

**Effect of an applied electric current in epitaxial growth of GaAs layer
on patterned GaAs substrate**

Mouleeswaran Deivasigamani, Tadanobu Koyama and Yasuhiro Hayakawa *

Research Institute of Electronics, Shizuoka University, 3-5-1 Johoku, Naka-ku, Hamamatsu,
Shizuoka 432-8011, Japan

**** Corresponding author:***

Yasuhiro Hayakawa

Research Institute of Electronics, Shizuoka University, 3-5-1 Johoku, Naka-ku, Hamamatsu 432-
8011, Japan

Tel/Fax: +81-053-478-1310

Email: royhaya@ipc.shizuoka.ac.jp

Abstract

Selective epitaxial growth of a GaAs layer on SiN_x masked Si doped semi-insulating (100) GaAs substrate was performed by current controlled liquid phase epitaxy (CCLPE) in the conventional liquid phase epitaxy. Experiments were carried out with and without the application of electric current. Surface morphology of (100) facet of the grown layer and the vertical and lateral growth rates were significantly improved under applied electric current. A thick layer of about 330 μm was achieved at relatively low growth time of 6 h with a current density of 20 Acm⁻². The epitaxial growth is realized by both electromigration of the solute and supercooling under a constant rate of furnace cooling. The dislocation density of the grown layer was significantly reduced, compared with that of the substrate ($4 \times 10^4 \text{ cm}^{-2}$).

Keywords: A1. Electromigration; A3. Current controlled liquid phase epitaxy; A3. Liquid phase epitaxy; A3. Selective epitaxy; B2. Semiconducting gallium arsenide

PACS: 66.30.Qa; 81.15.Lm; 81.05.Ea

1. Introduction

GaAs has long been recognized as an important high-frequency material and it has been used in field effect transistors since the 1970s. The electron drift velocity of GaAs is significantly higher than that of silicon. GaAs technology has advanced significantly in the past two decades, and the material now rivals silicon in terms of purity, size, and ease of growth. GaAs has potential applications in various electronic and optical devices, such as X-ray imaging for medical applications [1-2], emission of terahertz-frequency electromagnetic radiation for spectroscopic detection and location of concealed explosives [3-4] and blocked impurity band (BIB) detectors in the far-infrared region [5]. For these applications, dislocation-free thick GaAs layers on the order of few hundred micrometers to a few millimeters are required.

Bulk-grown materials contain a large concentration of dislocations and have heterogeneous electrical properties, which vary from the center of the wafer to its edges. Although significant improvement in bulk material growth has been achieved, the quality is not yet sufficient for medical imaging or terahertz applications. Epitaxial layers grown by molecular beam epitaxy (MBE), metal organic chemical vapor deposition (MOCVD), liquid phase epitaxy (LPE), and current-controlled liquid-phase epitaxy (CCLPE) exhibit homogeneity of electrical properties for using in imaging applications. To achieve the desired thickness in molecular and vapor phase epitaxy, the consumption of gases would increase dramatically, which would have adverse effects on the environment due to the hazardous nature of the gasses.

LPE and CCLPE are viable techniques to achieve thick epitaxial layers with no adverse environmental effects. Unfortunately, substrate defects can propagate into the grown epitaxial layers. Recently special attention has been paid to the selective epitaxial growth of III-V compound semiconductors to restrict defect propagation into the grown epitaxial layer. A

number of recent articles have reported the selective growth of binary and ternary III-V semiconductors by LPE [6-16] and CCLPE [17-20]. Selective growth by LPE with changing mask layers and mask openings was also investigated [21-22]. Naritsuka et al. grew thick GaAs epitaxial layers of about 360 μm in 100 h by a temperature-difference LPE method using H_2 cooling gas at a flow rate of 1200 ml/min [23].

