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SILICON PRODUCTION IN AN AEROSOL REACTOR

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Jin Jwang Wu and Richard C. Flagan
Division of Engineering and Applied Science
California Institute of Technology
Pasadena, CA 91125

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INTRODUCTION

The production of bulk solar-grade silicon by homogeneous gas-phase pyrolysis of silane has been the subject of a number of investigations, beginning with work at Union Carbide Corporation (1) and at the Jet Propulsion Laboratory.(2) While very high efficiencies of conversion of silane to silicon were achieved in those early studies, the silicon powder generated consisted of low density agglomerates of submicron particles. This powder was difficult to collect and melt. Moreover, the product purity was inadequate for the intended use.

In 1980, a study of the factors limiting particle growth in the so-called free space reactor was undertaken. This work has led to an improved understanding of the fundamental processes involved in the formation of low vapor pressure particles by gas phase chemical reactions, and, as a result of this understanding, to the development of a new type of aerosol reactor for the processing of high purity materials. The focus of recent work under this program has been on elucidating the operating regimes in which particles can be grown to large enough size to facilitate separation of the product from the gas. In this paper we summarize the major developments of this program.

LIMITATIONS OF THE FREE SPACE REACTOR

The Union Carbide reactor was called a "free space" reactor because the silane decomposition reactions are carried out in the volume of the reactor rather than on a substrate as in the conventional Siemens process for producing polycrystalline silicon. The choice of silane as a reactant rather than a chlorosilane allows complete conversion of the silane to silicon in a single pass through the reactor.

The reaction kinetics of silane pyrolysis are not completely understood. The initial steps in the reaction sequence are thought to be the reactions first hypothesized by Purnell and Walsh (3), i.e.,

$$SiH_4 \longrightarrow SiH_2 + H_2$$

$$SiH_2 + SiH_4 \rightleftharpoons Si_2H_6$$

$$SiH_2 + Si_2H_6 \rightleftharpoons Si_3H_8$$

The rate of silane disappearance of silane was found to be

$$\frac{d[SiH_4]}{dt} = -k_1[SiH_4]^{3/2} \quad : \quad k_1 = 10^{14} \exp(-30000/T) \ (M^3/Kmol)^{\frac{1}{2}} sec^{-1}$$

Ring and coworkers (4) suggest that these experiments were in the pressure fall-off regime of the dissociation reaction, Since the free-space reactor experiments have been conducted at atmospheric pressure, the kinetic expression of Purnell and Walsh provide a reasonable approximation to the rate of silane disappearance. The subsequent reactions leading to the production of condensible products are not understood. From the large activation energy of the initial pyrolysis reaction, it appears reasonable to assume that this is the rate limiting step in the formation of silicon by silane pyrolysis.

To achieve complete conversion of silane to silicon in a reactor of reasonable size, the Union Carbide reactor was operated at a temperature of about 1200 K. At this temperature, the characteristic time for the silane pyrolysis reaction on the order of microseconds, so the pyrolysis should be complete as soon as the reactant is heated. Assuming that vapor phase silicon is produced in this mechanism, this rapid reaction would lead to extremely high levels of supersaturation and, consequently, the homogeneous nucleation of large numbers of very small particles. With condensation taking place quickly, the only mechanism by which these nuclei can grow is by coagulation. Assuming residence times on the order of several seconds, particle growth by Brownian coagulation is limited to the production of particles smaller than one micron in diameter. Enhancement of the coagulation rate by turbulence is difficult because of the large drag to inertia ratio of these small particles. Thus, the free-space reactor is limited to the production of a powder comprised of submicron particles.

THE AEROSOL REACTOR

These results suggest immediately an alternate approach to the growth of large particles by direct gas phase chemical reactions in a flow reactor. It is clear that the growth of particles to supermicron sizes by coagulation is not feasible in reasonable residence times. If, however, a small number of particles could be grown by vapor deposition it should be possible to produce the desired large particles within a residence time of a few seconds. The size to which this small number of particles could be grown is determined by a simple mass balance. Assuming all particles grow to the same size, the volume of the final particle is simply the total volume of condensed phase products of gas phase reactions divided by the number of particle on which these products are deposited.

The problem with this approach is that the products of the silane pyrolysis reactions nucleate readily due to their low vapor equilibrium vapor pressures. If such nucleation takes place, large numbers of small particles are again generated and the growth of the initial particles to the desired size is prevented. There exists a limiting rate of production of condensible species below which nucleation is suppressed and above which significant new particle formation occurs. This rate is determined by the rate at which the products of reaction diffuse to the surfaces of the growing particles. If that diffusion is sufficiently fast, the condensible species are not allowed to accumulate to the point that nucleation is inevitable.

The procedure for the growth of large refractory particles in an aerosol reactor is, therefore:

(1) Generate seed particles by some means such as the homogeneous nucleation of the products of reaction of a small amount of the precursor gas.

(2) Dilute the seed particles with sufficient precursor to allow them to be grown to the desired volume by vapor deposition.

(3) React the precursor at a rate that is, at all times, kept slow enough that the diffusion of reaction products to the seed particles keeps significant supersaturation from developing.

To determine the limiting reaction rate, it is necessary to understand the process of homogeneous nucleation in the presence of growing aerosol particles. The classical theory of homogeneous nucleation(5) treats the formation of particles in a homogeneous system. Vapor diffusion to growing particles creates localized inhomogeneities around the particles. The depletion of vapor in these regions suppresses nucleation locally. If the number concentration is sufficiently high relative to the rate at which condensible species are generated, nucleation can be supressed. This problem has been examined theoretically, beginning with the use of an artificial construct, the "clearance volume" which is a measure of the ability of an isolated particle to inhibit nucleation but which is not rigorously valid in the limit of complete supression of nucleation.(6,7) We have recently developed a "cell model" which is more rigorously applicable to the problem at hand, the complete supression of nucleation. (8)

These models of the influence of growing aerosol particles on the rate of homogeneous nucleation are based on the classical theory of homogeneous nucleation. The low vapor pressures of the reaction products with which we are dealing make important assumptions of the classical theory questionable, notably the assumption that a quasi-steady-state population of molecular clusters is established before the onset of significant nucleation. According to the classical theory, the smallest thermodynamically stable cluster size has diameter d^*, where

$$d^* = \frac{4\sigma v_m}{kT\ln S}$$

and σ is the surface tension, v_m is the molecular volume, and S is the saturation ratio. For silicon in the silane pyrolysis aerosol reactor, we estimate that the number of molecules in the critical cluser, g , is less than 10. At this small size the use of the surface tension of the bulk material is clearly questionable. Moreover, an examination of the kinetics of nucleation indicates that the assumption of a quasi-steady cluster distribution is inappropriate. We have, therefore, recently developed a kinetic model to describe more accurately the nucleation process in the aerosol reactor.

REACTOR DESIGN AND EVALUATION

Two aerosol reactor systems have been constructed in our efforts to grow large silicon particles by silane pyrolysis and to understand the fundamental processes that limit aerosol reactor operation. The first reactor consisted of two stages: (i) a seed generator in which a small amount of silane was pyrolyzed to generate seed particles by homogeneous nucleation; and (ii) a growth reactor in which the seed particles were grown by rate-controlled silane pyrolysis. This system is illustrated in Figure 1. To achieve acceptable velocities and residence times with the small amounts of silane used in these experiments, nitrogen was added to the flows as a diluent.

