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Abstract: We report on the growth (using metal-organic vapour phase epitaxy) and optical characterization of single and multiple layers of InGaN quantum dots (QDs), which were formed by annealing InGaN epilayers at the growth temperature in nitrogen. The size and density of the nanostructures have been found to be fairly similar for uncapped single and three layer QD samples if the GaN barriers between the dot layers are grown at the same temperature as the InGaN epilayer. The distribution of nanostructure heights of the final QD layer of three is wider and is centred around a larger size if the GaN barriers are grown at two temperatures (first a thin layer at the dot growth temperature, then a thicker layer at a higher temperature). Micro-photoluminescence studies at 4.2 K of capped samples have confirmed the QD nature of the capped nanostructures by the observation of sharp emission peaks with full width at half maximum limited by the resolution of the spectrometer. We have also observed much more QD emission per unit area in a sample with three QD layers, than in a sample with a single QD layer, as expected.

Response to Reviewers:

"Growth and optical characterization of multilayers of InGaN quantum dots"
Zhu *et al.* CRYS-D-11-01302R1

Response to referee's comments and list of changes made to manuscript:

We thank the referee for his/her careful reading of the paper and appreciate the comments given by the referee. We will respond to his/her specific comments (quoted in italics) below.

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The referee comments: "*The only one not very important comment is about the following sentence in the abstract: "The size and density of the nanostructures have been found to be fairly similar for uncapped single and three layer QD samples if the GaN barriers between the dot layers are grown at a single temperature."*

In the main body of the paper the "single temperature" growth sequence is described in details, then "quasi-two temperature" method is described in the same way, and only below authors use a short term "single temperature GaN barriers". So, in the main text it is O'K. In contrast, inside the abstract, "single temperature" appears the first and thus is unclear. It seems that it would be better to write "The size and density of the nanostructures have been found to be fairly similar for uncapped single and three layer QD samples if the InGaN QD layers and GaN barriers between the dot layers are grown at the same temperature." or something equivalent."

The referee's suggested correction has been made. The sentence in the abstract now reads as follows:

"The size and density of the nanostructures have been found to be fairly similar for uncapped single and three layer QD samples if the GaN barriers between the dot layers are grown at the same temperature as the InGaN epilayer."

****

All the changes listed above have been highlighted in blue in the revised manuscript. We hope that the revised manuscript is now acceptable for publication.

Your sincerely

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9 Sep 2011

Dear Editor,

Title: Growth and optical characterization of multilayers of InGaN quantum dots

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I, the corresponding author Tongtong Zhu, hereby confirm on behalf of myself and other authors, that this manuscript is our original work and has been neither published, nor is being considered for publication elsewhere. All the authors have read and approved the manuscript and have agreed to the submission.

Your sincerely,

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*Highlights

Research Highlights:

- Growth and optical characterization of single and multiple layers of InGaN quantum dots.
- Effect of the number of InGaN QDs layers on metallic nanostructure height and density.
- Effect of the GaN barrier growth temperature on metallic nanostructure height and density.
- Observation of much more QD emission per unit area in a 3 QD layer sample.

Growth and optical characterization of multilayers of InGaN quantum dots

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ABSTRACT

We report on the growth (using metal-organic vapour phase epitaxy) and optical characterization of single and multiple layers of InGaN quantum dots (QDs), which were formed by annealing InGaN epilayers at the growth temperature in nitrogen. The size and density of the nanostructures have been found to be fairly similar for uncapped single and three layer QD samples if the GaN barriers between the dot layers are grown at the same temperature as the InGaN epilayer. The distribution of nanostructure heights of the final QD layer of three is wider and is centred around a larger size if the GaN barriers are grown at two temperatures (first a thin layer at the dot growth temperature, then a thicker layer at a higher temperature). Micro-photoluminescence studies at 4.2 K of capped samples have confirmed the QD nature of the capped nanostructures by the observation of sharp emission peaks with full width at half maximum limited by the resolution of the spectrometer. We have also observed much more QD emission per unit area in a sample with three QD layers, than in a sample with a single QD layer, as expected.

