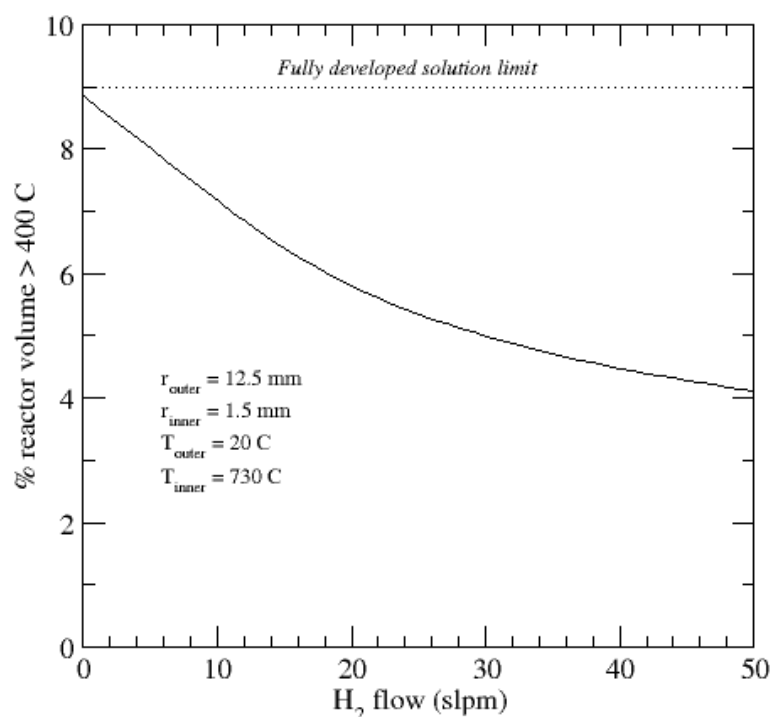


Fig. A6. Volume of reactor above 400°C as a function of carrier gas flow.

temperature and velocity profiles (expressed in terms of T_{bulk} and v_{critical}) for a flow of 15 slpm. As expected for a value of the Prandtl number $Pr < 1$, the thermal profile evolves more quickly than the velocity profile.

Finally, the simultaneous evolution of T , v , and the mass fraction of silane was modeled. Following Hashimoto *et al.* [27], it was assumed that the reaction at the surface is first-order in silane with a rate equation

$$r_s = k_s C_{AS}, \text{ units of mol m}^{-2} \text{ s}^{-1}, \quad (\text{A27})$$

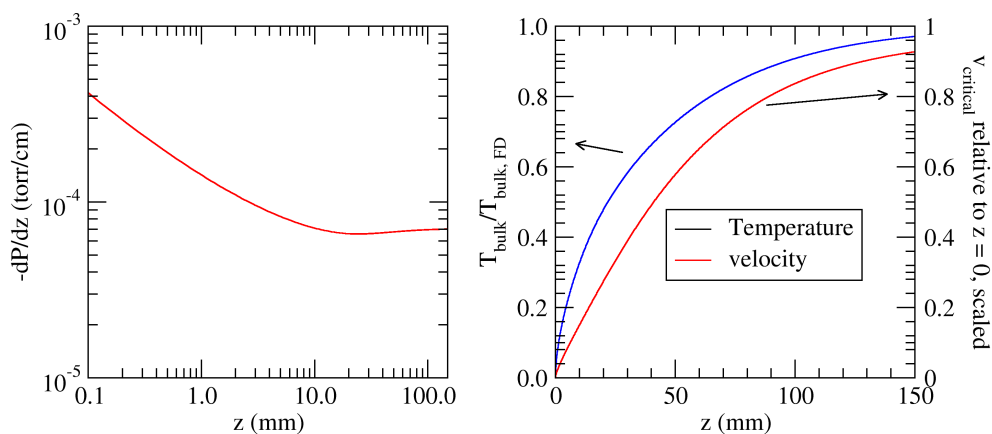


Fig. A7. Calculated pressure gradient (left) and temperature and velocity profiles (right) as a function of distance in the reactor for a carrier gas flow of 15 slpm. The mean velocity for these conditions is 55 cm/s and the Prandtl number is 0.71.

