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Increased size selectivity of Si quantum dots on SiC at low substrate temperatures: An ion-assisted self-organization approach


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A simple, effective, and innovative approach based on ion-assisted self-organization is proposed to synthesize size-selected Si quantum dots (QDs) on SiC substrates at low substrate temperatures. Using hybrid numerical simulations, the formation of Si QDs through a self-organization approach is investigated by taking into account two distinct cases of Si QD formation using the ionization energy approximation theory, which considers ionized in-fluxes containing Si1+ and Si2+ ions in the presence of a microscopic nonuniform electric field induced by a variable surface bias. The results show that the highest percentage of the surface coverage by 1 and 2 nm size-selected QDs was achieved using a bias of $-20$ V and ions in the lowest charge state, namely, Si1+ ions in a low substrate temperature range ($227–327$ °C). As low substrate temperatures ($=500$ °C) are desirable from a technological point of view, because (i) low-temperature deposition techniques are compatible with current thin-film Si-based solar cell fabrication and (ii) high processing temperatures can frequently cause damage to other components in electronic devices and destroy the tandem structure of Si QD-based third-generation solar cells, our results are highly relevant to the development of the third-generation all-Si tandem photovoltaic solar cells. © 2010 American Institute of Physics. [doi:10.1063/1.3284941]

I. INTRODUCTION

Recently, third-generation all-silicon (Si) tandem solar cells have attracted much attention due to the many advantages that they exhibit over conventional solar cells. The tandem cell structure acts as multiple photovoltaic cells connected in series, which provides higher open circuit voltages than conventional solar cells; this can be further enhanced by increasing the number of stacked cells. Moreover, the utilization of quantum dots (QDs) with different sizes in alternating layers, i.e., the top layers featuring smaller QDs (which will absorb higher-energy photons from the sunlight) while the lower layers feature progressively larger QDs (to absorb lower-energy photons), as illustrated in Fig. 1, is a key feature in third-generation all-Si tandem cells. Hence, one is able to use a wider range of the solar spectrum, resulting in the higher efficiencies and output voltages reported for third-generation photovoltaic devices compared to conventional solar cells.

Silicon is one of the best QD materials due to its high abundance and nontoxicity. The substrate material chosen for this paper is silicon carbide (SiC) due to its many benefits over other Si-based substrates such as Si$_3$N$_4$ or SiO$_2$. This is because the lower barrier height of SiC ($\sim 2.5$ eV) compared to SiO$_2$ ($\sim 9$ eV) or Si$_3$N$_4$ ($\sim 5.3$ eV) results in both better carrier transport property between the adjacent Si QDs due to an exponential increase in the tunneling probability of the carriers. In addition, more effective luminescence of Si QDs can be generated due to the strong overlap of electron-hole wave functions, which significantly enhances the radiative electron-hole recombination rates. As such, Si-based materials hold outstanding promise as the basis of renewable photovoltaic energy sources.

To realize all-Si tandem solar cells, the fabrication of alternating layers of size-uniform QDs (each individual layer contains QDs of a specific size) at low substrate temperatures is an important prerequisite. The conventional fabrication approach for such structures is to anneal alternating layers of near-stoichiometric (SiC$_{x}$SiO$_{2-x}$Si$_{3}$N$_{4}$) and nonstoichiometric [Si$_{1−x}$(C$_{y}$O$_{z}$N)$_{x}$] silicon-based materials. The QD size is controlled by the height of the layer. This approach provides quite limited QD size control and requires a very high-temperature range from 800 to 1000 °C, which hinders the path toward commercialization. Here, we propose an alternative approach that may ultimately be used to fabricate

![FIG. 1. (Color online) Schematic of the adopted self-organization model. The three main surface processes accounted for are adatom diffusion into the QD, 2D detachment from the QD, and 3D evaporation from the substrate. The ultimate goal here is to generate size-selective QD seed patterns suitable for eventual implementation in third-generation all-Si QD tandem solar cells.](Image 318x144 to 401x150)

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silicon-based QD tandem structures via layer-by-layer deposition and by utilizing self-organization processes, where one must be able to fabricate size-uniform/size-selected QDs at low substrate temperatures.