Keywords:
B2. InGaN quantum dots
A1. Photoluminescence
B1. Nitrides
A3. Metal-organic vapour phase epitaxy

I. INTRODUCTION

Semiconductor quantum dots (QDs) have recently attracted much attention for a variety of optoelectronic applications and for exploration of their fundamental physics [1]. By using a high density of uniformly distributed self-assembled QDs, laser diodes (LDs) have been realized with a much enhanced density of states and a much less temperature-dependent threshold current compared to LDs based on quantum well structures [2]. Conversely, emission from a single QD can be isolated and exploited to be used in single photon sources for quantum cryptography and quantum computing [3]. Nitride based QDs have been suggested to be a particularly attractive option for single photon sources [4] since their high piezoelectric constants allow the QD emission to be tuned across a wide range of energies by the application of an external bias [5]. Additionally, the large range of bandgaps in the nitride semiconductor family provides potential for single photon emission at room temperature [6].

Whilst self-assembled InGaN QDs have been grown by molecular beam epitaxy (MBE) via Stranski-Krastanov (SK) growth [7], there are a number of different methods to grow InGaN QDs in metal-organic vapour phase epitaxy (MOVPE), such as pre-treatment of the surface by a silicon precursor [8], and growing InGaN thin films at two different temperatures [9]. Our approach for the growth of InGaN QDs (modified droplet epitaxy) involves a post-growth anneal of the InGaN epilayer at the growth temperature in molecular nitrogen [10]. We have postulated [9] that QD formation in this method occurs first via the decomposition of the InGaN epilayer to form nanoscale metallic droplets, containing indium and gallium. These droplets then re-react with ammonia during the growth of the GaN cap, to form InGaN QDs. QDs formed in this way have been shown to act as single photon emitters [10] and have been successfully incorporated into micro-cavity structures exploiting AlN/GaN distributed Bragg reflectors [11] and microdisks [12], which allows more efficient light extraction from the QD layer.

In this paper, we investigated the growth of multilayers of InGaN QDs using the modified droplet epitaxy approach. It is hoped that this could lead to an increase in QD density, which could increase the probability of spatial and spectral resonance within a cavity structure. In addition, increased QD densities may also be of relevance to laser diode growth, in order to achieve an increased density of states in the active region. The effect of the number of QD-containing layers and barrier growth temperature on nanostructure height and density will be discussed. Optical properties of capped samples containing one and three QD layers will be studied by micro-photoluminescence (μPL).

II. EXPERIMENTAL DETAILS

All samples were grown by MOVPE in a 6 x 2 in. Thomas Swan close-coupled showerhead reactor on sapphire (0001) substrates with a miscut of (0.25±0.10)° towards (11-20). Trimethylgallium (TMG), trimethylindium (TMI), and ammonia were used as precursors. The pseudo-substrates consist of approximately 4.5 μm of GaN grown at 1020 ºC, following deposition of a 30 nm GaN buffer layer at 540 ºC [13]. InGaN epilayers of ~10 ML thickness were grown at 710 ºC with N_2 as the carrier gas at a reactor pressure of 300 Torr. The ammonia flux was kept the same as the N_2 flux at 10 slm (standard liters per minute). Immediately after the InGaN epilayer growth, samples were annealed for 30 s in an N_2 atmosphere under the same conditions of temperature and pressure that were used for InGaN epilayer growth. Details on this modified droplet epitaxy method for the growth of InGaN QDs can be found elsewhere [10].

As a control, a single QD epilayer, with no GaN cap (sample A) was first grown, as described above. For samples with 3 QD layers (referred to hereafter as 3 x QD samples), three InGaN epilayers were grown and annealed the same way as the sample with a single QD layer, with the InGaN layers separated by ~10 nm GaN barriers. To allow atomic force microscopy (AFM) examination of the InGaN surface, three 3 x QD samples were grown (samples B, C and D, see also Table. 1) in which the third and final InGaN QD layer was left uncapped. For sample B, the GaN barriers were grown under the same conditions as the InGaN epilayers by switching off the TMI flow solely. Another two samples with 3 x QD layers (sample C and D) were grown using a quasi-two temperature (Q-2T) growth method. For this latter growth method, an initial GaN capping layer of ~2 nm thickness was grown at the same temperature of 710 ºC after each InGaN QD layer, after which the temperature was ramped and stabilized at 860 (sample C) or 910 ºC (sample D) for the rest of the barrier growth (~8 nm) while maintaining a constant TMG flux. The higher GaN growth temperature was thought to be beneficial for the material quality while the thin GaN capping layer was designed to prevent indium evaporation during the temperature ramp.

