Growth mechanisms for InAs/GaAs QDs with and without Bi surfactants

X Y Chen[1], Y Gu[*, 1], Y J Ma[1], S M Chen[2], M C Tang[2], Y Y Zhang[2], X Z Yu[2], P Wang[1], J Zhang[1], J Wu[2], H Y Liu[2], Y G Zhang[1]

[1]*State Key Laboratory of Functional Materials for Informatics, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, Shanghai 200050, China*

[2]*Department of Electronic and Electrical Engineering, University College London, London WC1E 7JE, UK*

Abstract: We report systematic study of growth of self-assembled InAs quantum dots (QDs) on GaAs substrate at various temperatures with and without exposure of bismuth surfactants. Results show that the coalescence amongst InAs QDs is considerably inhibited by the exposure of bismuth flux during growth in the temperature range from 475 to 500 °C, leading to improved dot uniformity and a modified dot density. The mechanism of the suppression effect by bismuth surfactants on the strain-induced islanding through inhibiting the indium adatom mobility and the evaporation rate on the surface kinetically is thus clarified for the growth of InAs QDs. The photoluminescence peak wavelength for the InAs QDs with Bi exposure red shifted slightly due to the suppression of Bi atoms on the QD dissolution during the capping process at higher temperatures. Moreover, by investigating the temperature-dependent quenching processes with and without Bi exposure, it is observed that the the weak carrier confinement occurred in QDs with the presence of Bi caused broadness in the linewidths.

[*] Corresponding author. Tel.: +86-21-62511070; fax: +86-21-52419931.
Email address: ygu@mail.sim.ac.cn (Y. Gu).

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1. Introduction

Owing to the small segregation coefficient and low solid solubility in host lattice [1], bismuth (Bi) is considered as an ideal surfactant for the material growth and has recently been widely studied in different systems such as III-V quantum dots (QDs) [2], quantum wells (QWs) [3], heteroepitaxy of Ge on Si [4], and Co/Cu multilayers [5], etc. Most of these researches are devoted to improve the perfection of structures in aspects of ordering, interfaces, and surfaces. Self-assembled InAs QDs on GaAs (001) are favorable for devices operating in the optical telecom wavelength bands as the improved height/diameter aspect provides a deeper confinement of the charge carriers as compared to other nanostructures [6–8]. Given that QD-based device performances will be affected by the dot density and dimension, the QD size, uniformity, and density should be well tuned to guarantee optimum performances of QD-based devices. For example, an improvement in QD density and uniformity has the potential to increase the differential gain and modulation bandwidth for QD lasers as well as the interband and intersubband absorption strength for QD-based photodetectors. While the preserve of the shape and the improvement of uniformity of InAs QDs using Bi surfactants have been verified in previous works either by molecular beam epitaxy (MBE) or metal organic chemical vapor deposition (MOCVD) [9, 10], whether Bi decreases or increases the surface migration of indium (In) adatoms during the growth is still unclear since the effect of Bi surfactants during InAs QD growth has been interpreted inconsistently. Some researchers hold the point that Bi, acts as a reactive surfactant, can kinetically limit the surface adatom mobility and decrease the In adatom diffusion length and thus increase the QD density [9, 10]. Others argue an opposite effect of Bi on the QD density and dimension [11]. Since the QD density of uncapped QDs is greatly affected by not only the In adatom diffusion length but also by the evaporation rate of InAs nuclei on the surface. Both processes can be influenced by presence of Bi atoms and depends strongly on temperature. That would be the reason why the controversy exists.

Here, we reconcile these apparent contradictions by comparing InAs QDs grown with and without Bi exposure over the temperature range from 475 to 500 °C. It is observed that the Bi surfactant leads to a decrease in QD density for lower growth temperatures (475 - 485 °C), but an increase for higher growth temperatures (492 - 500 °C). The variations of the dot density are ascribed to the suppressing effect of Bi surfactants on the In adatom surface diffusion length during MBE growth regardless of growth temperatures, as is expected for a reactive surfactant [12]. Moreover, using Bi as a surfactant enables an improvement in QD uniformity, suggesting that the Bi surfactant-mediated growth of QDs has the potential to improve the performance of QD-based optoelectronic devices.

