Nucleation of silicon nanocrystals in a remote plasma without subsequent coagulation
Iker Doan, Stephen L. Weeks, Sumit Agarwal, and Mauritius C. M. van de Sanden

Citation: Journal of Applied Physics 115, 244301 (2014); doi: 10.1063/1.4885195
View online: http://dx.doi.org/10.1063/1.4885195
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/115/24?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
In-situ high resolution transmission electron microscopy observation of silicon nanocrystal nucleation in a SiO2 bilayered matrix

Crystalline Si nanoparticles below crystallization threshold: Effects of collisional heating in non-thermal atmospheric-pressure microplasmas

Ultrahigh throughput plasma processing of free standing silicon nanocrystals with lognormal size distribution
J. Appl. Phys. 113, 134306 (2013); 10.1063/1.4799402

Synthesis of silicon nanotubes by DC arc plasma method

Ellipsometry investigation of the amorphous-to-microcrystalline transition in a-Si:H under hydrogen-plasma treatment
J. Appl. Phys. 107, 083509 (2010); 10.1063/1.3393273
Nucleation of silicon nanocrystals in a remote plasma without subsequent coagulation

Ilker Doğan, Stephen L. Weeks, Sumit Agarwal, and Mauritius C. M. van de Sanden

1Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600MB Eindhoven, The Netherlands
2Department of Chemical and Biological Engineering, Colorado School of Mines, Golden, Colorado 80401, USA
3Dutch Institute for Fundamental Energy Research (DIFFER), P.O. Box 1207, 3430BE Nieuwegein, The Netherlands

(Received 24 March 2014; accepted 14 June 2014; published online 23 June 2014)

We report on the growth mechanism of spherical silicon nanocrystals in a remote expanding Ar plasma using a time-modulated SiH₄ gas injection in the microsecond time range. Under identical time-modulation parameters, we varied the local density of the SiH₄ gas by changing its stagnation pressure on the injection line over the range of 0.1–2.0 bar. We observed that nanocrystals were synthesized in a size range from ~2 to ~50 nm with monocrystalline morphology. Smaller nanocrystals (~2–6 nm) with narrower size distributions and with higher number densities were synthesized with an increase of the SiH₄ gas-phase density. We related this observation to the rapid depletion of the number density of the molecules, ions, and radicals in the plasma during nanocrystal growth, which can primarily occur via nucleation with no significant subsequent coagulation. In addition, in our remote plasma environment, rapid cooling of the gas in the particle growth zone from ~1500 to ~400 K significantly reduces the coalescence rate of the nanoparticles, which makes the coagulation process highly unlikely. Our observations on nanocrystal formation via nucleation indicated that subsequent coagulation for further growth is not always an essential step on nanoparticle formation. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4885195]

I. INTRODUCTION

Size dependent properties of nanoparticles and their potential technological applications have boosted interest in these materials among researchers from various disciplines. As a result of the multi-disciplinary approach on nanoparticles, a variety of synthesis techniques have been developed, which include solution synthesis, sputtering, ion implantation, laser pyrolysis, and microfluidic synthesis. In addition to these techniques, plasma-chemical synthesis techniques are particularly appealing as these techniques have potential to reach higher throughputs with respect to the other techniques while still preserving size dependent optical, electronic, and chemical properties. Various nanoparticle systems, including silicon nanocrystals (Si-NCs), have been synthesized in inductively coupled plasmas, radio-frequency discharge plasmas, direct-current discharge plasmas, atmospheric pressure plasmas, non-thermal plasmas, and very high frequency plasmas. These plasmas offer much flexibility on varying the process parameters and material morphology, and there is basically no limit on the type of the gas mixture used and the plasma environment created. An important consideration on the plasma synthesis of nanoparticle systems, however, is the dynamics of nanoparticle formation.

In the literature, detailed experimental analyses and theoretical approaches with different nanoparticle formation dynamics in plasmas are reported. A widely referred theory claims that formation of nanoparticles starts with nucleation of stable small clusters from polymerization of the monomer species of the feed gas. Once stable nuclei start to appear in the plasma, a nucleation burst occurs until reaching an almost complete depletion level of the nucleating species. Following this nucleation burst, subsequent growth up to the sub-micrometer scale particles occurs by means of coagulation.

Nanoparticle morphologies can greatly differ at different stages of the growth, especially in their crystal structures. As a result of the exothermic nature of the growth reactions that take place during nucleation, nanoparticles have monocrystalline, defect-free morphology. On the other hand, during post-nucleation stage, depending on the temperature, nanoparticles coagulate ending up with polycrystalline morphology, which contains defects and discontinuities due to the grain boundaries. In this case, embodied individual nanoparticles can be imaged by using electron microscopy. For a detailed review on how nanoparticle formation and growth takes place, the reader is recommended to check Ostrikov et al.

