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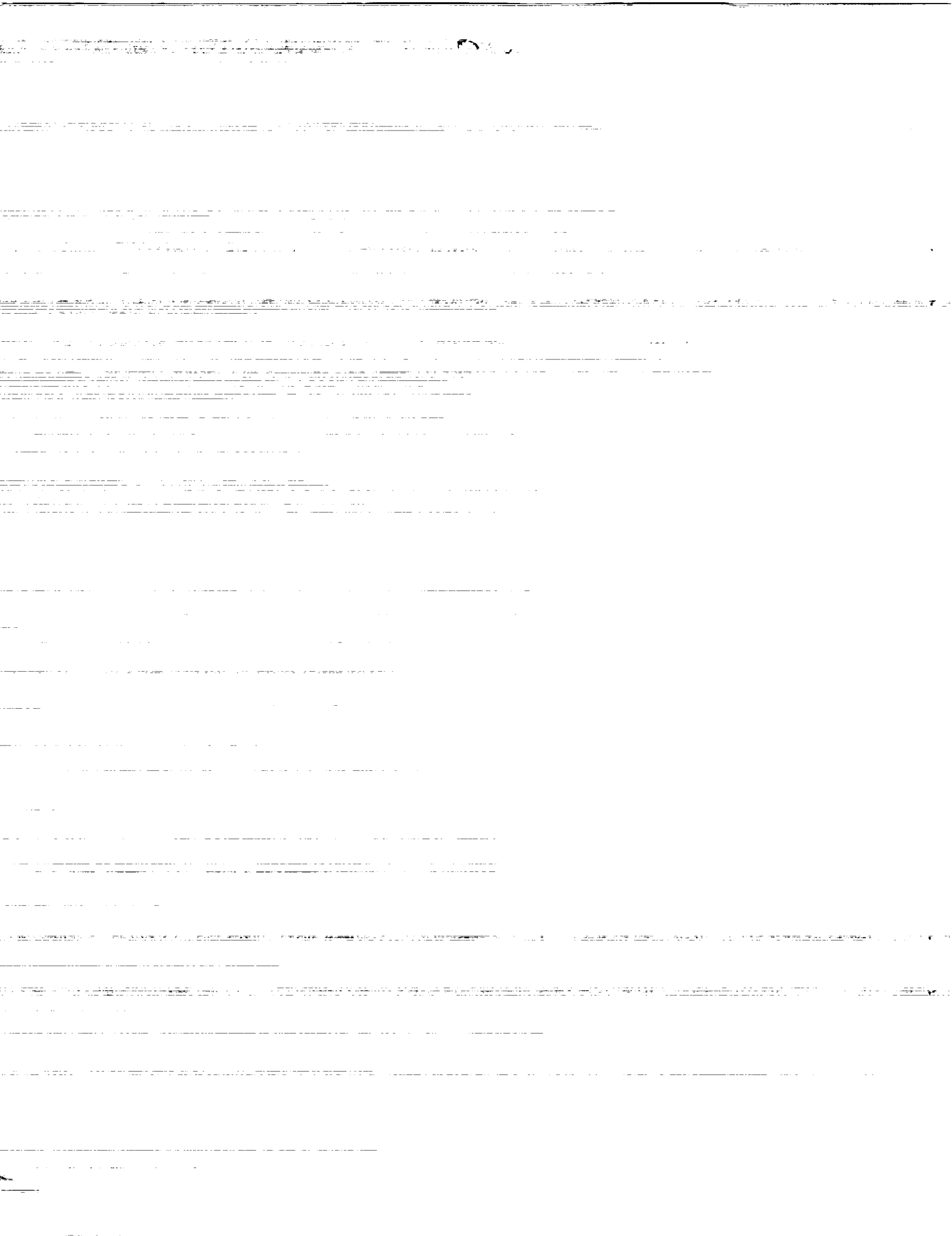

A NUMERICAL AND EXPERIMENTAL ANALYSIS OF REACTOR PERFORMANCE AND DEPOSITION RATES FOR CVD ON MONOFILAMENTS

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SUMMARY

The CFD code FLUENT is adopted to simulate a cylindrical upflow reactor designed for CVD on monofilaments. Equilibrium temperature profiles along the fiber and quartz reactor wall are experimentally measured and used as boundary conditions in numerical simulations. Two-dimensional axisymmetric flow and temperature fields are calculated for hydrogen and argon; the effect of free convection is assessed. The gas and surface chemistry is included for predicting silicon deposition from silane. The model predictions are compared with experimentally measured silicon CVD rates. Inferences are made for optimum conditions to obtain uniformity.