These uncapped samples A to D were examined by AFM using a Veeco Dimension 3100 operated in TappingMode™. The size and density of metallic nanostructures formed by the annealing of InGaN epilayers in N_2 were examined using ten 1 μm x 1 μm AFM images from each sample and the data were analyzed using the WSxM freeware [14].

Additional single layer (sample E) and 3 x QD (sample F) wafers for μPL studies were grown and were capped with ~10 nm GaN at 710 ºC in N_2 and another ~10 nm GaN at 1020 ºC in H_2. The main differences between the samples are summarised in Table. 1. Sample F had single temperature GaN barriers between the QD layers, similar to sample B. Micro-PL measurements were carried out using a two photon excitation technique employing a picosecond mode-locked Ti-sapphire laser emitting at 790 nm. Samples were mounted in a cold-finger cryostat that could be cooled down to 4.2 K and the laser was focused through a microscope objective lens to a spot size of ~1 μm with an excitation power density of 7.64 MW cm^{-2}. A more detailed description of this two-photon excitation technique is available elsewhere [15]. Luminescence from the samples was dispersed using a 1200 l/mm grating in a 0.3 m spectrometer with a Peltier cooled Si-based charge-coupled detector.

III. RESULTS AND DISCUSSION

1. Growth and morphology of single and 3 x InGaN QD layers

The surface morphologies of samples A and B are shown in Fig. 1(a) and (b). Surface pits in the InGaN layer and a number of small metallic nanostructures are seen for both the single layer and the 3 x QD sample [10]. The formation of nanostructures is observed both in the surface pits and on top of the InGaN layer. It is found that the nanostructure density is very similar between the two samples at ~1 x 10^{10} cm^{-2} and that the average nanostructure height is 1.5±0.4 nm for both samples. The only notable difference between the two samples is the observation of a raised defect and a number of prominent dislocation pits in Fig. 1(b) (indicated by circles on the figure), which are absent from Fig. 1(a). Raised defects have been observed previously in InGaN multiple quantum well structures [16], and they can also be seen in AFM images of the sample with a single, capped QD layer (sample E).

For the growth of 3 x QD layers, we varied the growth conditions of the GaN barriers by using a Q-2T growth method. It is shown in Fig. 1(c) and (d) that the general surface morphology of 3 x QD samples with Q-2T GaN barriers grown at 860 and 910 °C (samples C and D) looks fairly similar to the 3 x QD sample with GaN barriers grown at 710 °C (sample B), with surface pits and small metallic nanostructures formed after the annealing process. However, much larger nanostructurs are also seen and the nanostructure density appears to be much reduced in sample C and D. Whilst both dislocation pits and raised defects were observed for sample C [Fig. 1(c)], only dislocation pits were seen in sample D [Fig. 1(d)], which may be due to the improved material quality of the GaN barrier.

For samples with 3 x QD layers, we investigated the effect of Q-2T barrier growth temperature on the size distribution of the nanostructures in the third uncapped QD layer. Figure 2(a) shows that the distribution of heights of these nanostructures is fairly similar for single (sample A) and 3 x QD layers (sample B) with the InGaN epilayer and GaN barrier both grown at 710 °C. For the 3 x QD samples with Q-2T barrier growth at 860 and 910 °C, the distribution appears to be much wider and is centred around a much larger size. In addition, it is shown in Fig. 2(b) that the dot density also decreases as the growth temperature of the Q-2T barrier growth increases. This suggests that the use of multilayer samples employing single temperature GaN barriers is a better way to achieve an increased density of fairly uniform QDs for the purpose of achieving both spatial and spectral resonance of QD emission with a cavity.

