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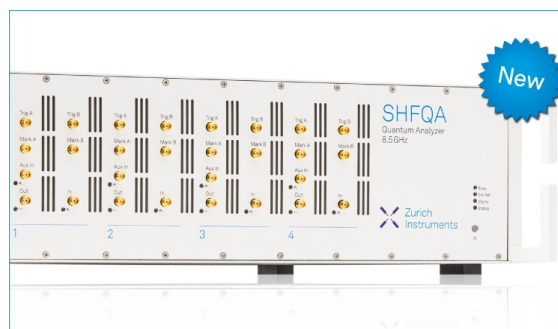
Surface fluxes of Si and C adatoms at initial growth stages of SiC quantum dots

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Self-assembly of highly stoichiometric SiC quantum dots still remains a major challenge for the gas/plasma-based nanodot synthesis. By means of a multiscale hybrid numerical simulation of the initial stage (0.1–2.5 s into the process) of deposition of SiC/Si(100)quantum dot nuclei, it is shown that equal Si and k_{st} atom deposition fluxes result in strong nonstoichiometric nanodot composition due to very different surface fluxes of Si and C adatoms to the quantum dots. At this stage, the surface fluxes of Si and C adatoms to SiC nanodots can be effectively controlled by manipulating the Si/C atom influx ratio and the Si(100)surface temperature. It is demonstrated that at a surface temperature of 800 K the surface fluxes can be equalized after only 0.05 s into the process; however, it takes more then 1 s at a surface temperature of 600 K. Based on the results of this study, effective strategies to maintain a stoichiometric ([Si]/[C]=1:1) elemental ratio during the initial stages of deposition of SiC/Si(100) quantum dot nuclei in a neutral/ionized gas-based process are proposed. © 2007 American Institute of Physics. [DOI: 10.1063/1.2433752]

I. INTRODUCTION

Nanostructured silicon carbide is a very promising material due to its many favorable characteristics such as resistance to corrosion and thermal shock, robust chemical, thermal and mechanical properties, high elastic modulus, specific stiffness, and fracture toughness.[1–9] These properties make it an ideal candidate for use in high-temperature, high-voltage, and chemically reactive environments.[7] Such strength and stability also lead to application of *a*-SiC in molecular sieves for high-temperature gas separation.[10] Presently, there is great excitement[8,11–13] regarding the wide band gap and photoemission properties of nanostructured SiC. This gap lends itself to blue light emission, which has recently been the subject of extensive research endeavors. Enhanced field emission from SiC capped Si nanotip arrays has also been noted as very promising for field emission displays.[14] Furthermore, SiC is not only of interest in optoelectronics but is also an important material in the burgeoning field of bionanotechnology. Utilization of SiC quantum dots as nanostructured labels of biological material is an example of one of the applications of the biocompatibility of SiC.[12] Studies show that both surface structure and composition play a crucial role in determining the stability and optical properties of SiC quantum dot arrays.[12]

Different approaches to fabrication of nanostructured SiC films have been put forward[9,15]; however, reliable and robust methods for fabrication of stoichiometric and hydrogen-free SiC quantum dots and associated nanopatterns are still in their infancy. While some methods make it possible to achieve fairly stoichiometric SiC thin films,[9,16] such films are in most cases hydrogenated. Achieving a 1:1 ratio of Si to C without any hydrogen, in the case of SiC/Si quan-

tum dots (QDs), is inherently more difficult. Moreover, this elemental ratio is required throughout the entire quantum dot structure, from the internal core to the outer shell. Unfortunately, it presently appears quite challenging, if possible at all, to control and characterize the elemental composition of ultrasmall nano-objects.[17–19]

The difficulty in obtaining stoichiometric SiC QDs is ultimately due to the fact that it is a complex binary system and thus more complex and harder to control than Si/SiC,[20] Ge/Si(100),[21] or Ge/SiO$_2$.[22] Given that Si and C atoms are subject to different conditions on the surface (different characteristic energies, migration rates, etc.), great care must be taken, not only to deliver the right amount of each type of atom to the surface but also to use an appropriate substrate temperature as it will affect surface reaction rates. Moreover, because of their different behavior on the substrate (Si, for example is more likely to epitaxially recrystallize on a Si surface than C), it is difficult to separately control the delivery and incorporation of Si and C atoms into SiC QDs.