2. Experiments

All the InAs/GaAs QD samples were grown by gas-source MBE in a VG Semicon V90H system on semi-insulating GaAs (001) substrates. The structures were started with a 200 nm GaAs buffer layer grown at 580 °C after desorption of the native oxide layer. Then the substrate temperature was ramped down for the growth of the first layer of InAs QDs with a thickness of nominal 2.8 monolayers (MLs) and deposition rate of 0.07 ML/s. This QD layer was used for photoluminescence (PL) measurements. A 10 nm GaAs capping layer was grown immediately at the same temperature. Then the temperature was ramped up to 580 °C for the deposition of a 110 nm GaAs spacing layer. At last, the InAs QD layer was repeated on the surface of the GaAs spacer for dot morphology studies. To investigate the effect of Bi exposure on the InAs QDs, the Bi shutter was only opened during the deposition of QDs with the Bi flux of 1.09 nA (Beam equivalent pressure ~ 8.8×10^{-9} torr), which has been proved to be helpful for the growth of triangular highly strained InAs/InGaAs QWs on InP [3], otherwise the Bi shutter remained closed during the growth. The substrate temperatures of 475, 485, 492 and 500 °C were adopted for the deposition of InAs QD layers. At such relatively high growth temperatures, Bi atoms tended to segregate, floated on the growth surface without incorporating into the host material [13], and acted evidently as a reactive surfactant. For comparison, another set of InAs QD samples without Bi exposure was also grown on GaAs under nominally identical growth conditions. Note that no deliberate growth interruption was used for both sets of samples after the deposition of InAs QDs in an attempt to maintain the similarity between the buried QDs and the uncapped QDs to the utmost, as well as to avoid artificial impacts on the surface adatom (especially In) diffusion length. In this way, the contrast between the two sets of QDs with and without Bi exposure would also be enhanced. The nominal growth rate of GaAs was 0.16 nm/s. The V/III ratio was far higher than 20 in this experiment according to our previous calibration, and As_2 species were used for all layers.

The InAs QD morphology was measured by a Bruker Icon atomic force microscope (AFM) in the contact mode. The scanned area was 1 × 1 μm^2. PL spectra were measured with a Nicolet IS50 Fourier transform infrared spectrometer (FTIR). Samples were excited by a diode-pumped solid state (DPSS) laser (λ = 532 nm). Temperature-dependent PL measurements were carried out by mounting samples into a continuous-flow helium cryostat, and a Lake Shore 330 temperature controller was used to adjust the temperature from 10 to 300 K. The laser spot area was about 4.5 × 10^{-2} cm^2. The laser power used in RT and temperature-dependent PL measurements were about 340 and 136 mW, respectively.

