Title: Dramatic reduction of dislocations on a GaN point seed crystal by coalescence of bunched steps during Na-flux growth

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Keywords: A2. Growth from solutions; A2. Natural crystal growth; A2. Single crystal growth; A3. Selective epitaxy; B1. Nitrides; B2. Semiconducting III-V materials

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ABSTRACT:

In our study, we found that threading dislocation density (TDD) in GaN crystals naturally reduced from $\sim 10^9$ cm⁻² in a seed to less than $\sim 10^3$ cm⁻², just by using the small-sized seed called a “point seed”. However, the mechanism of the dramatic reduction was unclear. In order to reveal the mechanism of this substantial reduction of TDD, we investigated the relationship between TDD and the crystal habit during the growth. Cathodeluminescence (CL) and scanning electron microscopy (SEM) images showed that TDD was dramatically reduced after the *c* face became small ($< 50 \times 50$ μm²) in the habit-change process caused by changes of supersaturation during growth, in which bunched steps growing from the edge of the *c* face coalesced at the center. It is thought that the shrinking of the *c* face in the growth process enabled the coalescence of bunched steps, which led to the gathering of threading dislocations (TDs), and resulted in the dramatic reduction of TDD. We concluded that the natural reduction of TDs was caused by coalescence of bunched steps, which easily occurs in during the Na-flux growth on small-sized “point seeds”, and which allowed fabrication of low-dislocation-density GaN wafers.

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Original Article Statement

“Dramatic reduction of dislocations on a GaN point seed crystal by coalescence of bunched steps during Na-flux growth”

This manuscript is the authors' original work and has not been published nor has it been submitted simultaneously elsewhere.

That all authors have checked the manuscript and have agreed to the submission.

Masayuki Imanishi, Osaka University

Dear Editors,

We are pleased to submit our manuscript entitled, “Dramatic reduction of dislocations on a GaN point seed crystal by coalescence of bunched steps during Na-flux growth” for consideration for publication in *Journal of Crystal Growth*.

In this paper, we investigated the behaviors of dislocations propagating from a multipoint-seed-GaN substrate, in which threading dislocation density was dramatically reduced from $\sim 10^9 \text{ cm}^{-2}$ in the point seed to $\sim 10^2 \text{ cm}^{-2}$ during the growth. Many studies have reported the reduction of dislocations using tools like a sapphire or SiO_2 mask. This technique is interesting, however, in that it dramatically reduced dislocations propagating from a small point seed without using any tools. We revealed that the reduction of dislocation was caused in the habit-changing process, where the dislocations gathered into one. This should be considered a unique technique in solution growth such as the Na-flux method. The reduction of dislocations could lead to fabrication of large-diameter GaN wafers with low dislocation density.

We believe our work will be of particular interest to the readers of *Journal of Crystal Growth*. All the authors contributed to the work described in the letter and all take responsibility for it. Moreover, none of the work in the study has been published in any other journal.

Thank you for considering our study for publication in *Journal of Crystal Growth*. We look forward to hearing from you at your earliest convenience.

Sincerely,

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Graphics for which color is requested

Figure 1, Figure 2, Figure 3, Figure 4, Figure 5, Figure 6, Figure 7

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Abstract:

In our study, we found that threading dislocation density (TDD) in GaN crystals naturally reduced from $\sim 10^9 \text{ cm}^{-2}$ in a seed to less than $\sim 10^3 \text{ cm}^{-2}$, just by using the small-sized seed called a “point seed”. However, the mechanism of the dramatic reduction was unclear. In order to reveal the mechanism of this substantial reduction of TDD, we investigated the relationship between TDD and the crystal habit during the growth. Cathodeluminescence (CL) and scanning electron microscopy (SEM) images showed that TDD was dramatically reduced after the *c* face became small ($< 50 \times 50 \text{ }\mu\text{m}^2$) in the habit-change process caused by changes of supersaturation during growth, in which bunched steps growing from the edge of the *c* face coalesced at the center. It is thought that the shrinking of the *c* face in the growth process enabled the coalescence of bunched steps, which led to the gathering of threading dislocations (TDs), and resulted in the dramatic reduction of TDD. We concluded that the natural reduction of TDs was caused by coalescence of bunched steps, which easily occurs in during the Na-flux growth on small-sized “point seeds”, and which allowed fabrication of low-dislocation-density GaN wafers.