Ideally, the stoichiometry of a binary quantum dot should be controlled from the earliest possible growth stage, when the initial composition and structure of the QD nucleus effectively dictates its future evolution. In the case considered, controlling the balance between delivery and consumption of Si and C atoms ["building units" (BUs)][23] is clearly important when attempting to fabricate stoichiometric quantum dots. The delivery and relative amounts of Si and C on the substrate are determined by the precursor influx ratio $k_p = P_{Si}/P_C$, where P_{Si} and P_C are the incoming fluxes of Si and C atoms, respectively. On the other hand, the consumption of Si and C (e.g., by the quantum dot nuclei) depends on the number of BUs on the solid surface and surface conditions, such as the surface temperature and morphology. The surface temperature is clearly important, in part because it largely determines the rates of adatom migration about the surface.

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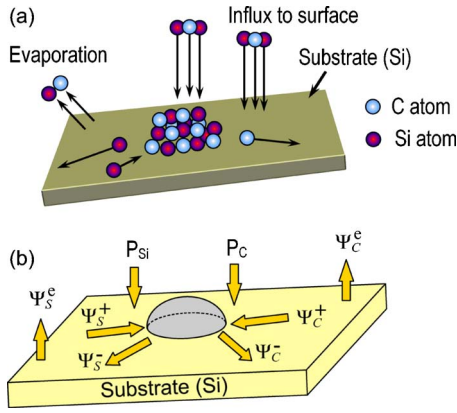
FIG. 1. (Color online) (a) Schematics of SiC QD growth on silicon surface and (b) atom/ion and adatom fluxes to/from the quantum dot.

This suggests that the precursor influx ratio and the substrate temperature would be the most effective controls to achieve a stoichiometric ($[Si]/[C]=1:1$) elemental ratio of Si and C on smooth silicon surfaces. We stress that existing numerical efforts on modeling quantum dot growth, while accounting for the effects of incoming fluxes and surface temperature, in most cases sidestep the important issue of the elemental composition and stoichiometry, which are essential for binary, ternary, etc., quantum dot systems.[24]

Here, we determine the conditions necessary to obtain stoichiometric SiC/Si(100) QDs at the initial stage of growth, by investigating the surface fluxes of Si and C adatoms to SiC QD nuclei (QDNs) consisting of 20 atoms or less. Our results suggest that the Si/C elemental ratio at the initial growth stage is time dependent and is controlled by the precursor influx ratio, deposition rate, and the substrate temperature. Intuitively, one would expect that by setting $k_p=1$, it might be possible to obtain stoichiometric SiC QDNs. However, as our simulation results suggest, this is not the case at the early stages of nanodot self-assembly when the core is formed. This article proposes various strategies aimed at achieving stoichiometric elemental ratios of Si and C in SiC quantum dot nuclei at the early stages of self-assembly. These approaches can also be applicable to other binary nanodot systems (e.g., GaAs, InP, InAs, self-assembled quantum dots).

The article is structured as follows. In the following section, we introduce the simulation geometry and numerical model of quantum dot growth in a neutral/ionized gas-based deposition process. In Sec. III, the results of the numerical study of the effect of various process parameters on the adatom surface fluxes and elemental composition of binary SiC nanodots are presented. Section IV is devoted to the discussion of the main results obtained and elaboration of the most efficient control strategies of the neutral/ionized gas-based nanofabrication of stoichiometric binary SiC quantum dot nuclei. Finally, in Sec. V, the main findings of this work are summarized and the outlook for future research is given.

II. MODEL AND NUMERICAL DETAILS

Figure 1(a) is a schematic representation of the simulation geometry of SiC quantum dot nuclei deposition in a neutral/ionized gas-based process. Silicon and carbon atoms/ions are delivered from the neutral/ionized gas phase and after becoming (charge neutral) adatoms on the substrate are redistributed about the Si(100)surface via surface diffusion processes. Depending on the surface temperature, the adatoms can also re-evaporate from the QD surfaces to the two-dimensional adatom field on the surface and/or back to the gas phase as shown in Fig. 1(a).

The QDN growth model implemented in this work is based on a set of species balance equations on the surface, which take the incoming fluxes from the gas phase into account. Such an approach has been widely used in surface science and is very suitable for describing the surface growth processes examined here.[25,26] In this case, an extended two-component (Si and C) system covering all the most important surface processes,[27] as sketched in Fig. 1(b), was used. The surface processes taken into account include atom attachment to and detachment from QDN surface borders, as well as atom evaporation from the substrate surface (Fig. 1). Clusters of two atoms and more are treated as immobile for the range of surface temperatures simulated. As can be seen in Fig. 1(b), the balance of adsorbed atoms (adatoms) takes into account the Si and C atom influx from the neutral/ionized gas phase $P^+=P_{Si}+P_C$, flux of Si and C atom evaporation from the substrate surface $\Psi^e=\Psi^e_S+\Psi^e_C$, flux of Si and C adatoms to the QDN $\Psi^+=\Psi^+_S+\Psi^+_C$, and flux of Si and C adatoms from the QDN $\Psi^-=\Psi^-_S+\Psi^-_C$. Here, $k_{st}=\psi^+_S/\psi^+_C$ and P_C are the incoming Si and C fluxes to the solid surface, $\Psi^e_S=n_k\nu_0\exp(-\varepsilon_{a.S}/kT)$ and $\Psi^e_C=n_k\nu_0\exp(-\varepsilon_{a.C}/kT)$ are the fluxes of silicon and carbon evaporation, respectively; $\varepsilon_{a.S}$ and $\varepsilon_{a.C}$ are the silicon and carbon adatom evaporation energies, n_k is the adatom surface density, T is the substrate temperature, k is Boltzmann's constant, Ψ^+_S and (s) are the Si surface adatom fluxes to and from the QDN, respectively, Ψ^+_C and Ψ^-_C are defined similarly for carbon.