One possible origin for the differences in the size and density of nanostructures formed on GaN barriers grown by single temperature and Q-2T methods, might be changes in the morphology of the surface on which the QDs are grown, altering the density of nucleation sites for the nanostructures. To investigate the influence of the underlying surface morphology on QD growth, we compared the surface morphology of a standard GaN pseudo-substrate and a sample with a single InGaN QD layer capped with 10 nm GaN grown at 710 °C in N_2. These two morphologies represent the surfaces on which InGaN QD layers were grown for Sample A [Fig. 1(a)] and B [Fig. 1(b)], respectively. Unlike the normal smooth surface observed for the GaN pseudo-substrate [Fig. 3(a)] which has been grown at 1020 °C in H_2, the low temperature GaN cap grown at 710 °C in N_2 [Fig. 3(b)] appears to be much rougher with a number of raised defects and dislocation pits, and with significant step-pinning by the dislocation pits. However, it has been shown in Fig. 1 (a) and (b) that the size and distribution of nanostructures seems very similar for the samples A and B, suggesting that the nanostructure formation is not significantly affected by the surface morphology of the underlying GaN layer in this case. Therefore, the variation in nanostructure formation (both size and density) observed in Fig. 1 is unlikely to be attributable to variation of surface roughness and hence of surface nucleation centres of the GaN barriers. A possible alternative explanation is that the underlying QD layers influence the strain at the GaN surface, and hence influence the growth of subsequent QD layers (as is seen in SK growth of QD multilayers [17]). If the Q-2T barrier growth has affected the underlying InGaN epilayer, perhaps via increased interdiffusion between the dots and the barriers at the higher temperature, then the influence of the underlying layer on the surface strain of the GaN cap may change, altering the observed QD layer's morphology. Growth conditions during capping layer formation are known to influence the morphology of the underlying dot layer in both the nitrides [18] and other materials systems [19] for other dot growth mechanisms.

2. Optical properties of single and 3 x InGaN QD layers

Initial room temperature PL measurements have confirmed that the luminescence intensity more than doubled by the use of 3 x QD layers (sample F) compared to the single QD layer (sample E) (data not shown here). Figure 4 shows μPL spectra from single and 3 x QD samples after the illuminated sample area has been reduced by an Au mask with an aperture size of ~1 μm. Sharp emission peaks have been observed for both samples, which are characteristic of carriers strongly confined in QDs [10]. The narrowest full width at half maximum (FWHM) of these sharp peaks is ~0.16 nm, which is limited by the spectral resolution of the spectrometer. Based on a number of similar spectra from different areas of each sample, it appears that there are more sharp peaks per unit area in the 3 x QD layer sample (F) than in the single QD layer sample (E), suggesting that we have achieved formation and inclusion of a much increased QD density in the structure by growing multilayers of InGaN QDs.

IV. CONCLUSIONS

In summary, we have demonstrated the growth of single and multiple InGaN QD layers by MOVPE using a modified droplet epitaxy method. Increasing the number of QD layers does not appear to affect the size and density of the nanostructures formed after the annealing of the InGaN epilayer in N_2, if the GaN barriers are grown at the InGaN growth temperature. However, growing the GaN barrier using a Q-2T method appears to have a significant impact on the dot height and density. The observation of sharp emission peaks with FWHM as small as ~0.16 nm at 4.2 K in μPL has confirmed the formation and inclusion of QDs in both single layer and 3 x QD samples. We have observed much more QD emission per unit area in the 3 x QD layer sample, suggesting that the growth of InGaN QD containing multilayers appears to be beneficial for achieving higher QD densities in order to achieve spatial and spectral resonance with a cavity structure.

ACKNOWLEDGMENTS

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REFERENCES

[1] A. D. Yoffe, Adv. Phys. **50**, (2001) 1.

[2] M. Henini and M. Bugajski, Microelectron. J. **36**, (2005) 950.

[3] N. Gisin, G. Ribordy, W. Tittel, and H. Zbinden, Rev. Mod. Phys. **74**, (2002) 145.

[4] A. F. Jarjour, R. A. Oliver, and R. A. Taylor, Phys. Status Solidi A **206** (2009) 2510.

