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Gas phase and surface kinetic processes in polycrystalline silicon hot-wire chemical vapor deposition

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Abstract

Experiments and numerical simulations have been conducted to determine critical parameters for growth of polycrystalline silicon via hot-wire chemical vapor deposition. Reactor-scale simulations performed using the Direct Simulation Monte Carlo (DSMC) method have revealed a number of important phenomena such as a sharp drop of 1700 K in the gas temperature from the wire to substrate. The gas-phase reaction of silicon atoms produced on the wire with ambient silane molecules has been studied using ab initio quantum chemical calculations. Results reveal that collisional stabilization of the adduct (H_3SiSiH) is unlikely under typical growth pressures, but an energetically favorable, low-pressure pathway has been found that leads to the formation of Si_2H_2 and H_2. Threshold ionization mass spectrometry measurements of radicals have revealed that at the pressure characteristic of growth (2-200 mTorr of 1% SiH_4 in He), the radical SiH_2 is predominant. Finally, film growth studies reveal that hot-wire-produced atomic hydrogen may preferentially etch amorphous silicon and suppress the formation of small nuclei. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hot-wire chemical vapor deposition; Direct simulation Monte Carlo; Threshold ionization mass spectrometry; Nucleation kinetics

1. Introduction

Synthesis of large-grained polycrystalline silicon at low temperatures with high throughput is critical to enabling a future polycrystalline thin-film silicon photovoltaics technology. A promising approach for low temperature, high throughput film growth is hot-wire chemical vapor deposition (HWCVD). To this end, experiments and numerical simulations are being used to explore the fundamental gas-phase and surface interactions of importance in HWCVD, with a final objective to optimize growth conditions for growth rate, crystal quality, and process uniformity.

The work presented here addresses several important issues in HWCVD. One major focus is to better understand how gas-phase chemistry alters the flux of species incident on the substrate. Gas-phase chemistry is thought to play a critical role in HWCVD of high-quality amorphous hydrogenated silicon (a-Si:H) [1,2] and is likely to be important for HWCVD of polycrystalline silicon as well. Recent work on numerical simulation of the HWCVD environment is described, including gas-phase chemistry, quantum chemical studies of the reaction of silicon atoms with silane molecules, and threshold ionization mass spectroscopic detection of radicals, all of which provide insights into the most important gas-phase processes in HWCVD of both amorphous and crystalline silicon films.

The second major area centers on measurements of the rates of important surface and gas-surface processes. Studies have been conducted on the etching of silicon films by atomic hydrogen, and have systematically explored the nucleation kinetics of Si on SiO_2 in HWCVD, with diluted silane (1% in He) and additional hydrogen. High deposition rate growth with no H_2 dilution has been achieved on a low-density array of seed nuclei produced using high H_2 dilution.

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2. Numerical simulation of HWCVD

2.1. Procedure

Numerical simulations were carried out to compute spatially-resolved gas temperature and species concentration distributions and the distribution of species arriving at the substrate for typical HWCVD conditions. The simulations were performed using the direct simulation Monte Carlo (DSMC) technique of Bird [3]. Two separate DSMC models were used, both of which include gas-phase and surface chemistry. The first is a one-dimensional model, in which the reactor is modeled as a long wire surrounded by a concentric cylinder that serves as the substrate [4,5] and is based on the FORTRAN program DSMC1, described by Bird [3]. The second model is two-dimensional, and for these simulations the program DS2V [6] was used. To treat elastic and reactive cross-sections, procedures outlined in Bird [3] were followed.

2.2. Wire chemistry

The primary reactions occurring at the wire are assumed to be the decomposition of SiH_4 and H_2 into atomic Si and H [7]. Silane is assumed to decompose with a probability of 0.7 [2], while the H_2 dissociation probability is taken to be 0.14 at 2000°C, leading to an H/H_2 flux ratio leaving the wire that is roughly the equilibrium value.

2.3. Substrate chemistry

Reactions at the substrate are treated using estimated reactive sticking probabilities taken from Perrin et al. [8]. The substrate is assumed to remain nearly fully hydrogenated during the deposition process. Incident atomic hydrogen is assumed to recombine to H_2, while incident SiH_3 may either abstract a surface hydrogen and leave as SiH_4 (probability 0.1), or be incorporated into the film with the evolution of 1.5 H_2 molecules (probability 0.18). Highly reactive species (e.g. Si) are assumed to be incorporated into the film with a probability of 0.7. An overall H balance is insured by making adjustments to the H_2 flux back into the gas for reactions involving surface hydrogen exchanges.