3. Results and Discussion

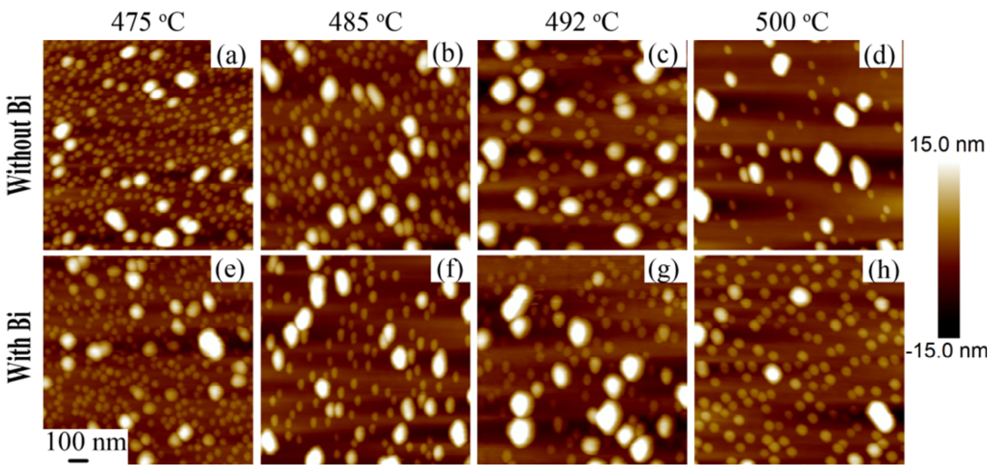

Figure 1. AFM images of InAs QDs grown at different temperatures with and without Bi exposure.

Topographical AFM images of the grown InAs QDs without and with Bi exposure are shown in figure 1. For the case of Bi-unmediated samples, at low substrate temperatures, the surface population of free In adatoms diffused relatively slowly due to a low surface energy and the average diffusion distance was short before they combined with dissociated As_2 molecules. This results in a high dot density with a small lateral size in general. At an elevated temperature, their diffusion distances elongated, and dots coalesced with each other intensely with an increase in surface energy of In adatoms, thus the dot density declined. As a concomitance of the dot growing up, the random aggregation of islands increased, corresponding to the piling up of bright circular features in figures 1(b) and 1(c). At the highest substrate temperature of 500 °C, it was observed that big dots evolved into larger islands leaving a few scattered dots surrounded, mostly caused by desorption of uncapped QDs and Ostwald ripening, as shown in figure 1(d). However, dissimilarities occurred in both the dot density and dimension for the case of Bi-mediated samples, as shown in figures 1(e)-1(h). The main difference can be found in the variation of dot densities in comparison to that without the Bi exposure ranging from 475 to 500 °C. The InAs dots formed under Bi exposure not only showed reduced variations in the dot densities but also became more homogeneous especially in the case of 500 °C, where the dislocated islands significantly suppressed, opposite to those without Bi exposure. These results indicate that the Bi surfactants significantly modified the growth kinetics of QDs. Bi atoms can preserve the dot dimension and density during cooling down, similarly to the property of Sb atoms [14, 15].

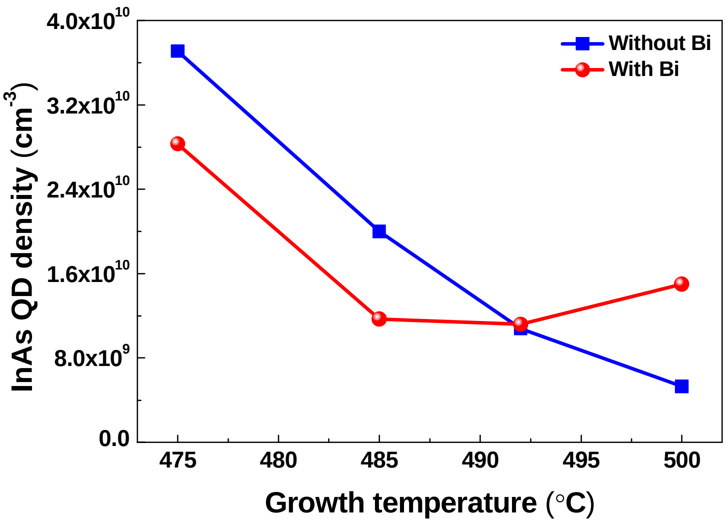

Figure 2. The temperature-dependent InAs/GaAs QD densities with and without Bi exposure.

