Enable a Facile Size Re-distribution of MBE-Grown Ga-Droplets via In Situ Pulsed Laser Shooting

Biao Geng1,2†, Zhenwu Shi1,2*, Chen Chen1,2†, Wei Zhang4, Linyun Yang1,2, Changwei Deng1,2, Xinning Yang1,2, Lili Miao1,2 and Changsi Peng1,2,3*

Abstract
A MBE-prepared Gallium (Ga)-droplet surface on GaAs (001) substrate is in situ irradiated by a single shot of UV pulsed laser. It demonstrates that laser shooting can facilely re-adjust the size of Ga-droplet and a special Ga-droplet of extremely broad size-distribution with width from 16 to 230 nm and height from 1 to 42 nm are successfully obtained. Due to the energetic inhomogeneity across the laser spot, the modification of droplet as a function of irradiation intensity (IRIT) can be straightly investigated on one sample and the correlated mechanisms are clarified. Systematically, the laser resizing can be perceived as: for low irradiation level, laser heating only expands droplets to make mergences among them, so in this stage, the droplet size distribution is solely shifted to the large side; for high irradiation level, laser irradiation not only causes thermal expansion but also thermal evaporation of Ga atom which makes the size-shift move to both sides. All of these size-shifts on Ga-droplets can be strongly controlled by applying different laser IRIT that enables a more designable droplet epitaxy in the future.

Keywords: Ga-droplet, In-situ pulsed laser, Thermal expansion, Thermal evaporation, Molecular beam epitaxy

Introduction
Currently with the increasing development of both fundamental physics and practical application, it is of great demands for people to achieve various devices. It has been widely demonstrated that various devices and structures can be constructed by applying of metallic nanoparticles [1–5]. As an important representative, droplet epitaxy which is based on metallic droplet (nanoparticles) has continuously attracted worldwide research interests and efforts since it is proposed by Koguchi et al. [6] in 1991 because it can nearly cover all kinds of low-dimensional nanostructures, including but not limited to quantum dots [7, 8], quantum rings [9–11] and quantum wires [12, 13]. Especially recently, some very peculiar structures of quantum-dot pairs [14, 15], quantum dot molecules [16, 17], double-rings [18] and multiple concentric rings [19, 20] are also successfully realized by droplet epitaxy. Generally, droplet epitaxy usually combines two steps, i.e., pre-formation of metallic droplet and subsequent crystallization [21, 22]. The size-control of droplets during the step of droplet formation is a key point for the whole droplet epitaxy since it not only determines the final size of quantum structure directly, but also defines what kind of nanostructure the droplets will target to become. For instance, a fast switch between quantum dots and quantum rings can be sensitively triggered by tuning the droplet size and the aforementioned multiple concentric rings is exclusively built on Ga-droplets of considerably huge size. As is well reported, temperature is the most essential factor for adjusting the size of droplets, in order to enlarge the droplet, the temperature must increase [23, 24]. Typically, Fuster et al. has
increased the temperature to as high as 500 °C to successfully obtain a huge Ga-droplet with 45 nm in height and 240 nm in width [25]. However, increasing temperature will intensify the droplet etching into substrate drastically [26–29]. By this kind of nano-drill, the elements of droplets will be consumed before the subsequent crystallization and also a parasitic structure of nano-hole will develop beneath the droplet which may pollute the target quantum structure. Zh. M. Wang et al. has proven that the Ga-droplets could totally disappear and be replaced by volcano-like nano-holes only after annealing at 500 °C for 80 s without Arsenic (As) supplying [30]. Obviously, to raise temperature may destroy the droplets, but to push them growing bigger makes people has to do so, it’s an irreconcilable contradiction in the traditional droplet epitaxy. Hence, it makes great significances to find a technology, with temperature-independence, to modify the droplet size.

In this paper, Ga-droplets, with an original morphology of density: $4.1 \times 10^{10}/\text{cm}^2$, width: 37–65 nm and height: 4–9 nm, were produced on GaAs (001) substrate (Sub) through MBE and then immediately we used a UV pulsed laser to in situ shoot the as-prepared surface. Impressively, the laser shooting behaves a good modification of the size of droplets and the involved principle of the resizing from the LIR is systematically presented as well. After irradiation, the height and width of the droplets broaden to a range of 1–42 nm and 16–230 nm, respectively, i.e., we have successfully achieved extreme huge droplets with width as long as 230 nm and height as high as 42 nm directly at a very low temperature of 180 °C. So a technology for resizing the droplets with both safety and efficiency is reported here. This must contribute great freedom of size-control to the current droplet epitaxy and make it more feasible and flexible.