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1 Dramatic reduction of dislocations on a GaN point seed 2 crystal by coalescence of bunched steps during Na-flux 3 growth

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11 ABSTRACT In our study, we found that threading dislocation density (TDD) in GaN crystals naturally
12 reduced from $\sim 10^9 \text{ cm}^{-2}$ in a seed to less than $\sim 10^3 \text{ cm}^{-2}$, just by using the small-sized seed called a
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21 reduction of TDs was caused by coalescence of bunched steps, which easily occurs in during the

Na-flux growth on small-sized “point seeds”, and which allowed fabrication of low-dislocation-density GaN wafers.

1. Introduction

Gallium nitride (GaN) has attracted significant attention for its material properties, which are useful for applications in both optical devices and high-power electronic devices such as light-emitting diodes (LED) [1,2], laser diodes (LD) [3,4], and high-power transistors [5]. In order to improve device performance and reduce the manufacturing costs of such electronic and optical devices, large-diameter and low-curvature GaN wafers with low-density dislocation are needed.

Several growth techniques have also been demonstrated for the reduction of threading dislocations (TDs) in 2-in. GaN wafers via metalorganic vapor-phase epitaxy (MOCVD) or hydride vapor-phase epitaxy (HVPE) [6-9]. Hiramatsu et al. proposed the facet-controlled epitaxial lateral overgrowth (FACELO) technique [6]. In this technique, selective growth begins at stripe windows formed in an SiO₂ mask. As a result, TDs of the seed propagate into the coalescence boundary of grains or into the areas above the windows [7], so that the threading dislocation density (TDD) in a grown GaN layer can drop to $\sim 10^6 \text{ cm}^{-2}$. Motoki et al. reported improvement of the process of TD elimination by epitaxial-growth with inverse-pyramidal pits (DEEP) [8,9]. In this method, TDs are concentrated toward the center of the hexagonal pit, and as a result, a large area with TDD as low as $5 \times 10^5 \text{ cm}^{-2}$ is formed. However, with these techniques, reduction of TDD less than 10^5 cm^{-2} is not still achieved.

In a previous study, we reported the reduction of TDs using a necking technique involving a sapphire mask [10], in which TDs terminated in a hole of the mask. Recently, we demonstrated 2-in. freestanding GaN wafers with extremely low TDD and low curvature using the Na-flux growth technique on a multipoint-seed-GaN (MPS-GaN) substrate [11]. With this technique, TDD was naturally reduced from $\sim 10^9 \text{ cm}^{-2}$ in the point seed to $10^2 - 10^6 \text{ cm}^{-2}$ in the growth layer during Na-flux growth just by using

small-size seed crystals. The dramatic reduction of TDD to less than 10^3 cm^{-2} , without the use of tools like a sapphire or SiO_2 mask, has not been reported in other growth techniques. However, in some growth conditions, TDs with a density of 10^6 cm^{-2} occasionally remain on a growth layer. The reason why the reduction rate of TDD differs in some cases is still unclear. Therefore, in order to reveal the mechanism of the dramatic reduction of TDs during the growth, in this study, we investigated the behavior of the TDs propagating from a point seed. A detailed investigation of the relationship between growth habit and TD behavior revealed that the TDs gathered into the center of the c face by coalescence of bunched steps growing from the edge in the habit-change process at the initial growth. This gathering of TDs by coalescence of bunched steps during the growth on a point seed has the potential to be extremely beneficial in fabricating extremely low-TDD GaN wafers with a large diameter and low curvature.

2. Experimental process

As shown in Fig. 1(a), a point-seed-GaN (PS-GaN) substrate was produced by etching an 8- μm -thick (0001) GaN layer, grown on a (0001) sapphire substrate by metalorganic vapor-phase epitaxy. The point seeds were 250 μm and 1000 μm in diameter. The two PS-GaN substrates were placed in an alumina-base-ceramic crucible with an 80-mm diameter, and the starting materials of metallic Ga (purity: 6N), metallic Na (purity: 4N), and granular graphite (purity: 6N) were added to the crucible in an Ar-filled glove box. The ratio of the carbon content to the total Ga+Na content was fixed at 0.5 mol%. The granular graphite was added in order to suppress the growth of polycrystalline material on the crucible wall [12]. The starting Ga:Na:C composition ratio was 27:73:0.5.