2.4. Gas-phase chemistry

To determine those gas-phase reactions important in HWCVD, simulations were first carried out with the one-dimensional model, using a moderate-sized gas-phase reaction mechanism. The mechanism was constructed from that of Ho et al. [9] for silane pyrolysis, and adding several reactions involving atomic hydrogen, with rates from Woiki et al. [10]. Not surprisingly, it was found that for most HWCVD conditions, only the direct reactions of Si and H from the wire with ambient silane were significant. The two gas-phase reactions identified as being the most significant were

$$H + SiH_4 = H_2 + SiH_3 \quad (1)$$

and

$$Si + SiH_4 = H_2 + Si_2H_2 \quad (2)$$

and these were chosen for use in the two-dimensional model.

Reaction (1) produces gas-phase silyl radicals, believed to be an important precursor for high-quality a-Si:H deposition and presumably important for polycrystalline silicon as well. The rate coefficient was taken to be k_1 (cm^3/mol s) $= 7.8 \times 10^{14} \exp(-E/RT)$, with $E = 4491$ cal/mol [10]. There is much more uncertainty surrounding the reaction of Si with silane. While it has been argued that this reaction plays the important role of blocking atomic silicon generated on the wire from reaching the substrate [1,2], the products of the reaction of $Si + SiH_4$ are not known with any certainty. Woiki et al. [10] have proposed that the reaction is fast, and they determine a best-fit rate coefficient of 4×10^{14} cm^3/mol s (at ~500 torr), corresponding to a reaction probability of 1 upon collision. There has also been recent work by Takahara et al. [11] which suggests a rate of 2.64×10^{14} cm^3/mol s (at 10 torr) for the consumption of Si atoms via reaction with silane. In neither study, however, were reaction products directly measured. For the purposes of the DSMC simulations, the rate coefficient of Takahara et al. [11] is used for Reaction (2), and the question of its rate will be further addressed in Section 3.

2.5. Results

Two-dimensional simulations were conducted under conditions relevant to amorphous or polycrystalline silicon growth by HWCVD. The simulation domain corresponds to a long square channel, 5 cm on a side, with a collinear wire in the middle. Gas enters from an opening at the left, at flowrates of approximately 90 sccm, and is exhausted to vacuum through two small openings at the upper and lower right corners. Film growth occurs on all four surfaces, maintained at a temperature of 300°C.

The conditions of this simulation were chosen to approximate those of Schropp et al. [12] for amorphous silicon growth, with a total silane pressure of 9 mtorr (1.2 Pa) and a flow rate of 90 sccm. The computed temperature distribution for the case of pure silane gas is shown in Fig. 1. The most noteworthy feature is that the gas temperature at the wire is approximately 1700° below the wire temperature. This is a consequence of the long mean free path compared to the wire diameter.

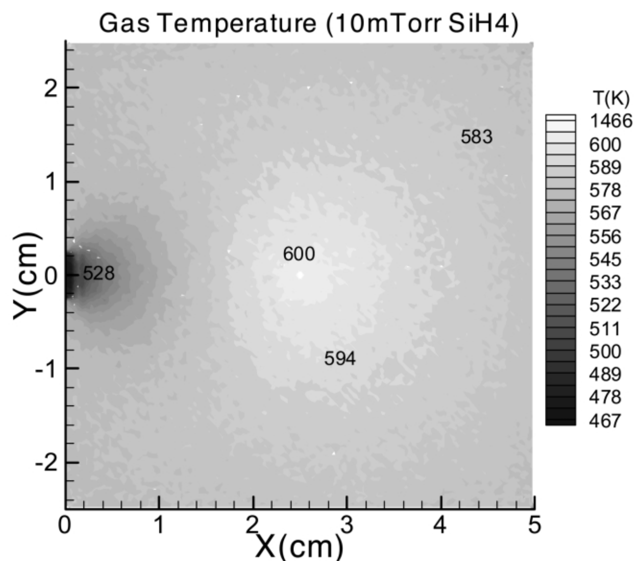


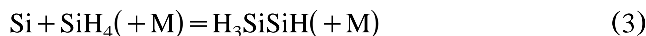
Fig. 1. Gas temperature contours for pure silane feedstock at a pressure of 10 mtorr and a wire temperature of 2000°C.