**Experimental Methods**

The experiments were performed on a special-designed MBE equipped with the laser viewport to in situ introduce pulsed laser beam into the chamber. At present, this prototype system only installs three source cells of Indium (In), Ga and As. The growth temperature is monitored by the pyrometer which is calibrated. For monitoring the growth, the reflection high energy electron diffraction is also comprised. First, a deoxidized GaAs (001) 2-inch quarter Sub was coated by a 300 nm GaAs buffer layer at 600 °C and the BEP of As$_2$ is set as $7.6 \times 10^{-6}$ Torr. Then, the As valve was full-closed and the Sub temperature was set down to 400 °C temporarily to wait the excess As atoms being sufficiently captured by the liquid nitrogen cold trap and meanwhile to avoid the absorption of As on the surface. Until the As-ambient pressure was reduced to about $1.2 \times 10^{-5}$ Torr that is nearly the same as the best pressure ($(9.5 \sim 11) \times 10^{-10}$ Torr) which can be obtained before growth to avoid the residual As$_2$, the Sub temperature was furtherly decreased to 180 °C to form the droplets respectively with Ga growth rate of 0.168 ML/s and total deposition thickness of 4 MLs. As soon as the Ga-droplet growth was finished, the sample was in situ irradiated by only single shot of mono-beam of a frequency tripled neodymium yttrium aluminum garnet laser (wavelength:355 nm/pulse duration: 10 ns) with an energy of 35 mJ. After irradiation, the sample was immediately taken out to undergo the surface morphology test by AFM in tapping mode. Because the laser spot (6 mm/Diameter) is much smaller than the 1/4 2-inch Sub, both non-irradiated region (NIR) and irradiated region (IR) can be put together to compare. For the IR, due to the laser spot has a Gaussian-like profiled intensity distribution, the morphology evolution of the droplet as a function of $IRIT$ can be all at once observed on this sample. So in the following discussion, five representative locations, defined as irradiation-1 ($IR1$) to irradiation-5 ($IR5$) in the $IRIT$ order of $E_{IR1} < E_{IR2} < E_{IR3} < E_{IR4} < E_{IR5}$, were selected from the IR for analysis and the exact positions of them related to the laser spot are marked in the top-draw of Fig. 1. As is shown, the position of $IR5$ is corresponding to the center of the laser spot (marked as O-position), then we linearly scanned rightward, after each movement of 0.5 mm, an AFM image was taken (corresponding to $IR4$-$IR1$ in sequence). At last, we completely moved outside of the spot and took the AFM image defined as $NIR$ (i.e., the original morphology of as-prepared Ga-droplets).

**Results and Discussion**

Figure 1a–f present the AFM morphology results of the droplets in $NIR$ and $IR1$–$IR5$, respectively. (g-l) and (m-r) are the corresponding histograms of width and height distribution. Since the droplets were fabricated at temperature as low as 180 °C, in $NIR$ (Fig. 1a), the original density reaches to as high as $4.1 \times 10^{10}/\text{cm}^2$ and the width and height are both typically Gaussian distributed with dominant mode of 45–55 nm and 4–8 nm (respectively shown in Fig. 1g, m). The maximum and minimum sizes are corresponding ~65 nm wide/ ~9 nm high and ~37 nm wide/ ~4 nm high. The droplets in $IR1$ (Fig. 1b) look very like with the $NIR$. There are no distinct changes can be distinguished in comparison of either Fig. 1h and (g) or (n) and (m). The droplets in $IR1$ have the same maximum and minimum size with the $NIR$. While in $IR2$ (Fig. 1c) and $IR3$ (Fig. 1d), the droplet size begins to be modified by the laser shooting. Some enlarged droplets emerge on the surface with a reduction of the density. Especially for $IR3$, the droplets beyond the former maximum width (65 nm) have
accounted to a proportion of 55% (Fig. 1j) and corresponding 37% for the proportion beyond the former maximum height (Fig. 1p). At the same time, the total density has reduced to only 1/3 of the original density. Overall, after the laser resizing, the size distribution of droplets in either of IR2 and IR3 is solely shifted to the large side, i.e., no droplets on the small side of the original distribution in NIR are observed. However, for the droplets in IR4 and IR5, the distributions not only shift to the large side but also extend to the small side: Fig. 1e, f display the results of IR4 and IR5, with continued reduction of the density, it is clear to see in Fig. 1k–l and q–r that the droplet size distributions are furtherly shifted to the large side. Particularly in IR5, the maximum droplet (width: 230 nm/height: 42 nm) is nearly four times larger than the maximum one (width: 65 nm/height: 9 nm) in NIR and such a large size is not reported elsewhere at so low a temperature. Besides, a few small droplets beneath the original minimum size are also generated and some of them even are ultra-mini only with width of 16 nm and height of 1 nm. So, the evolution of the laser modification of the
Ga-droplets with \textit{IRIT} is completely observed and it well demonstrates the laser shooting can facilely resize the Ga-droplets.