Between the two reactor stages, the primary silane flow was added to the seed aerosol and thoroughly mixed using a series of static mixers. Very efficient mixing is essential to the operation of the aerosol reactor since small inhomogeneities could allow nucleation to occur in localized regions of the growth reactor and interfere with particle growth. The growth reactor cosisted of a 9 mm i.d. quartz tube that was heated in five separately controlled zones. The temperature was increased along the length of the reactor by control of the separate heating zones, providing a temperature profile of

$$T = 755\text{K}\ (1 + 2.74\ \text{m}^{-1})^{\frac{1}{2}} \qquad (\pm\ 10\ \text{K})$$

The low initial temperature allowed for slow particle growth until the particles reached a size such that they became efficient vapor scavengers and could suppress nucleation at higher reaction rates. The high temperatures at the end of the process assured complete decomposition of the silane.

The silicon aerosols produced in these experiments were characterized using an electrical aerosol analyzer to determine the size distribution of submicron particles, TSI Model 3030, a condensation nuclei counter to determine the total number concentration, Environment One, and optical particle counters to determine the size distribution of particles in the 0.15 to 6 micron range, Royco Model 226, and in the 0.5 to 40 micron range, Particle Measurement Systems classical scattering probe. With these instruments it was shown that 0.1 micron seed particles could be grown to mass median diameters on the order of 6 to 10 microns,(8) as illustrated in Fig. 2.

To gain better control over the seed conditions in studies designed to elucidate the operating domain over which seed particles can be successfully grown, and to resolve questions about the density of the product particles, the larger three-stage reactor shown in Figure 3 was constructed. As in the original reactor, seed particles are generated in the first stage by homogeneous nucleation of the reaction products from the pyrolysis of a small amount of silane. The second stage is used to increase the size of the seed particles up to 2 microns. It consists of a 10 mm i.d., 350 mm long quartz tube that is heated in four separately controlled zones. The temperature is ramped along the length of this reactor to accelerate the reaction as the seed particles grow as in the original growth stage. The third stage grows these enlarged seeds to their final size in a 12 mm i.d., 850 mm long quartz tube. This reactor stage is heated in 5 separate zones. The first three zones are 50 mm long and are separated by 10 mm insulation to facilitate precise temperature control. These are followed by zones of 300 and 150 mm length that are heated by Lindbar silicon carbide heating elements. These heaters allow high temperature operation toward the end of the residence time in the reactor, making it possible to hear the aerosol to the melting point of silicon (1685 K) so the volume of silicon contained in individual particles can be determined unambiguously.

EXPERIMENTAL RESULTS

Several types of experiments have been conducted to characterize the reactor. In the following discussion, we focus on the behavior of the primary growth stage of the reactor. The first two stages are used merely as a controllable source of seed particles. Figure 4 shows typical size distributions of the seed aerosol after dilution at the exit of the second stage, after passing through the static mixers, i.e., at the entrance to the primary reactor stage, and at the end of the primary reactor without silane added for growth. The shift in the size distribution as the aerosol passes through the static mixers is due primarily to seed particle losses within the mixers (about 10 percent of the aerosol mass). The seed aerosol passes through the growth stage with little change in the size distribution due either to diffusional losses on the reactor wall or to coagulation. Thus, changes that occur when silane is added to the seed aerosol can be attributed to the results of silane decomposition.

To map the operating domain in which the seed particles could be successfully grown to large size, a series of experiments were performed with the temperature profile along the growth reactor wall fixed as illustrated in Figure 5. With this temperature profile, nucleation could be fully suppressed when 0.6 liters/min. of 1 percent silane in nitrogen was introduced into the reactor with 1 micron seed particles in a concentration of 2×10^5 particles/cc. The size and number concentration of seed particles was then varied to determine the sensitivity of nucleation control to the seed aerosol characteristics at otherwise constant reactor operating conditions.

The resultant operating map for this flow rate, temperature profile, and silane concentration is shown in Fig. 6. Two outcomes were possible in these experiments: (i) complete suppression of nucleation in which case the seed particles grew as indicated by the connected solid points; and (ii) runaway nucleation leading to a large increase in the number concentration and a corresponding decrease in the mean particle size. The latter experiments are indicated by open points. These results clearly demonstrate the sharp transition from one operating mode to the other. Also shown are theoretical predictions of the separation between the two operating modes. The solid line corresponds to the increase in the number concentration by a factor of two. The dashed line corresponds to the locus of conditions that lead to one half of the aerosol mass appearing as fine new particles.

A more direct illustration of the onset of nucleation is a series of experiments conducted with a fixed temperature profile and seed aerosol, but variable silane concentration. Figure 7 shows, the result of such an experiment with a seed concentration of 10^5 /cc, and a mean seed particle size of 0.7 micron. As the silane concentration was increased to 3 percent, the number concentration increased by less than a factor of two. Further increasing the silane concentration to 3.5 percent resulted in an increase in the number concentration of four orders of magnitude.

The results of a similar series of experiments are plotted on a mass distribution basis (as determined form optical sizing data) in Fig. 8. The mass median size increases rapidly to a silane concentration of 3.2 percent. Increasing the silane concentration beyond 4.9 percent does not appreciably enhance the size of the particles since the additional silicon increases the size of the large number of silicon nuclei only slightly and does not contribute to the growth of the seed particles.

PARTICLE CHARACTERISTICS

A scanning electron microscope photographs of the particles grown with a low final temperature in the growth reactor is shown in Fig. 9. The particle appears to be an agglomerate of approximately 0.1 micron spheres. The BET surface area of the collected powder was found to be 20.3 m^2/gm, indicating that this structure is uniform throughout the particle volume. The diffusivities of particles of that size are, however, so low that the observed growth of the seed particles and the small increase in the number concentration cannot be attributed to coagulation of these particles with the seeds. Instead, the structure of the particles must reflect the results of partial sintering of a low density particle which initially had a much finer structure.

This sintering can be accelerated by increasing the temperature in the final zone of the primary reactor. The reactor was designed so that this could be done without significantly altering the temperature profile in the upstream regions where the silane decomposition and particle growth take place. Figure 10 shows the effect of processing the grown particles to temperatures of 1523 K and 1673 K. The particles have densified appreciably during this heat treatment due to sintering.

Samples of the powders were also examined for crystallinity using X-ray diffraction. The spectra for samples treated in the reactor to three different temperatures are shown in Fig. 11. The material that was heated to no more than 973 K is clearly amorphous, but as the final processing temperature is increased the material clearly becomes crystalline.

One important concern with such powders is the possible contamination of the large surface area with oxide or, due to the nitrogen diluent used in the experiments, nitride layers. Infrared absorption spectroscopy was used to look for such contamination. Powder samples were collected under nitrogen and pressed into KBr pellets in a glove box under a nitrogen atmosphere. No silicon oxide or silicon nitride absorption was observed in the infrared spectra.