To quantify the influence of the Bi exposure on the QD densities, temperature-dependent InAs QD densities with and without Bi exposure were plotted in figure 2. Without Bi, the uncapped InAs QD densities decreased monotonically with the deposition temperature increasing from 475 to 500 °C mostly caused by the increase in desorption rates of In adatoms since they have additional time ~~to change on~~ for surface changes during cooling down, especially for samples grown at higher temperatures. Nevertheless, the dot dimension and density of buried QDs can be quite different. It may be much higher in ~~both size and~~ dot density but smaller in size! However, when Bi exposure was used, the variation of the QD density differed considerably over the whole temperature range of 475 - 500 °C. It is obvious that the Bi-mediated QD ripening process during cooling down is suppressed by Bi atoms. As a result, QDs with Bi exposure showed a decrease in the overall density at low temperatures but an increase at high temperatures compared to the QDs without Bi exposure.

It is well known that the InAs dot density and dimension depend strongly upon factors such as the surface diffusion length of In adatoms [16], the desorption rate of In adatoms from the substrate surface and the dissociation rate for the tiny InAs nuclei [17]. It is supposed that the dominant factors for QD density and dimension should be varied over the variation range of temperatures, which will be strengthened by the employment of Bi surfactants for the QD growth. At low temperatures, little desorption of In adatoms and dissociation for the tiny InAs nuclei occur. The dot density is probably dominated by the diffusion length of In adatoms on surface, and the reduction of the surface diffusion length of In adatoms due to the presence of Bi undoubtedly will defer the InAs QD formation by delaying the onset of QDs, leading to a decrease in the overall QD density with respect to the case without Bi exposure. At high temperatures, the desorption of In adatoms from the growth surface and the dissociation for the tiny InAs nuclei aggravate intensely, but they are ultimately suppressed by the presence of Bi. While the suppression effect of Bi exposure on the dot coalescence still exists due to the restrained surface diffusion length of In adatoms, thus leading to a higher QD density instead compared to that without Bi exposure.

These results demonstrate the suppression effect of Bi surfactants on the In adatom surface diffusion, which eventually leads to a suppression of QD coalescence and ripening, similar to the behavior of antimony (Sb) surfactants for QD growth [18, 19].

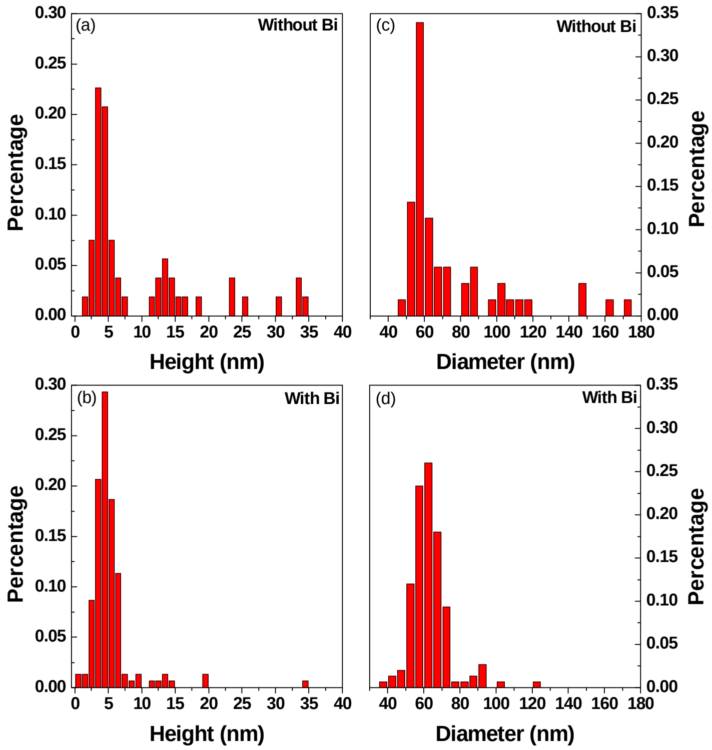

Figure 3. The histograms of the InAs QD height and diameter distribution grown at 500 °C with and without Bi exposure.