Previously, self-assembled QDs have been fabricated via the Staenski–Krastanov growth mode using neutral-gas-based techniques such as atomic beam deposition or molecular beam epitaxy.\textsuperscript{6} However, these techniques result in the formation of size nonuniform arrays of QDs and require very high substrate temperatures.\textsuperscript{3} Alternatively, plasma-aided\textsuperscript{8–12} or ion-assisted routes have been shown both theoretically\textsuperscript{13–16} and experimentally\textsuperscript{17–20} by many researchers to both provide better control of the size uniformity of QD arrays and to facilitate the formation of QDs at lower substrate temperatures compared to neutral-gas-based routes.\textsuperscript{16} Moreover, a plasma-aided or ion-assisted approach has been proven to be a versatile tool in many other nanofabrication processes such as the growth of nanowires,\textsuperscript{2} carbon nanotubes,\textsuperscript{22–26} carbon nanotips,\textsuperscript{27–29} and nanostructured thin films.\textsuperscript{30,31} Therefore, using hybrid numerical simulations, this paper (a) investigates the formation of size-selected Si QDs on a SiC substrate via ion-assisted self-organization and (b) explores the physical mechanisms involved in this simple and effective approach, which ultimately leads to the formation of size-selected QDs at lower substrate temperatures compared to conventional neutral gas routes.

Silicon carbide is typically regarded as an expensive material to work with given the difficulties in producing high quality, large area substrates. The main obstacle (aside from efficiency) to widespread photovoltaic solar cell usage is cost; hence, the choice of SiC as a significant component of solar cells may be somewhat controversial. The reasoning behind this choice is manifold; first, the favorable characteristics of SiC, namely, its suitability for high temperature, voltage, and current applications and its stability in chemically hostile environments,\textsuperscript{15,32,33} afford more flexibility where solar cells may be placed/implemented. Second, research is still being conducted into reliable methods of mass producing large area SiC substrates;\textsuperscript{34} with some success, SiC wafers with diameters of \( \sim 100 \) mm and defect densities of 1 cm\(^{-2}\) have been obtained.\textsuperscript{33} When robust and reliable methods of mass production for SiC substrates have been achieved, it can be expected that the cost will be much cheaper than that of other materials simply because the main components, namely, Si and C, are inexpensive. With that eventuality in mind, it is therefore worth exploring SiC as a possible major component of the next generation of solar cells.

One of the primary aims of this work is to demonstrate the possibility of tailoring the QD growth process by biasing the substrate surface and by controlling the charge state of the material being delivered. More specifically, here, using a base distribution of neutral Si atom clusters \( \text{Si}_n \) \((n > 1)\), we compare the deposition of three species: \( \text{Si}^{1+} \) ions (ions in the lowest charge state) and \( \text{Si}^{3+} \) ions (ions in the highest charge state) under a variable (negative) bias potential \( U_{\mathrm{app}} \) of \(-10\) and \(-20\) V, as well as neutral Si atoms in the absence of an applied bias. It is shown that in the plasma- or ion-assisted processes, the substrate temperature, the applied bias strength, and the nature of the depositing species (ions or neutral) play crucial roles in determining the characteristics of the QD arrays. We also investigate the effect of the different polarization effects that occur between the ions in different charge states in an ion-assisted self-organization process.

This paper is organized in the following manner; the model and numerical details are presented in Sec. II. The simulation results are described in Sec. III and are explained using the ionization energy approximation theory in Sec. IV. The conclusions and outlook for the future research are presented in Sec. V. This work will concentrate on the formation of Si QDs on a SiC substrate, which is highly relevant to the development of the third-generation all-Si tandem solar cells.

## II. MODEL AND NUMERICAL DETAILS

A hybrid numerical simulation was conducted based on a standard rate balance equation model described in detail elsewhere.\textsuperscript{16} The most important equations are described below,

\[
\frac{\partial \eta}{\partial t} = \Psi_i + \dot{\eta}_{\text{2D}} + \dot{\eta}_{\text{3D}},
\]

\[
\frac{\partial \eta}{\partial t} = P + P_{\text{ne}} - P_e - P_{\text{na}},
\]

where \( \partial \eta/\partial t \) is the rate of change in surface densities of \( i \)-atom islands and adatoms on the substrate with respect to time \( t \). Here, \( \Psi_i \) represents the deposition rate of \( i \)-atom clusters from the neutral or ionized gas phase; \( \dot{\eta}_{\text{2D}}, \dot{\eta}_{\text{3D}} \) are the rates of density variation in nanoclusters consisting of \((i)\) atoms due to adatom collisions with nanoclusters made up of \((i)\) and \((i-1)\) atoms, the rate of nanocluster density variation due to atom vaporization to the two dimensional (2D) surface vapor from nanoclusters of \((i)\) and \((i-1)\) atoms, and the rate of nanocluster density variation due to the atom evaporation to the external three dimensional (3D) vapor from nanoclusters consisting of \((i)\) and \((i-1)\) atoms, respectively.