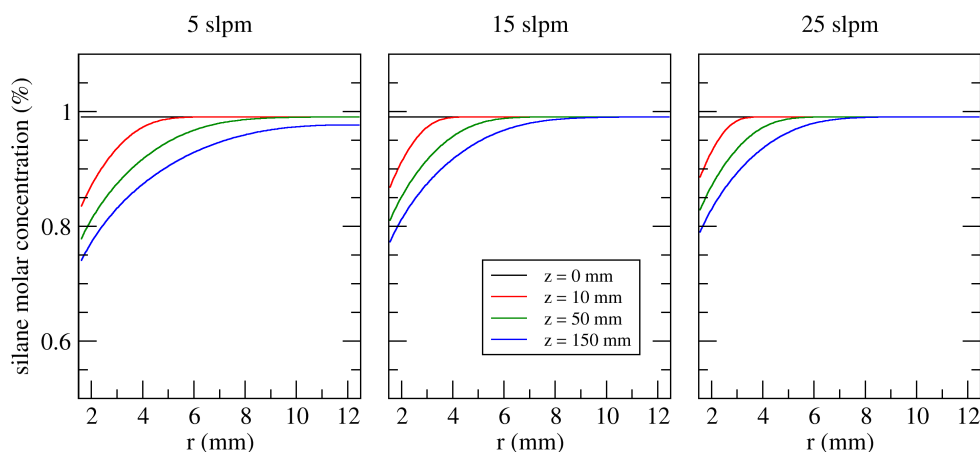


Fig. A8. Calculated radial silane concentration profiles as selected values of z for different carrier gas flows.

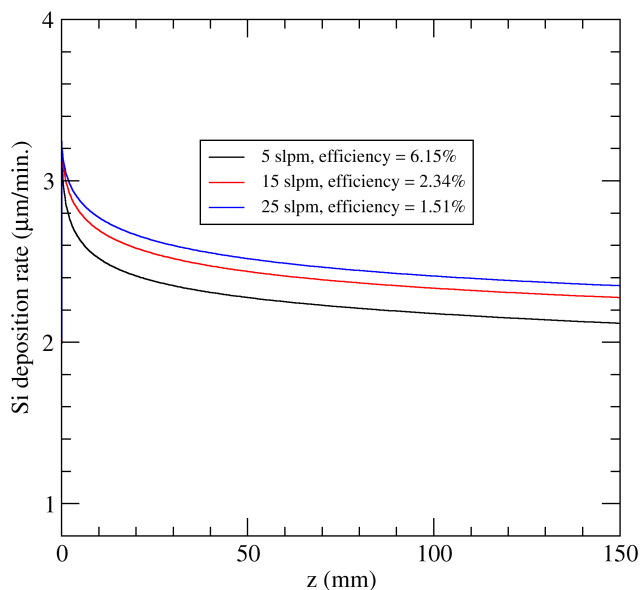


Fig. A9. Calculated silane deposition length as a function of axial distance z in the reactor for different carrier gas flows.

of silane at the surface [see Eq. (A5) for the relationship between concentration and mass fraction]. The deposition rate in units of distance per unit time is

$$\frac{dR_s}{dt} = \frac{M_{\text{Si}} r_s}{\rho_{\text{Si}}} \quad (\text{A28})$$

where M_{Si} is the atomic weight of Si and ρ_{Si} is its density (2.35 g cm^{-3}). The rate constant obtained by Hashimoto et al. was used:

$$k_s = 3.88 \times 10^6 \exp(-162,000 / RT) \text{ (units of m/s)}. \quad (\text{A30})$$

Radial concentration profiles for an initial silane concentration of 1% molar are shown in Fig. A8 and the predicted deposition rate as a function of z is shown in Fig. A9. At the slower flow (5 slpm), the silane radial concentration profile changes significantly as a function of z ; this is reflected in a deposition rate, which falls to 65% of its initial value by the end of the tube. This difference is less at higher carrier gas flows. The one pass efficiency also declines with increasing gas flow, as shown in the legend of Fig. A9.

Ultimately, a carrier gas flow of 15 slpm was selected for reaction operation. As shown in Figs. 7 and 8 this lead to very uniform deposition along the rod with an average deposition rate of about $5 \mu\text{m/min}$. This is in satisfactory agreement with the calculations, particularly given the uncertainties in the kinetic data used. It is possible that convective cooling of the rod leads to lower temperatures at small values of z (this effect can be seen in Fig. 6), leading to lower growth rates there and offsetting the trend predicted in Fig. A9.