Thus, the balance equation for adatom density on substrate η_j is

$$\frac{\partial \eta_j}{\partial t} = P^+_j - \Psi^e_j - \Psi^+_j + \Psi^-_j, \qquad (1)$$

where the subscript j represents either Si or C.

The state of the substrate surface influences QD growth mainly via the adatom diffusion activation energy ε_d. In this work there was no simplifying assumption of a defect-free surface; instead, an experimental value for the silicon atom surface diffusion activation energy $\varepsilon_{d.S}$ was used, which took the energy of adatom detachment from the surface defects, steps, etc., into account.[28] Reliable experimental data for the carbon atom surface diffusion activation energy $\varepsilon_{d.C}$ are not available, it was assumed to be $\varepsilon_{d.C}=1/3\varepsilon_{b.C}$, where $\varepsilon_{b.C}$ is the energy of a carbon-silicon bond. A complete set of the rate equations for SiC QD formation incorporates two balance equations describing Si and C atoms on the substrate surface, as well as equations for the density of SiC quantum dots consisting of 2, 3, ..., i atoms. Thus, the balance equations for the C and Si atoms are

$$\frac{\partial \eta_S}{\partial t} = P_{Si} - \Psi_S^e + \sum_{i=2}^{\infty} n_{S.i} \eta_i \mu_{S.i} - \eta_S \sum_{i=2}^{\infty} \sigma_i \eta_i v_{d.S}$$

$$- 2\sigma_1 \eta_S^2 v_{d.S} - \sigma_1 \eta_S \eta_C v_{d.S}, \qquad (2)$$

$$\frac{\partial \eta_C}{\partial t} = P_C - \Psi_C^e + \sum_{i=2}^{\infty} n_{C.i} \eta_i \mu_{C.i} - \eta_C \sum_{i=2}^{\infty} \sigma_i \eta_i v_{d.C}$$

$$- 2\sigma_1 \eta_C^2 v_{d.C} - \sigma_1 \eta_S \eta_C v_{d.C}, \qquad (3)$$

where $n_{S.i}$ and $n_{C.i}$ are the numbers of Si and C atoms at the borders of the QDN consisting of i atoms; η_i is the surface density of (i)-atom QDN; $\mu_{S.i}$ and $\mu_{C.i}$ are the frequencies of Si and C atom re-evaporation from borders of (i)-atom QDN; σ_i is the diameter of (ML) QDN. Here

$$v_{d.S(C)} = \lambda \nu_0 \exp(-\varepsilon_{d.S(C)}/kT)$$

are the linear velocities of Si and C adatom movement about the substrate surface, where λ is the lattice constant of the Si(100)substrate and $\varepsilon_{d.S(C)}$ is the Si or C adatom surface diffusion activation energies. The first sum in Eqs. (2) and (3) represents the surface influx of Si and C adatoms to the substrate surface due to adatom re-evaporation; the second sum represents the adatom flux from the surface due to the attachment to the QDN consisting of two and more atoms. The remaining two terms denote the adatom outflux from the surface due to the adatom-adatom collisions which lead to the formation of two-atom QDN.

The rate equations for the formation of i-atom QDN include the same surface processes, and thus have the following form:

$$\frac{\partial \eta_i}{\partial t} = \sigma_{i-1} \eta_{i-1} (\eta_S v_{d.S} + \eta_C v_{d.C}) - \sigma_i \eta_i (\eta_S v_{d.S} + \eta_C v_{d.C})$$

$$+ \eta_{i+1} n_{i+1} (\mu_{S.(i+1)} + \mu_{C.(i+1)}) - \eta_i n_i (\mu_{S.i} + \mu_{C.i}), \qquad (4)$$

where the first term describes the Si and C adatom collisions with ($i-1$)-atom QDN; the second term stands for the Si and C adatom collisions with the (i)-atom QDN consisting of atoms; the third term is related to the Si and C adatom detachment from the QDN consisting of ($i+1$) atoms; and the fourth term represents Si and C adatom detachment from (i)-atom QDN. Evaporation and diffusion activation energies for the Si and C atoms, as well as the energies of the Si-Si and Si-C bonds have been calculated using standard bond enthalpies (except where noted otherwise). The specific values for all the parameters used in our computations are listed in Table I.