INTRODUCTION

Structural fibers are currently being considered for the reinforcement of both ceramic and (inter)metallic matrices. There are, however, only a few commercially available fibers that could be used for this purpose. Many physical and chemical properties of existing and to-be-developed fibers need to be optimized for composites (ref. 1). It is expected that fibers themselves will have composite structures with specifically engineered coatings. Although CVD provides excellent opportunities as a versatile technique to fabricate new and novel materials, its success, especially for scaleup, depends on a sufficient understanding of the complex physicochemical processes. Hence, a CVD facility was built in our laboratory to study the process on monofilaments.

The experimental effort is complimented by modeling, whereby a computational fluid dynamics code FLUENT (ref. 2) is adopted to simulate the CVD reactor. This study improves our earlier model (ref. 3), by relaxing many of the restrictions.

The paper will focus on modeling and experimental results obtained for silicon deposition from silane in hydrogen or argon carrier gas at a fiber temperature of 1150 °C.

EXPERIMENT

The experimental reactor is a vertically oriented cylindrical quartz tube. Figure 1 shows the schematic with dimensions employed in this study. At the reactor inlet gases pass through porous carbon felt which damps the

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rather complicated entrance effects. The inlet and exit blocks are made of brass and are water-cooled. The reactor tube wall is not actively cooled. Textron SCS-6 silicon carbide fibers (~140 μm diam) are used as deposition substrates. The fiber is fed into the reactor through the mercury pools at the top and bottom. Mercury, which is held by surface tension, provides sealing and electrical contacts for the resistively heated fibers. The system can accommodate variable fiber lengths but is currently limited to electrically conducting single fibers for atmospheric pressure operation. This design is suited for possible continuous operation in the future. Recently, a similar design for batch operations, using a silicon rod substrate (4 mm diam), has demonstrated the feasibility of also doing gas and surface chemical kinetics studies (ref. 4).

The wall temperatures of the reactor is measured by chromel-alumel thermocouples which are surface-mounted at 1,2,3,4,5,10,15, and 20 cm from the tube inlet level, which is defined as the location where the fiber emerges out of the bottom mercury pool. The thermocouple junction thickness of 12.7 μm yields fast response due to its small thermal inertia. The temperature readings are automatically recorded by a data acquisition system. The fiber temperature is measured by a dual-wavelength optical pyrometer and has a lower limit of about 900 °C for this particular setup.

MODEL

FLUENT 3.02 is adopted for this study. This version of FLUENT incorporates many new phenomena relevant to CVD processes (ref. 2). Therefore, it has enabled us to improve our previous fiber CVD modeling work (ref. 3), by allowing (1) temperature dependent gas density, (2) gas phase reactions, (3) surface reactions, and (4) Soret diffusion. Furthermore, the uncertainties involved in the correct specification of temperature boundary conditions in the earlier model is now circumvented by employing the experimentally measured fiber and wall temperature profiles.

A two-dimensional geometry is used to approximate the reactor. The use of carbon felt at the tube inlet is assumed to dampen the three-dimensional disturbances and nonuniformities of the flow prior to that location. The results will be reported up to 20 cm from the inlet, so that they will be assumed to be independent of the actual exit conditions.