Growth on the PS-GaN substrates was carried out as follows. After the crucible was transferred into a stainless steel vessel in the glove box, the vessel was placed in a resistive heating unit set in a pressure-resistant chamber. The chamber was then evacuated to below $3.0 \times 10^{-1} \text{ Pa}$, and N_2 gas was introduced into the vessel through a gas line. The temperature was increased to 870°C over a 1-h period using a resistive heater. The temperature and N_2 pressure in the chamber were then maintained at 870°C

1 and 3.2 MPa, respectively, during the growth period of 96 h. The solution was then stirred in the
2 crucible by swing stirring the whole chamber in order to increase the supply of the nitrogen to the region
3 of low concentration around the seeds [13].

4 The vessel was allowed to cool naturally before the crucible was removed and immersed in cold
5 ethanol and water to dissolve the residual flux. In order to investigate the TDD of the grown crystals in
6 several growth thicknesses, the crystals were sliced parallel to the c face at the height of 500, 1000, and
7 1500 μm . Evaluation of TDD was performed using an etch-decoration technique on the cut surface after
8 treatment with a chemical mechanical polishing (CMP) process. A eutectic alloy of KOH-NaOH (50%
9 KOH and 50% NaOH), proposed by Weyher and previously shown to demonstrate good etching
10 behavior for GaN layers [14], was used as the etchant, at 450°C for 20 min. Etch pits were observed
11 using a scanning electron microscope (SEM). Distinction of the growth sectors and observation of the
12 hysteresis of the growth habit were performed via panchromatic cathodoluminescence (CL)
13 measurements (HORIBA, Imaging CL DF-100).

15 3. Results and discussion

16 This research demonstrated that pyramidal-shaped and well-faceted bulk GaN crystals could be grown
17 from GaN point seeds. Figures 1(b),1(c) are photographs of crystals (1000 and 250 μm , respectively)
18 grown on point seeds. We called the crystal grown from a 1000- μm point seed sample A, and that
19 grown from a 250- μm point seed sample B. The size of the c face on sample B was larger than that of
20 the crystal grown on sample A. These crystals were black in color; it is estimated that these were caused
21 by point defects such as impurities. In order to reveal the changes of TDD during growth, the etch
22 decoration technique with KOH-NaOH was performed on the surface treated with CMP after the
23 crystals were sliced at a height of 500, 1000, and 1500 μm from the seed, as shown in Fig. 2(a).

24 Before the etch pits were observed, growth sectors were distinguished using CL images. Figure 2(b)
25 shows the CL image of the c face of sample B at the height of 1000 μm , at which two growth sectors
26 with different emission intensities were observed. A schematic drawing of the cross-section parallel to

the m face of samples is shown in Fig. 2(c), and indicates that the crystals consist of two growth sectors: the c -growth sector inside and the $\{10\text{-}11\}$ -growth sector outside. In addition, the cut surface parallel to the c face has the two growth sectors equally. Thus, we can estimate that the sector inside, with the higher emission intensity in the CL image in Fig. 2(b), corresponds to c -growth sector, while the other sector outside with lower emission intensity corresponds to the $\{10\text{-}11\}$ -growth sector. A previous study also showed that the two different growth sectors exhibited different CL emission intensity [10].