Particles leaving the wire have translational energies characteristic of the wire temperature (2000°C), but those incident on the wire have come from cooler regions, roughly one mean free path away, and arrive with much lower translational energy. The temperature is defined as an average over all particles and therefore has an intermediate value at the wire.

The silane distribution showed the expected effects, with the concentration highest at the inlet at the left, and depleted near the wire. The depletion at the wire is due both to chemistry on the wire, and to the Soret effect, which drives heavier species toward cold regions. The atomic silicon profile, as expected, showed concentration near the wire where it is generated, and was depleted rapidly away from the wire, due both to reaction on the substrate and gas-phase reaction via Reaction (2). The distribution of SiH_3 was broader, since it is produced in the gas by reaction of H from the wire with silane.

Shown in Fig. 2 are the mole fraction profiles of several species along the horizontal line from the wire to the center of the right wall. Note that the simulations predict a buildup of Si_2H_2. This is undoubtedly an artifact of the assumption that it is produced by rapid reaction of Si and silane, but there are no equally rapid reactions included to remove it, either in the gas-phase or on the surface. As will be discussed below, mass spectrometry measurements detect very little of any species heavier than silane, which is consistent with previous reports [1,2].

A possible explanation is that the reaction of Si with silane occurs not only as represented by Reaction (2), but also via the formation of an intermediate (H_3SiSiH),



$$Si + SiH_4(+M) = H_3SiSiH(+M) \qquad (3)$$

which can be collisionally stabilized at high pressures (to be discussed in Section 3). In this case, the reaction may be in the fall-off regime at the pressures characteristic of HWCVD, and thus the experimental rate coefficients used for the simulation, which reflect the total rate of Si consumption via Reactions (2) and (3), may be too high. Since there are no other likely low-pressure products of $Si + SiH_4$ than those of Reaction (2), this would make it unlikely that any gas-phase reaction between silicon atoms and silane can be rapid enough to significantly block Si from reaching the substrate under HWCVD conditions. In addition, if Si_2H_2 was present in the amounts predicted by the simulation, its inclusion as a growth species would raise the growth rate several orders of magnitude beyond experimentally reasonable levels (i.e. ~1 nm/s). To investigate this reaction further, an ab initio quantum chemical study of $Si + SiH_4$ has been conducted, which is described in the next section.

3. Ab initio studies of the reaction of Si with SiH_4

3.1. Procedure

The possible reactions of a silicon atom with a silane molecule were investigated using density functional theory (DFT) [13,14] with the B3LYP functional [15] and the Dunning cc-pVTZ basis set [16]. For computational efficiency, *f*-functions were excluded from the basis set, a simplification that has been found to have a negligible impact on the energies or geometries resulting from these calculations. To determine the steady-state rate coefficients as a function of temperature and pressure, the microcanonical statistical theory of Rice and

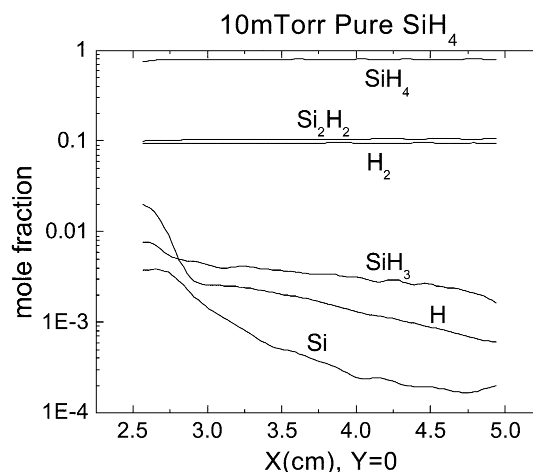


Fig. 2. 1-D species profiles along the gas-inlet axis ($Y = 0$) for conditions of 10 mtorr pure SiH_4, $T_{wire} = 2000°C$.