In CCLPE, epitaxial layer growth is achieved by passing an electric current through the substrate-solution interface, while the temperature of the system is kept constant. Two growth mechanisms can occur during CCLPE growth. One possible mechanism of CCLPE is current-induced Peltier cooling at the substrate-solution interface, which creates a temperature gradient and local supercooling at the interface. Similarly, there may be Peltier heating at the feed-solution interface at the top of the solution, also creating a temperature gradient in the solution. This Peltier-effect-induced temperature gradient in the solution creates a driving force for crystallization. An alternative mechanism for CCLPE involves electromigration of solute in the molten metallic solution. Two major effects drive electromigration: 1) the direct action of the electric field on the charged atoms or ions in the solution and 2) the frictional force or momentum exchange between flowing electrons and these atoms or ions. The total driving force is the sum of these two effects. The growth mechanism in CCLPE was investigated theoretically and experimentally, and it was concluded that electromigration dominates the growth mechanism in III-V compound semiconductor growth [24-30].

CCLPE offers a unique possibility for control of growth kinetics and properties of the epitaxial layers produced. In particular, electric current alters the solute distribution in the solution, which is important for selective epitaxial growth. This paper describes the effects of electric current on the selective growth of GaAs on a patterned GaAs substrate.

2. Experimental procedure

Si-doped semi-insulating (100) GaAs substrates (12×12 mm and about 350 μm thick) were used for this investigation. The substrates were ultrasonically cleaned in organic solvents prior to SiN_x deposition. A 0.2- μm -thick SiN_x layer was deposited on the substrate by plasma assisted chemical vapor deposition to form the pattern. A circular pattern with open windows 1 mm in diameter was fabricated using a combination of standard photolithography and reactive ion etching, as shown in Fig 1. The spacing between windows was 1 mm. Prior to mounting in the growth bin, the substrates were cleaned in organic solvents, and the native oxides were removed by etchant ($\text{H}_2\text{SO}_4\text{:H}_2\text{O}_2\text{:H}_2\text{O}$) for 30 sec at 60°C.

The growth bin is a modified version of a conventional liquid-phase epitaxy system that enables a flow of electric current through the growth interface. The challenges in using CCLPE were i) to achieve isothermal conditions during growth, and ii) to establish a uniform electrical back-contact to the substrate. In order to achieve isothermal conditions, the design of the growth bin is crucial. Uniform electrical back-contact can be established by using a metallic solution. In this work, we designed a suitable growth bin and used an Al+Ga back-contact solution. Two stainless steel electrodes were threaded: one on top of the graphite, and the other on the bottom of graphite. The graphite was electrically isolated by boron nitride. Monitoring thermocouples were positioned 1 mm from the substrate. Electric current could only flow when the solution was brought into contact with the substrate by sliding an upper graphite boat. An electric current was passed through the growth interface at a current density of 2-20 Acm^{-2} . The current density J was defined by the applied current divided by the window area opened on the substrate.

Three grams of 6N gallium, excess polycrystalline GaAs, and 9×10^{-4} atomic concentration of Te dopant were loaded into the growth bin. Then, H_2 was flowed at 300 cc/min until the end of the experiment. The loaded growth bin was heated to 825°C over 3 h, then held at this temperature for 4 h to homogenize the solution, and finally cooled to 800°C at a rate of 0.2°C/min. At this stage, a GaAs crust had formed on top of the solution. The solution was homogenized and equilibrated with the GaAs crust at the growth temperature of 800°C for 2 h. The crust acted as a feed, and continuously dissolved during growth. The temperature was lowered at a rate of 0.65°C/min, and the substrate was brought into contact with the solution after the furnace temperature was lowered by 3°C. The current flow started as soon as the substrate made contact with the solution. The growth was terminated by cutting the electric current and removing the solution from the substrate by sliding the upper graphite boat. The residual solution on the epilayer surface was removed by etching with HCl. The experiments were performed for various growth times and currents to understand the electromigration effect on selective growth. The selective epilayers were analyzed using a scanning electron microscope (SEM). The etch pit density was analyzed after etching with molten KOH at 350°C for 1 min.

3. Results and discussion

Figs. 2(a)-(d) show the top view of epilayers grown without current for 0.5, 2.0, 3.0, and 6.0 h. Initially growth started at the walls of the circular window and propagated slightly within the mask region. The selective growth depended upon the size and design of the mask opening and the orientation of the substrate. A pyramidal-type epitaxial layer was observed when using a circular seed opening of a few tens of micrometers in size [22]. In our case, box-like epitaxial layers with four sidewall {111} facets were grown using a 1 mm mask opening. Once the (100)

facet was formed at the top, growth proceeded inward due to the availability of growth steps or rough surface at the wall of the void. The area of the void was reduced due to enhanced crystallization at the rough surface by increasing the growth time.

