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Nucleation of silicon nanocrystals in a remote plasma without subsequent coagulation

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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.1–3 As a result of the multi-disciplinary approach on nanoparticles, a variety of synthesis techniques have been developed, which include solution synthesis,4 sputtering,5 ion implantation,6 laser pyrolysis,7 and microfluidic synthesis.8 In addition to these techniques, plasma-chemical synthesis techniques are particularly appealing as these techniques have potential to reach higher throughputs9,10 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,11 radio-frequency discharge plasmas,12 direct-current discharge plasmas,13 remote plasmas,14 atmospheric pressure plasmas,15 non-thermal plasmas,9,16,17 and very high frequency plasmas.18,19 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.20–23 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.24,25 Following this nucleation burst, subsequent growth up to the sub-micrometer scale particles occurs by means of coagulation.26–29

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 reactions30–32 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.33

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

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suppress them. Therefore, we should consider plasma-chemical techniques as possible environments where nanoparticle coagulation is an unfavorable mechanism during the growth. This can be possible either if the nanoparticles are strongly charged with the same polarity or if the nanoparticle growth occurs in a low temperature, rapidly cooling zone. In the first situation, the electrostatic repulsion forces between small nanoparticles prevent coagulation, and in the latter situation, coalescence rate of small nanoparticles is lower than their collision rate—so that the nanoparticles form web-like dendritic structures without merging into each other.10,19

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 end 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 \( v \approx 1000 \, \text{m/s} \)), 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 \( \tau_{\text{beam}} \lesssim 10.0 \, \text{ms} \), whereas the closed streamlines in the recirculation cells have residence times in the range \( \tau_{\text{recirc}} \approx 0.1–0.5 \, \text{s} \). 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

![Figure 1](image.png)

**FIG. 1.** Formation of Si-NCs in the ETP. Nanocrystal formation starts with dissociation of SiH₄ molecules via Ar⁺ ions. These silicon-containing ions and radicals undergo polymerization reactions, and form the first ionic clusters that will eventually be the cores of the stable clusters at the later stage of nanocrystal formation. When the stable size is reached, these clusters act as sinks for nucleation. A nucleation burst starts from this stage until the density of the nucleating species is quickly depleted. The final size of the nanocrystals is determined by the extent of the nucleation, and nucleation depends on the residence times in the plasma.
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 character of the ETP, the electron temperature in the downstream region is relatively low, i.e., $T_e \sim 0.1 – 0.3$ eV. Therefore, dissociation of SiH$_4$ by electron impact is inefficient and the plasma chemistry is initiated by Ar$^+$ ions emanating from the cascaded arc. Dissociation of molecular SiH$_4$ downstream of the ETP starts with Ar$^+$ ions by means of dissociative charge exchange reactions that leads to the formation of SiH$_n^+$ ($n \leq 3$) ions via

$$\text{Ar}^+ + \text{SiH}_4 \rightarrow \text{SiH}_n^+ + \text{H} + \text{mH}_2 + \text{Ar},$$

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

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

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

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

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

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

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$_2$H$_m^+$ and Si$_3$H$_n$) appear in the plasma.

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

$$\begin{align*}
\text{H} + \text{Si}_3\text{H}_n^+ &\rightarrow \text{Si}_3\text{H}_{n-1}^+ + \text{H}_2, \\
\text{H} + \text{Si}_n\text{H}_{m-1}^+ &\rightarrow \text{Si}_n\text{H}_{m-2}^+ + \text{H}_2
\end{align*}$$

Starting from the polymerization phase, H abstraction reactions produce H 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 $\sim 1$ 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 of 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 web-like 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 (P_{arc} = 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 ~ 10^{22} 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 plasma density in the downstream region is about 10^{21–10^{22}} m⁻³. SiH₄ gas was injected via an injection ring, which was placed in the subsonic region, 5 cm downstream. A valve was attached on the SiH₄ injection line, which was used for time modulation of the SiH₄ flow. The amount of SiH₄ injected downstream at each pulse was controlled by varying the stagnation pressure, Pₚ, upstream of the vessel, in the range of 0.1–2.0 bar. Stagnation pressure was monitored by using a baratron gauge. SiH₄ injection time during each pulse was t_{pulse} = 10.0 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, P_{stagnation}. The absolute amount of SiH₄ molecules delivered increases from ~5.0 × 10^{18} to 1.0 × 10^{20} 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

\[
D = \frac{I_{diff} - I_{on}}{I_{diff}},
\]

