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Numerical simulation of primary cluster formation in Silane plasmas

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1 Introduction

Higher rates and better quality of deposition of polymorphous, hydrogenated silicon films, and thereby better performance of solar cells can be achieved by operating at plasma conditions in which nano-meter sized silicon clusters are formed and deposited onto the film surface. Although dusty plasma behaviour in the regime of micrometer-sized particles is well understood today, the earlier stages of cluster formation, nucleation and coagulation are still open to experimental and theoretical investigation. The present work aims at obtaining a better understanding of the formation process of small particle clusters ranging in size from a few atoms to a few nano-meters. To this end, a simulation of the cluster formation process in its initial stages is attempted.

Cluster formation in gases passes through four distinct phases; 1) formation of primary clusters up to a critical size before nucleation, 2) growth of small particles, 3) formation of macroscopic particles by conglomeration of small particles and 4) growth of macroscopic particles into isolated multiply-charged particles. In this paper, we shall concentrate on the first stage of particle formation in capacitively coupled radio-frequency discharges in SiH_4, where the particles are neutral or singly charged anionic clusters.

There have been extensive experimental investigations aimed at determining the principal reaction pathways involved in the process. Existing literature leads to the conclusion that negative ions play a predominant role in powder formation in pure r.f. SiH_4 plasma at low or moderate power densities [1]. Negative ion formation by dissociative attachment on SiH_4 mainly produces SiH_3^- ions. Negative ions remain trapped in the plasma by the sheath potentials, accumulate and polymerize as follows to form larger particles.

$$\mathrm{Si_nH_{2n+1}^-} + \mathrm{SiH_4} \rightarrow \mathrm{Si_{n+1}H_{2n+3}^-} + \mathrm{H_2} \tag{1}$$

To begin with, only the above polymerization pathway is incorporated into the current simulation.

2 The model

A molecular dynamics (MD) based approach seems particularly suited to the simulation of the problem in view of the very small time and length scales involved. MD is a computer simulation technique where the time evolution of a set of interacting atoms is followed by integrating their equations of motion. Molecular dynamics is therefore a deterministic technique: given an initial set of positions and velocities, the subsequent time evolution is completely determined. However, it is a statistical technique in the sense that only the average values of physical parameters calculated within the constraints of the ensemble are meaningful. For an MD simulation, the physical system is represented by a potential,a function of the atomic positions and representing the potential energy of the system for the given configuration. On considering the predominant interactions,

$$\mathrm{E_{total}} \;=\; (\mathrm{E_{bond}} + \mathrm{E}_\theta + \mathrm{E_{U_B}} + \mathrm{E_{dih}} + \mathrm{E_{imp}}) \;+\; (\mathrm{E_{elec}} + \mathrm{E_{vdw}}), \tag{2}$$

where, the bonded potential includes the bond-stretching potential, the angle-bending potential, the Urey-Bradley term, the dihedral angle and the improper dihedral angle potential terms; the non-bonded potential includes the electrostatic potential due to the presence of charged particles, and the van der waals interatomic potential. In this work, MM3-2000 [2] parameter set has been used.

An initial ensemble of SiH_4 and SiH_3^- is considered to be present within a given volume, at a given neutral gas temperature. The MD simulation is then allowed to run in order to compute the trajectories of the molecules, and their orientations over time. In the absence of data for reaction rates of the reaction mechanisms along the specified polymerisation pathway, a simplifying assumption is made at this point. It is assumed that the if a neutral-anion pair reach within a critical distance of each other, and with favourable orientations, the event of their bonding is taken to be a certainty. The direct consequence of this assumption would be an over-estimation of the number of bondings, but is expected to still predict a realistic trend. Also, in order to be computationally feasible, the simulation runs are made with very high molecule densities. Typically, a cubic volume of 75^3 Å houses an ensemble of 125 neutrals and 27 single-Silicon negative ions, which makes a total of 733 atoms.

3 Results and discussion

It is observed that for a given neutral and ion density, the maximum particle size is seen to increase steadily over a period of time and then become steady, as can be seen in Fig. 1. The temperature was varied between 100K to 900K, and the variation in the saturation value with temperature was observed to be negligible (Fig. 2). As the polymerization proceeds, newer species of particles with greater masses are formed. The atomic mass spectra at 100K and 700K are shown in Figs. 3 and 4 respectively. The difference in the species concentrations does not seem significant.

It is observed that smaller particles (3—6 Si atoms) are initiated at about the same time, irrespective of temperature. However, medium (6—8 Si atoms) and heavy particles (more than 9 Si atoms) are initiated much earlier at higher temperatures. On the other hand, the maximum species mass is seen to have a curious evolution with temperature (Fig. 5) . Heavier particles are seen to be formed at an optimum temperature of around 300-400K, dropping off with increase as well as decrease of temperature, and rising again at much higher temperatures($>$ 700K). This optimum temperature zone is also seen to vary with gas density, being higher for lower densities and vice versa. Also, at lower densities particle formations of all species are seen to proceed at a much lower rate, as can be seen from Fig. 6 ($1.53 \times 10^{26}\, m^3$) and Fig. 7 ($12.16 \times 10^{26}\, m^3$). The time to depletion of SiH_4 neutrals decreases at high temperatures as may be seen in Fig. 8.