The etch pits in both the growth sectors at each cut surface of samples A and B were then observed using SEM, as shown in Figs. 3(a) and 3(b), respectively. In the case of sample A, many etch pits were observed in the c -growth sector at the region above the point seed in each of the growth thicknesses (Fig. 3(a)). The etch pit density (EPD) of the region was about $\sim 10^6 \text{ cm}^{-2}$. Some etch pits were also observed in the $\{10\text{-}11\}$ -growth sector. Interestingly, the shape of the etch pits in this sector was not a regular hexagon. This was different from the ones in the c -growth sector, indicating that the TDs in the $\{10\text{-}11\}$ -growth sector did not propagate parallel to the c axis, while the TDs in the c -growth sector propagated along the c axis. The EPD in the $\{10\text{-}11\}$ -growth sector was less than $\sim 10^3 \text{ cm}^{-2}$, indicating that almost TDs from a point seed existed in the c -growth sector, and propagated along the c axis. In contrast, in the case of sample B, only one etch pit was observed in the c -growth sector after 1000- μm -thick growth (Fig. 3(b)), so that the EPD was estimated to be $\sim 10^2 \text{ cm}^{-2}$, while EPD at 500- μm thickness was about $\sim 10^6 \text{ cm}^{-2}$. In the $\{10\text{-}11\}$ -growth sector, a few etch pits, whose density was less than 10^3 cm^{-2} , were observed at 500- μm thickness, but no etch pit was observed after the 1000- μm -thick growth. This result suggests that all TDs located in the $\{10\text{-}11\}$ -growth sector, which propagated from the periphery of a point seed in the initial growth stage, propagated into the $\{10\text{-}11\}$ -face surface as shown in Fig. 3(c), resulting the disappearance of TDs in $\{10\text{-}11\}$ growth sector at the cut surface of 1000 μm -thickness growth. From these, we found that TDs in the seed crystals ($\sim 10^9 \text{ cm}^{-2}$) were dramatically reduced during growth, especially in the case of sample B, which was mainly due to the dramatic reduction of TDs located in the c -growth sector of the crystal.

1 We then focused on the differences of the *c*-growth sector of the two samples during growth. In order
2 to clarify the changes in growth habits of both crystals, we investigated the size of the *c*-growth sector in
3 some growth thicknesses after the crystals were sliced at a height of 200, 500, 700, and 1000 μm .
4 Figures 4(a),(b) contain schematic drawings of the point seed and the CL images around the *c*-growth
5 sector, as well as schematic drawings of growth habits of the crystals at each of the growth thicknesses
6 of sample A and B, respectively. In sample A, the size of the *c*-growth sector gradually got smaller
7 compared to that of the point seed during growth (Fig. 4(a)). Conversely, in sample B, the *c*-growth
8 sector quickly shrank to less than 50 μm in diameter, and a pyramidal habit was formed in the initial
9 growth stage. After that, the *c*-growth sector gradually expanded (Fig. 4(b)). From Figs. 3(b),4(b), we
10 found that the TDs became as one after the formation of the pyramidal habit, which means that the
11 dramatic reduction of TDs occurred in the process in which the size of the *c*-growth sector gradually
12 became small. We also found that negative facets were formed at the center of the *c* face in the case of
13 the growth on 1000 μm -size point seed (Sample A) as illustrated in fig. 4(a) and seen in fig. 4(c), which
14 shows the cut surface SEM image at a height of 700 μm , including voids surrounded by negative facets
15 in the center. We discuss why these voids and negative faces were formed in the last section.

16 Here, we discuss why these changes of the habit occur during the growth. These were often reported
17 in our studies [15,16], and thought to occur due to the changes of flux composition and supersaturation
18 in a closed system. It is estimated that in the early growth stage, nitrogen poorly dissolves in the flux, so
19 that supersaturation is still low. In this growth condition, relative growth rate along $\langle 0001 \rangle$ direction
20 compared to $\langle 10\bar{1}1 \rangle$ direction becomes bigger, resulting in the formation of pyramidal facet as
21 previous paper reported [16]. As the growth proceeds, nitrogen dissolve enough in the flux and
22 supersaturation becomes higher. For the crystal growing from 250 μm -size seed, the size of the *c* face
23 decided by the later flux condition was predicted to be bigger than that decided by the early growth
24 stage. By contrast, in case of the crystal growing from 1000 μm -size seed, the size of the *c* face decided

1 by flux condition was estimated to be much smaller than that of the seed during the growth, so the c face
2 continued to be smaller.