The ratio of silicon and carbon adatom fluxes to the borders of quantum dots (the adatom balance factor) is defined as $k_{st} = \Psi_S^+ / \Psi_C^+$. Using Eq. (4), one obtains

$$k_{st}(t) = \sum_{i=1}^{N} \zeta_{S.i}/\zeta_{C.i}, \qquad (5)$$

where

$$\zeta_{S.i} = \eta_S v_{d.S} \sigma_i \eta_i - \eta_i n_i \mu_{S.i},$$

TABLE I. Parameters and representative values of computations.

Parameter	Value	Ref.
Physical constants		
Lattice atom oscillation frequency, ν_0, s^{-1}	1×10^{13}	29
Lattice parameter, λ, m	5×10^{-10}	30
Si atom diffusion activation energy, $\epsilon_{d.S}$, eV	1.35	28
Si atom evaporation activation energy, $\epsilon_{a.S}$, eV	3.04	31
Si atom bonding energy, $\epsilon_{b.S}$, eV	2.3	31
C atom diffusion activation energy, $\epsilon_{d.C}$, eV	1.1	30
C atom evaporation activation energy, $\epsilon_{a.C}$, eV	4.8	31
C atom bonding energy, $\epsilon_{b.C}$, eV	3.6	31
Si-C bonding energy, $\epsilon_{b.S-C}$, eV	3.3	32
Parameters of simulation		
Influx to surface, P^+, monolayers·s^{-1}	0.001–0.1	
Surface coverage, η, monolayers	0–0.5	
Number of quantum dot nuclei in pattern, K	1000	
Maximum number of atoms in QDN, N	2–25	
Substrate surface temperature, T, K	500–850	
Time of deposition, t, s	0–3	
Influx ratio, $k_p = P_{Si}/P_C$	0–3	
Adatom balance factor, $k_{st} = \Psi_S^+/\Psi_C^+$	0–4	

$$\zeta_{C.i} = \eta_C v_{d.C} \sigma_i \eta_i - \eta_i n_i \mu_{C.i},$$

and N is the maximum number of atoms constituting the quantum dot nuclei. We emphasize that k_{st} is a differential ratio, i.e., it is computed at each instant and thus provides a time-dependent measure of the evolution of the QD composition and internal structure.

Numerical simulations have been conducted for different substrate surface temperatures T, deposition times t, and values of the precursor influx ratio k_p. Obtaining time-dependent behavior of the adatom balance factor k_{st} was the main objective of our investigation. In particular, we have studied the dependence of k_{st} on deposition time and the influx ratio factor with the surface temperature and deposition time as parameters.

III. RESULTS

In this section we consider the results of numerical simulation of silicon carbide quantum dot nuclei formation on a Si(100)surface. Let us first examine the dependence of the adatom balance factor k_{st} on time with the surface temperature and precursor influx ratio k_p as parameters (Figs. 2 and 3). The first important observation is that k_{st} starts from the zero point for all k_p values within the range of 0.2–4; thus the C adatom flux is much larger than the Si adatom flux at the beginning of the deposition process. The adatom balance factor k_{st} increases with time and eventually saturates at $k_p(k_{st} \rightarrow k_p)$ for longer deposition times. It is also notable that at higher k_p, k_{st} levels off more slowly. Indeed, at the same surface temperature $T=700$ K, the saturation level $k_{st}=k_p$ $=0.2$, is reached in 0.15 s whereas more than 1 s is required to reach $k_{st}=k_p=0.2$.

When the surface temperature increases, the k_{st} factor increases rapidly; it takes 2.5 s to reach $k_{st}=0.2$ at $k_p=0.2$ and $T=550$ K; however, the same process requires only 0.05 s at $T=800$ K. Therefore, clearly the general behavior of the
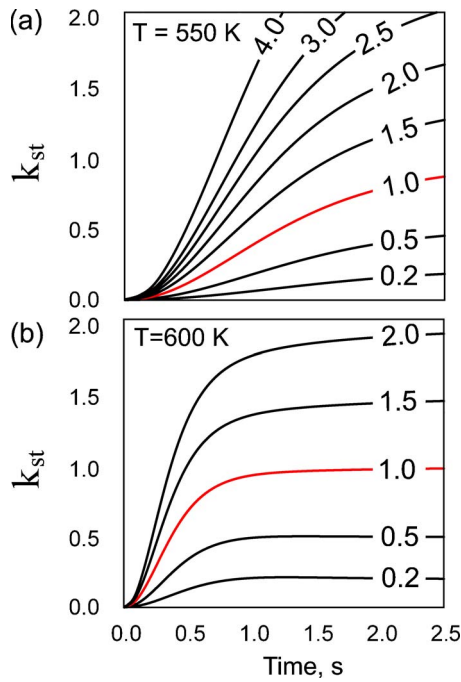
FIG. 2. (Color online) Dependence of adatom balance factor k_{st} on time with influx ratio k_p as a parameter, for the surface temperature $T=550$ (a) and 600 K (b).