[5] A. F. Jarjour, R. A. Oliver, A. Tahraoui, M. J. Kappers, C. J. Humphreys, and R. A. Taylor, Phys. Rev. Lett. **99**, (2007) 197403.

[6] S. Kako, C. Santori, K. Hoshino, S. Goetzinger, Y. Yamamoto, and Y. Arakawa, Nature Mater. **5**, (2006) 887.

[7] C. Adelmann, J. Simon, N. T. Pelekanos, Y. Samson, G. Feuillet, and B. Daudin, Phys. Status Solidi A **176**, (1999) 639.

[8] R. A. Oliver, N. K. van der Laak, M. J. Kappers, and C. J. Humphreys, J. Cryst. Growth **310**, (2008) 3459.

[9] T. Yamaguchi, K. Sebald, H. Lohmeyer, S. Gangopadhyay, J. Falta, J. Gutowski, S. Figge, and D. Hommel, Phys. Status Solidi C **3**, (2006) 3955.

[10] R. A. Oliver, G. A. D. Briggs, M. J. Kappers, C. J. Humphreys, S. Yasin, J. H. Rice, J. D. Smith, and R. A. Taylor, Appl. Phys. Lett. **83**, (2003) 755.

[11] A. F. Jarjour, R. A. Taylor, R. A. Oliver, M. J. Kappers, C. J. Humphreys, and A. Tahraoui, Appl. Phys. Lett. **91** (2007) 052101.

[12] H.A.R. El-Ella, F. Rol, M.J. Kappers, K.J. Russell, E.L. Hu, and R.A. Oliver, Appl. Phys. Lett. **98**, (2011) 131909.

[13] R. Datta, M. J. Kappers, M. E. Vickers, J. S. Barnard, and C. J. Humphreys, Superlattices Microstruct. **36**, (2004) 393.

[14] I. Horcas, R. Fernandez, J. M. Gomez-Rodriguez, J. Colchero, J. Gomez-Herrero, and A. M. Baro, Rev. Sci. Instrum. **78**, (2007) 013705.

[15] A. F. Jarjour, A. M. Green, T. J. Parker, R. A. Taylor, R. A. Oliver, G. A. D. Briggs, M. J. Kappers, C. J. Humphreys, R. W. Martin, and I. M. Watson, Physica E **32,** (2006) 119.

[16] S. M. Ting, J. C. Ramer, D. I. Florescu, V. N. Merai, B. E. Albert, A. Parekh, D. S. Lee, D. Lu, D. V. Christini, L. Liu, and E. A. Armour, J. Appl. Phys. **94**, (2003) 1461.

[17] J. Tersoff, C. Teichert, and M. G. Lagally, Phys. Rev. Lett. **76**, (1996) 1675.

[18] C. Tessarek, T. Yamaguchi, S. Figge, and D. Hommel, Physica Status Solidi C, **6**, (2009) S561.

[19] G. D. Lian, J. Yuan, L. M. Brown, G. H. Kim, and D. A. Ritchie, Appl. Phys. Lett. **73**, (1998) 49.

FIGURE CAPTIONS

Fig. 1. AFM images of uncapped InGaN epilayers on GaN following a 30 s anneal in N_2: a) single QD layer (sample A, ***h***=6.5 nm), b) 3 x QD layers with GaN barrier grown at 710°C (sample B, ***h***=16 nm), c) 3 x QD layers with Q-2T barriers grown at 860°C (sample C, ***h***=15 nm), d) 3 x QD layers with Q-2T barriers grown at 910°C (sample D, ***h***=12 nm).

Fig. 2. Variation in metallic nanostructures a) height and distribution with single and 3 x QD layers annealed in N_2 and b) density with different Q-2T barrier growth temperature for 3 x QD samples.

Fig. 3. AFM images of a) a standard GaN pseudo-substrate (***h***=4.3 nm) and b) a single InGaN QD layer with a 10 nm GaN cap at 710 °C (***h***=8 nm).