Finally, it is appropriate to comment on the limiting efficiency of a recirculating reactor. The recirculation factor n is the process gas flow divided by the exhaust flow. For a process gas flow of 15 slpm and an exhaust gas flow of twice the silane feed, the recirculation factor varied from 750 at the beginning of a run with 10 sccm silane feed to 150 at the end of a run with 50 sccm feed. The overall predicted efficiency is

$$1 - (1 - \eta)^n \quad (\text{A31})$$

where η is the one pass efficiency (predicted to be 2.3% for 15 slpm flow). Equation (A31) predicts an efficiency of close to 100% at the beginning of a run and to 97% at the end of a run. This is consistent with the observed efficiency of >95%.

References

- 1 W. S. Capinski, H. J. Maris, E. Bauser, I. Sillier, M. Asen-Palmer, T. Ruf, M. Cardona, and E. Gmelin, *Appl. Phys. Lett.* **71**, 2109 (1997).
- 2 P. L. Komarov, M. G. Burzo, G. Kaytaz, and P. E. Raad, *Microelectronics Journal* **34** 1115 (2003).
- 3 T. Ruf, R. W. Henn, M. Asen-Palmer, E. Gmelin, M. Cardona, H.-J. Pohl, G. G. Devyatych, P. G. Sennikov, *Solid State Commun.* **115**, 243 (2000).
- 4 A. V. Inyushkin, *Inorganic Materials* **38**, 427 (2002).
- 5 T. Ruf, R. W. Henn, M. Asen-Palmer, E. Gmelin, M. Cardona, H.-J. Pohl, G. G. Devyatych, and P. G. Sennikov, *Solid State Commun.* **127**, 257 (2003).
- 6 D. Karaiskaj, M. L. W. Thewalt, T. Ruf, M. Cardona, H.-J. Pohl, G. G. Devyatych, P. G. Sennikov, and H. Riemann, *Phys. Rev. Lett.* **86**, 6010 (2001).
- 7 D. Karaiskaj, M. L. W. Thewalt, T. Ruf, M. Cardona, and M. Konuma, *Phys. Rev. Lett.* **89**, 016401 (2002).
- 8 D. Karaiskaj, J. A. H. Stotz, T. Meyer, M. L. W. Thewalt, and M. Cardona, *Phys. Rev. Lett.* **90**, 186402 (2003).
- 9 B. E. Kane, *Nature* **393**, 133 (1998).
- 10 R. Vrijen, E. Yablonovitch, H. W. Jiang, A. Balandin, V. Roychowdhury, T. Mor, and D. DiVincenzo, *Phys. Rev. A* **62**, 0123306 (2000).
- 11 T. D. Ladd, J. R. Goodman, F. Yamaguchi, Y. Yamamoto, E. Abe, and K. M. Itoh, *Phys. Rev. Lett.* **89**, 017901 (2002).
- 12 A. M. Tyryshkin, S. A. Lyon, A. V. Astashkin, and A. M. Raitsimring, *Phys. Rev. B* **68**, 193207 (2003).
- 13 A. E. Dementyev, D. Li, K. MacLean, and S. E. Barrett, *Phys. Rev. B* **68**, 153302 (2003).
- 14 P. Becker, H. Bettin, P. De Bièvre, C. Holm, U. Kütgens, F. Spieweck, J. Stümpel, S. Valkiers, and W. Zulehner, *IEEE Trans. Instr. Meas.* **44**, 522 (1995).
- 15 K. Takyu, K. M. Itoh, K. Oka, N. Saito, and V. I. Ozhogin, *Jpn. J. Appl. Phys., Part 2* **38**, L1493 (1999).
- 16 A. D. Bulanov, G. G. Devyatych, A. V. Gusev, P. G. Sennikov, H.-J. Pohl, H. Riemann, H. Schilling, and P. Becker, *Cryst. Res. Technol.* **35**, 1023 (2000).
- 17 K. M. Itoh, J. Kato, M. Uemura, A. K. Kaliteyevskii, O. N. Godisov, G. G. Devyatych, A. D. Bulanov, A. V. Gusev, I. D. Kovalev, P. G. Sennikov, H.-J. Pohl, N. V. Abrosimov, and H. Riemann, *Jpn. J. Appl. Phys.* **42**, 6248 (2003).
- 18 L. D. Crossman and J. A. Baker, "Polysilicon Technology," in *Semiconductor Silicon 1977*, Electrochem. Soc., Pennington, New Jersey, 1977 pp. 18-31.
- 19 S. Wolf and R. N. Tauber, *Silicon Processing for the VSLI Era* (Lattice Press, Sunset Beach, CA, 1999), Vol. 1, pp.6-35.