adatom balance factor is also dependent on the surface temperature: k_{st} tends to the corresponding k_p value at lower temperatures (up to 700 K) but shows an oscillating behavior (exceeding a saturation level after the first rise followed by a decrease to the equilibrium level) at a temperature of 800 K as can be seen in Fig. 3(b).

Let us now consider the dependence of the adatom balance factor k_{st} on the influx ratio k_p with surface temperature and deposition time as parameters (Fig. 4). The general ten-
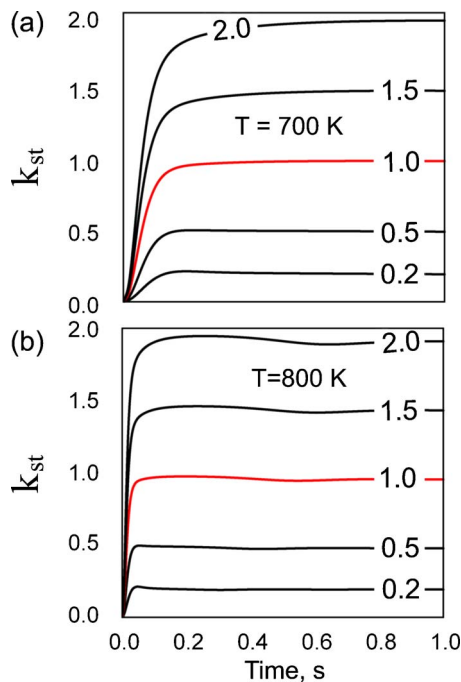

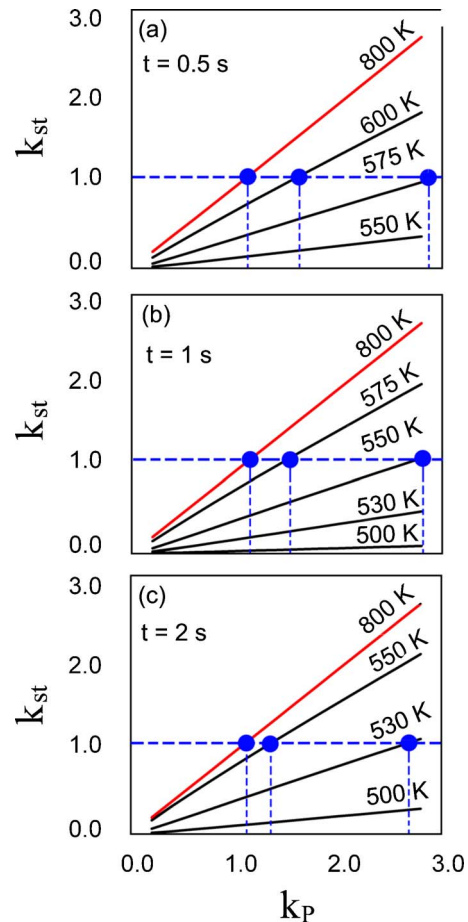FIG. 3. (Color online) Same as in Fig. 2 for the surface temperature T = 700 (a) and 800 K (b).

FIG. 4. (Color online) Dependence of adatom balance factor k_{st} on influx ratio k_p with surface temperature T as a parameter for a deposition time of 0.5 (a), 1.0 (b), and 2.0 s (c).

dency is that k_{st} increases with k_p. As can be seen from Fig. 4, when surface temperature decreases, k_{st} becomes smaller; this means there is a decreased influx of silicon adatoms to the QDN, compared to the carbon adatom influx. It is important to note that at surface temperatures equal to or exceeding 800 K, the saturation level $k_{st}=k_p$ is reached quickly (in less than 0.5 s); thus the upper red curve in Figs. 4(a)–4(c) is also the same for $T>800$ K. On the other hand, at lower surface temperatures (the range 500–600 K is shown in Fig. 4) the slope of the k_{st} versus k_p curves gradually increases with time; it takes longer to reach the saturation level at lower substrate temperatures.