Silicon deposition is predicted by using dilute silane source gas in hydrogen carrier gas. The reversible gas phase reactions considered for this chemical system are:

$$SiH_4 = SiH_2 + H_2 \qquad (R1)$$

$$Si_2H_6 = SiH_2 + SiH_4 \qquad (R2)$$

For surface reactions all three silicon-carrier species are accounted for on the fiber surface. Hydrogen flux on the fiber surface and all species fluxes on the wall are zero. Because silane is dilute in hydrogen, thermophysical and transport properties are justifiably calculated by treating the mixture essentially as hydrogen, naturally increasing computational efficiency.

The computational mesh has evenly distributed 115 cells in the axial direction and unevenly distributed 19 cells in the radial direction. Predicted rates depend on the correct resolution of the SiH_2 concentration profile near the fiber, which has required the first grid to be ~10 μm (still >> mean free path). The calculations require at least 8000 iterations for satisfactory convergence.

RESULTS AND DISCUSSION

For the results reported in this paper, the total flow rate will be fixed at 1 slm, the fiber temperature at 15 cm from the inlet at 1150 °C and inlet silane mole fraction of 0.3 percent in hydrogen.

Figure 2 shows the measured fiber and wall temperature axial profiles for both hydrogen and argon. Because of conduction losses into the cooled end-blocks and cool gases entering the reactor both the fiber and wall temperatures fall at the inlet region. Because hydrogen is a better thermal conductor than argon, the temperatures reach a plateau value much faster with hydrogen. The resulting wall temperatures for hydrogen is much higher for the same reason.

Figures 3 and 4 show the velocity profiles for hydrogen and argon, respectively. Hydrogen develops rapidly to a steady profile because of its thermophysical properties. However, for argon free convection causes flow reversal and creates a recirculating cell along the wall. This reduces the effective area available for upflow and creates a more or less stagnant layer near the wall. The fact that argon is a heavier gas and results in larger radial temperature gradients makes the system more prone to such complicating free convection effects even for a vertical upflow setup.

Figures 5 and 6 show the radial temperature profiles for the right-half of the reactor for hydrogen and argon, respectively. The temperature field for hydrogen develops much faster, as expected, within a few centimeters; whereas the argon case takes more than a third of the reactor length to develop fully. Note also that argon at 1 cm is even colder than the wall due to radiation from the fiber heating the wall, but not the gas.

Figure 7 depicts the axial depletion of SiH_4 with and without the effects of Soret diffusion. Note how Soret diffusion pushes SiH_4 away from the hotter fiber region with serious consequences in the resulting SiH_2 concentration and, hence, deposition rates.

Figure 8 is a magnified plot of the SiH_2 concentration near the fiber, showing the axial depletion effects. Note that the region near the fiber needs to be very carefully resolved to capture the correct behavior of SiH_2.

Figure 9 and 10 are the predicted and experimental Si deposition rates, respectively. The curves labeled "slow chemistry" and "fast chemistry" in figure 9 refer to rate constants taken from reference 5 or 6 for the gas phase reactions (R1) and (R2), respectively. (Even larger rate constant values are recently reported in reference 7 for the temperature range of interest of us.) The error bars in figure 10 indicate the standard deviation in deposit thickness measurements. Controlling the fiber temperature during the experiment is very difficult due to (1) the continuous change in the overall electrical

resistivity of the fiber, and (2) local variations in deposit thickness resulting in different local current densities and, hence, temperature variations. Furthermore, there is an uncertainty associated with the absolute fiber temperature measurement due to the small fiber diameter and time-dependent fiber surface emissivity. We currently believe that the temperature measurements may be as much as 100 K lower than the actual values. To depict the significant change in predicted rates, the "fast chemistry" is run at 1250 °C, rather than at 1150 °C, giving results similar in trends as the measured rates. Note that larger rates at the inlet zone lead to a source gas (SiH_4) depletion reflected as an axial reduction of rates. The unusually large Soret effects on deposition rates is attributed to the very high temperature gradients near the fiber, which is nontypical of other CVD systems. The resulting concentration profile of SiH_2, which govern the deposition rates in our case, is a consequence of the mentioned temperature profile, although a very fine computational resolution was necessary to make this determination. The Soret effect is expectedly larger at higher fiber temperatures and smaller fiber diameters.