Fig. 4. μPL spectra from the capped single (sample E) and 3 x QD layer (sample F) under the same excitation power density (7.64 MW cm^{-2}) using two-photon excitation at 4.2 K.

TABLES

Table. 1. Summary of sample description for A – F.

Table.1

Sample	Number of QD layer	Barrier growth temperature (°C)	Capping layer
A	1	710	No
B	3	710	No
C	3	710 – 860	No
D	3	710 – 910	No
E	1	710	Yes
F	3	710	Yes

Figure.1
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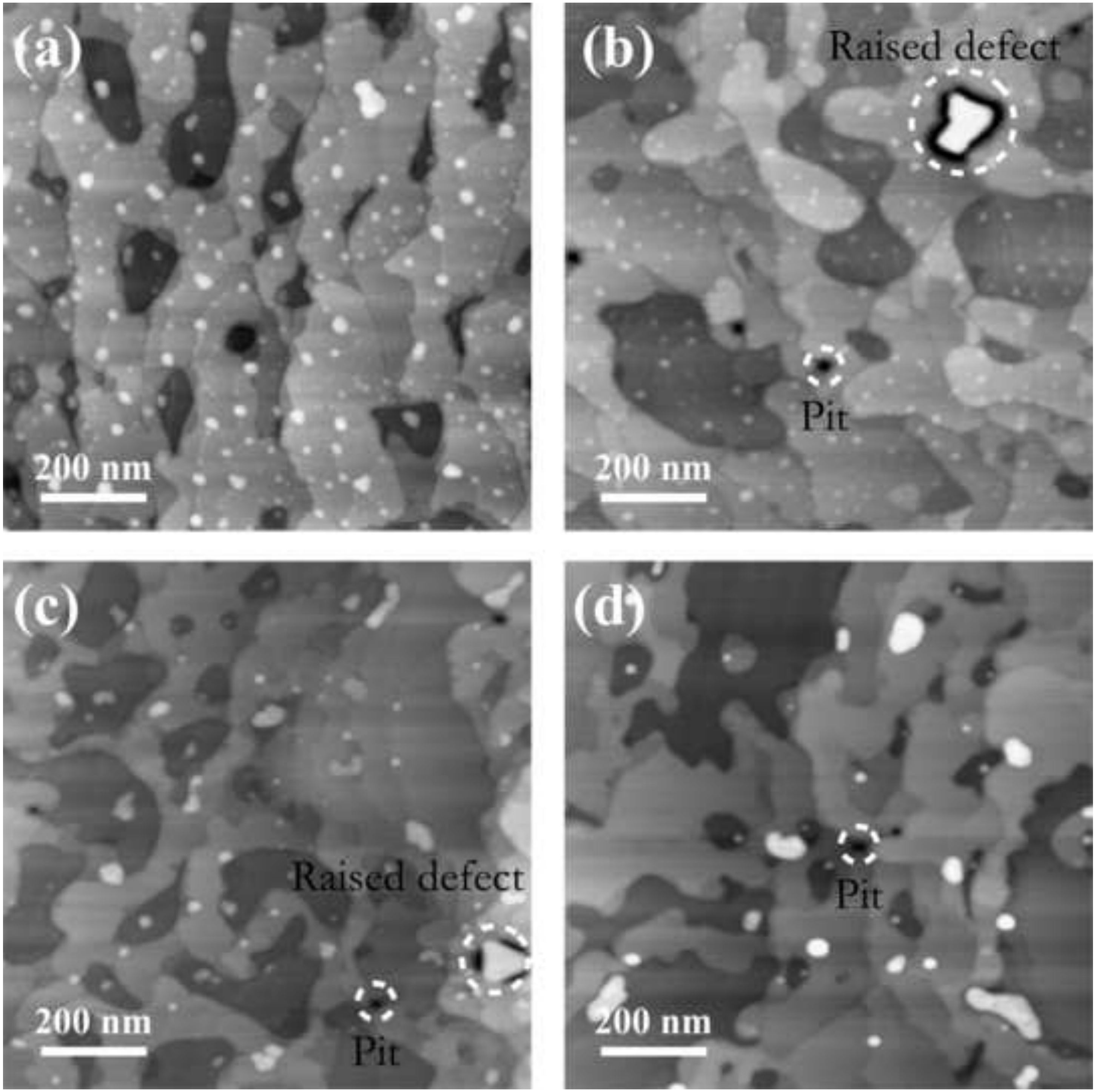