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 SiH$_4$ (Figure 3(b)) decreased from $\sim$80% to $\sim$40% with an increase in the absolute number of the SiH$_4$ molecules in the downstream region from $\sim5.0 \times 10^{18}$ to $1.0 \times 10^{20}$. Note that the equivalent SiH$_4$ flow within 10.0 ms corresponds to a flow rate of $\sim20–400$ sccs, which was much higher than the SiH$_4$ flow used under continuous plasma condition reported earlier. At the high equivalent flow rates, we expect relatively less efficient depletion of SiH$_4$ molecules since the number of Ar$^+$ ions emanating from the arc was limited by the plasma source settings (depletion decreases when the initial ratio of the Ar to SiH$_4$ density is reduced). By knowing the absolute amount of SiH$_4$ and its depletion, the absolute depleted amount of 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 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 SiH$_4$ density ($n_e/n_{SiH4}$). To demonstrate a simple comparison, we only consider the events that take place during SiH$_4$ injection ($\tau_{pulse} = 10.0$ ms). We know that electrons were produced only by the ionization of Ar in the cascaded arc. Assuming 10% ionization degree and 10 ms interaction time with injected SiH$_4$ in the central beam (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 Ar$^+$ ions) are available to initiate dissociative recombination reactions during 10 ms of interaction time (Eq. (2)). Referring back to the mass spectroscopy data, the amount of SiH$_4$ molecules increased from $10^{19}$ to $6 \times 10^{19}$ with stagnation pressure in the gas line. In other words, $n_e/n_{SiH4}$ decreases from $10^{-1}$ to $\sim1.6 \times 10^{-3}$. 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 SiH$_4$ has a linear dependency on the stagnation pressure, i.e., $D\times P_s$. 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 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, 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 SiH$_4$ injection (Figure 4(a)) as a benchmark. As we discussed above, and showed in our previous work, 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, $\tau_{beam} \leq 10.0$ ms) and large Si-NCs with sizes in the range of 50–120 nm are synthesized in the recirculation cells ($\tau_{recirc} \sim 0.1–0.5$ s). Figure 4(b) demonstrates that the size distribution of Si-NCs was still bimodal in the time modulated SiH$_4$ gas injection experiments. However, in contrast to the continuous SiH$_4$ flow experiments, the size of large Si-NCs synthesized in the time-modulated 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 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 SiH$_4$ injection. The stream lines in the recirculation cells were almost identical in the continuous and in the time-modulated injection of SiH$_4$, as the downstream properties were mainly determined by the supersonic 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 SiH$_4$ injection in the time-modulated injection was much shorter with respect to the characteristic residence times ($\tau_{pulse} \ll \tau_{rec}$), 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 reactor is observed when convective flow and
diffusion processes are responsible for particle transport through a finite growth regime in well-defined residence times.\textsuperscript{10,23} 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.\textsuperscript{27}

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.\textsuperscript{42}

C. Raman spectroscopy

Figure 6 demonstrates Raman spectra of Si-NCs synthesized at various stagnation pressures of the gas line during time-modulated SiH\textsubscript{4} flow experiments. Raman spectroscopy revealed that the analyzed material was fully crystalline as the broad Raman peak centered at 480 cm\textsuperscript{-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 \(\omega_{\text{c-Si}} = 521\) cm\textsuperscript{-1}, starting with the stagnation pressure of 0.2 bar (\(\sim 2 \times 10^{19}\) SiH\textsubscript{4} 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 SiH\textsubscript{4} 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\textsuperscript{43} 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 SiH\textsubscript{4} 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 SiH\textsubscript{4} 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.\textsuperscript{42} Figure 7 demonstrates the size distribution of small Si-NCs as a function of SiH\textsubscript{4} 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 \(P_s = 0.2\) bar, we observed Si-NCs in the size range from 2.5 nm to almost 16.0 nm, however, at \(P_s = 2.0\) bar, the sizes were in the range from 2.0 nm to 6.0 nm.