As we mentioned before, size dependent features of nanoparticles can potentially be used in various technological applications. Particularly for crystalline silicon nanoparticles, or silicon nanocrystals (Si-NCs), these properties depend on the structure of the nanocrystal—grain boundaries and disordered crystal structures within a nanocrystal can alter its optical and electronic properties, or even completely

---

Address: i.dogan@tue.nl and m.c.m.vandesanden@differ.nl

---

<image/image_data>
In our previous work, which concerns the formation of Si-NCs in a remote expanding thermal plasma (ETP) using an Ar/SiH₄ gas mixture, we elaborated that nucleation favors the growth of Si-NCs in low temperature growth zones with well-defined residence times that ends up with spherical shapes and monocrystalline morphologies according to the results obtained from transmission electron microscopy (TEM). This work deals with the systematic analysis of the Si-NC growth mechanism, which will show that nucleation is the primary nanoparticle formation mechanism in ETP. We synthesized Si-NCs in an Ar/SiH₄ mixture using a time modulated injection of SiH₄ to vary the local density of silane injected into the downstream plasma. We analyzed the depletion of SiH₄ from mass spectrometry, and the morphology and size distribution of Si-NCs using TEM and Raman spectroscopy. TEM analyses demonstrated the formation of small and large Si-NCs that are monocrystalline and free from any defects. Analysis of Raman spectroscopy data showed that there is an inverse relationship between the average Si-NC size and size distribution with the local density of SiH₄ in the downstream plasma, which indicated Si-NC growth by nucleation process without subsequent coagulation as a result of rapid depletion of the nucleating molecules, ions, and radicals at higher local densities of SiH₄ injected into the downstream plasma. In addition, we will comment on the role of different plasma species, i.e., positive ions and radicals, on polymerization and growth reactions of small and large Si-NCs grown in different parts of the downstream plasma.

This paper is organized as follows: Following the introduction, we will discuss the particular silane chemistry leading to synthesis of monocrystalline Si-NCs via nucleation. After that the ETP and the experimental details will be provided. We will show the results obtained from mass spectroscopy, TEM, and RS in the results section and discuss the observations. Finally, we will summarize and draw conclusions.

II. SILANE CHEMISTRY IN THE DOWNSTREAM REGION OF THE EXPANDING PLASMA

Formation of nanoparticles is observed in various plasmas. Although the formation mechanism may differ in different plasma environments, a general formation mechanism of nanoparticles can be envisaged, see Figure 1: First, dissociation of the precursor gas; second, polymerization reactions of the plasma species (i.e., ions, radicals, and neutrals containing one Si atom) on the molecular scale; and finally, nucleation and subsequent growth of stable nanoparticles. In this section, we will describe the particular plasma chemistry that leads to formation of Si-NCs in the ETP.

Figure 2(a) shows a schematic of the ETP setup. An Ar plasma generated in a cascaded arc with approximately 10% ionization degree expands supersonically into a low pressure downstream cylindrical vessel. After a stationary shock front located ~3 cm in front of the nozzle, the plasma expands subsonically (with a directed velocity of v ~ 1000 m s⁻¹), in the form of a central beam. As a result of the limited pumping capacity in the background of the plasma beam recirculation cells develop. This flow pattern in the ETP creates significant differences in residence times between the beam and background regions: the directed flow in the central beam has a residence time of τbeam ~ 10.0 ms, whereas the closed streamlines in the recirculation cells have residence times in the range τrecirc ~ 0.1–0.5 s. The residence times determine the final size of the nanoparticles synthesized in these plasma zones, and therefore, a bimodal size distribution of small and large nanoparticles is expected. The transport of Si-NCs between these two zones occurs via a
Therefore, dissociation of SiH$_4$ by electron impact is inefficient and the plasma chemistry is initiated by Ar$^+$ ions with a reaction rate of $k$ and the plasma temperature. At high plasma temperatures, the kinetic energy of Ar$^+$ ions is less than 1.0 eV).

The chemistry in the ETP is different from the usual electron dominated chemistries. As a result of the remote expansion of the plasma, the plasma expands in the form of a central beam that is surrounded by background recirculation cells. SiH$_4$ was pulsed through an injection ring located 5 cm downstream from the arc nozzle. A fast valve attached to the SiH$_4$ injection line, was used to modulate the gas flow. The amount of SiH$_4$ delivered in each pulse was controlled by varying the stagnation pressure, $P_s$, measured upstream the fast valve ($P_s = 0.1$–0.2 bar). (b) SiH$_4$ was pulsed for 10 ms and the time interval between each pulse was 10 s. (c) The time interval of 10 s was chosen to ensure that each pulse was isolated, that is, there was no residual silane signal ($m/z = 31$) observed by the quadrupole mass spectrometer prior to the next pulse. Five pulses were performed for each processing parameter to collect enough Si-NCs for transmission electron microscopy and Raman spectroscopy.