Figure.2

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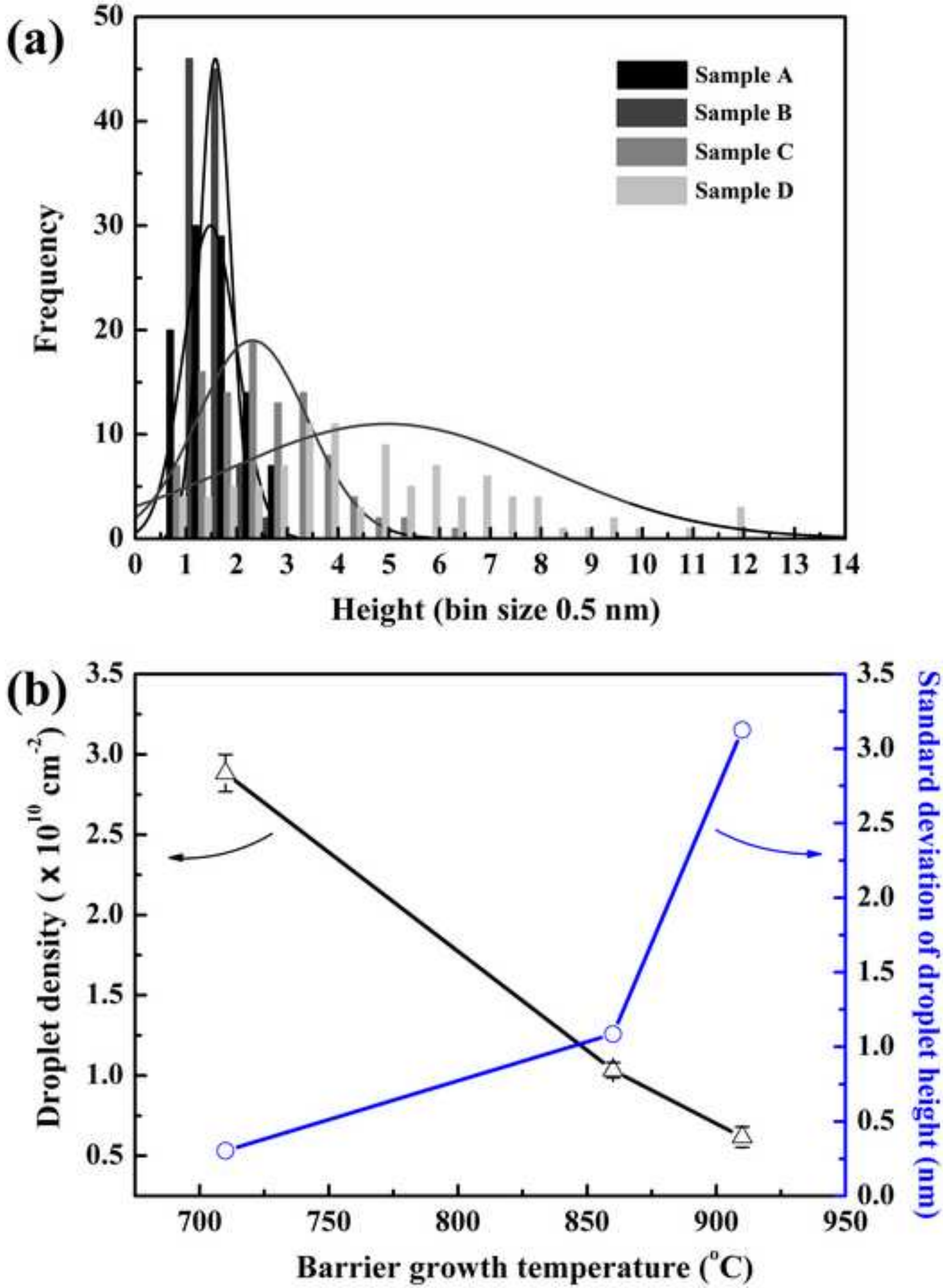