In order to interpret the above experimental data, firstly, five partial areas selected from \textit{NIR} and \textit{IR1-IR4} are enlarged and illustrated in Fig. 2a–e, respectively. Secondly, we additionally calculated the equivalent volume (\textit{EV}) of the Ga-droplets in \textit{NIR} and \textit{IR1-IR5}. In the calculation, the section profile of Ga droplet is approximately assumed as the mode of spherical cap [26], then the volume of each droplet can be given by

\[
V = \frac{\pi r^3}{3} \left( 2 - 3 \cos \theta + \cos^3 \theta \right) / 3 \sin^3 \theta
\]  

(1)

where \( r \) is the droplet radius and \( \theta \) is the contact angle, respectively, at last the \( \textit{EVs} \) for \textit{NIR} and \textit{IR1-IR5} were counted by summing up the volume of all the droplets in Fig. 1a–f correspondingly. Figure 2f shows the normalized \textit{EV} results (triangles) and the normalized density data (squares) is included as well. Then the whole evolution of laser resizing could be divided into three stages: at the first stage (\textit{NIR-IR1}): The original droplets in \textit{NIR} (Fig. 2a) inter-stand very close and the surrounding of each droplet is clear and flat (see the drawing) which is sketched in Fig. 2a. For \textit{IR1} (wherein is irradiated by a quite low intensity), comparing with the \textit{NIR}, the size distribution, density and \textit{EV} are almost unchanged, but an emerging structure of nano-ring is observed to surround the droplets which is marked by the white arrows in Fig. 2b. We attribute it to the expansion of droplets induced by laser-heating. As is shown in Fig. 2b, after the
irradiation, the laser will heat the droplets to expand (the well-known thermal expansion). Whereas the expansion is not strong enough to make coalescence of the droplets due to the limited intercross. As the heat dissipated, the droplets will relax back to the original equilibrium state but leaving the trails of expansion which is shaped as a ring encircling the relaxed droplet (see the black arrow). Therefore in this stage, the IRIT is too weak to resizing the droplets; at the second stage (IR2-IR3): In Fig. 2c for IR2, the experimental evidence of the droplet coalescence is observed and pointed out with a yellow dotted rectangle. The marked droplet is neighbored by a nano-hole (white arrow) and it is much larger than any of NIR with the size of 70 nm wide and 12 nm high. This can be explained by the coalescence of two droplets as is shown in Fig. 2c': for A_droplet and B_droplet, with the IRIT increasing, the expansion is enhanced which results in more cross-over between them and then the more inter-cross will probably push A_droplet merging into B_droplet randomly thus leaves a nano-hole pre-drilled by A_droplet at the same time. While compared with IR2, in Fig. 2d for IR3, coalescence of three (see yellow dotted rectangle/Fig. 2d') or even more droplets are discovered which reflects a more strong effect of laser resizing. Hence, for IR2 and IR3, the statistical data of size distribution and density could be explained as a result of the coalescence. Furthermore, as is seen in Fig. 2f, both of IR2 and IR3 still keep the same EV level with NIR in contrast to the sharp reduction of density. That means at this stage, the laser-shooting only resizes the droplets through thermal expansion without loss of Ga atoms. However, at the third stage of IR4-IR5: the EV of droplets begins to decrease sharply. It indicates that the LIR will not only expand the droplets but also accompanying with thermal evaporation of Ga atoms. Once the IRIT exceeds to a certain value, the pulsed laser may instantaneously heat the droplet to over the evaporation threshold of Ga. So the resizing of droplets in this stage is co-governed by coalescence and evaporation. Figure 2e' illustrates the interplay: if the coalescence not compensate the loss of Ga by thermal evaporation, the droplet size will shrink (see the mini droplet marked in Fig. 2e) and otherwise, it will increase. Especially, some huge droplets may be produced (see the huge droplet marked in Fig. 2e) by coalescence of multi-droplets under certain probability. Then this kind of competition can well explain why the size-shift of IR4 and IR5 specially broadens to both sides. So far, resizing of the droplets by in-situ pulsed LIR has been well investigated in the perspectives of both performance and principle. To make the work more well-organized, in the following we have carried out another two designed experiments.