FIG. 2. (a) The remote expanding thermal plasma setup. Due to the particular reactor geometry and processing parameters, the Ar plasma expands in the form of a central beam that is surrounded by background recirculation cells. SiH$_4$ was pulsed through an injection ring located 5 cm downstream from the arc nozzle. A fast valve attached to the SiH$_4$ injection line, was used to modulate the gas flow. The amount of SiH$_4$ delivered in each pulse was controlled by varying the stagnation pressure, $P_s$, measured upstream the fast valve ($P_s = 0.1$–0.2 bar). (b) SiH$_4$ was pulsed for 10 ms and the time interval between each pulse was 10 s. (c) The time interval of 10 s was chosen to ensure that each pulse was isolated, that is, there was no residual silane signal ($m/z = 31$) observed by the quadrupole mass spectrometer prior to the next pulse. Five pulses were performed for each processing parameter to collect enough Si-NCs for transmission electron microscopy and Raman spectroscopy.

diffusional process. However, large Si-NCs are strongly influenced by the convective processes that traps these nanocrystals in the recirculation cells for the duration of above-mentioned residence times.

The chemistry in the ETP is different from the usual electron dominated chemistries. As a result of the remote expansion of the plasma, the plasma expands in the form of a central beam that is surrounded by background recirculation cells. SiH$_4$ was pulsed through an injection ring located 5 cm downstream from the arc nozzle. A fast valve attached to the SiH$_4$ injection line, was used to modulate the gas flow. The amount of SiH$_4$ delivered in each pulse was controlled by varying the stagnation pressure, $P_s$, measured upstream the fast valve ($P_s = 0.1$–0.2 bar). (b) SiH$_4$ was pulsed for 10 ms and the time interval between each pulse was 10 s. (c) The time interval of 10 s was chosen to ensure that each pulse was isolated, that is, there was no residual silane signal ($m/z = 31$) observed by the quadrupole mass spectrometer prior to the next pulse. Five pulses were performed for each processing parameter to collect enough Si-NCs for transmission electron microscopy and Raman spectroscopy.

With a reaction rate $k \sim 10^{-16}$ m$^3$ s$^{-1}$, the dominant product of this reaction is SiH$_3^+$ ions (formation of SiH$_4^+$ ions with $n \leq 2$ requires Ar$^+$ ions with kinetic energies above 2.0 eV). In the downstream of the ETP, the kinetic energy of Ar$^+$ ions is less than 1.0 eV). Produced SiH$_4^+$ ions can involve in two different polymerization reaction pathways depending on the electron density to SiH$_4$ density ratio ($n_e/n_{SiH4}$). When $n_e/n_{SiH4} < 10^{-3}$, the first reaction pathway is a radical polymerization path that starts with a dissociative recombination reaction of an SiH$_3^+$ ion with an electron

$$\text{SiH}_3^+ + e^- \rightarrow \text{SiH}_2 + \text{H} + \text{H}_2$$

(2)

with a reaction rate $k \sim 10^{-13}$ m$^3$ s$^{-1}$, and $l + 2m + p = 3$ and proceeds further with the addition of SiH$_4$ molecules, e.g., for $p = 2$

$$\text{SiH}_2 + \text{SiH}_4 \rightarrow \text{Si}_2\text{H}_2 + \text{H}_2$$

(3)

with a reaction rate $k \sim 10^{-16}$–$10^{-15}$ m$^3$ s$^{-1}$. In the second pathway, when $n_e/n_{SiH4} > 10^{-3}$–$10^{-2}$, SiH$_3^+$ ions initiate an ion polymerization path—they react with SiH$_4$ via an associative charge exchange reaction

$$\text{SiH}_3^+ + \text{SiH}_4 \rightarrow \text{Si}_2\text{H}_5 + \text{H}_2$$

(4)

with a reaction rate, $k \sim 6.0 \times 10^{-16}$ m$^3$ s$^{-1}$. Further addition of radicals and ions drives the polymerization, and first molecular clusters (Si$_4$H$_{10}^+$ and Si$_6$H$_{14}^+$) appear in the plasma.

During silane polymerization, atomic H is generated abundantly in association reactions, which can abstract an H from the molecular Si$_3$H$_m^+$ and Si$_6$H$_m$ clusters, forming H$_2$ molecules, e.g., for Si$_6$H$_m^+$

$$\text{H} + \text{Si}_6\text{H}_{m+1}^+ \rightarrow \text{Si}_6\text{H}_{m+1}^+ + \text{H}_2$$

(5)

Starting from the polymerization phase, H abstraction reactions produce H$_2$ poor Si clusters, which are indeed observed experimentally.

Growth of molecular clusters proceeds until these clusters reach sizes which can no longer be considered molecular. Beyond this critical size, these clusters become stable nanoparticles with well-defined surfaces that provide sites for further nucleation of the molecules, ions, and radicals in the plasma (the critical size for Si-NCs is $\sim 1 \text{nm}$). Nucleation of nanoparticles continues until the density of nucleating species is depleted.

During the nucleation of silicon nanocrystals (Si-NCs) in the ETP, all reactions (radical and ion polymerization reactions, hydrogen abstraction reactions, and collisional stabilization of excited species) involved in growth are exothermic. The energy released from these reactions locally heats the particles at their nucleation sites and most probably is responsible for maintaining the crystallinity during the growth process.