CONCLUSIONS

An aerosol reactor system has been developed in which large particles of silicon can be grown by silane pyrolysis. To grow particles to sizes larger than one micron, vapor deposition must be used to grow a relatively small number of seed particles. To maintain that small seed concentration requires that homogeneous nucleation be suppressed. This is achieved by limiting the rate of gas phase chemical reactions such that the condensible products of gas phase chemical reactions diffuse to the surfaces of the seed particles as rapidly as they are produced. This prevents high degrees of supersaturation and runaway nucleation during the growth process.

The dividing line between runaway nucleation an successful growth of the seed particles is very sharp. In one experiment, a 17 percent increase in the silane concentration resulted in an increase in the number concentration at the reactor outlet of 4 orders of magnitude. Thus, if the reactor is operated near the maximum feasible growth rate, small excursions in operating conditions can have catastrophic results.

If the peak temperature in the reactor is kept low, the particles have a fine structure, appearing to be agglomerates of very small particles. Calculations of particle growth kinetics clearly indicate that this structure is not the result of coagulation of particles the size of the fine structure. Instead, the structure results from partial sintering of particles that initially had a much finer structure. Heating the particles to higher temperatures for times on the order of one second are sufficient to fuse the particles, eliminating the structure observed in the low temperature aerosol. In practical applications of this technology, that would be useful since the densified particles would be easier to separate from the gas and to process.

Particles on the order of 10 microns have been grown repeatedly with the present aerosol reactor. Particles approaching 100 microns in size have been grown on numerous occasions, although deposition on the reactor walls became a problem under those conditions. The nucleation controlled aerosol reactor is, therefore, a suitable system for the production of powders that can readily be separated from the gas by aerodynamic means.

The process is not limited to silane decomposition. As long as the reaction kinetics are well enough understood that the rate can be limited to control nucleation, other reaction systems can be applied in the nucleation controlled aerosol reactor. For silicon processing, halo-silanes might have important advantages since the etching reaction, e.g., the reaction of HCl with solid Si, reduce the potential for supersaturation and nucleation. Powders of controlled size particles of other materials should also be attainable in aerosol reactors by applying mechanisms that are commonly used for chemical vapor deposition.

ACKNOWLEDGEMENTS

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FIGURE CAPTIONS

Figure 1. Schematic of the two-stage aerosol reactor of Alam and Flagan.(8)

Figure 2. Particle size distribution of the silicon aerosol produced in the two stage reactor experiments of Alam and Flagan.(8)

Figure 3. Schematic of the present three-stage aerosol reactor.

Figure 4. Size distribution of the seed particles used in the three stage reactor experiments.

Figure 5. Measured wall temperature profile on the growth stage of the three stage reactor.

Figure 6. Map of operating conditions that led to successful growth of seed particles (initial and final sizes and concentrations are indicated by connected solid points) and those experiments that resulted in runaway nucleation (open points).

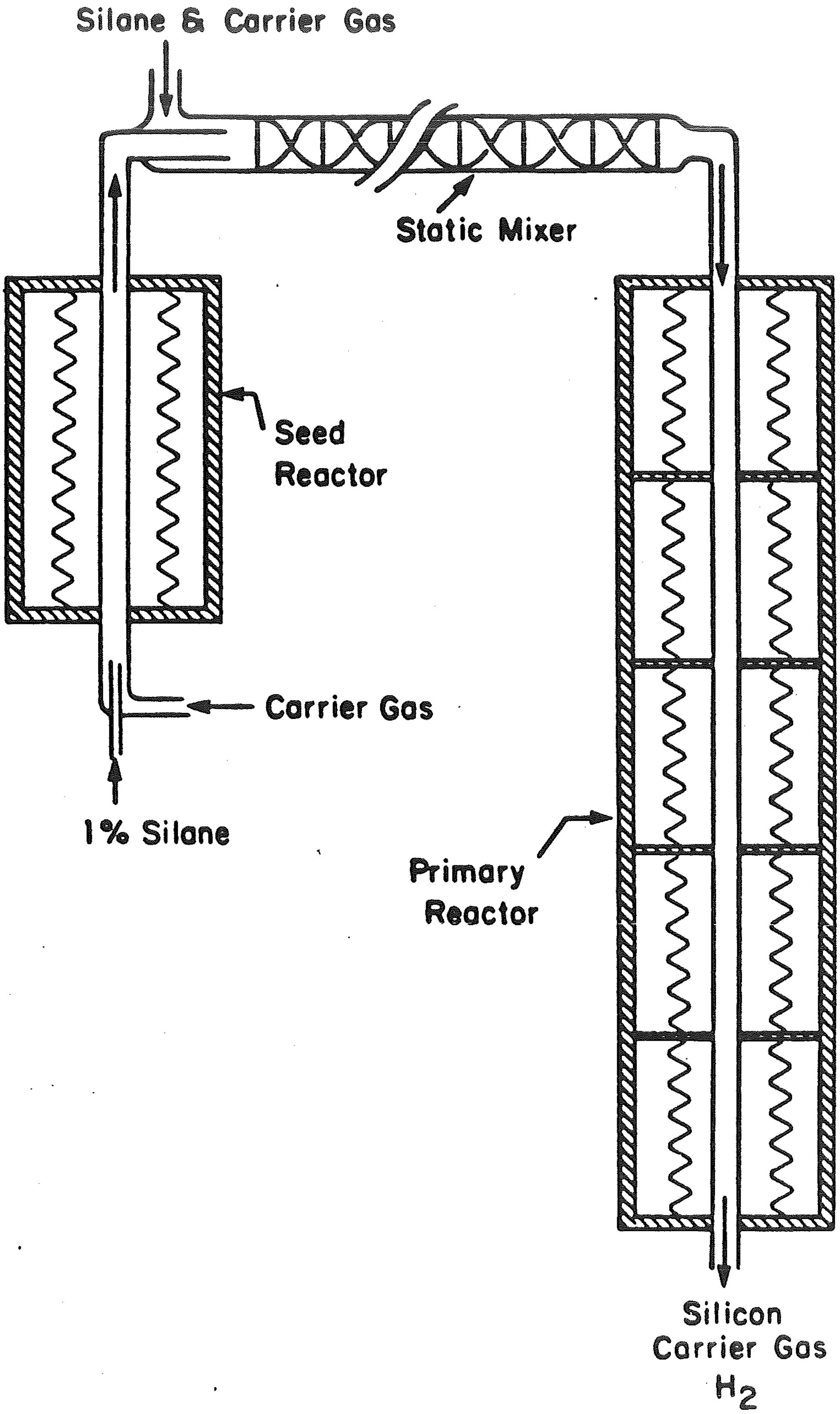
Figure 7. Variation of final number concentration with percent silane in the feed gas for fixed temperature profile, flows, and seed aerosol.

Figure 8. Mass distributions measured with three stage reactor for various silane concentrations.

Figure 9. SEM photograph of the product particles generated with a maximum reactor temperature of 973K.

Figure 10. SEM photographs of product particles following post-growth processing at elevated temperatures for approximately one second. (a) 1523 K; (b) 1673 K.

Figure 11. X-ray diffaction patterns for the silicon powders processed at various peak temperatures.