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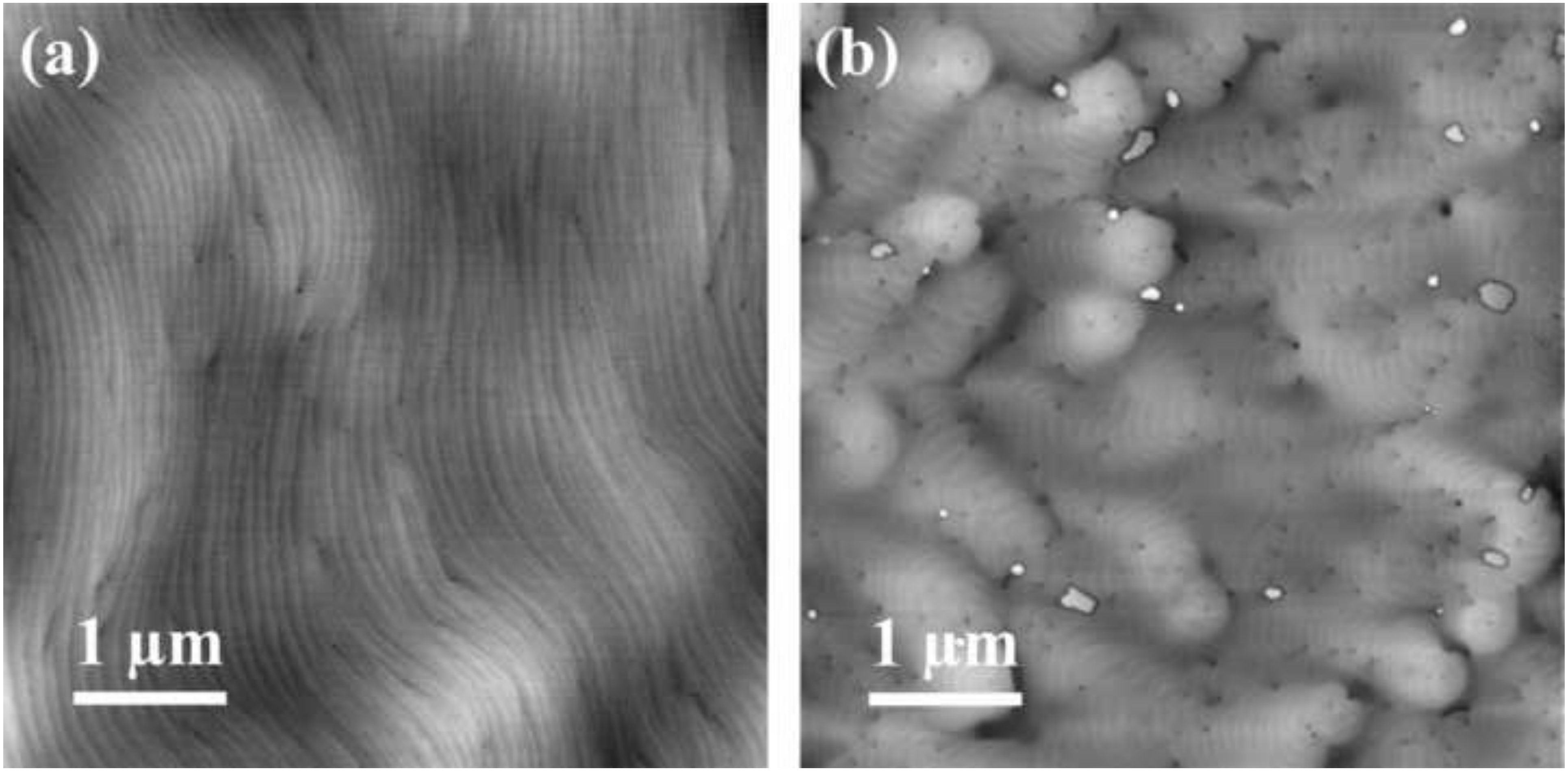

Figure.4
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