Further growth of nanocrystals can be possible depending on the plasma temperature. At high plasma temperatures,
TABLE I. Process parameters for the expanding thermal plasma.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Processing values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar flow</td>
<td>20 sccs</td>
</tr>
<tr>
<td>Plasma power</td>
<td>1.3–1.8 kW</td>
</tr>
<tr>
<td>Arc pressure</td>
<td>0.1–0.2 bar</td>
</tr>
<tr>
<td>SiH₄ stagnation pressure</td>
<td>0.1–2.0 bar</td>
</tr>
<tr>
<td>Downstream pressure</td>
<td>1.0 millibar</td>
</tr>
<tr>
<td>Pulse ON time</td>
<td>10 ms</td>
</tr>
<tr>
<td>Pulse OFF time</td>
<td>10 s</td>
</tr>
<tr>
<td>Number of pulses</td>
<td>5</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>25 °C</td>
</tr>
</tbody>
</table>

in which colliding nanocrystals are in a molten state, coalescence (mutual merging of particles) rate is high. As a result of collision between small nanoparticles, large nanoparticles with sizes of hundreds of nanometers can be formed. This process is defined as the coagulation phase of the particle growth. During the coagulation, large particles roughly maintain a spherical shape (in fact, the surface that is considered spherical is made up of crystal facets that can only be distinguished from the high resolution view of nanocrystal surfaces) and individual small nanoparticles are distinguished. If the temperature in the plasma is not high enough to initiate the coalescence, collided nanoparticles do not coagulate. Instead, they stick to each other and form weblike dendritic structures. Individual nanoparticles could be decomposed via a post-separation process without affecting their morphology. Thus, in a low-temperature plasma, nucleation and further growth by monomer addition on the nanocrystal surface (growth by molecular collisions) are the primary nanoparticle growth processes.

III. EXPERIMENT

Silicon nanocrystals (Si-NCs) were synthesized in a remote ETP by using an Ar/SiH₄ gas mixture (see Figure 2(a)). A DC plasma was generated in a cascaded arc with a fixed Ar flow rate of 20.0 sccs under subatmospheric pressures (Pₐrc = 0.1–0.2 bar). The total power generated in the arc was over the range of 1.3–1.8 kW. Both electron and gas temperatures in the cascaded arc were ~1.0 eV, with an electron density of nₑ ~ 10²² m⁻³. The downstream region is pumped down to a pressure of ~1.0 millibar. The diameter of the cylindrical vessel was about 50 cm, and the distance between the nozzle and the substrate holder was 40 cm. The distance of the cylindrical vessel was about 50 cm, and the distance from the nozzle to the arc was ~1.3–1.8 kW. The plasma power was monitored using a baratron gauge. SiH₄ injection time during each pulse was 10 ms. A time interval of 10.0 s with no SiH₄ flow between each isolated pulse ensured that residual SiH₄ in the vessel was pumped out prior to the next pulse (Figure 2(b)). The depletion of SiH₄ was determined by means of a quadrupole mass spectrometer by monitoring the ion current signal at m/z = 31 (Figure 2(c)). Our previous studies with similar processing parameters showed that the gas temperature is ~1500 K at the location of injection ring and decreases down to ~400 K close to the substrate and the reactor walls. Si-NCs were collected onto plastic or crystalline silicon substrates and transferred via a load lock. Substrates were protected by a shutter during the startup of the plasma. A list of setup parameters are provided in Table I.

TEM was performed after transferring the Si-NCs to carbon grids. Beam intensities were chosen sufficiently low to prevent any electron-beam related artifacts on Si-NCs. Raman spectroscopy was performed by using a 514 nm Ar⁺ laser. During the Raman measurements, laser power was fixed at 0.3 W mm⁻², which is sufficiently low to prevent any laser induced shift and broadening on the Raman spectra of silicon nanocrystals. The Raman spectra were deconvoluted using Lorentzian line shapes to determine the size distribution of small Si-NCs using an analytical, size-dependent phonon confinement model.

IV. RESULTS AND DISCUSSION

A. Mass spectrometry

Figure 3 demonstrates the amount of SiH₄ delivered into the downstream region for each pulse and its depletion as a function of the stagnation pressure, Pₛ. The absolute amount of SiH₄ molecules delivered increases from ~5.0 × 10¹⁵ to 1.0 × 10¹⁶ with an increase of the stagnation pressure from 0.1 bar to 2.0 bar. Thus, we were able to control the SiH₄ density injected in the downstream plasma by tuning the stagnation pressure. We determined the depletion of SiH₄ from the relative amount of dissociation, D (by the Ar⁺ ions emanating from the arc) with respect to the SiH₄ content under plasma-off condition using

$$D = \frac{I_{\text{off}} - I_{\text{on}}}{I_{\text{off}}}$$  

FIG. 3. (a) Absolute number of SiH₄ molecules delivered into the downstream region of the plasma during each pulse, (b) the percent depletion of SiH₄, and (c) the absolute amount of depleted SiH₄ in the downstream region of the expanding Ar plasma as a function of SiH₄ stagnation pressure.
where \(I_{on}\) and \(I_{off}\) are the ion current signals at \(m/z = 31\) when the plasma was on and off, respectively.