3 We also paid attention to the CL contrast in the c -growth sector. In the c -growth sector of sample A
4 (Fig. 4(a)), star-like contrasts were observed, which were remarkably similar to InGaAs grown with the
5 epitaxial overgrowth technique on patterned GaAs substrates and reported by Hayakawa et al. [17].
6 These contrasts indicate that bunched steps grew from the edge to the center of the c face. It can be
7 estimated that the growth of bunched steps was caused by the difference in supersaturation between the
8 center and edge of the c face in the finite crystals, which is known as the Berg effect [18]; the growth
9 mode called “hopper growth” is often observed in crystals grown on point seeds in Na-flux growth.

10 In order to reveal the reduction mechanism of TDs in the habit-change process, cross-sectional CL
11 mapping was performed on the other crystal grown on a 250- μm point seed sliced parallel to the a face
12 at the growth thickness around 700 - 900 μm , as shown in Fig. 5(a) and the magnification image around
13 700- μm thickness in Fig. 5(b) with the schematic drawing of the growth mode in Fig. 5(c). The
14 cross-sectional CL image in Fig. 5(b) corresponds to the region in which the c face gradually became
15 smaller, as shown in Fig. 4(b). It was thought that the dark spots in this CL image were due to TDs, as
16 reported by Rosner et al. [19], and that they gathered in the region with high-emission intensity as the
17 growth proceeded, as shown in Fig. 5(c). This region corresponded to the front surface of the bunched
18 steps, as shown in our previous study [20], and the TDs were located at the boundaries between the
19 c -growth sector and the front faces of the bunched steps as illustrated in Fig. 5(d), indicating that TDs
20 were led to propagate toward the center of the c face along the bunched steps growing from the edge to
21 the center of the c face as shown in Fig. 5(c),5(d). That propagation of TDs by bunched steps was often
22 observed in the Na-flux method as demonstrated by Kawamura et al. [15], which was also reported in
23 the GaN molecular beam epitaxy (MBE) growth on a vicinal sapphire by Shen et al. [21]. As the result,
24 all TDs propagating in the c face were led to gather at the center of it. We also focused on the
25 cross-sectional CL images more than 700- μm thickness as shown in Fig. 5(a), and found that CL

1 emission in *c*-growth sector became brighter than the other sectors while *c* face became larger, which
2 was different from the CL contrast while *c* face shrank. It is estimated that these were caused by
3 increase of impurity capture and formation of CL active defects in the *c* face due to the changes flux
4 condition in the later growth stage.

5 Finally, we discuss why TDs in the *c*-growth sector merged into one only in the case of crystals grown
6 on 250- μm point seeds. Figure 6 compares schematic drawings of crystals grown on three sizes of point
7 seeds: (a) 250 μm , (b) 1000 μm , and (c) 2 inch. Bunched steps from the edge of the *c* face grew during
8 the growth on any size of point seed. In the case of growth on the 250- μm point seeds, after the *c* face
9 grew some degree smaller (in this case, less than $50\text{ }\mu\text{m} \times 50\text{ }\mu\text{m}$) as shown in Fig. 6(a), bunched steps
10 began to coalesce at the center of the *c* face. As a result, TDs were gathered at the center of the *c* face in
11 the process in which the bunched steps coalesced. In contrast, in cases where the *c* face was wide, as in
12 the crystals grown on point seeds larger than 1000 μm , bunched steps started to grow on former ones
13 before they coalesced. As a result, “negative” facets were formed at the center of the *c* face, especially
14 in the case of 1000- μm point seeds (Figs. 4(a),4(c),6(b)), because bunched steps at the bottom barely
15 advanced due to lack of a nitrogen source. Therefore, TDs in the crystals grown on larger point seeds
16 are predicted to remain in the *c*-growth sector. It was also estimated that TDs in GaN crystals grown on
17 1000- μm point seeds would have the potential to gather and dramatically reduce after longer growth
18 periods, because the size of the *c* face tended to become smaller during the growth; this is shown in Figs.
19 4,6(b), where the coalescence of bunched steps occurs. In the case of growth on 2-in. seed crystals (our
20 previous technique [15]; see Fig. 6(c)), nitrogen sources were sufficient on the *c* face so that remarkable
21 negative facet was hardly formed, although TDs in the seed propagated into the *c* face. In this case,
22 reduction of TDs by coalescence of a lot of facets bounded by $\{10\text{-}11\}$ at the early growth stage was
23 reported. However, a lot of coalescence regions also formed and TDs remain in each regions (TDD:
24 $\sim 10^6\text{cm}^{-2}$). This is quite different from the reduction mechanism of TDs on a point seed, in which TDs
25 gather in a single coalescence point of bunched steps in the center, resulting in further dramatic
26 reduction of TDs compared to the growth on 2-in. seed crystals.