In Eq. (2), \( \partial \eta/\partial t \) is the density variation of adatoms on the substrate with respect to time. Here, \( P \) represents the external flux of atoms or ions, and \( P_{\text{ne}}, P_e, \) and \( P_{\text{na}} \) are the rates of adatom detachment from QDs to 2D vapor, 3D evaporation from the substrate, and attachment into the growing QDs, respectively. The surface coverage, \( \zeta \), is calculated using the following equation:\textsuperscript{35}

\[
\zeta = \sum_{i=1}^{N_{\text{max}}} \eta_i \sigma_i,
\]

where \( N_{\text{max}} \) is the maximum number of atoms in a QD and \( \eta_i \) and \( \sigma_i \) represent the surface density of an \( i \)-atom cluster and the surface area covered by \( i \)-atom islands on the substrate, respectively. The relevant parameters are included in Table I.
In our model, we have assumed a stress and defect free surface, which is justified given the low coverages considered (<0.007 and 0.02 ML for the 1 and 2 nm cases, respectively; see Table I). Recall here that we examine a nucleation stage, i.e., submonolayer growth, with very small nanoclusters on the surface and small coverages considered. Under such conditions, crystallographic issues (and also the surface stress, island nucleation via fragmentation of wetting layers as in the Stranski–Krastanov mode, etc.) are less important than the kinetic issues. In this case, the system does not consist of any large fragments of a film and thus does not exhibit a long-range order where the heterointerfaces play a key role. At this stage, such complications do not affect the accuracy of the model used. We mostly concentrate on the estimation of possible bonding configurations in order to obtain the activation energies. We estimate the activation energies using the following logic. It is clear that Si-surface-based atoms have just one dangling bond available, following from the experiments in hydrogen termination of growing nanostructures. Thus, we consider the configurations with three bonds engaged. Hence, in this case, a sole adatom can have only two possible bonding configurations, as shown in Fig. 2(a).

The main processes considered in the model are as follows: adatom attachment to QDs, atom detachment to 2D (surface) vapor from QDs, and atom evaporation to 3D (external) vapor. Here, we treat the adsorbed atoms on a surface as a 2D vapor and atoms in the space above the substrate as a 3D vapor. Both 2D and 3D vapors are involved in similar processes (diffusion, evaporation, and condensation) on the surface and in external (to the substrate) space, respectively. When the energy of an adatom/adion deposited on the surface exceeds the diffusion activation energy, \( \epsilon_d \), the adatom may move freely about the substrate surface until it finds a favorable site to reside where it will attach (by forming bonds) to either the substrate itself or to an \( i \)-atom island. If the energy of the atom/ion exceeds a bonding activation energy, \( \epsilon_{b0} \) (where \( i \) is the number of atoms in an island), it may detach from the \( i \)-atom island and undergo surface diffusion again. We denote this surface vapor of atoms/ions as a 2D vapor in our model. If an adatom/atom possesses energy exceeding \( \epsilon_{ao} \), the energy required to break its bonds with the substrate/\( i \)-atom island, the adatom escapes to the gas phase external to the substrate (referred to here as the 3D vapor) and will not undergo surface diffusion again.

The effective bonding and evaporation activation energies were estimated as follows, using Fig. 2 as a guide: In our calculations, we assumed that the Si–Si bond energy is \( \epsilon_{bSi-Si}=2.3 \text{ eV} \) (Ref. 37) and the Si–C bond energy is \( \epsilon_{bSi-C}=3.3 \text{ eV} \). It is clear that the Si adatom diffusing on the surface will have bonds with the surface-located Si and C atoms. Assuming equal probability of the adatom attachment to Si and C (since the crystalline structures of Si and SiC are very similar, even taking into account the variety of the available SiC polytypes), the effective bonding activation energy for Si on SiC can be written as \( \epsilon_{bef}=(\epsilon_{bSi-Si}+\epsilon_{bSi-C})/2=2.8 \text{ eV} \) [Fig. 2(a)].