CONCLUSIONS

The conclusions of this work for our particular, but typical, fiber reactor setup for silicon deposition are: (1) Soret diffusion is found to have a very significant (>100 percent) effect on deposition rates, (2) the predicted deposition rates are governed by SiH_2 flux to the fiber surface, (3) a careful numerical resolution of the immediate vicinity of the fiber is essential based on our first two conclusions, (4) depending upon the physical (and chemical) properties of the carrier gas (H_2 versus Ar), the prevailing flow and temperature (and concentration) fields are substantially different, and (5) existing uncertainties in chemical kinetic and transport parameters combined with the difficulties associated with accurate fiber temperature measurement and control render the absolute comparison of predictions with experimental deposition rates unfeasible.

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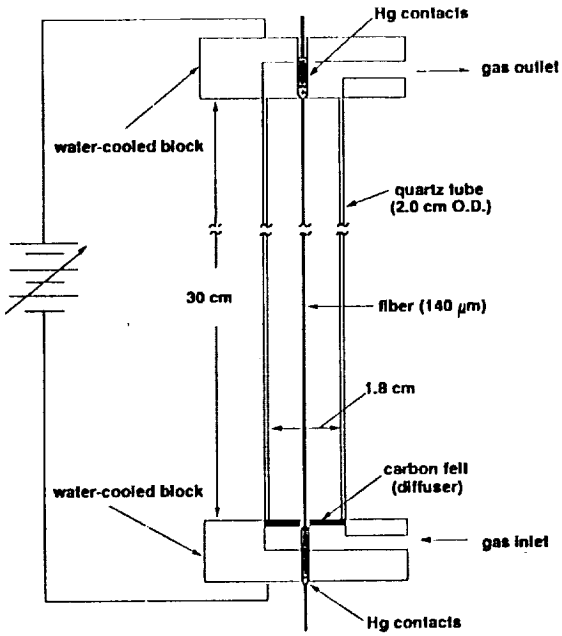

FIGURE 1. - SCHEMATIC OF THE EXPERIMENTAL REACTOR.

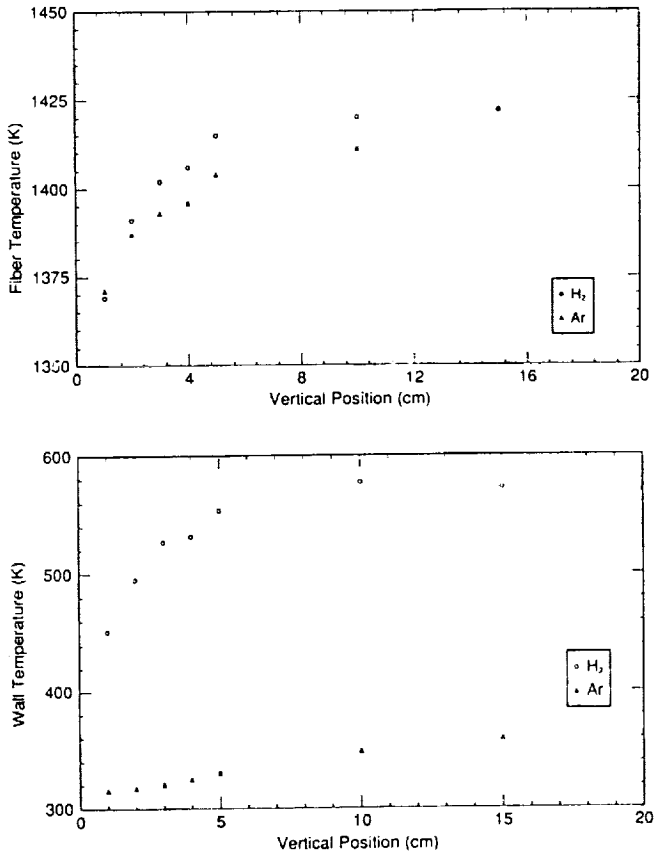

FIGURE 2. - EXPERIMENTAL FIBER AND WALL TEMPERATURES FOR HYDROGEN AND ARGON.