Silane & Carrier Gas
Static Mixer
Seed Reactor
Carrier Gas
1% Silane
Primary Reactor
Silicon
Carrier Gas
H_2

FIG. 1

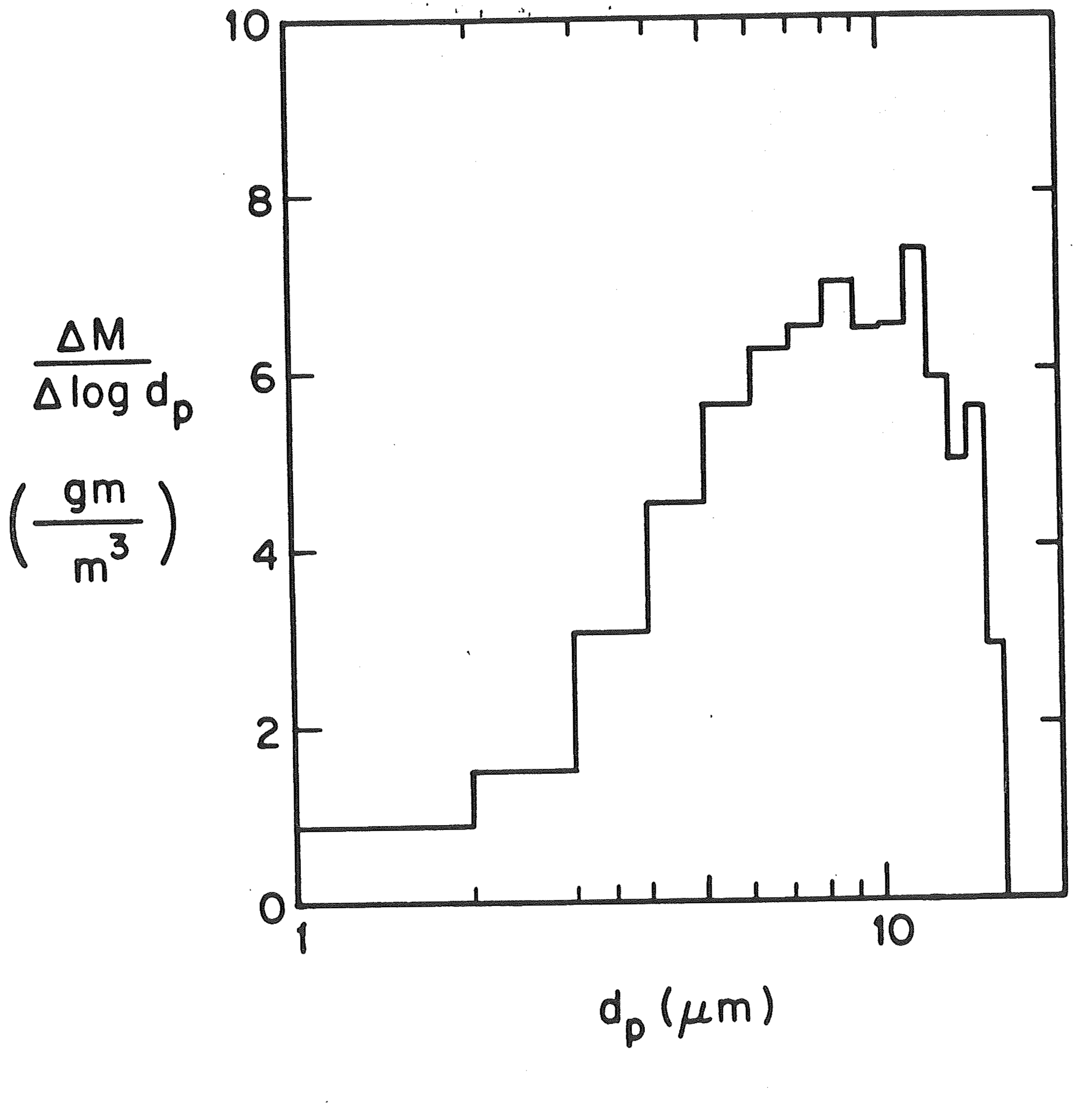


FIG. 2

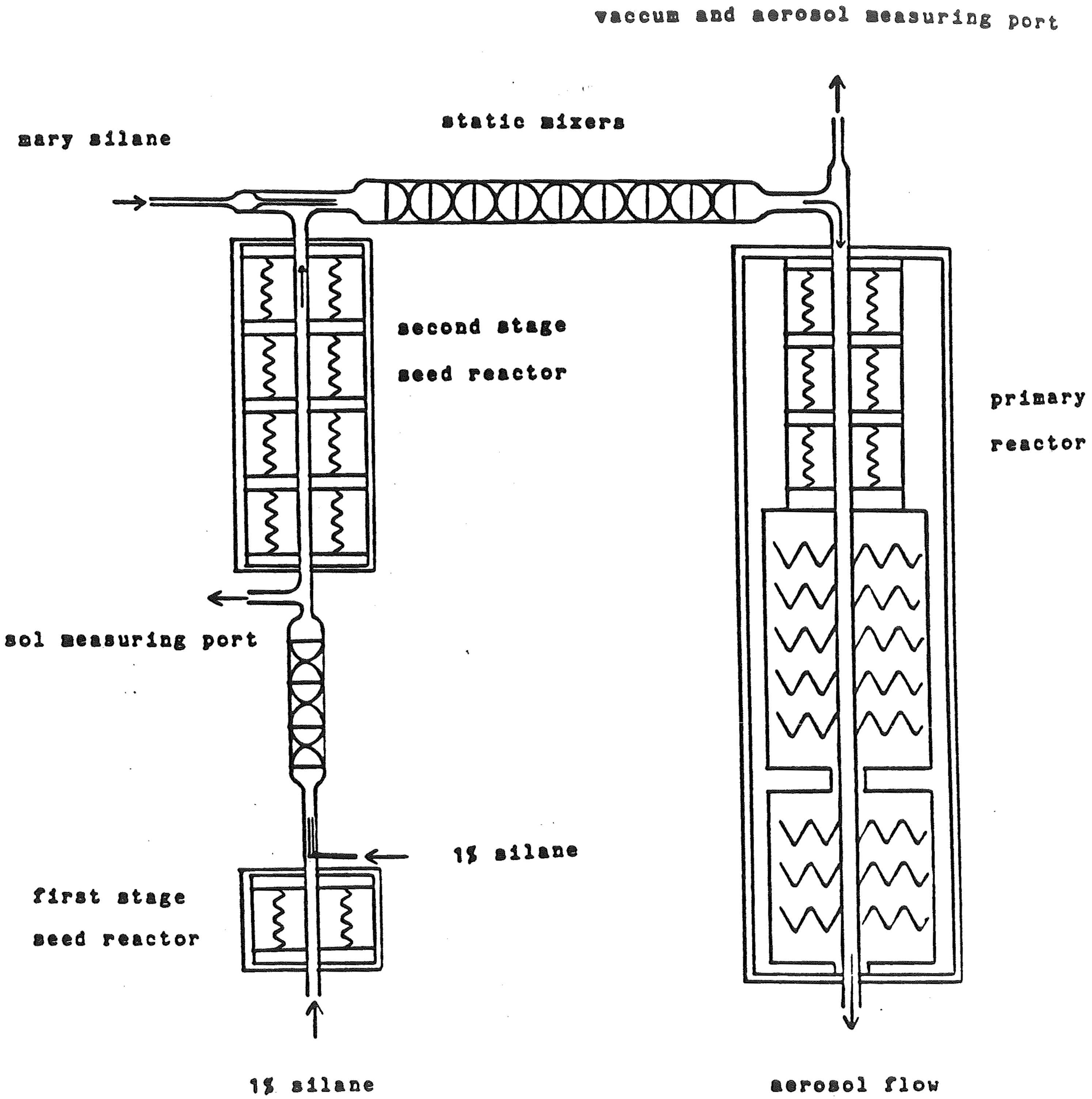


Figure 3. Schematic of the present three-stage aerosol reactor.