To estimate the surface diffusion activation energy for Si on SiC, we take into account that usually a parabolic energy potential on the surface is assumed. During the jump between neighboring surface sites, an adatom is tunneled without being completely evaporated from the surface; thus, the diffusion activation energy is a fraction of the bond energy, and it is often assumed to be 1/3 of the bond energy. Indeed, it is clear that in the case of a parabolic potential, a fraction of 1/3 significantly decreases the width of tunneling. Thus, we have assumed that \( \epsilon_d=\epsilon_{bef}/3=0.93 \text{ eV} \). Hence, the adatom diffusion speed is given by \( v_d=v_0\lambda \exp[-\epsilon_d/(k_BT)] \), where \( T \) is the substrate temperature, \( k_B \) is Boltzmann’s constant, and \( v_0 \) is the lattice oscillation frequency, which varies with the substrate temperature as \( 2k_BT/h \), where \( h \) is Planck’s constant. In our approximation for \( \epsilon_d \), we have considered the Si–C terminated faces of 6H–SiC, 4H–SiC, 2H–SiC, and 3C–SiC polytypes. These Si–C terminated polytypes have equal probabilities for a Si adatom to be adsorbed or bonded with Si or C atom on the substrate surface, which is further reinforced by the fact that the surface mobility of Si is higher compared to C. \( ^{34} \)
The evaporation activation energy [to the 3D (external) vapor, see Figs. 2(b) and 2(c)] is $e_{ai}$, where $i$ is the number of atoms in the cluster. For a Si-Adatom, three bonds (2Si+1C or 1Si+2C) with the surface are assumed (Si is a four-valent element, thus, our assumption of three surface bonds and one dangling bond); taking the average of the two possibilities gives $e_{ai}=8.4$ eV. Extending these arguments to a cluster of two atoms, one can assume two bonds for atoms that form a cluster consisting of two adatoms. In this case, each atom can have two Si-Si bonds to two Si-C bonds. Therefore, for an atom that is in the cluster consisting of two atoms, we can assume $e_{ai}=e_{Si-Si}+e_{Si-C}/2$, and two bonds with Si may follow for $i=3$ atoms that after evaporation, two new bonds with the surface are created $(e_{Si-Si}+e_{Si-C})/2$ and two bonds with Si (“cluster” atoms) are broken $(2e_{Si-Si})$; hence, $e_{ai}=e_{Si-Si}+e_{Si-C}/2-2e_{Si-Si}$. The above model of surface diffusion was combined with the ionization energy approximation theory, which gives a proportionality relationship between the ionization energy of an atom and the ionization potential, which can be found in detail elsewhere.34

Briefly, the origin of the ionization energy in the polarizability and diffusivity equations (explained below) is from the Schrödinger equation based on the ionization energy theory, given below,

$$H\psi = (E_0 \pm \xi)\psi,$$

where $E_0$ is the total energy of a system at $0$ K and $\xi$ is the energy level difference in a real system. The microscopic and mathematical details of the Hamilton operator, $H$, are given in Ref. 43. However, the ionization energy approximation allows one to claim that $\xi$ is proportional to $E_0$, where $E_i$ is the atomic energy level difference or the atomic ionization energy for isolated or free atoms. Using this approximation, one can calculate the average $E_0$ for all the constituent atoms in a given system. To calculate the effect of different ions on the diffusivity is to average the $E_i$ of that particular ion, namely, Si$^{1+}$ (first ionization energy), Si$^{2+}$ (averaged value from the first two ionization energies), and Si$^{3+}$ (averaged value from the first three ionization energies). We then input these values accordingly into our numerical model to obtain the relevant diffusivities as functions of temperature and applied electric fields. Note here that the ionization energy approximation theory implies that the most mobile species on any given nonmetallic surfaces are the species with the lowest averaged ionization energy, i.e., Si in the lowest charge state. Furthermore, we can also explain why large applied bias voltage can be used to further reduce the temperature required to grow QDs.

Then, the effects of different charge states of ions or atoms were incorporated alongside with the effect of the variable electric field, which was induced by the variable bias applied to the surface. The relationship between the microscopic electric field, $E_{app}$, and the applied bias, $U_{app}$, is given by $E_{app}=(U_{app}/r)$, where $r$ is the radius of the QD and was estimated to be $2 \times 10^{-7}$ V m$^{-1}$ for $U_{app}=-20$ V and $1 \times 10^{-7}$ V m$^{-1}$ for $U_{app}=-10$ V. It was also assumed that the external bias did not have any effect on Si clusters $Si_n$ ($n > 1$). The most important equation of this approximation is

$$\bar{\xi} = \frac{\lambda e^2}{k_BT M} \left[ \exp\left(\frac{\lambda_0 (E_0^0 - \bar{\xi})}{\alpha_{ph}}\right) \right] \frac{dE_{app}}{dr} \left[ E + E_{app} \right],$$