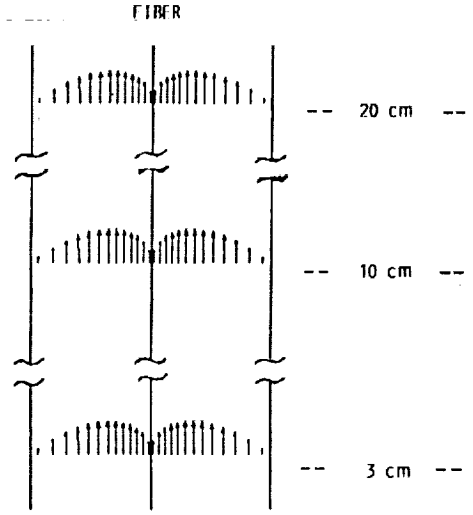

FIGURE 3. - VELOCITY PROFILES FOR HYDROGEN AT THE INDICATED HEIGHTS.

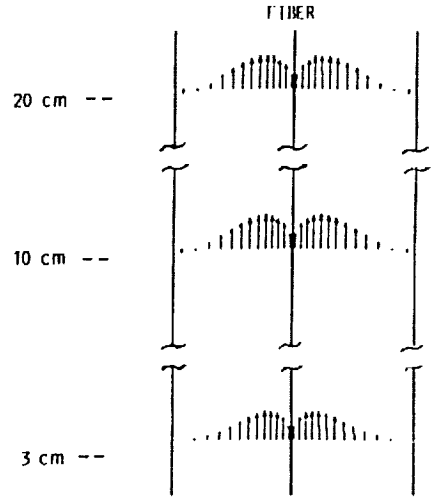

FIGURE 4. - VELOCITY PROFILES FOR ARGON AT THE INDICATED HEIGHTS.

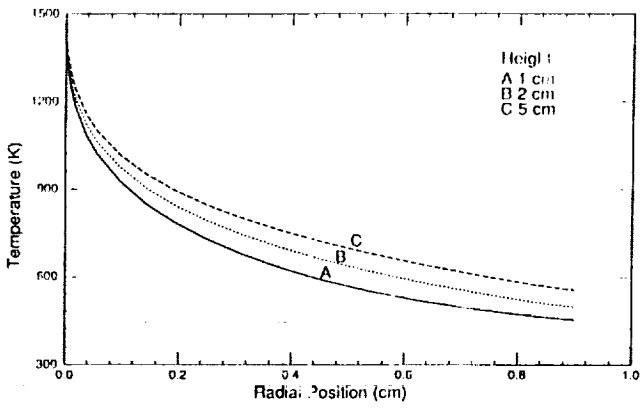

FIGURE 5. - RADIAL TEMPERATURE PROFILES FOR HYDROGEN AT THE INDICATED HEIGHTS.

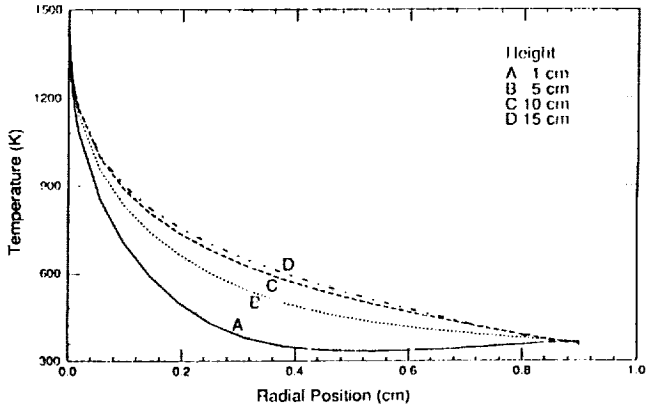

FIGURE 6. - RADIAL TEMPERATURE PROFILES FOR ARGON AT THE INDICATED HEIGHTS.

