Synthesis and on-line size Control of 
Silicon Quantum Dots

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Abstract

The synthesis of silicon quantum dots is performed in the [3-5 nm] range using CO₂ laser pyrolysis of SiH₄. This size range is particularly relevant for potential applications in photovoltaic devices and biomedical imaging. The laser pyrolysis technique offers convenient control of the synthesis parameters in the case of nanoparticle production. However, controlling the size of small silicon objects remains difficult. The original approach consists here in a time-control of the energy injected into the reaction by gating the laser. The laser gate-on duration is adjusted in the range of 10 to 80 µs while keeping the average power constant. In parallel, supersonic expansion and on-line time-of-flight mass spectrometry are performed for on-line size characterization. A monotonic increase of the size as a function of the gate-on duration is observed for several SiH₄ volume concentrations. The results are discussed qualitatively.

Keywords: Gas-phase nanoparticle synthesis, silicon quantum dots, on-line size control, laser pyrolysis, aerosol characterization by TOF-MS

1. Introduction

Controlling the size of quantum dots is a key issue for applications requiring materials with precisely adjustable properties brought about by nanostructuration. A typical example is the case of Silicon Quantum Dots (Si-QDs), which exhibit strong size-dependent properties. Various applications are expected in different domains including optical and electronic devices, photovoltaic solar cells and markers for in vivo biological structures imaging. The band gap can be adjusted as a function of the size below 8 nm according to the quantum confinement model prediction, which correctly fits the experimental observations for sizes down to about 3 nm. In addition, in the case of silicon, the spatial confinement of the exciton induced by an incident UV photon leads to an efficient photoluminescence (PL) of surface-passivated Si-QDs at room temperature.

Most of the applications require sufficient quantities (more than a few hundred mg) of small and high-quality Si-QDs in terms of purity, average size control and size distribution. CO₂ laser-driven pyrolysis is an efficient method to synthesize various high-purity nanopowders, oxides and non-oxides, in a gas-phase bottom-up approach. It has been proven to be an efficient way to synthesize and deposit photoluminescent Si-QDs using a nanosecond-pulsed CO₂ laser. It was recently found that this method could be optimized for relatively large production rates of small Si-QDs using a microsecond-gated CO₂ laser. However, as their properties change rapidly as a function of their size, a precise control at the synthesis stage and on-line diagnostics are needed for specific applications. The aim of the present paper is to investigate the ability of a gated CO₂ laser, in combination with Time-of-Flight Mass Spectrometry (TOF-MS), to control the size of Si-QDs on-line. The idea is to gain better control over the growth of nanoparticles by varying the amount of energy available for the reaction in time.

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The laser pyrolysis method

Laser pyrolysis, also called Laser Chemical Vapor Pyrolysis (LaCVP), is a gas-phase process first introduced in 1982\(^{10}\). It is currently used for the synthesis of various kinds of nanoparticles\(^7\). It is based on the resonance between the emission of a laser, usually a CO\(_2\) laser at 10.6 µm, and the absorption by a gaseous (or liquid) precursor molecule. In this thermal process, the CO\(_2\) laser is used as a spatially well-defined and easily adjustable heat source allowing collision-induced decomposition of precursor molecules. The pyrolysis mechanism at the microscopic level was detailed earlier\(^{11, 12}\). Experimental descriptions are given elsewhere\(^7, 10\). A significant improvement and upscaling of the technique was recently proposed\(^{12}\). Briefly, the precursor’s flow, guided by a coaxial inert gas flow, intersects the laser beam orthogonally in a reaction chamber kept under controlled pressure. The temperature increases rapidly in the laser-crossing region. If the particle formation temperature is reached, nucleation occurs from dissociated species and particles grow rapidly. The reaction zone shows a luminescent flame originated by the thermal emission of the particles and possible emission contributions from excited radicals. The confinement by the inert gas flow avoids any reaction with the chamber walls and thus prevents particles from contamination.