Fig. 3 shows the thickness of the grown epitaxial layer grown both with and without current (4 Acm^{-2}) for different growth times. For growth without current, temperature gradient induced by constant-rate furnace cooling brought solute to the window region by diffusion. In other words, transport of solute was driven only by the concentration gradient of the arsenic atoms along the growth direction in the solution. All arsenic atoms that reached the window region of the substrate were eventually used for growth. When an electric current was introduced, the solute distribution in the solution was affected. The electric current brought solute to the window region from the surrounding areas by electromigration. Solute enrichment occurred in the window region, which led to supersaturation, and caused crystallization on the substrate. The additional driving force from electromigration in association with diffusion enhanced the thickness of the epitaxial layer when current was applied during growth. The enhancement of epitaxial layer growth caused by the applied current was clearly evident.

Figs. 4(a)-(d) show epitaxial layers grown by various current densities, such as 2, 4, 12, or 20 Acm^{-2} , for 6 h. The surface morphology of the (100) facet was improved by increasing the applied current density. When the applied current density was 2 Acm^{-2} , the void on the (100) facet covered nearly half of the surface. The void on (100) facet was significantly reduced when the applied current density was increased, until it was completely filled at 20 Acm^{-2} . This occurs because the walls of the void have growth steps, which attract solute atoms from the solution. The increased electromigration of solute atoms with increasing applied current density made more solute atoms available to the growth front. The higher availability of solute atoms led to

crystallization at the growth front on the walls of void, and the applied electric current enhanced the growth kinetics.

The vertical growth rate of epitaxial layer versus the applied current density after 6 h is shown in Fig. 5. The growth rate increased with increasing applied current density, although it was not linearly proportional. The change in vertical growth rate is explained as follows: Initially, the electric current distribution over the circular window region was isotropic, since the mask layer was an insulating film and the growth area was fixed. When the growth exceeded the mask film thickness, the surface area of the epitaxial layer increased due to the four side {111} surfaces. Then, the current distribution was along the four side {111} surfaces and the top (100) surface. The entire side surface attracted solute atoms, due to its conducting nature, by electromigration, which enhanced solute transport in the lateral direction. At higher current density, the side surfaces attracted more solute atoms due to increased electromigration, and became supersaturated compared to lower current density. As a result, the lateral growth was enhanced by the higher current density. Since the area of the epitaxial layer increased, the effective current density decreased, in other words the applied current remained constant while the area of the epitaxial layers increased along with the applied current. Lateral growth enhancement decreased the increment of the vertical growth rate of the epitaxial layer at higher current density.

Figs. 6(a)-(b) show a substrate cleaved along the [0-1-1] direction in order to estimate the lateral growth with and without applied current after 6 h of growth. The dotted line in the inset shows the cleave orientation. The dashed white line shows the window region of the substrate and the symbol A shows the lateral grown area. The lateral growth layer was 30 μm without

current, but was $268\text{ }\mu\text{m}$ at 20 Acm^{-2} . This clearly demonstrates that the lateral growth was enhanced by the applied current.

The surfaces of the GaAs substrate and GaAs layer grown with a current density of 20 Acm^{-2} for 6 h after molten KOH etch are shown in Figs. 7(a)-(b). The substrate had an etch pit density of $4 \times 10^4\text{ cm}^{-2}$. In this sample, the top surface of the epitaxial layer had no etch pits in the centre but did have some on the edges. Some dislocations propagated from the walls of the circular patterned substrate to the epitaxial film, and they were observed at the corner of the grown epitaxial layer. The top surface was directly above the exposed area of the substrate, and was expected to have some dislocations, but no dislocations were observed on top of the epitaxial layer. To understand this phenomenon, the internal structure of the epitaxial layer was observed. The sample was cleaved and polished with fine alumina powder. The resulting cross section revealed that a void was present in the center of the epitaxial layer, as shown in Fig. 8. The void played a key role in defect filtration.