FIG. 5. (a) Transmission electron microscopy images of large Si-NCs demonstrate a spherical morphology without and internal defects in the structures. Scale bar is 50 nm. High resolution transmission electron microscopy images of large Si-NCs in (b) and (c) demonstrate the monocrystalline morphology that indicates the primary growth mechanism was nucleation in ETP. Scale bars in (b) and (c) are 10 nm and 5 nm, respectively.

FIG. 6. Raman spectra of Si-NCs for different stagnation pressures in the gas line. The Raman peak position shifts to the lower wavenumbers with increasing stagnation pressure, indicating a decrease in the average size of the Si-NCs. Moreover, increased asymmetry of the line shapes, which is especially apparent for stagnation pressures of 1500 and 2000 millibars, indicates that a bimodal size distribution still exists. Inset shows the full scan.
nucleation and subsequent growth of these nuclei via SiH4 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 SiH4 available in the recirculation cells are sufficient for the nucleation and growth of nanocrystals via monomer addition up to hundreds of nanometers in size.

Figure 8 shows that higher stagnation pressures on the SiH4 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 SiH4 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 nanostructures (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 monocristalline 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 ~1500 (at the position of the injection ring) to ~400 K in the vicinity of the substrate and in the recirculation zones. 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 SiH4 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 SiH4 available in the recirculation cells are sufficient for the nucleation and growth of nanocrystals via monomer addition up to hundreds of nanometers in size.

Another remarkable observation is the inverse relation between the amount of SiH4 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 $5.0 \times 10^{18}$ SiH4 molecules were injected, and 3.2 nm when $1.0 \times 10^{20}$ SiH4 molecules were injected in the downstream plasma. In addition, the volume fraction of small Si-NCs increase from ~60% to ~85% as the SiH4 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. 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. Higher local densities of SiH4 (i.e., higher stagnation pressure on the SiH4 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. 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 SiH$_4$ increases with stagnation pressure with a linear relationship. However, depletion of SiH$_4$ decreases from $\sim$80% to $\sim$40%. In other words, the absolute number of SiH$_4$ molecules also increases with stagnation pressure. If SiH$_4$ molecules are consumed by addition reactions, the total surface area of Si-NCs should compensate for the available SiH$_4$ molecules. Considering $\sim$40 nm average size of large Si-NCs, and the volume fractions of 85% and 60%, respectively, the available surface area during the growth of 3.2 nm Si-NCs was 2.4 times larger than that of 6.3 nm Si-NCs. This observation indeed indicates that addition reactions of SiH$_4$ 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 SiH$_4$ injected downstream. In addition, the distribution shapes became less asymmetric when their widths became narrower. Observation of a finer size distribution is related to the nucleation time. We illustrate this with the following assumption:\footnote{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., lognormal 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 SiH$_4$ 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 SiH$_4$ 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 SiH$_4$ radical is 0.27–0.33 for $n = 3^{-10}$ and 0.35–0.40 for $n = 2$. For the polisilane 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 SiH$_4$ density ratio, $n_e/n_{SiH_4} < 10^{-3}–10^{-2}$, as mentioned earlier. This is observed at higher amount of SiH$_4$ injections. Indeed, increased surface area for SiH$_4$ addition, and linear dependency of SiH$_4$ 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 SiH$_4$ into the downstream region. First of all, with time modulation of the SiH$_4$ injection, we had a full control on the time, and the amount of SiH$_4$ molecules injected via varying the stagnation pressure with a linear relationship. However, depletion of SiH$_4$ becomes dominant over the radical creation rate if electron to SiH$_4$ density ratio, $n_e/n_{SiH_4} < 10^{-3}–10^{-2}$, as mentioned earlier. This is observed at higher amount of SiH$_4$ injections. Indeed, increased surface area for SiH$_4$ addition, and linear dependency of SiH$_4$ 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.

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 dendritc groups. Analyses on size distribution of small Si-NCs showed an inverse relation between the SiH$_4$ density and the final nanocrystal size under identical SiH$_4$ 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.

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