Figure 5 shows the dependence of k_{st} on k_p with surface temperature as a parameter, for the invariable precursor influx ratio $k_p=1$.[33] Similar to Figs. 2 and 3, the k_{st} factor starts from the zero point at all temperatures. Therefore, at the beginning of the process, the carbon flux is much larger than that of silicon. Eventually, the adatom balance factor levels off at 1. This transition process typically lasts from 0.1 to 0.4 s at higher temperatures (650–800 K) and 1–5 s at temperatures below 600 K. It should be noted that the earlier dependencies have been calculated using a total atom influx P^+ of 0.1 ML/s.

To elucidate the influence of the total atom influx on the process, we have plotted the dependence of adatom balance factor k_{st} on influx ratio k_p with the total atom influx to
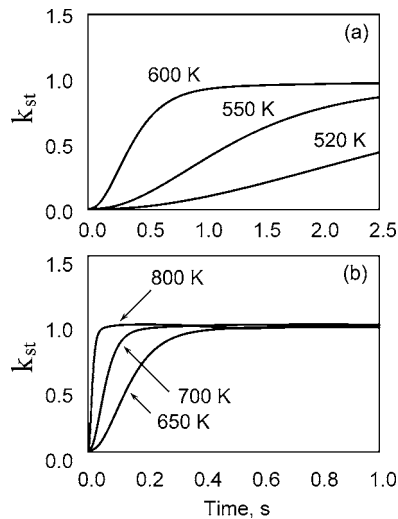
FIG. 5. Dependence of balance factor k_{st} on time with surface temperature T as a parameter for influx ratio $k_p=1$.

substrate surface as a parameter, for deposition time $t = 1.0$ s and surface temperature $T=600$ K (Fig. 6). From this figure it can be seen that the general behavior of the $k_{st}(k_p)$ curves is quite similar to that shown in Fig. 4. With the total influx equal to 0.1 ML/s, k_{st} is approximately equal to k_p for any k_p value. On the other hand, when the total influx is less than 0.1 ML/s (0.01 and 0.001 ML/s in this simulation), the k_{st} factor is much smaller than k_p; thus, the carbon adatom flux well exceeds the silicon adatom flux under lower deposition rate conditions.

IV. DISCUSSION

We recall that the subject of our study is the diffusion fluxes of carbon and silicon adatoms on the substrate surface at the initial stage of SiC QD formation. Apparently, the compositional structure of the quantum dots (crystalline structure, polytype, etc.) develops continuously, from the moment when the precursor species are let in to when the desired surface coverage (up to ~ 0.5 in this work) is achieved.[34]

Here, the dependence of the adatom balance factor k_{st} on the process parameters is studied with the aim of discovering the parameter range and conditions that provide stoichiometric QD composition and avoid unwanted QD formation from unbalanced ("nonstoichiometric") silicon and carbon
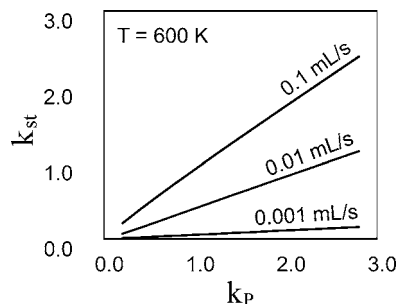

FIG. 6. Dependence of flux balance factor k_{st} on influx ratio k_p with the atom influx to substrate surface P^+ as a parameter. Time of deposition $t = 1.0$ s.

fluxes. The most important fact discovered is that, if one keeps the precursor influx ratio k_p constant at very early process stages, the ratio of surface fluxes of Si and C adatoms is time dependent, and, moreover, nonstoichiometric. As Figs. 2 and 3 show, the equilibrium level of the balance factor k_{st} can be reached after some time lag, ranging from 0.05 s to several seconds; this time lag depends on the surface temperature and the precursor influx ratio k_p.

Therefore, at early deposition stages it is not possible to synthesize stoichiometric SiC nanodot cores on a Si(100)surface by using time-invariable and equal fluxes of Si and C atoms or ions and special arrangements should be made to ensure that the surface fluxes of Si and C adatoms are properly balanced at every growth stage. In brief, this can be achieved by transiently increasing the surface temperature or silicon atom influx with respect to that of carbon. One more possibility would be to appropriately control the deposition rate P^+. Let us now re-examine the results shown in Figs. 2–6 and propose specific strategies to mediate the unwanted self-assembly of nonstoichiometric SiC quantum dot nuclei at initial growth stages.