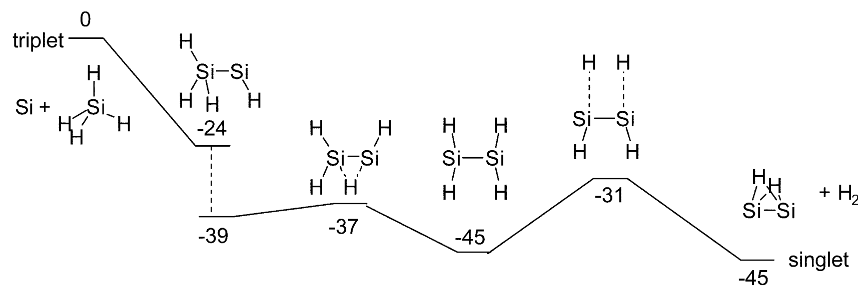


Fig. 3. Energy profile (kcal/mol) for the insertion, rearrangement, and H_2 elimination process that leads to Si_2H_2.

Ramsperger [17], Kassel [18], and Marcus [19] (RRKM) was used.

The calculations were adjusted with zero-point energy (ZPE) corrections and Gibbs free energy adjustments, obtained from the vibrational frequencies using a harmonic approximation. A temperature of 1200 K was used to estimate free energies for the reactions considered here, which is between the wire temperature and the substrate temperature. These calculations are performed using the Jaguar program suite [20] as well as ChemRate [21].

3.2. Results

The objective of the ab-initio study was to identify energetically favorable pathways for the reaction of Si with SiH_4 that do not require collisional stabilization, and therefore can be rapid even at very low pressure. There are two possible bimolecular reactions between Si and SiH_4: abstraction of an H atom from SiH_4 to form SiH and SiH_3, and insertion of Si into a Si–H bond of SiH_4 to form H_3SiSiH.

The energetics for the abstraction of an H atom by Si from SiH_4 were found to be significantly uphill, and thus not likely to be of importance under HWCVD conditions. Fig. 3 shows the insertion of a Si atom into an Si–H bond of SiH_4. The ground spin state of the Si atom has triplet multiplicity, and the ground state of SiH_4 is a singlet; hence, the spin-conserved product will have triplet multiplicity. Calculations show that this process occurs without a significant barrier, and is substantially downhill energetically. The formation of the triplet species was predicted to be exothermic by 24.30 kcal/mol in energy, and is slightly endothermic by 1.01 kcal/mol in free energy at 1200 K.

There is also a singlet state of the resulting H_3SiSiH product, which is significantly more stable than the triplet state. Calculations show that the singlet H_3SiSiH species is 38.95 kcal/mol in energy and 13.36 kcal/mol in free energy at 1200 K below the reactant energies. These calculations show that the insertion of Si into a Si–H bond of SiH_4 is a very exothermic process. The initial species will be a triplet state. The determination of the rate at which the triplet state can intersystem cross to the singlet state is beyond the scope of the current study.

However, whether H_3SiSiH is in the triplet or singlet state, it will still have the full energy of the reactants, which must be carried away by subsequent collisions in order to stabilize the H_3SiSiH product. In the absence of such collisions, the highly excited H_3SiSiH is likely to dissociate in a few vibrational periods, either back to the reactants or to other products. To confirm this expectation, calculations [21] were performed to determine the rate at which Si and SiH_4 will react to form collisionally stabilized H_3SiSiH. The characteristic time for this process was found to be of order 0.1 s, much longer than the 10-μs transit time of this species from the wire to the substrate. Therefore, Si_2H_4 (either as H_3SiSiH or H_2SiSiH_2) is not expected to be a significant product of the reaction of Si and SiH_4 under typical HWCVD conditions; in other words, the reaction is in the fall-off regime.