Studies on the dynamics of particle formation by gas-phase processes were carried out\(^4, 10\). The thermal decomposition of SiH\(_4\) was studied experimentally and numerically\(^{16, 17}\). In the pyrolysis process, nucleation occurs when the dissociation temperature threshold of precursor molecules is reached. Particles then grow either by coagulation of nuclei and atom addition to their surface induced by vapor condensation in a supersaturated environment\(^4\), or by chemical heterogeneous reactions on their surface\(^{19}\). A second step of coagulation between grown particles may occur after the first primary particle growth step. In that case, a second growth mechanism occurs by melted particle-particle collision or by solid-state diffusion between two hot solid particles. This leads to relatively large and non-agglomerated particles. If the reaction temperature is relatively low, or if it drops quite rapidly after the first growth process, then primary particles may only agglomerate or aggregate in larger fractal-like objects\(^{20, 21}\). The growth process, the primary particle size and phase, plus the structure and size of agglomerates, are the consequence of the reaction temperature history. In the laser pyrolysis process, controlling the synthesis parameters, such as precursor molecules flow, pressure in the reaction chamber and laser power and focusing, provide the opportunity, to a large extent, of controlling the temperature history. Instantaneous temperature at a point of the reaction zone is the result of a balance between the heat generated by absorption of the laser radiation and the cooling brought about by radiation from hot particles and gas diffusion. In some cases, energy release or absorption by chemical reactions may also play a significant role.

In addition to these usual parameters, it is possible to dilute the reactant precursor flow. Simple dilution in an inert gas flow induces different changes in the reaction zone. First, if the amount of reacting precursor molecules is kept constant, the total gas flow is increased, leading to a decrease of the residence time in the laser zone and thus to a decrease of the reaction duration and temperature. Second, if the total flow rate is kept constant, the dilution gas acts as a thermal bath. The collision frequency between dissociated species is lowered, as the partial pressure of reactant molecules is smaller. The energy in the reaction is also decreased because of less absorption of the laser radiation. The balance tilts in favor of the cooling process. Furthermore, the cooling rate of the reaction can be increased by making a careful choice of the thermophysical properties of the diluting gas. The diffusion coefficient of He in gases is more than 3 times higher than that of Ar\(^{20}\). It is 0.617 cm\(^2\)/s for He at room temperature. In addition, the thermal conductivity of He is about a factor of 10 higher than that of Ar\(^{22}\). It is 156 mW/m.K for He at room temperature. It is then a good candidate for accelerating the growth quench of Si-QDs.

3. Experimental set-up optimization

The basic pyrolysis reactor was upgraded by instrumentation and equipment that provide on-line characterization of the particles size (see Fig. 1), aiming at an optimization for small Si-QDs synthesis. It is composed of three vacuum chambers. The first one is a source chamber that includes the pyrolysis reactor. The second one is an on-line film deposition chamber and the third one is a TOF-MS chamber. Previous work\(^{20}\) inspired the general configuration of this set-up.

3.1 Source chamber design

The synthesis itself takes place in the flow reactor placed in the source chamber as shown in Fig. 1. The precursor molecule is SiH\(_4\), which is a very ef-
ficient absorber of the 10.6 µm wavelength radiation used here. SiH₄ is diluted in He. The volume concentration of SiH₄ is set at several fixed values from 3.2% to 9.6%. It is introduced into the flow reactor from the bottom. The laser is focused and crosses the precursor flow at 90 degrees above the injection nozzle. The pressure in the flow reactor is set at 200 mbar in order to minimize the growth rate. It is maintained constant with the help of an electronically controlled valve and a closed-loop system. The pressure in the source chamber is set at 10⁻³ mbar with a turbo-molecular pump (TMP). A fraction of the Si-QDs flow is collected on a filter placed downstream in the pumping line on the top of the flow reactor. The remaining fraction is extracted horizontally through a skimmer-shaped extraction nozzle by the pressure difference between the flow reactor and the source chamber. The extraction nozzle axis is placed orthogonally with respect to the gas flow. Its aperture is positioned at 5 to 10 millimeters above the top of the pyrolysis flame (see Fig. 1). A supersonic beam of gas carrying the Si-QDs is then formed with a second differential pumping system through a skimmer between the source chamber and the deposition chamber.