The depletion of \(\text{SiH}_4\) (Figure 3(b)) decreased from \(~80\%\) to \(~40\%\) with an increase in the absolute number of the \(\text{SiH}_4\) molecules in the downstream region from \(~5.0 \times 10^{18}\) to \(1.0 \times 10^{20}\). Note that the equivalent \(\text{SiH}_4\) flow within 10.0 ms corresponds to a flow rate of \(~20–400\) sccs, which was much higher than the \(\text{SiH}_4\) flow used under continuous plasma condition reported earlier.\(^{10}\) At the high equivalent flow rates, we expect relatively less efficient depletion of \(\text{SiH}_4\) molecules since the number of \(\text{Ar}^+\) ions emanating from the arc was limited by the plasma source settings (depletion decreases when the initial ratio of the \(\text{Ar}\) to \(\text{SiH}_4\) density is reduced).\(^{36}\) By knowing the absolute amount of variation of \(\text{SiH}_4\) and its depletion, the absolute depleted amount of \(\text{SiH}_4\) in the downstream increased from \(5.0 \times 10^{18}\) (for \(P_s = 100\) millibars) to almost \(4.0 \times 10^{19}\) (for \(P_s = 2000\) millibars) with a linear trend (Figure 3(c)).

Note that the absolute increase of the amount of depletion (which quenches the electron density) and the absolute amount of \(\text{SiH}_4\) species in the plasma is in favor of ion-molecule reactions (Eq. (4)), which promote ion polymerization path. Here, we compare the ratio of electron to \(\text{SiH}_4\) density (\(n_e/\rho_{\text{SiH}_4}\)). To demonstrate a simple comparison, we only consider the events that take place during \(\text{SiH}_4\) injection (\(\tau_{\text{pulse}} = 10.0\) ms). We know that electrons were produced only by the ionization of \(\text{Ar}\) in the cascaded arc. Assuming \(10\%\) ionization degree and 10 ms interaction time with injected \(\text{SiH}_4\) in the central beam (\(\text{Ar}\) flow is 20.0 sccs, 1 sccs is \(2.5 \times 10^{19}\) particles per second under standard conditions), \(5 \times 10^{17}\) electrons (and also \(\text{Ar}^+\) ions) are available to initiate dissociative recombination reactions during 10 ms of interaction time (Eq. (2)). Referring back to the mass spectrometry data, the amount of \(\text{SiH}_4\) molecules increased from \(10^{16}\) to \(6 \times 10^{19}\) with stagnation pressure in the gas line. In other words, \(n_e/\rho_{\text{SiH}_4}\) decreases from \(10^{-1}\) to \(\sim 1.6 \times 10^{-3}\). Thus, ion polymerization path (Eq. (4)) was promoted at higher stagnation pressures on the gas line. According to Figure 3(c), the depleted amount of \(\text{SiH}_4\) has a linear dependency on the stagnation pressure, i.e., \(D \propto P_s\). As we will discuss later on, this linearity of \(D\) together with decreased Si-NC size at higher stagnation pressures is an important indication that addition of \(\text{SiH}_4\) plays a critical role on the growth of Si-NCs in the ETP.

**B. Transmission electron microscopy**

We used TEM to analyze the morphology and size distribution of Si-NCs. Figure 4 demonstrates Si-NCs synthesized in ETP, which have a spherical shape and a fully crystalline morphology (in a previous report,\(^{10}\) we have demonstrated that synthesized Si-NCs have three main diffraction peaks of bulk crystalline Si, namely, (111), (220), and (311)). First, we show Si-NCs synthesized using a continuous \(\text{SiH}_4\) injection (Figure 4(a)) as a benchmark. As we discussed above, and showed in our previous work,\(^{10}\) Si-NCs (Figure 4(a)) have a bimodal size distribution as a result of the specific reactor geometry: small Si-NCs with sizes in the range of 2–10 nm are synthesized in the central beam (beam residence time, \(\tau_{\text{beam}} \leq 10.0\) ms) and large Si-NCs with sizes in the range of 50–120 nm are synthesized in the recirculation cells (\(\tau_{\text{recirc}} \sim 0.1–0.5\) s). Figure 4(b) demonstrates that the size distribution of Si-NCs was still bimodal in the time-modulated \(\text{SiH}_4\) gas injection experiments. However, in contrast to the continuous \(\text{SiH}_4\) flow experiments, the size of large Si-NCs synthesized in the time-modulated \(\text{SiH}_4\) injection experiments were noticeably smaller (20–50 nm, see Figure 4(d)) than the sizes observed in continuous silane gas injection (50–120 nm, Figure 4(c)) as a result of the finite amount of \(\text{SiH}_4\) present in the downstream region—the averaged flow between two pulses varies in the range of \(2 \times 10^{-4}–4 \times 10^{-3}\) sccs.