The issue then is to determine if there are other possible dissociation pathways for excited H_3SiSiH, which requires looking at rearrangements of Si_2H_4 compounds. It has been found that there is a large barrier ($\sim$30 kcal/mol) for triplet H_3SiSiH to rearrange to triplet H_2SiSiH_2. However, singlet H_3SiSiH has a barrier of only $\sim$1 kcal/mol to rearrange to singlet H_2SiSiH_2, which is also more stable than the triplet form. Then, the only energetically accessible dissociation pathway for excited Si_2H_4 is H_2 elimination. Although this is uphill in energy from the H_2SiSiH_2 ground state, it is only necessary for the energy of every intermediate state to be lower than the initial $Si+SiH_4$ energy to proceed. Fig. 3 shows the overall energetics of Si insertion into SiH_4, H_3SiSiH triplet to singlet conversion, rearrangement to H_2SiSiH_2, and H_2 elimination to produce Si_2H_2 and H_2 as the final reaction products. It may be seen that there is no intermediate state with higher energy than the initial state. Furthermore, it was found that there were no substantial free energy barriers. All steps in this process are likely to be rapid, with the possible exception of the H_3SiSiH triplet-to-singlet inter-

level crossing, the rate of which is the subject of current work.

In conclusion, there are two possible outcomes of reaction of silicon atoms with silane molecules that can proceed under HWCVD conditions. The intermediate energetic Si_2H_4 may dissociate back to $Si + SiH_4$, or else to $Si_2H_2 + H_2$. The latter pathway will only be significant if the interlevel crossing is sufficiently fast. If it is not, then it is unlikely that Si is sufficiently reactive with silane for this reaction to be able to shield the substrate from Si atoms, as has been proposed [1,2]. In this case, other explanations would be required to account for the improvement in a-Si:H quality noted previously for conditions where Si atoms experience a few collisions between the wire and the substrate. Further work will be required to resolve this issue.

4. Radical species measurements

The relative fluxes of radicals to the film have a major influence on the resulting film quality. For HWCVD of a-Si:H, the radicals H, Si and SiH_3 have received the greatest attention. However, other radicals may be significant as well. For example, for crystalline silicon deposition, the relative abundance of the radicals SiH_2 and SiH_3 is thought to determine the balance between rough, island surface growth vs. epitaxial silicon growth [22].

Experiments have been initiated to detect radicals arriving at the substrate using threshold ionization mass spectrometry (TIMS). Experiments have been carried out for conditions of 2–200 mtorr total pressure, with 1% SiH_4 in He. Wire temperatures between 1750°C and 1900°C (200–300 W, 40 V across wire) were used, with a wire-to-substrate distance of 2.5 cm. For these experiments, the flow rate was relatively low (2–17 sccm), resulting in high silane depletion (75–90%).

Under these conditions, the dominant radical species observed is SiH_2. Fig. 4 shows the SiH_2 signal as a function of electron energy, with the wire at 1900°C, and with the wire at room temperature (off) under conditions of 2 mtorr dilute SiH_4. Due to depletion of the SiH_4 gas with the wire on, the wire off signal is normalized such that the two signals are equal at high energies (30 eV); this relies on the assumption that the dominant contribution to the SiH_2^+ signal at high energies is from SiH_4 dissociation. As a result, the net radical signal is the difference between the 'wire on' and normalized 'wire off' signals. The dominance of SiH_2 for these conditions is attributed to heterogeneous pyrolysis of SiH_4 on hot surfaces other than the wire (i.e. the amorphous silicon-coated walls of the chamber), given that the wire temperature is well into the regime at which complete silane dissociation on the wire is suggested [7] and that pressures are well below the regime at which gas-phase collisions could produce this

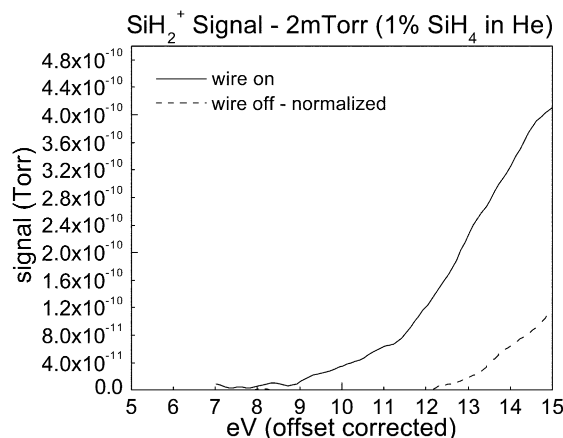


Fig. 4. SiH_2^+ signal vs. electron energy with the wire on (1900°C) and off (room temperature).

species. In addition, the production of SiH_2 via reaction of silane with a silicon surface has been previously suggested [23]. This result underscores the importance both of limiting the silane residence time in the reactor and substrate thermal management during HWCVD growth to insure that the environment seen by the film is dominated by silane cracking on the wire, rather than thermal CVD at the substrate. At higher pressures (200 mtorr), the radical SiH_3 is also detected, consistent with Reaction (1).