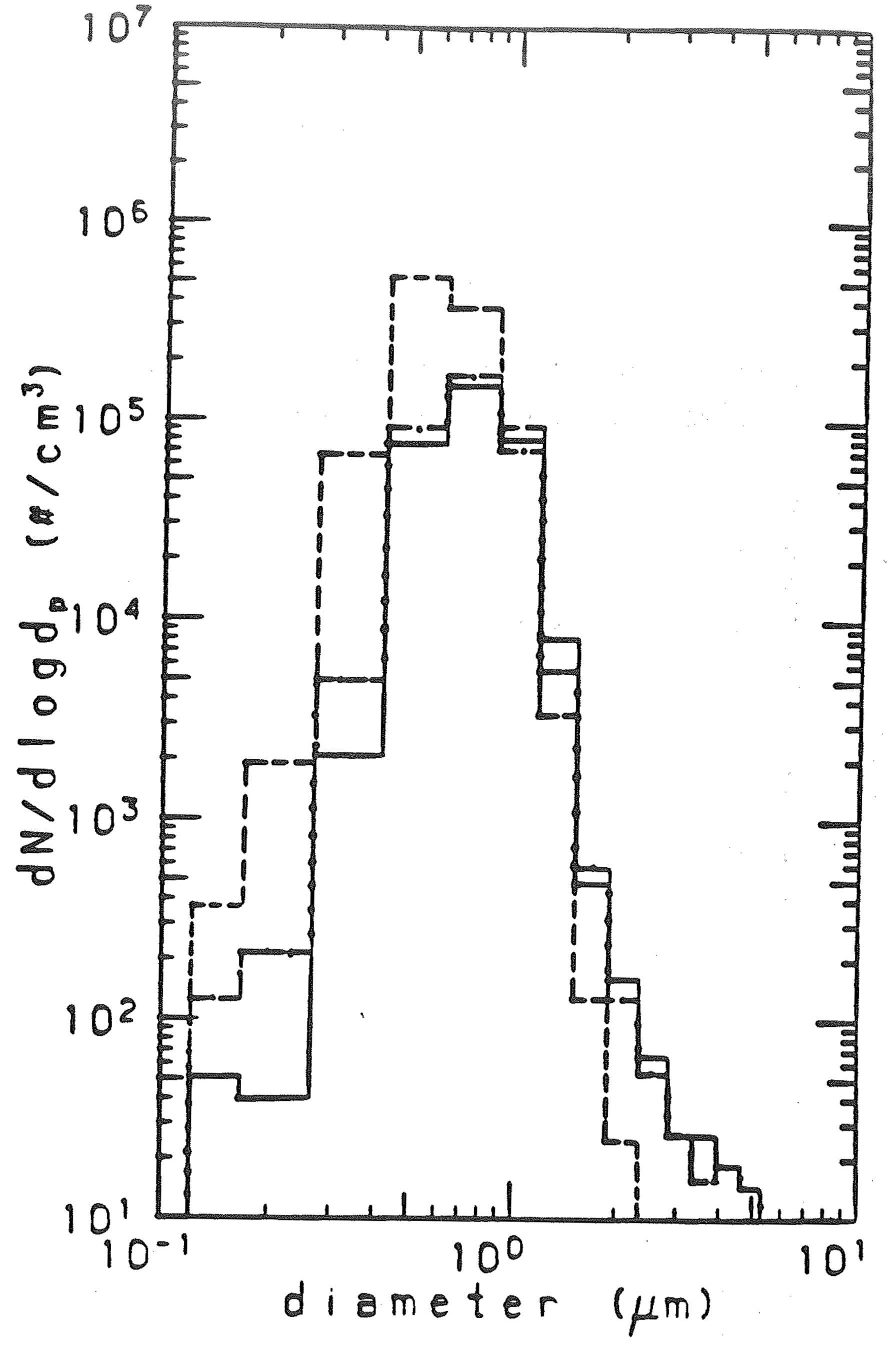


figure 4. aerosol samples monitored by ROYCO OPC

----- aerosol from the exit of the seed growth reactor

-·-·- aerosol from the entrance of the primary reactor

——— aerosol from the end of the primary reactor

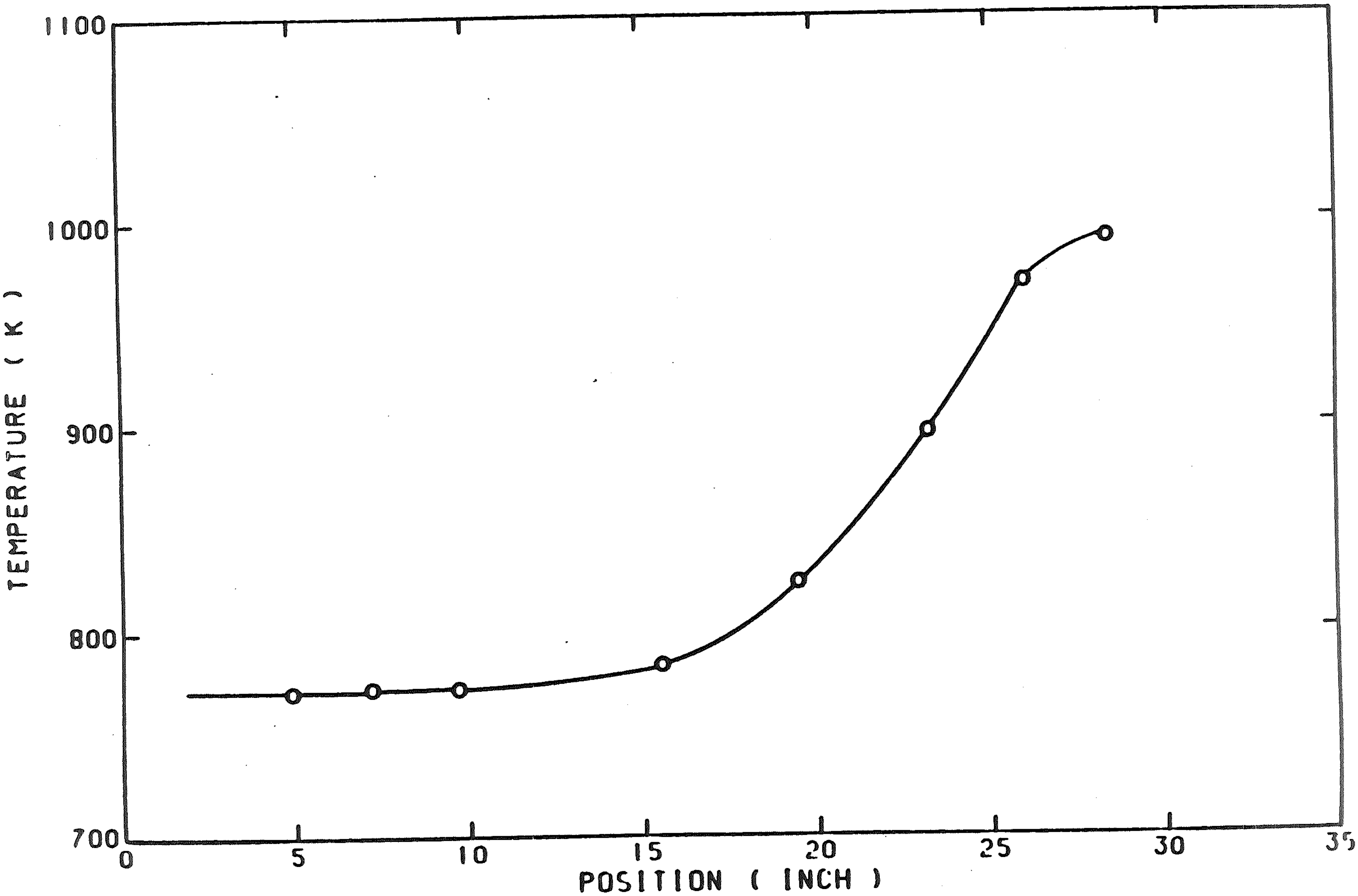