3.2 Deposition process

The pressure in the deposition chamber is 10⁻⁵ mbar so that nanostructured films can be prepared by deposition of particles carried by the supersonic gas jet. It is simply achieved by introducing a substrate on the sample holder in front of the jet. With a 10-mm deposition spot diameter, a routine deposition rate around 12 nm/min is observed during more than 4 hours. Fig. 2 shows Scanning Electron Microscopy (SEM) micrographs of a nanostructured film realized by the deposition of 4 nm Si-QDs on a quartz substrate. The experimental settings correspond to those given in section 3.5. The laser is used in the gated mode (Tₜₐₜ = 20 µs, duty cycle = 0.2) detailed in section 3.5. The average power is 400 W. The total flow rate is 0.64 l/min. The SiH₄ volume concentration in He is 7.2%. The film thickness is about 180 nm for 15 min. continuous wave operation. Fig. 2(a) is an edge view of the nanostructured film and Fig. 2(b) is a normal to surface view. It illustrates the porous feature of the layer. The deposition rate is measured with a calibrated quartz crystal microbalance Maxtek model TM-200 that can be introduced into the particle beam during the deposition process. This instrument measures a mass deposited on a known area by measuring the change in frequency of a quartz crystal resonator. The calibration is realized by measuring the thickness of a film deposited during a determined time by SEM. With a deposition rate of 12 nm/min., a film porosity of 70% was estimated by the quartz crystal microbalance calibrated with bulk silicon data. This value is comparable to measured values reported elsewhere.

If only dry powder is needed, the extraction nozzle can be removed, so that the total particle production is collected on the filter. In both cases, Transmission Electron Microscopy (TEM) analyses are carried out with the help of a fast sampling system (see Fig. 1). This system allows deposition on TEM grids exposed...
to the aerosol flow during very short times (down to 30 ms) by fast translation of a pneumatic cylinder. It allows direct analysis of the shape and morphology of agglomerates from the gas phase.

3.3 Laser beam spatial management

The laser focusing spot is 0.5 mm high and 3 mm wide. The height is as short as possible in order to limit the reaction time while the width is chosen large enough to maintain a good overlap with the reactant gas flow. Reactant molecules flow out from the 2-mm circular injection nozzle. The spatial shaping of the laser spot is realized with the help of a tandem cylindrical lens system illustrated in Fig. 3. Both lenses have a focal length of 500 mm. The first lens focuses in the vertical direction, and is placed at 500 mm from the reaction zone. The second lens focuses in the horizontal direction, and is placed at an adjustable distance from the reaction zone. An elliptical and width-adjustable spot is obtained in the reaction region. This allows short growth times and high production rates of small particles. With the extraction nozzle removed, a typical production rate of 300 mg/h is achieved for 4-nm Si-QDs. The production rate can be dramatically increased when larger sizes are needed. Larger sizes are obtained by increasing the vapor pressure of dissociated species. It is achieved, for example, by increasing the laser average power.

Fig. 2 Scanning electron micrographs of a Si-QDs-based film on a quartz substrate. The edge view (a) shows the film thickness. The normal to surface view (b) illustrates its nanostructured porous feature.
by decreasing the absolute precursor flow rate or by increasing the SiH₄ volume concentration. For example, a production rate for 9.5-nm Si-QDs about ten times larger than that for 4.2 nm Si-QDs was observed earlier⁹. The distance between the nozzle end and the laser spot horizontal axis is chosen at 2.5 mm with the help of computational fluid dynamics investigations (see below).

### 3.4 Aerodynamic flow modelling

We performed simple 3-dimensional (3D) aerodynamic flow modeling illustrated in Fig. 4. The calculations were carried out with commercial software FLOW-EFD V5 and took into account the true 3D geometry of the flow reactor, as well as the actual initial conditions (pressure, respective volume flows) and gas characteristics. Fig. 4(a) is a 2-dimensional (2D) velocity map in the vertical plane along the injection axis. The scale is limited to the 0 – 2 m/s range for a better visualization in the laser reaction zone. The injection gas tube provides diluted reactant molecules to the flow reactor. A second 10-mm diameter tube for argon coaxial flow surrounds it. The total flow (He + SiH₄) in the 2-mm inner diameter injection nozzle is 0.64 l/min. The coaxial argon flow is 1.74 l/min. The SiH₄ volume concentration in He is 7% in these calculations. Reactant and coaxial flows are numerically optimized in order to obtain a laminar, well-confined and smooth flow rate in the laser interaction region.