where $\bar{\xi}$ is the nondimensional energy of an adatom and $\lambda$, $k_B$, $e$, $T$, and $M$ represent the lattice parameter, Boltzmann’s constant, electron charge, substrate temperature, and effective ionic mass, respectively. Here, $\lambda_0=(12\pi e^2/n)^1/2$, where $e_0$ is the permittivity of space. Furthermore, $E_0^0$ stands for the ground state energy level at $T=0$ and $\xi$ represents the atomic ionization energy. Ions in different charge states would have different values of $\xi$, which would ultimately affect the polarizability of an ion. Here, $\alpha_{ph}$, which denotes the lattice oscillation frequency, is given by $2k_BT/h$. The internal electric field is represented by $E$. This equation, which was derived from the ionization energy approximation theory and the model of surface diffusion, allows one to take into account the effect of difference in the degree of polarizability, which originates from the different charge states of depositing ions. Therefore, one can now write the equation for the surface diffusivity by incorporating the ionization energy approximation as

$$D_s = \frac{\lambda^2 \omega_{ph}}{2\pi} \exp\left[ \frac{\bar{\xi} - \bar{\xi}_j}{k_BT} \right],$$

where $D_s$ and $\bar{\xi}_j$ represent the surface diffusivity and surface diffusion activation energy, respectively.

As one can see from Eq. (5), $\bar{\xi}_j$ is dependent on the ionization energy of the particular ion, which varies between different charge states of the ions. The negative sign in $\xi$ allows one to predict that a higher ionization energy will result in a lower nondimensional energy, $\bar{\xi}_j$. Also, the key parameter, $E_{app}$, in this equation is proportional to $\xi$, where $\bar{\xi}_j$ takes into account the effect of different charge states and the applied electric field strength (which in turn is proportional to the applied bias strength) was calculated and is shown in Table II. In this calculation, the ionization energy values for Si$^{1+}$ and Si$^{3+}$ ions were 786.5 and 3231.6 kJ mol$^{-1}$, respectively.

Two cases were considered: synthesis of (a) 1 nm (0.96–1.04 nm or 22–28 atoms were regarded as a 1 nm QD) and (b) 2 nm (1.96–2.04 nm or 189–215 atoms were classified as
TABLE II. Decrease in energetic term, $\bar{E}_n$.

<table>
<thead>
<tr>
<th>Ion</th>
<th>$U_{\text{app}}$ (V)</th>
<th>$\bar{E}_n$ 1 nm (eV)</th>
<th>$\bar{E}_n$ 2 nm (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si$^{+1}$</td>
<td>10</td>
<td>0.15</td>
<td>0.08</td>
</tr>
<tr>
<td>Si$^{+1}$</td>
<td>10</td>
<td>0.05</td>
<td>0.03</td>
</tr>
<tr>
<td>Si$^{+1}$</td>
<td>20</td>
<td>0.30</td>
<td>0.16</td>
</tr>
<tr>
<td>Si$^{+1}$</td>
<td>20</td>
<td>0.10</td>
<td>0.05</td>
</tr>
</tbody>
</table>

a 2 nm QD) Si QDs on SiC. To that end, two atom/cluster influx distributions were used, as shown in Fig. 1, based on a Gaussian distribution centered around 25 and 202 atoms for the 1 and 2 nm QD cases, respectively—with an appreciable number of influx atoms and smaller clusters. A deposition time of 0.01 s was used, with the total surface coverage remaining under 0.007 and 0.02 for the 1 and 2 nm cases, respectively.

III. RESULTS

Figures 3 and 4 plot Si adatom surface diffusivity against $1/T$, with ion charge and applied bias as parameters for 1 and 2 nm QDs, respectively. It is shown that the highest surface diffusivity in the low-temperature region was achieved using Si$^{+1}$ ions in the presence of an applied bias of $-20$ V for both 1 and 2 nm QD formation cases, followed by the Si$^{+3}$ ion case, with the lowest surface diffusivity being that of the neutral Si atom.

Figures 5 and 6 plot the number of 1 and 2 nm Si islands, respectively, as a percentage of the total surface coverage, $\xi$, at different substrate temperatures. The general trend shows an increase in the percentage of the surface coverage by 1 and 2 nm islands, with increasing the substrate temperature before reaching a saturation in the higher substrate temperature region ($\geq 675$ K). The key trend in Figs. 5 and 6 is that the use of Si$^{+1}$ ions under the influence of the applied bias ($-10$ or $-20$ V) made it possible to achieve the highest percentage of 1 and 2 nm QDs on the substrate in the lower substrate temperature region between 500 and 600 K. This was followed by the Si$^{+3}$ ion case (ion in a high charge state) in the presence of an applied bias of $-10$ or $-20$ V. Furthermore, the lowest percentage of the total surface coverage by 1 and 2 nm islands was achieved by depositing neutral Si atoms in the absence of any applied bias.