To analyze the effects of the Bi surfactant on QD uniformity, the typical height and diameter histograms of the InAs QDs grown at 500 °C with and without Bi exposure were extracted from the AFM images, as shown in figure 3. From the histograms of height distribution, as shown in figures 3(a) and 3(b), an extremely large proportion of QDs with the height beyond 12 nm was suppressed markedly after the Bi exposure. The dot height in the presence of Bi showed less size fluctuation than that without Bi. The average heights were deduced to be 6.3 and 10.5 nm for InAs QDs with and without Bi exposure, respectively. Similarly, QDs grown without Bi exhibited a wider distribution in the diameter, as shown in figure 3(c). While the fluctuation in the diameter was diminished for the InAs QDs in the presence of Bi, and the average QD diameters were deduced to be 64.0 and 74.2 nm for InAs QDs with and without Bi exposure, respectively. This means that the Bi surfactant decreased the typical QD size through suppressing the free surface diffusion of In adatoms during InAs QD growth. This also coincides with the QDs grown with Sb as a surfactant [18, 19].

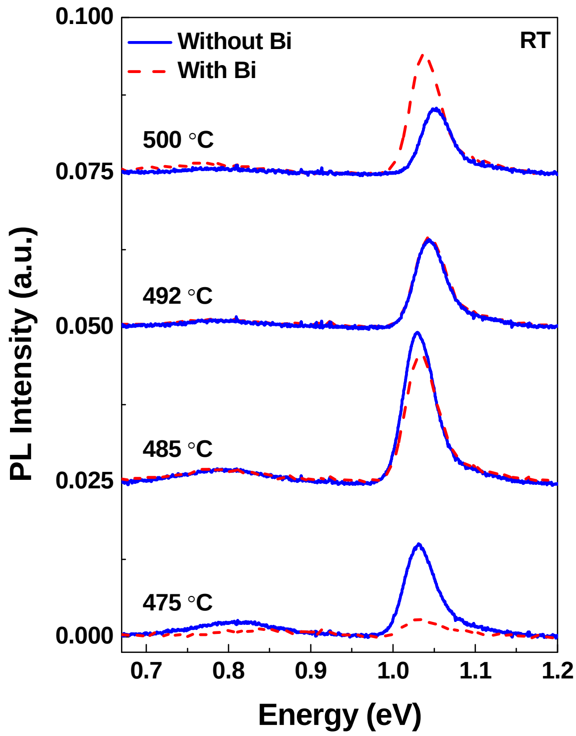

Figure 4. PL spectra of InAs QDs grown at different temperatures with and without Bi exposure.

Figure 4 shows the room temperature (RT) PL spectra for the InAs QDs with and without Bi exposure deposited at different temperatures. The output voltage of the DPSS laser was set to 2.5 V with an excitation power of about 340 mW. As shown in figure 4, the ground state emission occurred at about 1.03 eV for both sets of QD structures at RT. The broad signal located in the 0.75-0.87 eV range fell off linearly as the temperature increased, corresponding well with the features of the lateral associated InAs QDs [20, 21]. It is noticeable that the peak position of the ground state emission for the InAs QDs with Bi exposure shifted slightly to the red, especially for the InAs QDs and the GaAs capping layer grown at higher temperatures (500 °C) with respect to those without Bi exposure as shown in figure 3. This phenomenon can be explained by the fact that QDs will be partly dissolved ~~with a lower height~~ during the capping process [22, 23], and as a result their height is lower, but the presence of Bi atoms can definitely influence this process by suppression of QD dissolution and then increase the height of resulting QDs, which is similar to Sb atoms [14, 15]. As a result, this shifts the wavelength of InAs QDs grown with Bi to lower energies. It is worth noting that the bigger hillocks may not show any PL since they are relaxed and contain ~~annihilation centers~~ dislocations. The PL spectrum originated only from the small QDs with the height not bigger than 10 nm - the first maximum in the histogram for both samples shown in figures 3 (a) and (b). This redshift of PL agrees well with the first maximum shifted to bigger QD size for sample grown with Bi at higher temperatures, as shown in figure 5.