4. Conclusions

Current flow from the substrate to the solution in temperature-controlled selective LPE growth of GaAs greatly improved the surface morphology. Selective growth occurred due to electromigration of the solute species and supercooling brought by decreasing furnace temperature. The vertical epitaxial growth and lateral growth were enhanced by the applied current. A thick layer of about $330\text{ }\mu\text{m}$ was achieved at relatively low growth time of 6 h with a current density of 20 Acm^{-2} . The EPD of the grown epitaxial layer was dramatically reduced due to the presence of a void in the center of the layer. CCLPE proved a good method to grow thick GaAs semiconductor epitaxial layers in a relatively low growth time.

Acknowledgement

The authors are grateful to Prof. A. Tanaka for providing plasma CVD, and Prof. M. Tabe and Mr. T. Mizuno for providing a photolithography facility. One of the authors, Mouleeswaran D., acknowledges MHRD, India and financial support from the Japan Ministry of Education, Culture, Sports, Science, and Technology.

References

- [1] J.C. Bourgoin, Nucl. Instr. and Meth. A 460 (2001) 159.
- [2] G.C. Sun, et al., Nucl. Instr. and Meth. A 546 (2005) 140.
- [3] J. Heyman, N. Coates, A. Reinhardt, G. Strasser, Appl. Phys. Lett. 83 (2003) 5476.
- [4] M. Nagai, K. Tanaka, H. Ohtake, T. Bessho, T. Sugiura, T. Hirosumi, M. Yoshida, Appl. Phys. Lett. 85 (2004) 3974.
- [5] B.L. Cardozo, L.A. Reichertz, J.W. Beeman, E.E. Haller, Infrared Phys. Technol. 46 (2005) 400.
- [6] T. Nishinaga, T. Nakano, S. Zhang, Jpn. J. Appl. Phys. 27 (1988) L964.
- [7] Y. Hayakawa, S. Iida, T. Sakurai, Y. Yanagida, M. Kikuzawa, T. Koyama, M. Kumagawa, J. Crystal Growth 169 (1996) 613.
- [8] S. Iida, Y. Hayakawa, T. Koyama, M. Kumagawa, J. Crystal Growth 200 (1999) 368.
- [9] Z.R. Zytewicz, Cryst. Res. Technol. 34 (1999) 573.
- [10] Y. Hayakawa, K. Balakrishnan, S. Iida, Y. Shibata, T. Koyama, M. Kumagawa, J. Crystal Growth 229 (2001) 158.
- [11] W. Huang, T. Nishinaga, S. Naritsuka, Jpn. J. Appl. Phys. 40 (2001) 5373.
- [12] S. Naritsuka, T. Nishinaga, J. Crystal Growth 222 (2001) 14.
- [13] K. Balakrishnan, S. Iida, M. Kumagawa, Y. Hayakawa, Semicond. Sci. Technol., 17 (2002) 729.
- [14] M. Kaneko, S. Nakayama, K. Kashiwa, S. Aizawa, N.S. Takahashi, Cryst. Res. Technol. 37 (2002) 177.

- [15] S. Nakayama, M. Kaneko, S. Aizawa, K. Kashiwa, N.S. Takahashi, J. Crystal Growth 236 (2002) 132.
- [16] G. Zhang, K. Balakrishnan, T. Koyama, M. Kumagawa, Y. Hayakawa, J. Crystal Growth 256 (2003) 243.
- [17] X.F. Yang, L. Huang, H.C. Gatos, J. Electrochem. Soc. 129 (1982) 194.
- [18] S. Saki, Y. Ohashi, Y. Shintani, J. Appl. Phys. 70 (1991) 4899
- [19] M.G. Mauk, J.P. Curran, J. Crystal Growth 225 (2001) 348.
- [20] Z.R. Zytckiewicz, D. Dobosz, Y.C. Liu, S. Dost, Cryst. Res. Technol. 40 (2005) 321.
- [21] H. Zhang, L. Hu, Y. Tian, X. Sun, X. Liang, S. Pan, J. Crystal Growth 295 (2006) 16.
- [22] H. Zhang, L. Hu, Y. Tian, X. Sun, X. Liang, H. Zhang, S. Pan, J. Crystal Growth 307 (2007) 294.
- [23] S. Naritsuka, Y. Tejima, K. Fujie, T. Maruyama, J. Crystal Growth 310 (2008) 1642.
- [24] T. Bryskiewicz, J. Lagowski, H.C. Gatos, J. Appl. Phys. 51 (1980) 988.
- [25] K. Nakajima, J. Crystal Growth 98 (1989) 329.
- [26] K. Nakajima, J. Appl. Phys., 61 (1987) 4626.
- [27] Y.C. Liu, Y. Okano, S. Dost, J. Crystal Growth 244 (2002) 12.
- [28] H. Sheibani, S. Dost, S. Sakai and B. Lent, J. Crystal Growth 258 (2003) 283.
- [29] D. Mouleeswaran, R. Dhanasekaran, Mater. Sci. Eng. B, 112 (2004) 91.
- [30] D. Mouleeswaran, R. Dhanasekaran, Mater. Sci. Eng. B, 130 (2006) 137.