The effect of hydrogen dilution has also been investigated via mass spectrometry. Results confirm the expectation that atomic hydrogen is produced at the wire, and reveal that etching is significant enough to regenerate SiH_4 from silicon-coated areas of the reactor. Finally, Si_2H_x species have been detected at dilute SiH_4 pressures between 500 and 2000 mtorr. These higher silanes, however, constitute only 1% or less of the total silicon-containing species (except SiH_4). Whether this is produced by gas-phase chemistry, or by H etching of the film on the walls and substrate, or by pyrolysis of SiH_4 on surfaces is not yet known. Experiments are in progress to isolate these factors. However, the apparent lack of abundance of Si_2H_x effectively confirms the arguments presented above that $Si + SiH_4 = Si_2H_4$ is not significant under HWCVD conditions. It may also indicate that $Si + SiH_4 = Si_2H_2 + H_2$ is slow.

5. Film growth experiments

All film growth experiments were performed using dilute silane (1% in He) and a 0.25-mm-diameter tungsten wire (at 2000°C) at a wire-to-substrate distance of 2.5 cm. Thermal radiation from the wire heated the substrates of 100 nm SiO_2 on Si to 300°C. Dilutions in H_2 are referenced to 1 mtorr of SiH_4 in 99 mtorr He (at a flowrate of 8 sccm), and all gases used are ultrahigh purity.

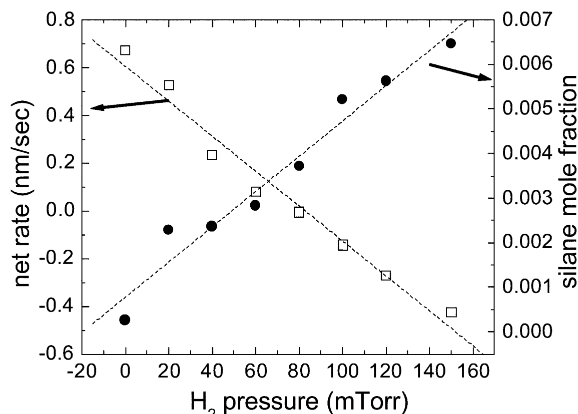


Fig. 5. Net deposition rate and SiH_4 mole fraction, as a function of H_2 partial pressure in 100 mtorr of dilute SiH_4 (1% in He).

The net growth rate was measured in separate experiments using a quartz crystal oscillator, cooled to approximately 250°C and located at the substrate position, with H_2 dilution between 0 and 150:1 (H_2 flowrate up to 15 sccm). As seen in Fig. 5, the net growth rate decreases with increasing H_2 partial pressure, due to etching by atomic H. The SiH_4 signal was measured at the same H_2 dilutions with the mass spectrometer, and was observed to increase with the addition of H_2, due to etching from the walls. A transition from net growth to net etching of the amorphous Si grown on the quartz oscillator is observed near 80:1 H_2 dilution, though the transition dilution is likely higher during polycrystalline film growth due to a slower hydrogen etch rate for crystalline Si than amorphous Si [24].

Transmission electron microscopy (TEM) of films grown on SiO_2 substrates confirmed that, at a H_2 dilution of 20:1, Si films are fully polycrystalline, with no amorphous interface layer. These continuous microcrystalline films have a columnar grain structure, and grain size increases from 40 to 85 nm upon H_2 dilution (20:1 H_2:SiH_4), due to the etching of initially-deposited amorphous silicon regions by atomic H. Experiments were also carried out to study the initial nucleation of silicon on SiO_2 under HWCVD conditions. Nucleation took place on Si(100) at 300–450°C, using 1 mtorr SiH_4 (in 99 mtorr He) at H_2 pressures from 0 to 100 mtorr. The nucleation density at low silicon coverage on a 100-nm-thick SiO_2 layer was determined using contact-mode atomic force microscopy (AFM) on the substrate region nearest the wire. As seen in Fig. 6, the nucleation density increased sublinearly with time, and decreased with H_2 dilution. The decrease with H_2 dilution is consistent with the reported increase in grain size for continuous films. The nucleation rate is initially high, until a critical density of nuclei is reached, at which time the nucleation rate is sharply reduced and grain growth begins. To further elucidate the role of atomic hydrogen etching in the growth process, an SiO_2 substrate was exposed to 60 mtorr H_2 for 20 min, after which growth was allowed to proceed with a non-hydrogen diluted silane mixture. The resulting nucleation densities shown in Fig. 6 were similar to those for undiluted growth without previous H_2 exposure, suggesting that H_2 does not significantly roughen the SiO_2 substrate.