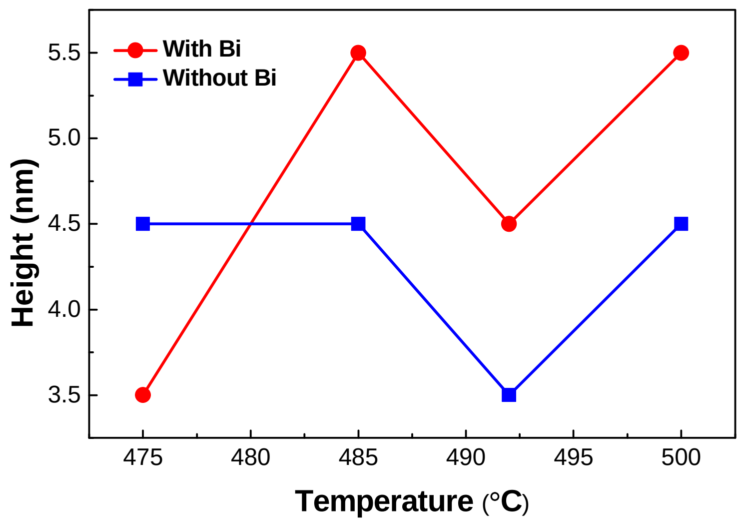

Figure 5. The peak height value for smaller QDs and its dependence on the

temperature.

Additionally, the PL intensity of the ground state transition for InAs/GaAs QDs with Bi exposure was weaker at a deposition temperature of 475 °C but comparable at temperatures of 485 - 500 °C with respect to those without Bi exposure. Since Bi induced layer-by-layer growth in the InAs/GaAs strained systems by reducing the interface energy, and thus the three-dimensional (3D) islands in the Stranski-Krastanov (S-K) growth mode was suppressed. This would lead to postponement of the wetting layer formation before the growth mode changing from 2D to 3D during the S-K growth process due to the decrease in the strain energy [9, 24]. Then the critical thickness of the wetting layer would be extended, which delayed the formation of InAs QDs. If this wetting layer was modified properly, it would improve the optical property of InAs QDs, but a much thicker one, in turn, could damage it by serving as a channel for thermally activated carriers [25]. The influence could change with the growth temperature due to the variation of the critical thickness of the wetting layer. The inferior PL of InAs QDs grown with Bi exposure at 475 °C could be caused by the insufficiently developed QDs at this low temperature with the presence of Bi atoms.