The decrease in the size of the large Si-NCs is also related to the duration of \(\text{SiH}_4\) injection. The stream lines in the recirculation cells were almost identical in the continuous and in the time-modulated injection of \(\text{SiH}_4\), as the downstream properties were mainly determined by the supersonic \(\text{Ar}\) plasma expansion in the axial direction and by the limited pumping capacity, resulted in the formation of the recirculation cells. However, one key difference is that the duration of \(\text{SiH}_4\) injection in the time-modulated injection was much shorter with respect to the characteristic residence times (\(\tau_{\text{pulse}} \ll \tau_{\text{rec}}\)), which also limited the growth of large Si-NCs in the recirculation cells. An analysis of the size distribution in Figures 4(c) and 4(d) shows that large Si-NCs had a lognormal distribution. Lognormal distribution in gas phase synthesis reactors is observed when convective flow and
diffusion processes are responsible for particle transport through a finite growth regime in well-defined residence times. Depending on the competition between the convective flow and diffusion processes, the shape of the distribution could be either highly asymmetric (limited convection) or almost symmetric (limited diffusion).

As we mentioned above, all Si-NCs synthesized in the ETP have fully crystalline morphology. High resolution TEM images in Figure 5 demonstrate that large Si-NCs have ordered crystal structures. In other words, Figure 5 concludes that these large Si-NCs do not have polycrystalline morphology, indeed they have monocrystalline morphology. In addition, the dendritic shape of small and large Si-NCs (Figure 4(b)) implies that the temperature in the plasma was insufficient to initiate particle coalescence. This observation concludes that the rate of a possible coalescence mechanism was lower than the rate of collision during the transport of nanocrystals in the downstream plasma.

Size analysis of small Si-NCs with TEM is only possible if only these nanocrystals could be separately distinguished. As small Si-NCs were found in dense dendritic-like structures, size analysis was unreliable and time consuming by using TEM. Nonetheless, an accurate analysis of the average size and size distribution of small Si-NCs is essential to understand the particle formation mechanisms in the plasma beam. As we demonstrated in a previous paper, Raman spectroscopy can be excellently used as an alternative analysis tool.

C. Raman spectroscopy

Figure 6 demonstrates Raman spectra of Si-NCs synthesized at various stagnation pressures of the gas line during time-modulated SiH₄ flow experiments. Raman spectroscopy revealed that the analyzed material was fully crystalline as the broad Raman peak centered at 480 cm⁻¹, which is the fingerprint of the amorphous silicon (a-Si:H), was not detected. The peak position of Raman spectra departed from the optical phonon mode of bulk crystalline silicon, which is located at ʋₜ₅ = 521 cm⁻¹, starting with the stagnation pressure of 0.2 bar (~2 x 10¹⁹ SiH₄ molecules per injection). Moreover, we observed that the red-shift increases with an increase in the stagnation pressure. In other words, the average size of Si-NCs had an inverse relation with the density of SiH₄ injected downstream. In addition, we observed an asymmetric peak broadening together with the peak shift: for each Raman spectra, the average shift in the low wavenumber part of the peak was more pronounced than the average shift in the high wavenumber part (Figure 6). Observed peak shapes differ from the peak shape of Si-NCs with monodisperse size distribution and indicates the presence of a bimodal size distribution, which was also observed from TEM images. We observed smaller Si-NCs at higher stagnation pressures on the SiH₄ gas line (which shift the low wavenumber part of the spectra); however, large Si-NCs were still present in the mixture (which makes the high wavenumber part of the spectra almost unshifted). The presence of bimodal size distribution became clearer from the Raman spectra as the stagnation pressure, or SiH₄ density, got higher.

The way to determine the size distribution of small Si-NCs is to deconvolute the measured Raman spectra to find the particular Raman peaks of small and large Si-NCs, and determine the parameters required to plot the size distribution. The deconvolution procedure is explained in detail in our previous work. Figure 7 demonstrates the size distribution of small Si-NCs as a function of SiH₄ stagnation pressure. Results of the analyses conclude that, at higher stagnation pressures, the average size of small nanocrystals decreased and nanocrystals had possession of a narrower size distribution, e.g., at Ps = 0.2 bar, we observed Si-NCs in the size range from 2.5 nm to almost 16.0 nm, however, at Ps = 2.0 bar, the sizes were in the range from 2.0 nm to 3.0 nm.
local densities of SiH\textsubscript{4} injected in the plasma. This observation is related of small Si-NCs decrease with increased stagnation pressure, i.e., higher spectroscopy analyses. Figure demonstrates that the peak size and the width of small Si-NCs determined from the Raman spectra using the analytical phonon confinement model demonstrated in our previous work.\textsuperscript{42} Increasing stagnation pressure—or increasing the local density of SiH\textsubscript{4} for each pulse—results in smaller Si-NCs with a narrower size distribution.