Figure 5. Measured wall temperature profile on the growth stage of the three-stage reactor.

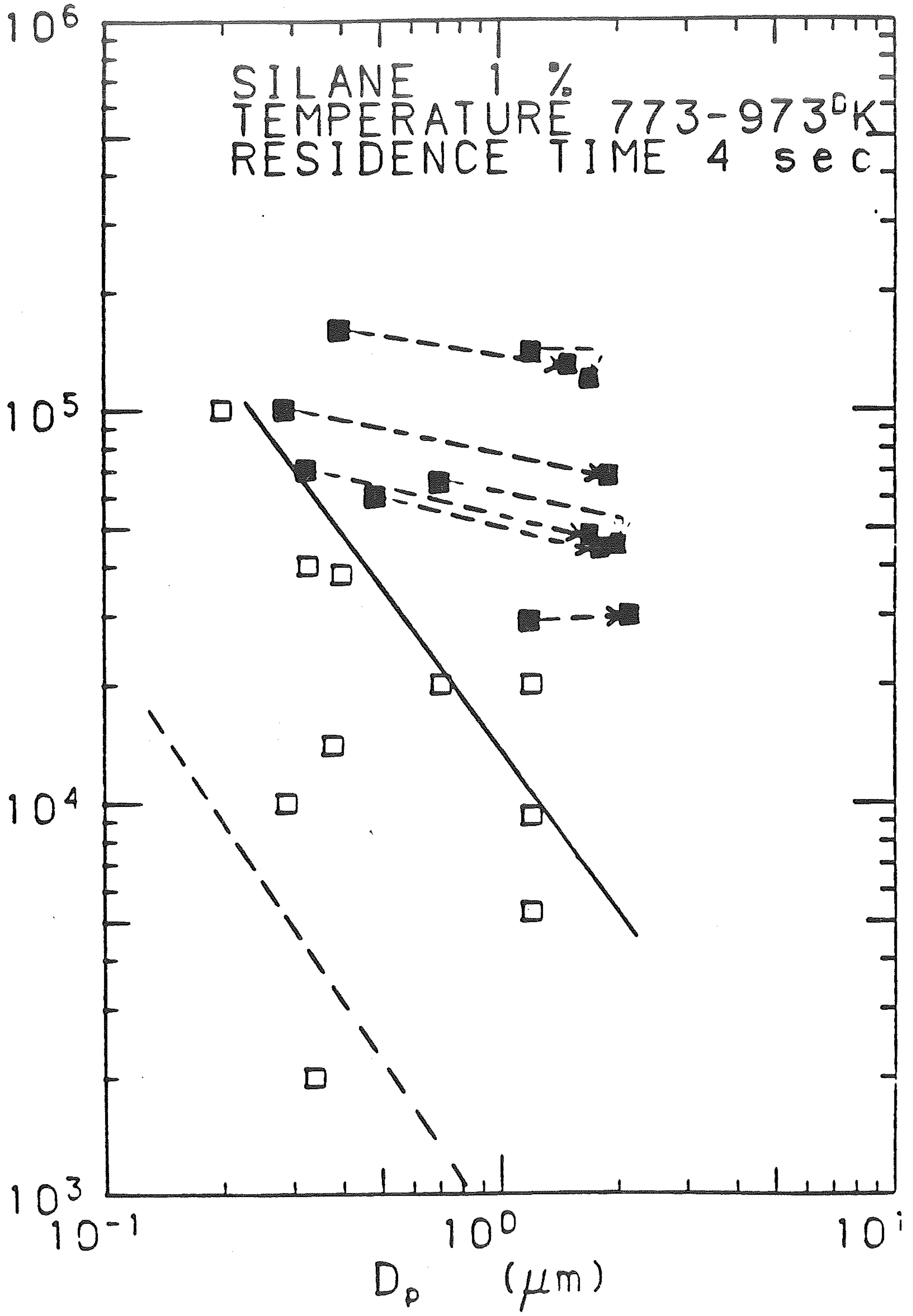


Figure 6. Map of operating conditions that led to successful growth of seed particles (initial and final sizes and concentrations are indicated by connected solid points) and those experiments that resulted in runaway nucleation (open points).

