Silicon Nanoparticle Evaporation and Crystallization in Plasma Synthesis

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Abstract: Plasma synthesis of crystalline nanoparticles (NP) occurs through in-situ annealing due to selective heating and cooling of the NPs. We report on the modeling of plasma synthesis of silicon NPs including evaporation and crystallization through tracking of NP temperatures in capacitively and inductively coupled plasmas (CCPs and ICPs). The impact of plasma type and operating conditions on NP melting and crystallization will be discussed.

1. Introduction

Group IV nanoparticles (NPs) have a wide range of applications in the semiconductor, catalyst and biomedicine fields due to their favorable electrical and optical properties. Nonthermal plasma synthesis is a method to control NP size uniformity and produce crystalline NPs. Prior experimental and computational work [1,2] have proposed that the crystallinity of NPs synthesized in plasmas is likely the result of stochastic particle heating by surface reactions. In this paper, we report on a computational investigation of silicon NP synthesis while tracking particle temperature to assess conditions that optimize crystallinity. The simulations combine a 2-dimensional plasma hydrodynamics model with a 3-dimensional kinetic NP growth model.

2. Description of the Models

The plasma chemistry and discharge dynamics were addressed by the Hybrid Plasma Equipment Model (HPEM) which contains modules that iteratively exchange information using multi-physics, time-slicing algorithms. The Dust Transport Simulator (DTS) utilizes plasma properties computed by HPEM to temporally and spatially track NP properties. The DTS has been improved to track the temperature of individual NPs through ion and neutral particle interactions. An evaporation model has been implemented to predict silicon NP growth and loss of mass at elevated temperatures (1600 – 2600 K). The test systems of interest are cylindrical flowing plasmas sustained in Ar/SiH_4 mixtures in capacitively-coupled and inductively coupled formats. Plasma conditions are a pressure of a few Torr and powers of 1 to 10 W.

3. NP Evaporation, Annealing and Growth

NPs in nonthermal plasmas grow by accretion of radicals and are heated through stochastic neutral chemistry and ion-driven collisions, and cooled by radiation and elastic gas collisions. Small particles (< a few nm) can be heated above their annealing temperatures, after which crystallinity is maintained by epitaxial growth. The NPs can also be heated to the degree that they will evaporate, thereby reducing their size. Particles must statistically survive this intense heating and evaporation stage in order to grow to sizes greater than several nm. For example, NPs 0.75 nm in radius may statistically evaporate in 0.35 ms (Fig. 1a) while 1 nm NPs grow steadily (Fig. 1b). The complete evaporation of NPs is less likely to occur in CCPs compared to ICPs due to their lower plasma density. However, almost all NPs with a starting radius of 0.5 nm in various operating conditions evaporate.

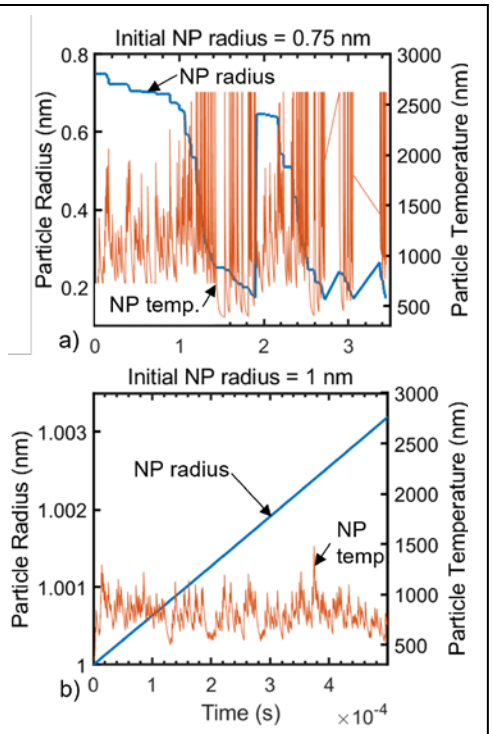

Fig. 1. Temperature and growth of Si NPs flowing through a 1 Torr, 1 W CCP rewith initial radii of a) 0.75 nm and b) 1 nm.

4. Concluding Remarks

Modeling of NP temperatures during plasma synthesis has provided insights into formation of crystalline silicon NPs. Smaller NPs are more likely to crystallize yet they are also statistically more prone to evaporation. It is probable that only a small fraction of NPs overcome the evaporation stage and achieve stable growth in high plasma density systems. A balance between evaporation and crystallization occurs for stable synthesis of nanocrystals in nonthermal plasmas.

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References

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