These calculations are in good agreement with experimental observations. Fig. 4(c) shows the velocity profile along the injection axis. The maximum velocity in the reactant injection tube is more than 6 m/s, although the average velocity is around 3.4 m/s in this region. This is due to friction on the inner wall and to the small dimensions of the injection tube. It causes an important radial velocity gradient in the tube. The consequence is an important and fast drop of the longitudinal velocity at the entrance of the flow reactor that even begins before the nozzle end. The distance between the laser position and the nozzle end is chosen at 2.5 mm in order to have the interaction region in a smoother longitudinal velocity zone while the SiH₄ volume fraction is still high. This distance should be kept constant from one experiment to another. It is checked by a digital camera (Basler A102) equipped with high magnification collection optics that images the interaction region.

The calculated gas velocity profile in the laser horizontal plane is given in Fig. 4(b). The minimum velocity is less than 0.6 m/s on the sides, the maximum is close to 1 m/s on the axis and the average velocity is 0.78 m/s. Considering this calculated result and the 0.5-mm-high laser beam, the average residence time of reactant molecules in the laser region is about 640 µs.
3.5 Laser beam temporal management

The CO\textsubscript{2} laser used for this work is a Trumpf TLF 2400. It provides up to 2400 W output power and delivers either a Continuous Wave (CW) radiation or a time-gated one. The gate-on duration control \( T_{\text{on}} \) is adjustable from 10 µs to continuous. The gate-off duration control \( T_{\text{off}} \) is adjustable from 40 µs. However, the true temporal power profile is significantly different from the gate control. Different temporal profiles of the laser output power are given from the supplier and reported in Fig. 5 for \( T_{\text{on}} = 10, 20 \) and 50 µs. The duty cycle control \( T_{\text{on}}/(T_{\text{on}}+T_{\text{off}}) \) is kept constant and equal to 0.2, so that \( T_{\text{off}} \) is adjusted proportionally. The maximum power and the power rise time increase as a function of \( T_{\text{on}} \). For example, for \( T_{\text{on}} = 20 \) µs, the maximum power (arbitrary units) and power rise time are 0.54 and 18.5 µs, respectively. For \( T_{\text{on}} = 50 \) µs, the corresponding values are 0.70 and 47 µs, respectively. The fall time appears to be also slightly dependent on \( T_{\text{on}} \). It can be as long as 160 µs for very large \( T_{\text{on}} \) (not shown in Fig. 5). Longer \( T_{\text{on}} \) inevitably induces greater maximum power. In spite of this, the average output power delivered by the laser at the reaction point, measured with the help of a classic water-cooled calorimeter Coherent model LM-2500, is approximately constant (400 W in this case) if the duty cycle control is constant.

Fig. 4 Aerodynamic modelling of the gas injection region in the laser pyrolysis flow reactor. 2D velocity map in the vertical plane (a), longitudinal velocity profile in the laser position horizontal plane (b), and longitudinal velocity profile along the gas injection axis (c).
3.6 On-line size measurement by TOF-MS

TOF-MS is used for on-line size characterization of the synthesized particles. The ionization is performed by an Nd:YAG laser at 266 nm wavelength. The ionized part of the particle beam is slightly deflected after acceleration with the help of polarized deflection plates in order to avoid deposition of the neutral component on the micro-channel plate (MCP) detector (see Fig. 1). The TOF spectra show two separated components. The first component is related to Si$_n$ peaks ($n = 1 - 12$), which are ascribed to fragments formed from small nanoparticles during the ionization step, as reported elsewhere. The second is related to Si-QDs. The ionization laser intensity is kept sufficiently low to make sure that multi-photon induced multi-ionization processes can not occur so that the higher mass distribution is only related to singly charged nanoparticles.