6.0 nm. In addition, we estimated the volume fraction of small Si-NCs with respect to the total analyzed volume using the integrated areas of the deconvoluted peaks. For the lowest (5.0 $\times$ 10\textsuperscript{18}) and highest (1.0 $\times$ 10\textsuperscript{20}) amount of SiH\textsubscript{4} molecules injected into the downstream, we determine the volume fraction of small Si-NCs as 60% and 85%, respectively. Figure 8 shows that higher stagnation pressures on the SiH\textsubscript{4} gas line reduced the peak size and the distribution width of Si-NCs from 6.2 nm to 3.2 nm and from 5.0 nm to 1.7 nm, respectively. Size distributions became less asymmetric at high stagnation pressures. Decreased asymmetry of the nanocrystal size distribution indicates that the contribution of diffusion as a key process in Si-NC formation became smaller with respect to convective flow (limited diffusion) at higher local densities of the SiH\textsubscript{4} gas injected into downstream region.

D. Discussion

From the results of TEM and Raman spectroscopy, we observed distinctive phenomena, which helped us to reveal the underlying mechanism, on the formation of silicon nanocrystals (Si-NCs) in the remote ETP. First of all, we observed a bimodal size distribution of spherically shaped small and large Si-NCs. Considering the residence time differences in the plasma as mentioned above, small Si-NCs were synthesized in the central beam and large Si-NCs were synthesized in the recirculation cells. TEM images demonstrate that, together with small Si-NCs, large Si-NCs had monocrystalline morphology. In other words, large Si-NCs were free from any discontinuities in their crystal structures, such as dislocations, grain boundaries, or randomly distributed atomic planes (Figure 5). The dendritic behavior indicated that individual nanocrystals did not combine and form large Si-NCs. Downstream expanding plasma cools rapidly from $\sim$1500 (at the position of the injection ring) to $\sim$400 K in the vicinity of the substrate and in the recirculation zones.\textsuperscript{35} These temperatures in nanocrystal formation regions were insufficient to promote the coalescence that might result in the formation of Si-NCs with various sizes. Therefore, under these observations, we conclude that nucleation and subsequent growth of these nuclei via SiH\textsubscript{4} addition with suppressed coagulation is the only responsible formation mechanism of small and large Si-NCs in the ETP. Indeed, the residence times and the density of SiH\textsubscript{4} available in the recirculation cells are sufficient for the nucleation and growth of nanocrystals via monomer addition up to hundreds of nanometers in size.\textsuperscript{10}

Another remarkable observation is the inverse relation between the amount of SiH\textsubscript{4} in the plasma and the average size of small Si-NCs formed in the central beam. According to the Raman spectroscopy results, average size of small Si-NCs was 6.2 nm when 5.0 $\times$ 10\textsuperscript{18} SiH\textsubscript{4} molecules were injected, and 3.2 nm when 1.0 $\times$ 10\textsuperscript{20} SiH\textsubscript{4} molecules were injected in the downstream plasma. In addition, the volume fraction of small Si-NCs increase from $\sim$60% to $\sim$85% as the SiH\textsubscript{4} amount in the plasma increases. Instead of reaching larger sizes at higher local densities of the feed gas injected in the downstream region, nanocrystals got smaller and their number densities increased. The question is why and how?

Nucleation of nanoparticles starts with polymerization reactions of the molecules, ions, and radicals in the plasma, which leads to formation of stable ionic clusters.\textsuperscript{26} Formation of these clusters and their population in the growth region depends on the supersaturation degree of the feed gas (including ions, radicals, and neutrals) in the plasma.\textsuperscript{22,23} Higher local densities of SiH\textsubscript{4} (i.e., higher stagnation pressure on the SiH\textsubscript{4} gas line) shortens the required time for appearance of stable clusters, and increase their number densities in the growth region as a result of the increased supersaturation degree. These clusters act as sinks for the nucleation of the species available in the plasma during the nucleation burst.\textsuperscript{25} A high number density of clusters provide a large surface area for further nucleation, which in turn depletes the density of plasma species in the growth zone faster than a depletion by a low number density of clusters. Therefore, higher number density of clusters results in
rapid depletion of plasma species that reduces the nucleation time and results in the formation of smaller nanocrystals. These observations from Raman spectroscopy can only be explained in such a way if nucleation is the responsible nanocrystal formation mechanism in the ETP.

According to the mass spectroscopy data, total absolute amount of directly consumed SiH₄ increases with stagnation pressure with a linear relationship. However, depletion of SiH₄ decreases from ~80% to ~40%. In other words, the absolute number of SiH₄ molecules also increases with stagnation pressure. If SiH₄ molecules are consumed by addition reactions, the total surface area of Si-NCs should compensate for the available SiH₄ molecules. Considering ~40 nm average size of large Si-NCs, and the volume fractions of 85% and 60%, respectively, the available surface area during the growth of 3.2 nm Si-NCs was 2.4 times larger than that of 6.3 nm Si-NCs. This observation indeed indicates that addition reactions of SiH₄ molecules play an important role on the growth of small Si-NCs at higher stagnation pressures.