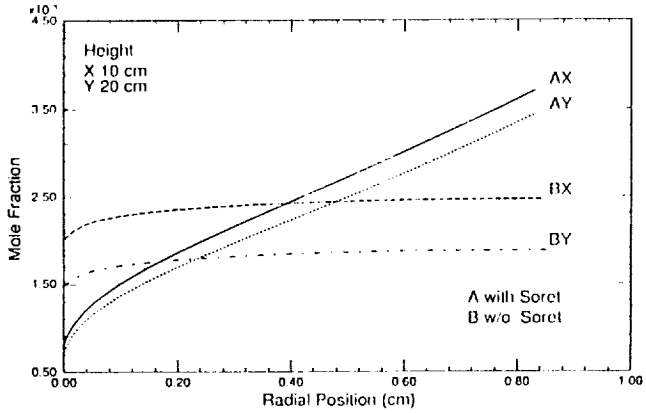

FIGURE 7. - RADIAL SiH_4 MOLE FRACTION PROFILES, WITH AND WITHOUT SORET, AT THE INDICATED HEIGHTS.

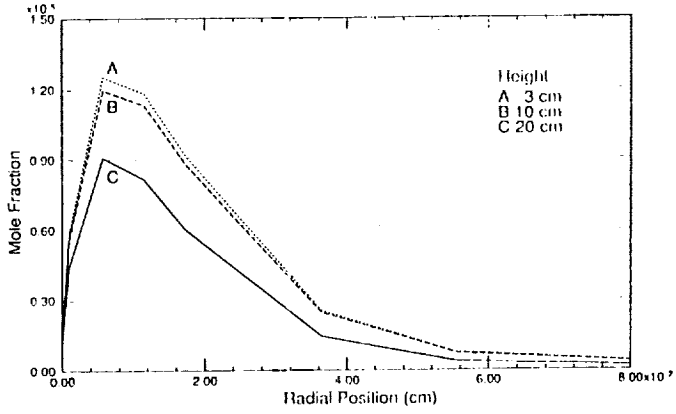

FIGURE 8. - RADIAL SiH_2 MOLE FRACTION PROFILES WITH SORET, AT THE INDICATED HEIGHTS. (RADIAL MAGNIFICATION).

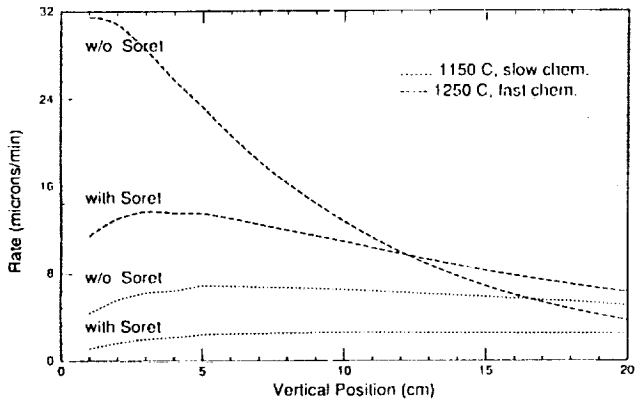

FIGURE 9. - PREDICTED SILICON DEPOSITION RATES SHOWING CHEMICAL AND SORET EFFECTS.

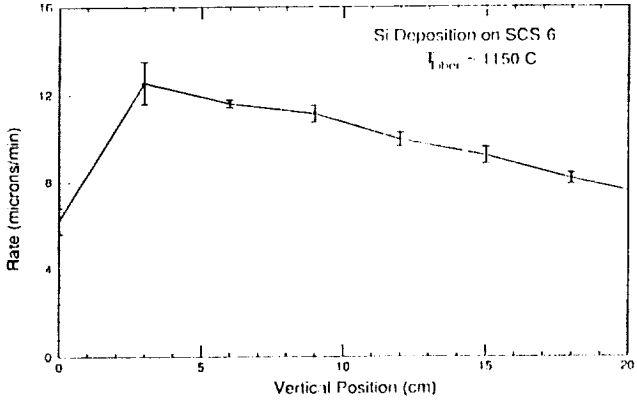

FIGURE 10. - EXPERIMENTAL SILICON DEPOSITION RATE FOR A ONE MINUTE RUN TIME.

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16. Abstract

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