The initial kinetic energy of neutral nanoparticles in the supersonic beam is not negligible when compared to the energy given by TOF-MS acceleration potentials. Measurement of this initial kinetic energy is then necessary to establish a correct correspondence between time of flight and mass. It is achieved by deliberately changing the acceleration potentials of the spectrometer, so that the acceleration energy given to the ions is changed proportionally in the case of singly charged particles. We measure two most probable time-of-flights (time at maximum signal) $t_1$ and $t_2$, $t_1$ with the normal acceleration energy $U_1$, and $t_2$ with the modified acceleration energy $U_2$. It is then easy to retrieve the initial kinetic energy using the classic TOF-MS equations. Considering that the acceleration time is small compared to the total time of flight for very high masses, the simple following expression of the most probable initial kinetic energy $K_{E0}$ is deduced:

$$K_{E0} = \frac{(t_1^2 U_1 - t_2^2 U_2)}{(t_2^2 - t_1^2)}$$

(1)

Fig. 6 shows an example with two mass spectra for different acceleration energy conditions. In the first one (solid line), $U_1 = 1.9$ keV. In the second one (dotted line), $U_2 = 0.95$ keV. The deduced average initial kinetic energy from equation (1) is 1.4 keV. This high value is due to the dense and high-speed supersonic...
gas beam that carries the particles. $K_{0}$ is then introduced into TOF-MS equations to obtain the most probable size corresponding to $t_{1}$. In this example, the most probable size of the Si-QDs is 4 nm. Size measurements by TOF-MS, taking into account the initial kinetic energy, are in good agreement at 4 nm with high-resolution TEM observations of a TEM grid exposed to the supersonic jet during a few seconds.

The signal intensity is less in the lower acceleration energy case in Fig. 6. We assume it is due to the lower detection efficiency of MCP when the incoming ion speed decreases.

4. Characteristics of the synthesized Si nano-crystals

4.1 Comparison between CW and gated laser modes

In order to evaluate the interest of the gated-mode of the laser in terms of quality of products, a comparison between nanoparticles obtained in the CW beam mode and some obtained in the gated beam mode is proposed. In both cases, other synthesis parameters are similar, and the laser average power is about 660 W. SiH₄ is highly diluted in He (SiH₄ volume concentration about 7%), and the reactant total flow is 0.64 l/min. The laser beam focusing conditions are the ones presented in the experimental optimization part. Fig. 7 shows TEM micrographs in each mode (CW mode on the left; gated mode on the right) and the corresponding primary particle size distributions obtained by software analysis of 50 particles for each representative TEM micrograph. The software is Image J (open source). The particle size can be visualized by the outer lines drawn around two particles on each micrograph. The primary particle size and morphology of agglomerates can be compared with the same scale in both modes.

In the CW mode, the minimum average primary particle size we are able to reach is about 8 nm, even in this optimized parameter regime for the production of small particles. The average size of the primary particles is 8.3 nm and the sample standard deviation is 1.3 nm. Particles are partially sintered in a strongly agglomerated form. Agglomerates are quite compact. The laser CW mode is well-suited to the synthesis of high quantities of Si nanocrystals, but the size range available is still too high to observe significant quantum confinement. In addition, control of the average size of small primary particles in this mode is not precise.

Typical particles produced in the gated laser mode are shown on the right TEM micrograph of Fig. 7.
The corresponding primary particle size distribution is given. In this experiment, the gate-on duration was 50 μs and the duty cycle was 0.33. These conditions appeared to be suitable for a relatively high production rate (400 mg/h) of highly crystalline Si-QDs. The average size is 6.6 nm and the sample standard deviation is 0.9 nm. Particles are still highly agglomerated. Fig. 7 (right TEM micrograph) clearly shows that they are more individualized. Moreover, the size distribution is narrower. These particles were found to be adequate as a starting material for biomedical imaging applications, for which a photoluminescence maximum is needed in the near infrared. The final material is obtained by chemical post-treatment and functionalization.

4.2 Controlling the size of Si-QDs

The influence of the CO₂ laser gate-on duration control $T_{on}$ on the Si-QDs size is studied for $T_{on}$ values in the 10 to 80 μs range, with a constant duty cycle of 0.2 and with different SiH₄ volume concentrations $C_{SiH_4}$. The Si-QDs most probable sizes are deduced from the TOF spectra taking into account the initial kinetic energy for each measurement point. Si-QDs agglomerates may be present in the supersonic beam as well as individualized primary particles. We assume that the detected particles are initially individualized primary particles or primary particles from agglomerates that are separated at the ionization stage in the TOF mass spectrometer. As the mass of agglomerates is too high to be detected, it is not possible to measure their size by TOF-MS.
Si-QDs most probable size as a function of the laser gate-on duration control $T_{on}$ for different values of SiH$_4$ volume concentration $C_{SiH4}$ and for a constant duty cycle $T_{on}/(T_{on} + T_{off}) = 0.2$. Size increases monotonically with the laser gate-on duration at a constant laser average power for a given $C_{SiH4}$.