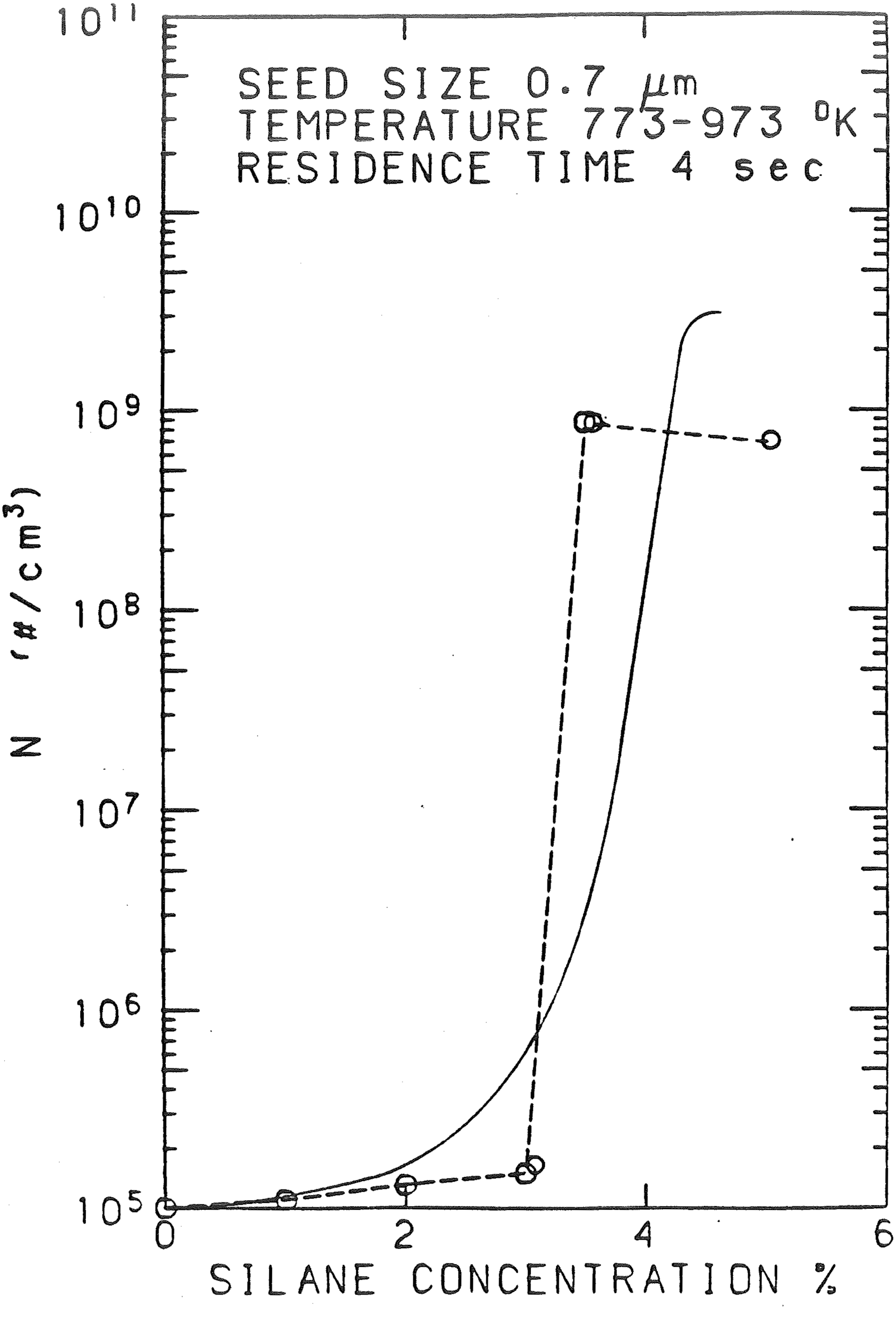


Figure 7. Variation of final number concentration with percent silane in the feed gas for fixed temperature profile, flows, and seed aerosol.

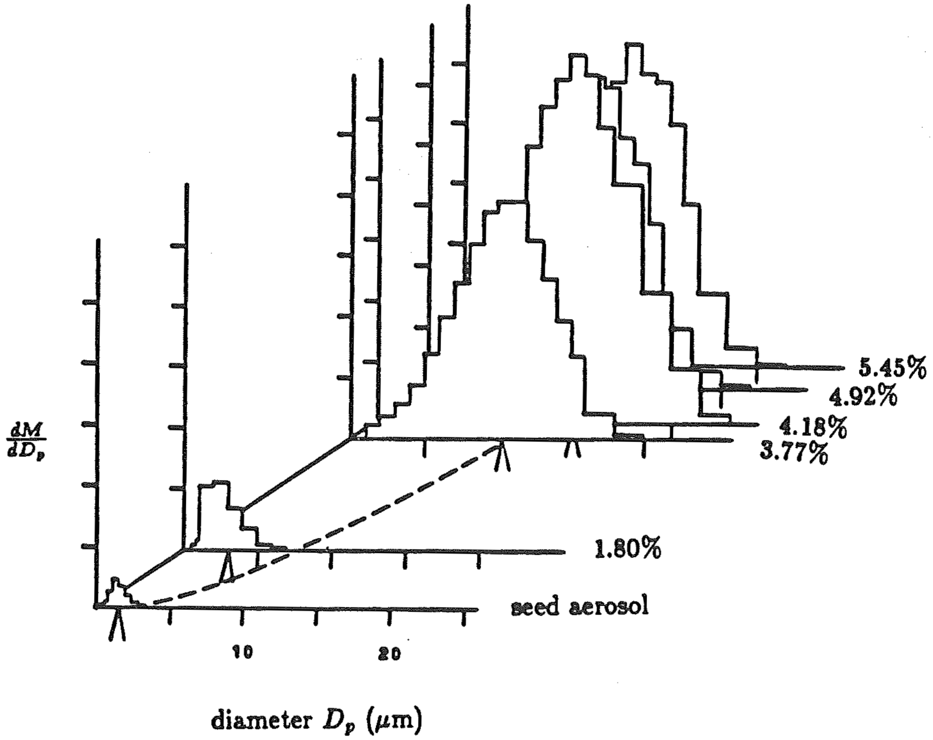


figure 8. seed aerosol growth by increasing primary silane concentration (seed particles were monitored by ROYCO OPC and CNC, particle growth was measured by CSPC)

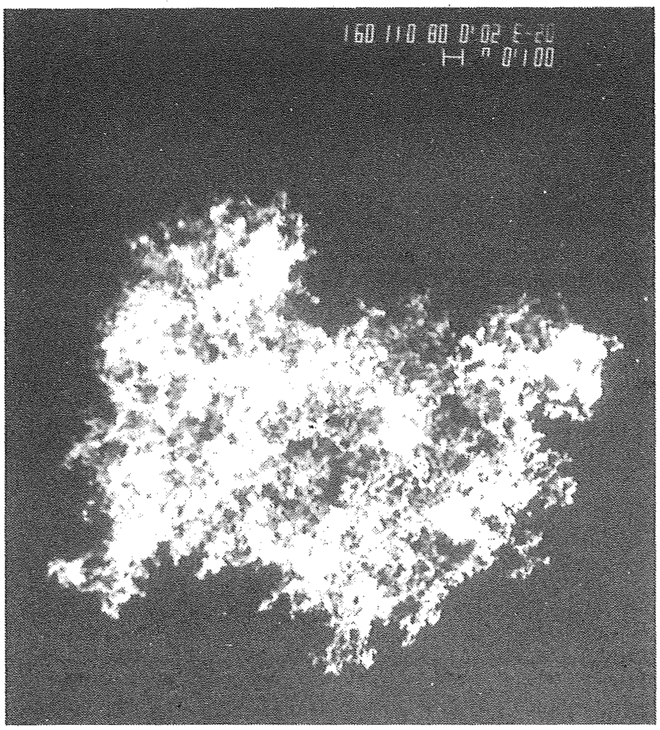


Figure 9. SEM photograph of the product particles generated with a maximum reactor temperature of 973 K.

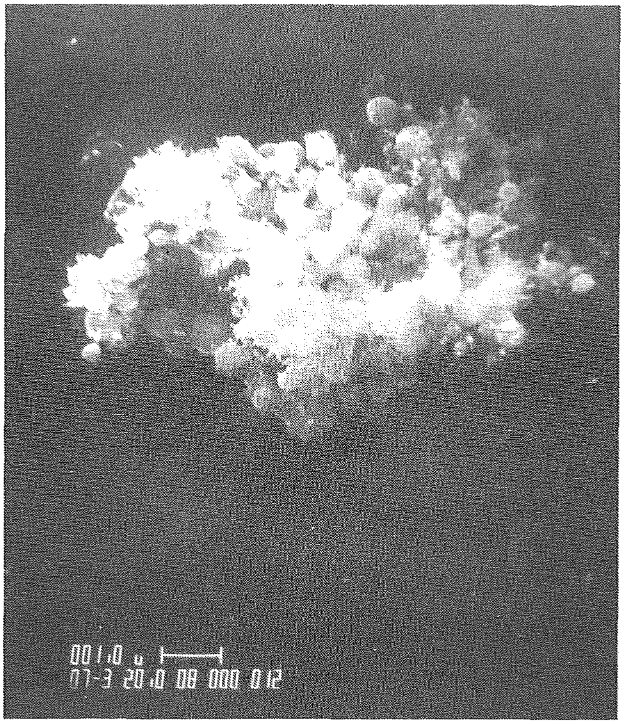


Figure 10a. SEM photograph of product particle following post-growth processing at elevated temperature (1523K) for approximately one second.