Figure captions:

Fig. 1: Schematic diagram of the patterned substrate.

Fig. 2: Growth morphologies of GaAs layers grown without electric current as a function of time a) 0.5, b) 2, c) 3, and d) 6 h.

Fig. 3: Dependence of GaAs layer thickness as a function of growth time with 4 Acm^{-2} and with no applied current.

Fig. 4: Growth morphologies of GaAs layers grown with electric current as a function of current density a) 0.2, b) 4, c) 12, and d) 20 Acm^{-2} for 6 h.

Fig. 5: Dependence of vertical growth rate of GaAs layers grown with an applied electric current as a function of current density for 6 h.

Fig. 6: Substrates cleaved along the [0-1-1] direction after 6 h of growth a) without current, and b) with 20 Acm^{-2} .

Fig. 7: EDP profiles of a) (100) GaAs substrate, b) GaAs layer grown with current density of 20 Acm^{-2} for 6 h.

Fig. 8: Cross-section of a GaAs layer grown with a current density of 20 Acm^{-2} .

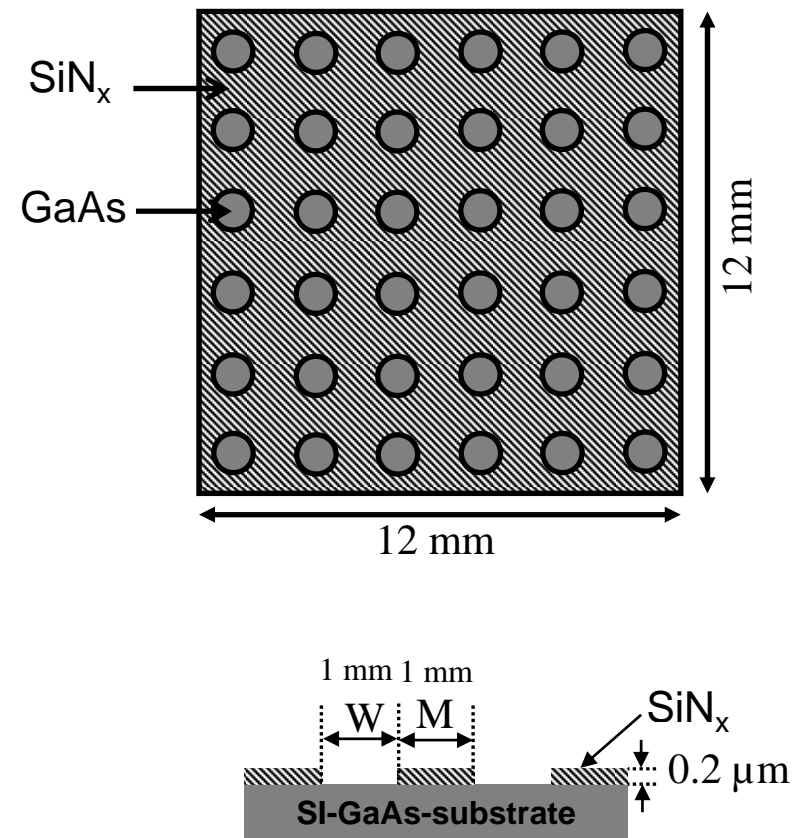


Figure 1
Mouleeswaran D et al.