The effect of increasing the strength of the applied bias resulted in an increase in the percentage that 1 and 2 nm islands made up of the total surface coverage compared to the lower applied bias case. The effect of different charge states under different applied biases is strongly pronounced in the low-temperature region between 500 and 600 K, and
these effects diminish at higher substrate temperatures around 675 K for both 1 and 2 nm QD cases, which implies that bias control in the low-temperature regime is essential to achieve higher percentages of the total surface coverage in our preselected size range (namely, 1 and 2 nm islands) at low substrate temperatures.

For completeness, the surface coverage distribution has been included as Fig. 7—the effect is very subtle, much less noticeable than the trends presented in Figs. 5 and 6. Figures 7(a) and 7(b) show that adatoms/adions under different charge states ($Q_i$) and applied bias ($U_{app}$) conditions exhibited different surface coverages at $T = 500$ K, following the trend [$5 > 3 > 1$], where 5 is the case where $U_{app} = -20$ V and $Q_i = +1 e$ and 1 represents an adatom in the absence of an applied bias [as in Figs. 5 and 6; here, data series 2 and 4] have been omitted for the sake of readability]. This implies that the rates of surface diffusion of adatoms into the QDs follow the trend [i.e., $1 > 3 > 5$], where the smallest number of adatoms is attached to the QD in the absence of an applied bias. As adatoms/adions attach to our preselected size clusters, this leads to the observed surface coverage trend [i.e., $1 > 3 > 5$] in our preselected size region for 1 nm (22–28 atoms) or 2 nm (189–215 atoms) QDs, as shown in Figs. 7(a) and 7(b), respectively. However, this surface coverage trend is much less noticeable for the 2 nm case than for the 1 nm case because of the scale difference between the number of atoms (horizontal axis) in the 1 and 2 nm sized QDs. Hence, as we observed previously, at low substrate temperatures, using Si$_n^{2+}$ under an applied bias of $-20$ V leads to a greater surface coverage in our preselected size region, compared to neutral atoms in the absence of an applied bias.

One of our main assumptions was that the only mobile species on the surface were adatoms/adions. However, a more complete description of the surface coverage could be obtained if surface processes involving the movement of neutral Si$_n$ clusters ($n \geq 2$) were also considered. Moreover, a better understanding (and perhaps further enhancement) of this effect could be obtained if we considered the deposition of ionized Si$_n$ clusters ($n \geq 2$) as well as neutral Si$_n$ clusters. This effect could be further enhanced if we considered the deposition of a higher initial influx of Si adions and considered longer deposition times.

IV. DISCUSSION

We will now discuss the main results obtained and the physical mechanisms behind them by applying the ionization energy approximation theory. The simulation results presented in Sec. III, which are in good agreement with the initial growth stage model$^{16}$ and the ionization energy approximation,$^{34}$ show that ion-assisted self-organization provides a way to obtain higher percentages of size-selected 1 and 2 nm islands at lower substrate temperatures than are typically needed for size-uniform QD formation using a neutral-gas-based approach.

We recall here that the primary aim of this work is to demonstrate the possibility of tailoring the QD growth process by biasing the substrate surface and controlling the
charge state of the material being delivered. To illustrate this, as noted in Sec. III, we have plotted first of all the dependencies of the surface diffusivity on temperature (in the low-temperature range), with the ion charge as a parameter, for 1 nm (Fig. 3) and 2 nm (Fig. 4) cases. As noted in Sec. III, the highest surface diffusivity in the low-temperature region was achieved using Si\(^{1+}\) ions in the presence of an applied bias of \(-20\) V for both 1 and 2 nm QD formation cases, followed by the Si\(^{3+}\) ion case, with the lowest surface diffusivity being that of the neutral Si atom. This effect can be explained by noting that since the Si\(^{1+}\) ions have a smaller ionization energy compared to Si\(^{3+}\) ions, Si\(^{1+}\) ions gain the highest energy \(\bar{e}\) on the surface. This, in turn, leads to the greatest reduction in the surface diffusion activation energy \(e_d\) resulting in a higher surface diffusivity compared to Si\(^{3+}\) ions or neutral Si atoms, as follows from Eqs. (5) and (6).

The noticeable trend, as shown in the plots of the percentages that 1 and 2 nm islands comprise of the total surface coverage in Figs. 5 and 6, respectively, is that the Si\(^{1+}\) ion (ion in the lowest charge state) under the influence of the applied bias (which in turn induces an applied electric field \(E_{app}\)) resulted in higher percentages of both 1 and 2 nm islands in the lower substrate temperature region (between 500 and 600 K) compared to Si\(^{3+}\) (ion in a high charge state) in the presence of the applied bias or neutral Si atoms without any applied bias before reaching almost a steady state. This result may be explained using the ionization energy approximation theory\(^{34}\) as outlined below.