Si-QDs most probable size as a function of $T_{on}$ is plotted in Fig. 8 for four different $C_{SiH4}$ values: 3.2%, 5.6%, 7.2% and 9.6% with a constant total flow rate. As expected, we observe a significant increase of the production rate when $C_{SiH4}$ increases. For $C_{SiH4} = 3.2\%$, only one point is recorded at $T_{on} = 80$ µs because no signal was detectable for lower values. We have an equivalent observation for $C_{SiH4} = 5.6\%$ for $T_{on}$ values lower than 30 µs. For $C_{SiH4} = 9.6\%$, it was not possible to record data for $T_{on}$ values above 30 µs because of the extraction nozzle clogging in these high production rate regimes. In addition, for the measurement points reported in Fig. 8, important signal amplitude fluctuations are experimentally observed in TOF-MS spectra with this high volume concentration. We assume it is due to intermittent and partial obstruction of the extraction nozzle. The size measurement may then present significant errors caused by erratic fluctuations in the particles’ kinetic energy in the supersonic beam. The absolute values obtained with $C_{SiH4} = 9.6\%$ in Fig. 8 should be treated with caution.

The size distribution width is not strictly deducible from the TOF-MS spectra because the initial kinetic energy is slightly dependent on the size (see experimental part). Nevertheless, the size distribution width is included in $\pm 15\%$ (FWHM) of the most probable size. This value is usually observed in laser-pyrolysis-produced nanopowders and is in good statistic agreement with HRTEM observations of 4-nm-sized Si-QDs. The error bars are related to the uncertainty on the most probable size determination by the TOF-MS and the analyzing process. It is estimated at $\pm 5\%$ of the most probable size, based on the uncertainty on the determination of the most probable time of flight and the initial kinetic energy measurement. This uncertainty should not be confused with the size distribution.

5. Discussion

5.1 Laser gate-on duration effect

For a given SiH$_4$ volume concentration and with a constant duty cycle, a monotonic increase of Si-QDs size as a function of $T_{on}$ is observed (Fig. 8). The first steps of nucleation involve numerous physical and chemical processes detailed elsewhere. If the nucleation threshold temperature is reached in given conditions of pressure and dilution, nucleation starts and growth occurs rapidly. The thermal decomposition of silane was studied in the range of 100 ppm...
to 10% volume fraction in different carrier gases\textsuperscript{27).}

Limited in He or in Ar, the particle formation threshold temperature was found to be between 770 K and 800 K for a volume concentration of SiH\textsubscript{4} in the 1 to 10% range. This threshold temperature is much lower than the melting point temperature of the bulk phase at 1687 K. If the temperature goes back below the threshold, the nucleation process stops by closing key physical and chemical pathways. Thus, growth can only occur by coagulation of particles, which leads to full coalescence in cases of liquid-liquid or liquid-solid particles collisions. It was shown that temperatures approaching the melting point of the bulk phase (1687 K) or higher are necessary to achieve full coalescence of previously grown solid crystallites of a few nm in size\textsuperscript{21).} At temperatures higher than 1687 K, particles are non-agglomerated single crystals with a quite large (a few tens of nm) diameter depending on the vapor pressure of the dissociated species. At temperatures lower than 1687 K, particles are either small (a few nm) agglomerated monocrystals, or non-agglomerated polycrystalline spherical particles resulting from the sintering of several primary particles. In our experimental conditions, particles are small (a few nm) and agglomerated, as shown in Fig. 7. Previous works showed that they were monocrystalline in similar synthesis conditions\textsuperscript{28).} Therefore, we assume that the maximum reaction temperature during gate-on slots in our case is between 770 K and 1687 K, and depends on \(T_{\text{on}}\). In these conditions, the size is essentially governed by two parameters, i.e. the reaction temperature and the reaction time. The reaction temperature is directly related to the SiH\textsubscript{4} dissociation efficiency, and thus to the vapor pressure of dissociated species. Higher temperature leads to higher vapor pressure, more nuclei and faster growth rate. For a given reaction time, a higher reaction temperature, corresponding to a higher laser power, leads to a larger Si-QDs diameter in the considered temperature range\textsuperscript{21).} The reaction time controls the nucleation duration while SiH\textsubscript{4} is not completely decomposed. In our experiment, the decomposed fraction of SiH\textsubscript{4} is 3% at most. The reaction time then controls both nucleation and growth durations. At a given temperature, a larger reaction time leads to a larger Si-QDs diameter. Considering the temporal profiles of the laser power given in Fig. 5, the maximum amplitude increases as a function of the gate-on duration \(T_{\text{on}}\). The direct expected consequence is a higher maximum reaction temperature with longer \(T_{\text{on}}\). Moreover, the total reaction time is the same for all values of \(T_{\text{on}}\). As the duty cycle is constant, the integrated time spent above the nucleation temperature threshold is about the same or slightly higher as a function of \(T_{\text{on}}\) during the total reaction time. It is then reasonable to think that the increase of Si-QDs size as a function of \(T_{\text{on}}\) is due primarily, to an increase of the average vapor pressure of dissociated species as a consequence of an increase in the maximum reaction temperature.