5. Summary

In this work, we investigated the behaviors of TDs propagating from two sizes of GaN point seed crystals (250 μm and 1000 μm) in the Na-flux growth. TDD in the crystal grown on the 1000- μm point seed was about $\sim 10^6 \text{ cm}^{-2}$, while that on the 250- μm point seed was less than $\sim 10^3 \text{ cm}^{-2}$; this showed the dramatic reduction of TDs from the 250- μm point seed (TDD: $\sim 10^9 \text{ cm}^{-2}$) compared to the 1000 μm -size point seed. CL images of the c face at three growth thicknesses revealed that the size of the c face had a tendency to become small during the growth in both samples. The source of the dramatic reduction of TDs in the crystal grown on the 250- μm point seed was found in the habit-change process, in which TDs on the c face were led to gather at the center of the c face by coalescence of bunched steps growing from the edge to the center. Some TDs located in the $\{10\text{-}11\}$ -growth sector were found to propagate along the $\langle 10\text{-}11 \rangle$ direction. It was also thought that the size of the c face of the crystal grown on the 1000- μm point seed was too large for coalescence of bunched steps. As a result, many TDs remained. Shrinking of c face in the habit-change process, causing the coalescence of bunched steps from the edge, is the key for the dramatic reduction of TDs. We concluded that TDs naturally reduced in the habit-change process, which is a unique phenomenon in the Na-flux growth on small-sized “point seeds”, and which allowed fabrication of low-dislocation-density GaN wafers.

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Figure captions

Fig. 1. (a) Schematic drawings of the process for fabricating point seeds and GaN crystals grown from (b) 1000- μm (Sample A), and (c) 250- μm (Sample B) point seeds.

Fig. 2. (a) Schematic drawing of the slice of grown crystals parallel to the c face; (b) the CL image of the sample B which was cut parallel to c face at a 1500- μm thickness showing CL of different growth sectors; (c) a schematic drawing of the m face of crystals grown on a point seed shows that crystals consist of two growth sectors: the c -growth sector inside and the $\{10\text{-}11\}$ -growth sector outside.

Fig. 3. SEM images of the c -face cut surface at c - and $\{10\text{-}11\}$ -growth sector in (a) sample A, and (b) sample B at three growth thicknesses—500, 1000, and 1500 μm —after wet etching with KOH-NaOH melt. (c) The schematic drawing of the propagation of TDs along $\langle 0001 \rangle$ and $\langle 10\text{-}11 \rangle$ direction from a point seed.

Fig. 4. CL images of the c -growth sector, schematic drawings of the size of point seed, and of the growth habits of crystals at each of the growth thicknesses of (a) sample A, and (b) sample B, respectively. In (c) the sliced c -face SEM image of sample A at the height of 700 μm , voids surrounded by negative facets can be seen in the center.

Fig. 5. (a) The cross-sectional CL image of a GaN crystal on a 250- μm point seed sliced parallel to the a face at a growth thickness of around 700 - 900 μm , and (b) the magnification image around 700- μm thickness with (c) the schematic drawing in which the c -growth sector gradually becomes smaller as the growth proceeds. (d) The schematic drawings of the TDs propagating to the center of the c face along the bunched steps growing from the edge toward the center of the c face.

1 **Fig. 6.** Schematic drawings of the GaN crystals grown on three kinds of point seeds: (a) 250 μm , (b)
2 1000 μm and (c) 2 inch. Coalesce of the bunched steps from the edge of the c face easily occur in case
3 of the growth on smaller-size point seeds.

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1 **Fig. 1.**

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1 **Fig. 2.**

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Fig. 3.

(a)

Scale bar: 20 μm

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(b)

Scale bar: 20 μm

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1 **Fig. 3.**

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Fig. 4.

(a)

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(b)

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Fig. 4.

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1   **Fig. 5.**

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1 **Fig. 6.**

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