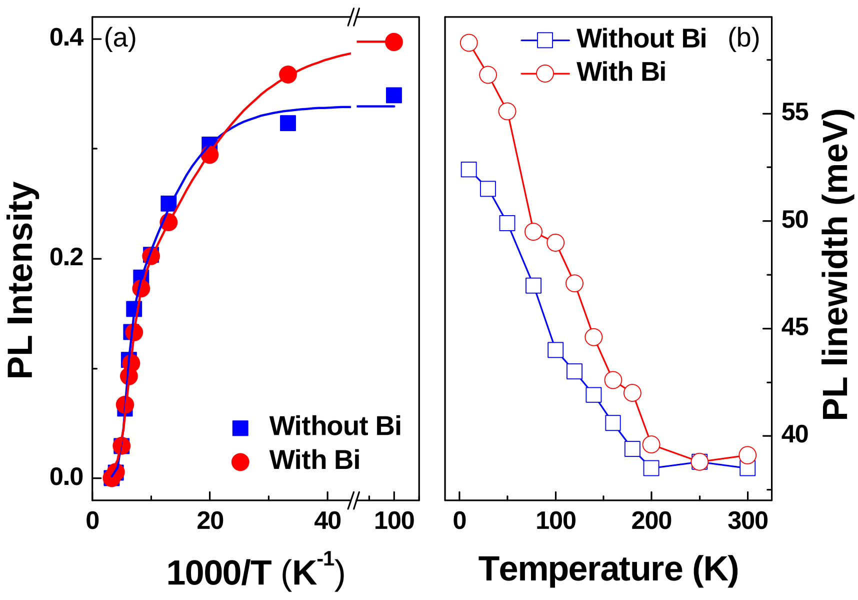

Figure ~~5~~ 6. (a) Integrated PL intensities for InAs QDs grown at 492 °C with and without Bi exposure as a function of reciprocal temperature from 10 K to 300 K. The lines are the least squares fit of the data. (b) PL linewidths for InAs QDs with and without Bi exposure versus temperatures. The lines are drawn as a guide.

To have a deeper understanding of the effect of Bi surfactants on the optical properties of QDs, the change of carrier confinement in both sets of QDs should be investigated further by measuring temperature-dependent PL quenching processes. Therefore, the InAs QDs grown at 492 °C with similar RT PL spectra under both Bi-mediated and unmediated conditions to eliminate the impact coming from different dot densities were measured. The integrated PL intensities, excited under low-pump conditions, were plotted in figure ~~5~~ 6(a) as a function of reciprocal temperature. The fits are derived by applying equation [26], $I(T) = I(0)/[1 + C_1\exp(-E_1/k_BT) + C_2\exp(-E_2/k_BT)]$ (Eq. (1)), where C_1 and C_2 represent the strengths of the both quenching processes, $I(T)$ and $I(0)$ are the PL integrated intensity at temperature T and 0 K, k_B is Boltzmann' constant and E_1, E_2 are the thermal activation energies corresponding to the highest required energies for carriers to escape from the active region in low- and high- temperature regions respectively. Experimental data were well fitted as shown in figure ~~5~~ 6(a), and the fitting parameters calculated from the Arrhenius plots were listed in table 1.

It can be observed that calculated activation energies were 14.6 and 9.0 meV in low-temperature regions, 156.1 and 105.0 meV in high-temperature regions for the InAs QDs without and with Bi exposure respectively. The reduction in activation energies of E_1 and E_2 suggested weaker carrier confinement for InAs QDs with Bi exposure. This reduced confinement potential can be explained by the fact that the size of QDs at lower temperatures with Bi as surfactant is smaller, which decreases the confinement barrier for carriers in QDs [11].

Lastly, the PL linewidths for InAs QDs grown at 492 °C with and without Bi exposure as a function of temperature from 10 to 300 K were plotted in figure ~~5~~ 6(b). The linewidths of both spectra substantially increased in low-temperature regions due to the appearance of emission from small QDs [27]. While at high temperatures, the QDs with high localization energies will be preferentially occupied by carriers and thus dominated the spectra, resulting in narrow linewidths. It is noted that the linewidths were broadened lightly for QDs with Bi exposure over the temperature range of 10-300 K, which also indicates that a weak carrier confinement occurred in the QDs grown with the presence of Bi.

Table 1. Fitting parameters for the measured temperature-dependent integrated PL intensities of InAs QDs with and without Bi.

Table 1.

Sample	$I(0)$	E_1	C_1	E_2	C_2
Without Bi	0.34	14.6	3.4	156.1	73943
With Bi	0.40	9.0	2.7	105.0	3951.9

4. Conclusions

The influence of Bi exposure on the self-assembled InAs/GaAs QDs has been investigated by comparison of dot density and dimension at varying substrate temperatures. It is shown that the dot density decreases but large, defective InAs islands accumulate as the growth temperature increases under the Bi-unmediated condition. By contrast, for the Bi-mediated growth, the dot areal density decreases at low temperatures but increases at high temperatures, which reveals essentially the suppression effect of Bi on the surface migration and desorption of In adatoms. Furthermore, the QD dimensions become more uniform and homogeneous at higher temperatures for Bi atoms suppressing the formation of larger dislocated islands. If the negative effect of Bi can be avoided, Bi-mediated QDs could show great application potential for photonic and optoelectronic devices in the future.

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