Thus it may be concluded that temperature fails to have any significant effect on the maximum achievable particle sizes. Higher thermal energies at higher temperatures however do encourage faster initial clustering rate and cause earlier initiation of medium and heavier particles. However, faster depletion of neutral molecules discourages further cluster growth. This could explain the presence of an optimum temperature convivial for production of heavier particles. Surprisingly, this effect is also observed experimentally, where a temperature increase from room temperature upto 450 K delays and finally inhibits particle growth [3]. The fact that in spite of production of heavier particles, the particle sizes are not significantly affected is somewhat unexpected; this could be due to the formation of linear molecules at lower temperatures, and the heavier particles at higher temperatures folding on to themselves to form dehydrogenated ring-like molecules. However the species concentrations at depletion is not significantly different at moderately different temperatures, as has been observed by Bhandarkar *et al* [4]. Increased density has a considerable effect on both clustering rates as well as concentration of species.

It is important to remember that very high densities have been used in the present study, in order to keep the computation times practical, but to assign quantitative values to the trends would require calibration with experimental data.

4 Conclusion

The anion-neutral pathway is thus seen to be a viable polymerization route. The present simulation model seems to produce valid and meaningful trends. Further studies are planned to observe the effect of ionic densities, as well as the presence of positive ions. Alternate pathways may be incorporated to obtain the effect of competing pathways. An ab initio modelling of the neutral-anion reaction mechanism, if incorporated into the existing model would enhance its accuracy considerably.

References

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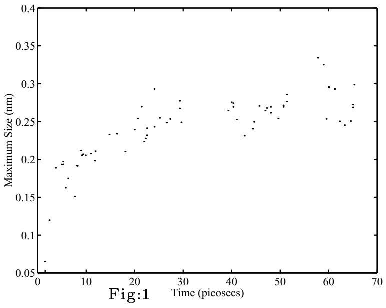


Fig:1

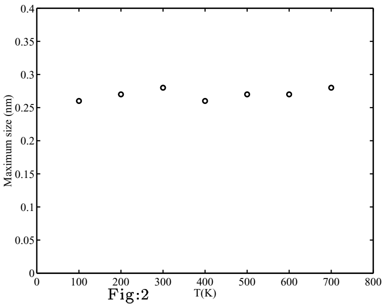
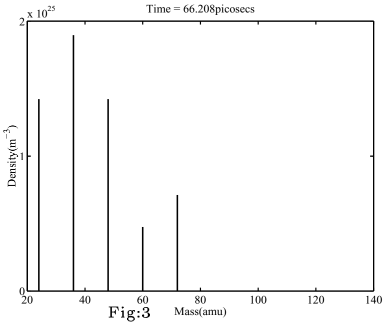


Fig:2



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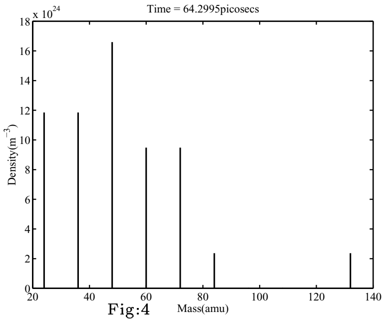

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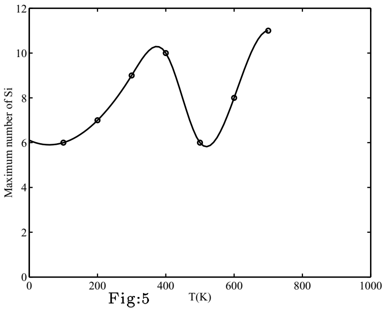
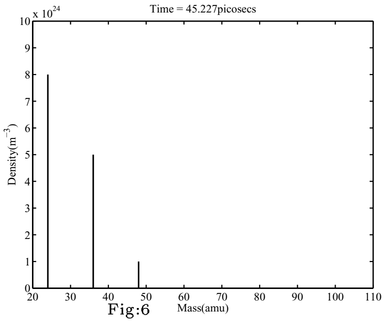


Fig:5



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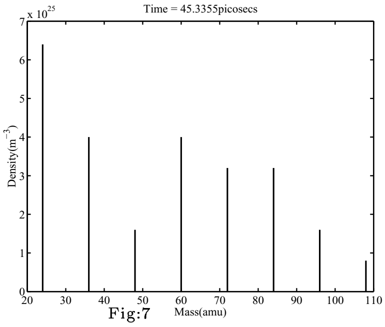

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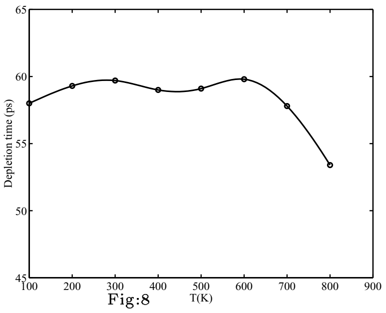

Fig:8