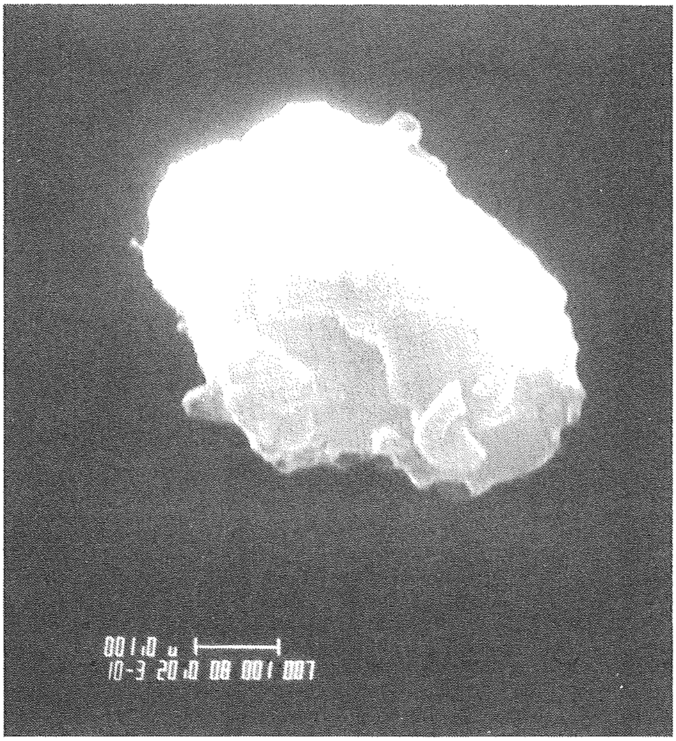


Figure 10b. SEM photograph of product particle following post-growth processing at elevated temperature (1673K) for approximately one second.

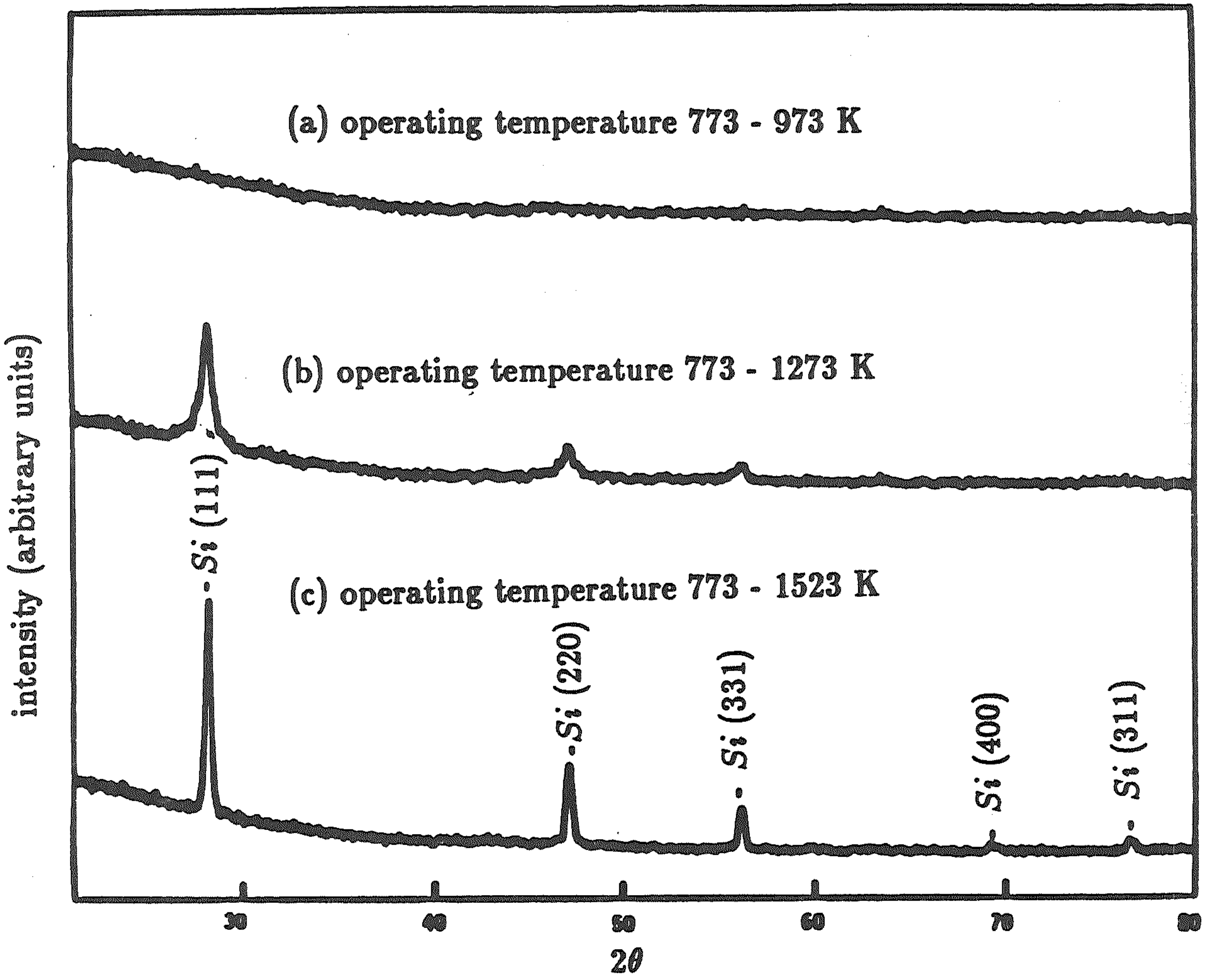


figure 11. structure of silicon particles with different operating temperature ranges

Copper Kα X - ray diffraction patterns

omit

DISCUSSION

LORD: What is the diameter reduction you get when the particles are densified?

FLAGAN: It has been a factor of about 3 to 4.

LORD: Does that mean that the size is reduced from 10 µm to about 2 µm?

FLAGAN: We have also produced dense 10 µm particles.

LORD: Is 10 µm size the largest dense particles you have produced?

FLAGAN: We have produced dense particles of 100 µm, although not for extended periods of time. The reactor plugs very quickly at that point due to the very slow flow in our small-scale reactor.

LORD: Just to follow up on the plugging, did you find out that the particles go to the wall?

FLAGAN: They go to the wall at the exit of the hot zone, but not in the hot zone itself.

AULICH: What is your hydrogen content of your submicron-fine particles?

FLAGAN: I do not have that number. Our focus has been on the characterizaton of the particle formation process itself, and we simply don't have those data.