Examining Figs. 2 and 3, one can conclude that at lower surface temperatures (550 and 600 K) and a "stoichiometric" ratio of Si and C atom fluxes to the surface [curves labeled "1.0" in Figs. 2(a) and 2(b))], the C adatom flux to the SiC quantum dots is almost twice as large as that of silicon adatoms during the first 0.5–1.0 s into the process. With a total influx of 0.1 ML/s, the total amount of deposited material in this time interval is $\sim 0.05-0.1$ ML. Under such conditions, QDN consisting of 10–20 atoms are formed by highly unbalanced fluxes of Si and C adatoms. As a result, the quantum dot nuclei will be rich in carbon with a strongly nonuniform elemental composition.

As Figs. 2 and 3 suggest, this effect is more pronounced at lower substrate temperatures. Thus, in low-temperature-demanding processes, such as polymer processing, one could expect highly nonstoichiometric (carbon-rich) SiC nanodot cores. At higher surface temperatures, this effect is less important, but still plays a role at $T=700$ K. However, when $T \geq 800$ K, the time required to reach the saturation level $k_{st}=k_p=1$ is less than 0.05 s. During this time, the total number of atoms deposited is $\sim 2 \times 10^{16}$ m^{-2}.

It is worth emphasizing that in this study we have focused on the process conditions when the precursor influx rate k_p does not change in time. It is clear that, if the re-evaporation of adatoms from the substrate surface and surfaces of quantum dots is low, the adatom balance factor k_{st} should eventually reach k_p as a result of species (mass) balance on the substrate surface. In the temperature range considered (from 500 to 800 K) the re-evaporation is low in terms of the ratio of the characteristic re-evaporation time to the characteristic diffusion time. Thus, the rate of the mass loss of the diffusing species from the substrate surface is low, and the precursor influx ratio should eventually equalize with the ratio of surface fluxes of Si and C adatoms. The time dependence of k_{st} can be attributed to different Si and C adatom mobilities on the surface, which depend strongly on the substrate temperature. Hence, the undesired growth of nonstoichiometric QDs is unavoidable when adatoms of dif-

ferent elements (with very different surface diffusion activation energies) are involved and their incoming fluxes are not properly balanced.

The results of our simulations yield process conditions that result in stoichiometric ($k_{st}=1$) surface fluxes of Si and C adatoms. One possible way to achieve this is to increase the surface temperature during the initial stage of deposition. Indeed, at higher surface temperatures the difference in the Si and C adatom mobilities decreases.[35]

Thus, one of the ways to mediate the effect of nonbalanced adatom fluxes at the initial stage of deposition is to transiently increase the surface temperature during the time required for deposition of a submonolayer of 0.05–0.1 ML. For example, the surface temperature can be transiently increased during the first 0.01–0.1 s by using energetic ion bombardment in a pulsed substrate bias regime. After the pulse is turned off, the excess energy accumulated in the superficial layer of the substrate will then be dissipated in the substrate material without any significant heating of the substrate. It is clear that this method requires the use of a plasma-based process and cannot be implemented in a neutral gas-based environment.

Another way to achieve stoichiometric adatom fluxes at the initial stage of SiC nanodot self-assembly is to use an increased influx ratio k_p during the first 0.01–0.1 s of the process. In this case, as can be seen in Fig. 2, the equilibrium value of the balance factor $k_{st}=1$ can be achieved much faster. Thereafter, the influx ratio $k_p=1$ should be used to maintain the stoichiometrical composition of the SiC QDs.

Thus, two-step strategies can be used to fabricate stoichiometric SiC/Si(100)quantum dots. Specifically, the deposition can first be conducted at a higher surface temperature or increased precursor influx ratio k_p. Upon achieving the adatom balance factor $k_{st}=1$, the process should be continued by using equal fluxes of silicon and carbon atoms. At this stage, T can also be lowered to the most suitable surface temperature, which can be determined from the conditions of QD crystallization and/or thermal stability of the substrate.

Figure 4 evidences that the two major control parameters, the surface temperature and the precursor influx ratio k_p are highly interdependent. It becomes apparent that at lower temperatures, fluxes with a higher k_p should be used, and vice versa. In practice, there is no need to increase both parameters simultaneously to the limit, as the results can best be achieved by an optimal combination of slightly increased T and k_p. A number of suitable process "working points" are mapped in Fig. 4 and can be chosen depending on specific requirements. For example, our target is to obtain stoichiometric Si and (s^{-1}) adatom fluxes after 1 s into the process. As follows from Fig. 4(b), one can use, e.g., the following three options: (i) at $T=800$ K, a stoichiometric precursor influx ($k_p=1$) can be used; (ii) at $T=575$ K, k_p should be ~1.3; and (iii) at $T=550$ K, k_p should be ~2.7. These combinations are different at other time moments and can easily be worked out by using the results in Fig. 4.

We stress that since in practice it is quite inconvenient and sometimes technically challenging to rapidly change the influx ratio k_p, a transient increase of the surface temperature can be very effective in maintaining the stoichiometric flux

condition $k_{st}=1$. This possibility is evidenced by the results in Fig. 5, which corresponds to the time-invariable precursor influx with $k_p=1$.