Raman spectroscopy also demonstrated that the width of the nanocrystal size distribution decreases with increased amount of SiH₄ injected downstream. In addition, the distribution shapes became less asymmetric while their widths became narrower. Observation of a finer size distribution is related to the nucleation time. We illustrate this with the following assumption: Consider a constant flux \( \phi \), of plasma species on a newly formed nanocrystal with surface area \( A \). We can describe the increase of the nanocrystal volume per unit time as \( dV/dt = \phi A \). According to this assumption, the radius of the nanocrystal scales with time, i.e., \( r \propto t \). If there is an asymmetric residence time distribution for nanocrystal growth, which is observed when the nanocrystal transport is governed by convective flow and random diffusion, the size distribution of nanocrystals will also be asymmetric, i.e., log-normal under present conditions. Linked with the reasons stated above, smaller Si-NCs with a narrower size distribution is observed when nanocrystal growth stops in a shorter time, which was observed for a higher number density of clusters. On the other hand, depletion of the SiH₄ density in the plasma takes longer if the number density of clusters is lower as a result of reduced nucleation area on the cluster surfaces. Thus, differences in sizes increase and the final size distribution becomes wider and more asymmetric, and average size of Si-NCs increases.

We should also address the role of various plasma species on the formation of small and large Si-NCs as their mean free path, sticking coefficient, and reaction rate significantly differ from each other. Two groups of plasma species, i.e., radicals and positive ions, mainly react with each other or with SiH₄ during the initial polymerization and subsequent nucleation process in the ETP. Radicals have longer mean free path and lower sticking coefficients than positive ions. For instance, the sticking coefficient of a SiH₃ radical is 0.27–0.33 for \( n = 3 \) and 0.35–0.40 for \( n = 2 \). For the polysilyl radicals, the sticking coefficient roughly equals to 0.10–0.20. On the other hand, the positive ions have almost unity sticking coefficient and once they appear in the plasma, they immediately undergo ion-molecule reactions. During the plasma expansion process, therefore, one can expect that the radicals have a higher chance of reaching the recirculation cells via diffusional process, where the polymerization reactions and subsequent nucleation form large Si-NCs. Positive ions, however, likely stay within the central beam and undergo polymerization reactions that end up with the formation of small Si-NCs. Molecular ion creation rate becomes dominant over the radical creation rate if electron to SiH₄ density ratio, \( n_e/n_{SiH_4} < 10^{-3}–10^{-2} \), as mentioned earlier. This is observed at higher amount of SiH₄ injections. Indeed, increased surface area for SiH₄ addition, and linear dependency of SiH₄ depletion with stagnation pressure concludes that creation of molecular ions by charge exchange process is in favor of the formation of small Si-NCs since these species mostly stay within the central beam.

We finally discuss the main differences between the continuous and time-modulated injection of SiH₄ into the downstream region. First of all, with time modulation of the SiH₄ injection, we had a full control on the time, and the amount of SiH₄ molecules injected via varying the stagnation pressure in the gas line. Time-modulation experiment tracked the change of particle size and size distribution as a function of SiH₄ amount injected per unit time interval, and therefore revealed the underlying formation mechanism. In the case of continuous SiH₄ injection, these parameters are not very well defined. Although a bimodal size distribution of Si-NCs is observed both in the continuous and time-modulated SiH₄ injection, the final size of the large Si-NCs synthesized in the time-modulated injection was smaller. Another difference is the final size and size distribution of small Si-NCs. A high local density of SiH₄ in the downstream results in smaller Si-NCs in both cases as a consequence of growth via nucleation. In continuous SiH₄ injection, the maximum possible SiH₄ injection is in the order of tens of standard cubic centimeters per second (~10 sccs). During the time-modulation, as we mentioned before, we reached equivalent SiH₄ flows over the range of 20–400 sccs. In relation with the discussions on the particle size and size distribution, therefore, time modulated injection produces smaller nanocrystals during nucleation, with a narrower size distribution. This is a critical requirement for technological applications of Si-NCs in which the size dependent properties of nanocrystals are used for promoting optimum device performance.

V. CONCLUSION

According to the results from TEM and Raman spectroscopy, silicon nanocrystals (Si-NCs) synthesized in the remote expanding thermal plasma had monocristalline morphology, and they formed dendritic groups. Analyses on size distribution of small Si-NCs showed an inverse relation between the SiH₄ density and the final nanocrystal size under identical SiH₄ injection times. In addition, nanocrystal size distributions were lognormal and their widths became narrower at smaller sizes. Under these conditions, we conclude that formation of large Si-NCs with monocristalline morphology via coagulation is highly unlikely. Therefore, the only possibility of Si-NCs to reach sizes from a few to tens of nanometers is via nucleation and further growth of the...
molecules, ions, and radicals available in the plasma. These nanocrystals have monocrystalline morphology as the molecular exothermic reactions maintain crystallinity during growth. In addition, observed dendritic structures were easily separable, e.g., by means of sonication of Si-NCs. The observations of this work apply for all kind of plasma environments, where nucleation is the primary mechanism of nanocrystal formation.

ACKNOWLEDGMENTS

This work is part of the research programme of the Foundation for Fundamental Research on Matter (FOM), which is part of the Netherlands Organisation for Scientific Research (NWO). The authors of this work thank M. J. F. van de Sanden and J. J. A. Zeebregts for skillful technical assistance, and M. A. Verheijen for TEM images.