### 5.2 SiH\textsubscript{4} volume concentration effect

The dependence of the size of Si-QDs as a function of \(C_{\text{SiH4}}\) has already been reported by other authors\textsuperscript{29).} For a given gate-on duration, sizes are smaller as the \(C_{\text{SiH4}}\) decreases. For example, for \(T_{\text{on}} = 80 \mu s\), sizes are 5.3, 5.0 and 4.6 nm for \(C_{\text{SiH4}} = 7.2\%\), 5.6\% and 3.2\%, respectively. This is explained by lower laser absorption and a lower average collision rate between dissociated species when increasing SiH\textsubscript{4} dilution. Furthermore, for \(C_{\text{SiH4}} = 3.2\%\), no signal is detected below \(T_{\text{on}} = 80 \mu s\), and for \(C_{\text{SiH4}} = 5.6\%\), below \(T_{\text{on}} = 30 \mu s\). Increasing the dilution is equivalent to lowering the heating rate of the reaction which results in lowering the growth time. In addition, it has been shown that the threshold temperature for nucleation was dependent on the SiH\textsubscript{4} volume concentration\textsuperscript{27).} More highly diluted SiH\textsubscript{4} needs higher temperatures for particles formation. This explains why it is difficult to reach very small sizes with small \(C_{\text{SiH4}}\). In this case, the minimum temperature for nucleation onset is too high to be reached with small values of \(T_{\text{on}}\). It results in a limitation for lower \(C_{\text{SiH4}}\) to reach very small sizes. This introduces the idea of an optimum in SiH\textsubscript{4} volume concentration. In our experiment, this optimum is around 7\%, where a minimum probable size of 3.3 nm is obtained. However, the use of a higher volume concentration is limited by our experimental set-up due to the high production rate that induces clogging of the extraction nozzle. For \(C_{\text{SiH4}} = 7.2\%\), a simple visual guide suggests in Fig. 8 that the size can be controlled precisely between 3.3 and 5.3 nm by adjusting \(T_{\text{on}}\) with a constant duty cycle. This observation could be of importance for applications depending on the changing properties of Si-QDs in this size range.

### 6. Conclusion

Applications in various fields need large quantities of size-controlled Si-QDs. The CO\textsubscript{2} gated laser-driven pyrolysis of SiH\textsubscript{4} can provide a precise size control in the relevant range by adjusting the laser gate-on duration with a constant average power and on-
light TOF-MS. The size evolution as a function of $T_m$ and SiH$_4$ volume concentration in He is qualitatively discussed. We assume that the maximum reaction temperature reached during the laser gate-on slots mostly controls the Si-QDs size. This means controlling the average vapour pressure of the dissociated species in the reaction zone. In a more general consideration, controlling the time and amplitude of the input energy in the reaction zone should be convenient when small particles with a precise size control are difficult to obtain by other means.

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