The Si or C substrate atoms also exhibit a certain degree of polarization (although less than the adatom/adion on the surface) in the presence of an applied electric field. This directional polarization between the substrate atoms and the ions on the surface causes a repulsion between them. The degree of the repulsion depends on the degree of polarization of surface ions, which can be enhanced by increasing \(E_{app}\). Physically, Si\(^{1+}\) ions have more easily polarizable electrons under the influence of the electric field compared to Si\(^{3+}\) ions. Also, the electrons in Si\(^{3+}\) ions experience a stronger nuclear attraction force from the nucleus compared to the electrons in Si\(^{1+}\) ions inducing a weaker polarization strength. This induces a greater repulsion between the Si\(^{1+}\) surface ions and the substrate atoms compared to the Si\(^{3+}\) case, giving the surface ions a larger nondimensional energy \(\bar{e}\). Hence, as shown in Figs. 5 and 6, Si\(^{1+}\) ions (ions in the lowest charge state) are better suited to form QDs at lower temperatures compared to Si\(^{3+}\) ions (ions in a higher charge state).

In the ion-assisted self-organization process, the key parameters that one can control are the substrate temperature and the bias voltage, which can be modified to enhance the formation of size-selected QDs. We note that in practical applications, the surface bias is easier to control than the substrate temperature. Our results suggest that increasing the temperature or bias can increase the diffusion rate of QDs. However, it should be mentioned that this will also increase the 3D evaporation rate from the substrate, which is one of the reasons that we have emphasized the percentage that 1 and 2 nm QDs make up of the total amount of materials on the substrate (total surface coverage, \(\zeta\) in Sec. III, rather than explicitly focusing on the surface coverage in our pre-selected size range, as presented in Fig. 7.

The above trend (increased percentages of 1 and 2 nm islands for Si\(^{1+}\), \(U_{app} = -20\) V compared to neutral Si atoms in the absence of \(E_{app}\)) is less marked for the 2 nm QD case. This is because the surface diffusivity of surface atoms or ions for larger (2 nm) QDs is less than that for smaller (1 nm) QDs, as shown in Figs. 3 and 4. This is due to the lower electric field gradient \(\delta E_{app}/\delta r\) in Eq. (5) for the 2 nm QD case. As the radius \(r\) of the QD increases, the electric field effect is averaged over a larger volume leading to a lower \(\bar{e}\) of surface atoms or ions, which induces a lower surface diffusivity in all temperature ranges (for the 2 nm case compared to the 1 nm QD case). This leads to a smaller reduction in the surface diffusion activation barrier \(e_d\), which ultimately results in higher temperatures required for the formation of 2 nm Si QDs compared to the 1 nm case.

The physical mechanism behind this effect is illustrated in Fig. 8. As one can see, the neutral Si atom in the absence of an applied bias is unpolarized, meaning that the electric dipole moment of the atom is isotropic. However, charged ions on the surface such as Si\(^{1+}\) or Si\(^{3+}\) in the presence of an applied bias exhibit directional polarization. Therefore, the electric dipole moment of the ions is perturbed depending on the microscopic topography of the electric field \(E_{app}\).

We have assumed that there is an equal probability of surface ions or atoms forming a QD at either a silicon- or carbon-rich substrate atom surface site (or rather Si or C face of SiC). However, using the ionization energy approximation theory, one can predict that for a carbon substrate atom that has a higher average ionization energy (3571 kJ mol\(^{-1}\))\(^{37}\) compared to silicon (2488 kJ mol\(^{-1}\))\(^{37}\), the negative exponential term in Eq. (5) would be lower. This will induce a weaker polarization, leading to a less effective repulsion between the surface Si atoms or ions and the carbon substrate.