-
- 20 T. D. Kamins, in *Handbook of Semiconductor Silicon Technology*, edited by W. C. O'Mara, R. B. Herring, and Lee P. Hunt (Williams-Andrew, Norwich, NY, 1990), pp. 640-719.
 - 21 R. N. Flagella, and H. J. Dawson, U.S. Patent No. 4,921,026 (May 1, 1990).
 - 22 W. Hensel, in *Electrochemical Society Proceedings, Vol. 96-13*, edited by C. L. Claeys, P. Stallhofer, P. Rai-Choudhury, and J. E. Maurtis (Electrochemical Society, Pennington, NJ, 1996), pp. 3-14.
 - 23 S. M. Lord and R. J. Milligan, U.S. Patent No. 5,810,934 (Sept. 22, 1998).
 - 24 R. C. Flagan and M. K. Alam, U.S. Patent No. 4,642,227 (Feb. 10, 1987).
 - 25 B. Caussat, M. Hemati, and J. P. Couderc, *Chem. Eng. Sci.* **50**, 3615-3624 (1995).
 - 26 S. K. Iya, *J. Crystal Growth* **75**, 88-90 (1986).
 - 27 K. Hashimoto, K. Miura, T. Masuda, M. Toma, H. Sawai, and J. Kawase, *J. Electrochem. Soc.* **137**, 1000 (1990).
 - 28 A. M. Beers and J. Bloem, *Appl. Phys. Lett.* **41**, 153 (1982).
 - 29 E. Ibok and S. Garg, *J. Electrochem. Soc.* **140**, 2927 (1993).
 - 30 L. C. Rogers, in *Handbook of Semiconductor Silicon Technology*, edited by W. C. O'Mara, R. B. Herring, and Lee P. Hunt (Williams-Andrew, Norwich, NY, 1990).
 - 31 F. C. Eversteijn, *Philips Res. Repts.* **26**, 134 (1971).
 - 32 T. U. Murthy, *J. Crystal Growth* **33**, 1 (1976).
 - 33 S. K. Iya, R. N. Flagella, and F. S. DiPaolo, *J. Electrochem. Soc.* **129**, 1531 (1982).
 - 34 F. Sliotman and J.-C. Parent, *J. Aerosol Sci.* **25**, 15 (1994).
 - 35 Y. Yatsurugi, A. Yusa, and N. Takahashi, U.S. Patent No. 4,150,168 (Apr. 17, 1979).
 - 36 W. C. Breneman, R. N. Flagella, J. M. Gaston, and D. W. Hagan, U.S. Patent No. 4,826,668 (May 2, 1989).
 - 37 D. Karauskaj, M. L. W. Thewalt, T. Ruf, and M. Cardona, *phys. stat. sol. (b)* **235**, 63 (2003).
 - 38 M. L. W. Thewalt, private communication.
 - 39 A. N. Safonov, G. Davies, and E C. Lightfowlers, *Phys. Rev. B* **54**, 4409 (1996).
 - 40 R. K. Shah and A. L. London, *Laminar Flow Forced Convection in Ducts* (Academic, New York, 1978), pp. 284-321.
 - 41 J. H. Lienhard, *A Heat Transfer Textbook* (Prentice-Hall, Englewood Cliffs NJ, 1987), pp. 211-265.
 - 42 M. Kawase, private communication.
 - 43 R. E. Lundberg, P. A. McCuen, and W. C. Reynolds, *Int. J. Heat Mass Transfer* **6**, 495-529 (1963).
 - 44 H. S. Heaton, W. C. Reynolds, and W. M. Hays, *Int. J. Heat Mass Transfer* **7**, 763-781 (1964).
 - 45 V. L. Shah and K. Farnia, *Comput. Fluids* **2**, 285-294 (1974).
 - 46 R. W. Shumway and D. M. McEligot, *Nuc. Sci. Engin.* **46**, 394-407 (1971).