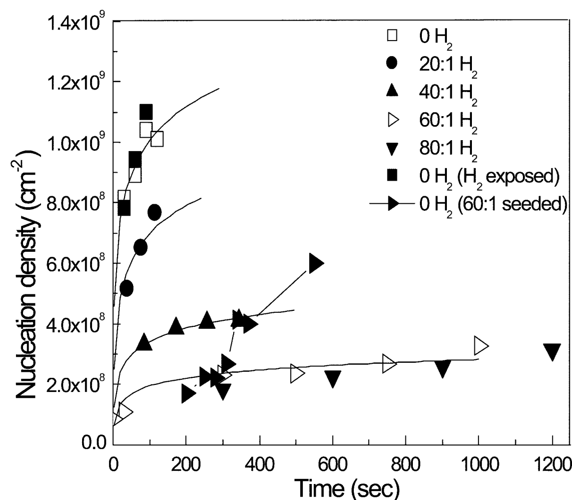


Fig. 6. Nucleation density variation with time during low coverage poly-Si growth on SiO_2, at various hydrogen dilutions.

One approach to synthesis of large-grained polycrystalline films at a high deposition rate is the production of a low-density array of Si seed crystals at high H_2 dilution, followed by growth at a high rate, with little or no H_2 dilution. To test this idea, a SiO_2 substrate was exposed to conditions of 60:1 H_2 dilution for 250 s, after which undiluted growth was allowed to proceed. As seen in Fig. 6, the resulting nucleation densities were higher than those previously observed for growth at 60:1 H_2 dilution, but lower than those observed for undiluted growth, suggesting that the high-dilution nucleation phase serves to suppress the formation of the numerous smaller nuclei that ordinarily form during undiluted growth.

6. Summary and conclusions

In this paper, results have been presented of an ongoing investigation into fundamental processes of importance for HWCVD of polycrystalline silicon films, many of which are relevant to a-Si:H as well. The approach taken combines numerical simulation of HWCVD processes, ab-initio quantum chemistry calculations, experimental detection of radical species to validate and improve the models, and basic studies of thin film nucleation and growth under HWCVD conditions.

Several important conclusions may be drawn from this work. First of all, the proposal that reaction of silicon atoms produced on the wire with ambient silane can shield the substrate from this flux of silicon atoms has been considered in some detail. The simulations show clearly that this is the case if Si reacts with silane with high probability upon collision, but not otherwise. The only viable low-pressure reaction pathway found is one that leads to formation of Si_2H_2 and H_2. This overall reaction is exothermic, but requires a triplet-to-singlet interlevel crossing. Whether this can occur rapidly enough to make this reaction significant in blocking Si from the substrate is not yet clear. If not, then non-chemical explanations for the known effect of pressure on a-Si:H quality must be sought. Threshold ionization mass spectrometry measurements show two things. First, a significant SiH_2 radical signal is detected for conditions of high silane depletion, indicating that pyrolysis may play a role in HWCVD, unless the process is designed to suppress it. Second, little Si_2H_x is detected, in agreement with previous reports [1,2]. Finally, film growth studies have shown clearly that high hydrogen dilutions can result in net etching of the film by incident H atoms. If the conditions are chosen so that the growth rate is still positive, this may enhance crystalline film quality by preferentially etching amorphous silicon. In particular, nucleation studies on SiO_2 show that hydrogen dilution has the beneficial effect of suppressing the formation of numerous small nuclei that occurs during undiluted growth.

Acknowledgements

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