As discussed earlier, there is a requirement that the adatom balance factor levels off at $k_{st}=1$ as early as possible in order to ensure that the SiC quantum dots have equal amounts of Si and C atoms from the innermost volume of the dot to its outermost layers, and at all stages of the self-assembly. Thus, one more convenient way to speed up this process would naturally be to synthesize the nanodots faster, at higher deposition rates. As Fig. 6 suggests, higher deposition rates at a constant precursor influx ratio indeed result in faster stoichiometrization of the Si and C adatom fluxes. However, this important process parameter cannot be increased indefinitely since at $T=600$ K the equilibrium condition $k_{st}=k_p=1$ is reached almost instantaneously when the deposition rate is 0.1 ML/s, which is the upper practical limit of the adatom balance control on the surface. Moreover, very high deposition rates may lead to undesired formation of continuous films rather than nanodot arrays.

Thus, from the arlier practical considerations we would suggest that at a given deposition rate, a balanced combination of a transiently elevated surface temperature and increased delivery of silicon atoms (with respect to carbon) to the surface can be the best way to obtain stoichiometric composition of SiC quantum dot nuclei at the initial stage of their self-assembly.

However, it should be noted that higher substrate temperatures while improving not only the stoichiometry but also the crystallinity of SiC QDs may also dramatically restrict the range of substrate materials that can be used. For example, Polyethylene terephtalate (PET) and PET/silica nanocomposites, widely used in biomedical applications, have very low melting points ~540 K.[36] For these and similar easily fusible materials the best way to maintain the proper elemental composition of the SiC QDs is to use larger ratios (P_{Si}/P_C) of incoming fluxes of silicon and carbon BUs.

Therefore, determining the k_p factor for which the ratio of Si and C adatom fluxes to the growing quantum dots tends to be 1 at all deposition stages, and then establishing the minimum substrate temperature necessary to achieve acceptably stoichiometric dots throughout the entire structure is a viable approach to active dynamical control of the nanoassembly process. It is worthwhile to reiterate that such a process can be applicable to other binary QD systems such as GaAs/Si(100)and a variety of BU delivery methods such as molecular beam epitaxy, chemical vapor deposition, atomic deposition and plasma-based methods (plasma enhanced chemical vapor deposition, reactive magnetron sputtering, pulsed laser deposition, etc.[37–39]).

V. CONCLUSIONS AND OUTLOOK

In this article, the dependence of Si and C adatom fluxes to SiC quantum dots at the initial stage of self-assembly on a Si(100)surface has been studied numerically. It was demonstrated that, owing to the different surface mobilities of silicon and carbon adatoms on a Si substrate, the Si and C

adatom fluxes to the quantum dots are not equal even in the case when the Si and C influxes from the neutral/ionized gas to the substrate surface are equal. Thus, the deposition process conducted at the equal Si and C influxes to the surface will result in the undesired formation of nonstoichiometric SiC nanodots. Based on the results obtained, the following conclusions may help to improve the predictability and controllability of nanofabrication of highly-stoichiometric SiC quantum dots on Si(100) surface:

- the surface temperature and the ratio of Si and C atom/ion influxes to the substrate surface are the main factors that determine the time dependence of the ratios of Si and C adatom fluxes k_{st};
- the use of a transiently increased surface temperature results in a faster "stoichiometrization" of the Si and C adatom fluxes but may be restricted by the substrate and quantum dot material characteristics;
- correction of the Si and C influx ratio by increasing Si atom flux to the substrate for 0.1–1 s is very effective in maintaining the Si and C adatom fluxes ratio close to unity; and
- a balanced combination of the elevated substrate surface temperature and increased precursor influx ratio k_p at the initial stage of deposition should be considered as the most promising way to sustain self-assembly of highly-stoichiometric SiC quantum dot nuclei.

The main challenge for future work is to consider the possibility of using a time-variable ratio of incoming Si and C atom fluxes to obtain perfectly stoichiometric Si/C adatom flux ratio during the entire nanoassembly process and eventually achieve SiC/Si(100) quantum dot arrays with the required elemental composition.

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[34] The duration of this stage can be estimated $t = \theta/P^+$, where θ is the required surface coverage.

[35] It should be stressed that the surface temperature by itself does not influence the *equilibrium* quantum dot composition provided that adatom re-evaporation from the surface is weak enough. After a certain time lag (which depends on the process conditions), the elemental composition of the QDs reproduces that of the precursor influx. However, the nonequilibrium QD composition at the initial stage of deposition can significantly affect the nanodot structure at later growth stages.

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