On the one hand, according to the principle of our explanation of thermal-expansion induced coalescence, besides the IRIT, the inter-droplet distance, i.e., the density of droplet, is the other key parameter. As is shown in Fig. 3a, if we separate two droplets in a larger gap (from d1 to d2), the coalescence should be relatively inhibited resulting from the reduced inter-cross during the same thermal expansion. Hence, we prepared a new droplet sample at the temperature of 280 °C. As the temperature increased, the droplet density of NIR (Fig. 3b) is rapidly decrease to 5 × 10^9/cm^2, nearly 1/8 of the sample at 180 °C and the interspace among droplets has been amplified effectively. After irradiation, as is seen in Fig. 3c, the droplets still have the equal density to the NIR but are encircled by very remarkable adjacent rings (see white arrows). It reflects that the coalescence is indeed prevented even with strong thermal expansion and thus further solidifies our explanation powerfully.

On the other hand, it is worth pointing out that the nano-holes (Fig. 4a) observed in our work are very shallow with depths of sub-nanometer (less than three atomic
layers) (see the inset). So impressively, the drill effect of droplets is strictly suppressed and could be almost neglected which benefits from the low Sub temperature. To present the potential risk of nano-drill as the temperature increasing for the droplets, we fabricated another sample at a high temperature of 350 °C. After the growth finished, the Sub temperature didn’t decrease immediately but with a short interrupt of only 2 min before rapid cooling down. Figure 4b shows the morphology result, we could see a serious drill effect has happened and it has destroyed the droplets badly. And some droplets (see arrows) are even completely eroded up and replaced by nano-holes with etching depth of several nanometers (see the inset). On the contrary, as is suggested in Fig. 4c, the droplets prepared at 180 °C can still keep stable after an interrupt as long as 15 min.

Conclusions

In conclusion, we have conducted a research on MBE in situ shooting on the Ga-droplets at 180 °C by pulsed laser and demonstrated that the laser-shooting can facilely and high-efficiently adjust the size distribution of droplets. The morphology evolution of the droplet as a function of \( IRIT \) is carefully studied and the involved mechanism is also systematically clarified: for low irradiation level, the droplet size distribution is solely shifted to the large side which can be explained by the only effect of droplet-coalescence induced by laser-thermal expansion of the droplets; While for high irradiation level, the size-shift will specially extend to both sides and this is resulting from a kind of competition between coalescence and thermal-evaporation. So herein, we have reported a technology by using pulsed laser-irradiation to in situ resize the droplets at such a low temperature that can nearly prevent the droplets etching into the Sub. Apparently, our technology is compatible with the common droplet epitaxy solution beautifully with free of pollution, oxidation and damage. And what is worth mentioning is, by upgrading the mono-beam irradiation into muti-beam interference irradiation, that we can easily realize patterned-modification of the droplet size for a more controlled droplet epitaxy in the future.

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Authors’ contributions

Biao Geng and Chen Chen prepared and tested the samples and also analyzed the results. Wei Zhang, Linyun Yang, Changwei Deng, Xinning Yang and Lili Miao help to grow and test the samples. Zhenwu Shi supervised the study and wrote the manuscript. Changsi Peng supervised the study and reviewed the manuscript. All the authors read and approved the manuscript.

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Availability of data and materials

Not applicable.

Declaration

Competing interests

The authors declare that they have no competing interests.

Author details

1 School of Optoelectronic Science and Engineering and Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University, Suzhou 215006, China. 2 Key Lab of Advanced Optical Manufacturing Technologies of Jiangsu Province and Key Lab of Modern Optical Technologies of Education Ministry of China, Soochow University, Suzhou 215006, China. 3 Institute of Research for Applicable Computing, University of Bedfordshire, Park Square, Luton LU1 3JU, UK. 4 AVIC Huadong Photo-electronics Co., Ltd, Wuhu 241002, China.
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