![Fig. 8. (Color online) Physical effects/phenomena occurring in the ion-assisted self-organization process. The size of the arrow represents the magnitude of the surface diffusivity. In the absence of an applied bias, the neutral adatom/adion’s electric dipole moment is isotropic. However, when an applied bias is introduced, the adion/adatom is polarized depending on the charge state of the adion (schematically represented by a distortion in shape). The weakest polarization occurs in the neutral Si atom. This polarization creates a repulsion between the substrate atom and the adatom/adion leading to the higher surface diffusivity at a given substrate temperature. The diffusivity of the adatom is enhanced further by introducing a stronger applied bias (leading to a greater distortion in shape) due to the greater distortion in the electric dipole moment of the respective ion/atom eventually resulting in a stronger repulsion between the adatom/adion and the substrate atom. The highest surface diffusivity is induced by the Si\(^{2+}\) ion (strongest polarization) followed by the Si\(^{1+}\) ion (moderate polarization), and the lowest is induced by the neutral Si atom (weakest polarization).](image-url)
atom compared to the case of a silicon substrate atom. This will lead to a lower $\varepsilon$, for the Si surface atom/ion, implying lower surface diffusivity in the C face case compared to the Si face case. Hence, diffusion on the C face would not be favorable compared to diffusion on the Si face of SiC. As a result, our model and the ionization energy approximation shape the understanding of surface processes involved in ion-assisted self-organization leading to a lower temperature formation of size-uniform and size-selected QDs for third-generation all-Si tandem solar cells.

Here, we have used a rate equation model to observe trends between ion charge, bias, deposition temperature, and surface coverage within a preselected size range (1 and 2 nm) for the purpose of finding ways to optimize the yield of size-selected QDs at low substrate temperatures. Further investigations, for example, on the effect of bias on nanostructure shape and strain between the nanostructure and substrate materials would require other models and approaches.

From a practical perspective, ions of different charge states can be generated via techniques such as ion-beam-assisted deposition and filtered cathodic vacuum arc.44–46 One can therefore easily produce multicharge states, making ion-assisted self-organization a highly feasible approach, which will pave the way toward the deterministic nanofabrication of the third-generation all-Si tandem solar cells.

V. CONCLUSIONS

We have performed a series of hybrid numerical simulations to investigate the viability of an ion-assisted self-organization route in fabricating size-uniform Si QDs of 1 and 2 nm on a SiC substrate, which will be one of the key components in the third-generation all-Si tandem solar cells. Specifically, our investigation was centered on the following points:

1. Ensuring that the highest percentage of the total surface coverage consisted of size-uniform 1 and 2 nm Si QDs and was achieved at the lowest possible substrate temperature.
2. Study of the atom/ion surface diffusion in a charged environment. Specifically, we have examined the effect of deposition of Si ions in different charged states ($\text{Si}^{1+}$ and $\text{Si}^{3+}$) under different magnitudes of microscopic electric fields (induced by applied negative biases) and compared this effect to the surface diffusion of neutral Si atoms in the absence of the electric field.
3. Understanding the fundamental physics behind how an ion-assisted self-organization process can facilitate the formation of size-selected QDs at lower substrate temperatures.

Our main findings in this work can be summarized as follows:

• Size-uniform 1 and 2 nm islands comprised the greatest percentage of the total surface coverage in the low substrate temperature region (227–327 °C) when $\text{Si}^{1+}$ ions (ions in the lowest charge state) were used. The next highest value was for $\text{Si}^{3+}$ (the highest charge state), and the lowest value was observed for the neutral Si atom case in the absence of $U_{app}$.
• Increasing the strength of the applied bias (from $-10$ to $-20$ V) enhanced the polarization effect of $\text{Si}^{1+}$ and $\text{Si}^{3+}$ resulting in a stronger repulsion between the adions/adatoms and the substrate atoms leading to higher diffusivity at a given substrate temperature. This resulted in higher percentages of 1 and 2 nm islands for stronger applied electric fields at given substrate temperatures.
• The ionization energy approximation theory was used to explain the reasons behind the higher adatom/adion surface diffusivity under low substrate temperature conditions by relating the difference in the ionization energy of specific atoms/ions to the differences in the degree of polarization among the ions in different charged states that deposit onto the substrate. As such, this knowledge enhanced the understanding of ion-assisted self-organization processes.

Our results thus suggest that by using an ion-assisted self-organization route, surface coverages with higher percentages of size-uniform islands within the preselected size range may be achieved at lower substrate temperatures than is typically achievable through neutral-gas-based self-organization.

We did not take into account the effect of the applied bias on the bonding energy and the evaporation energy; however, this effect will be investigated in the near future. Another possible investigation in ion-assisted/plasma-aided self-organization processes is examining the effect of the competing control factors such as the substrate temperature and the strength of the microscopic electric field in the low substrate temperature region. Future work will focus on finding ways to further enhance the yield of size-selected QDs, lower the processing temperatures required, and simultaneously increase the degree of determinism in the nanoassembly process. This research will ultimately pave the way toward facilitating the commercially viable incorporation of precisely tailored QDs in the third-generation all-Si solar cells.

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