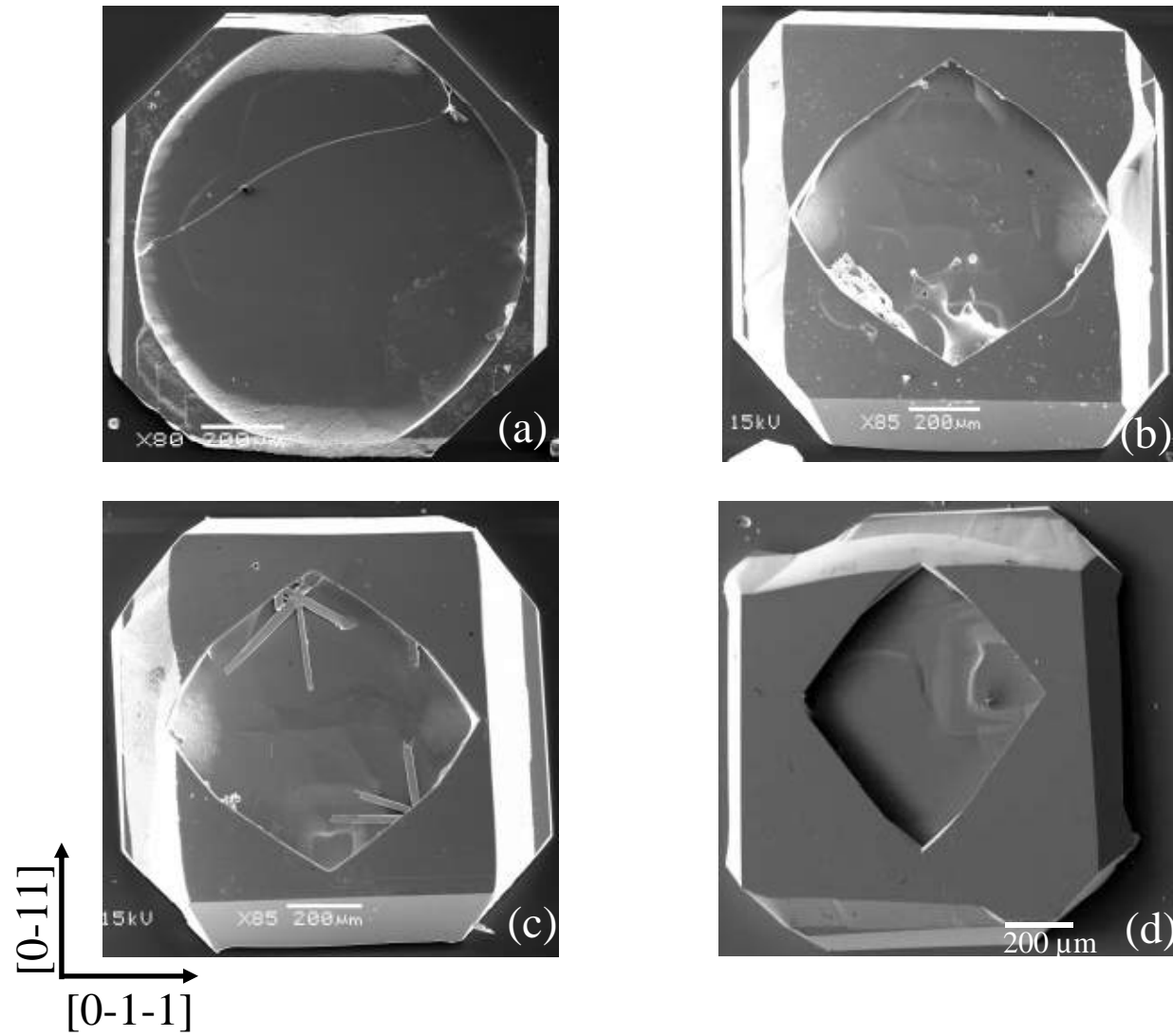


Figure 2
Mouleeswaran D et al.

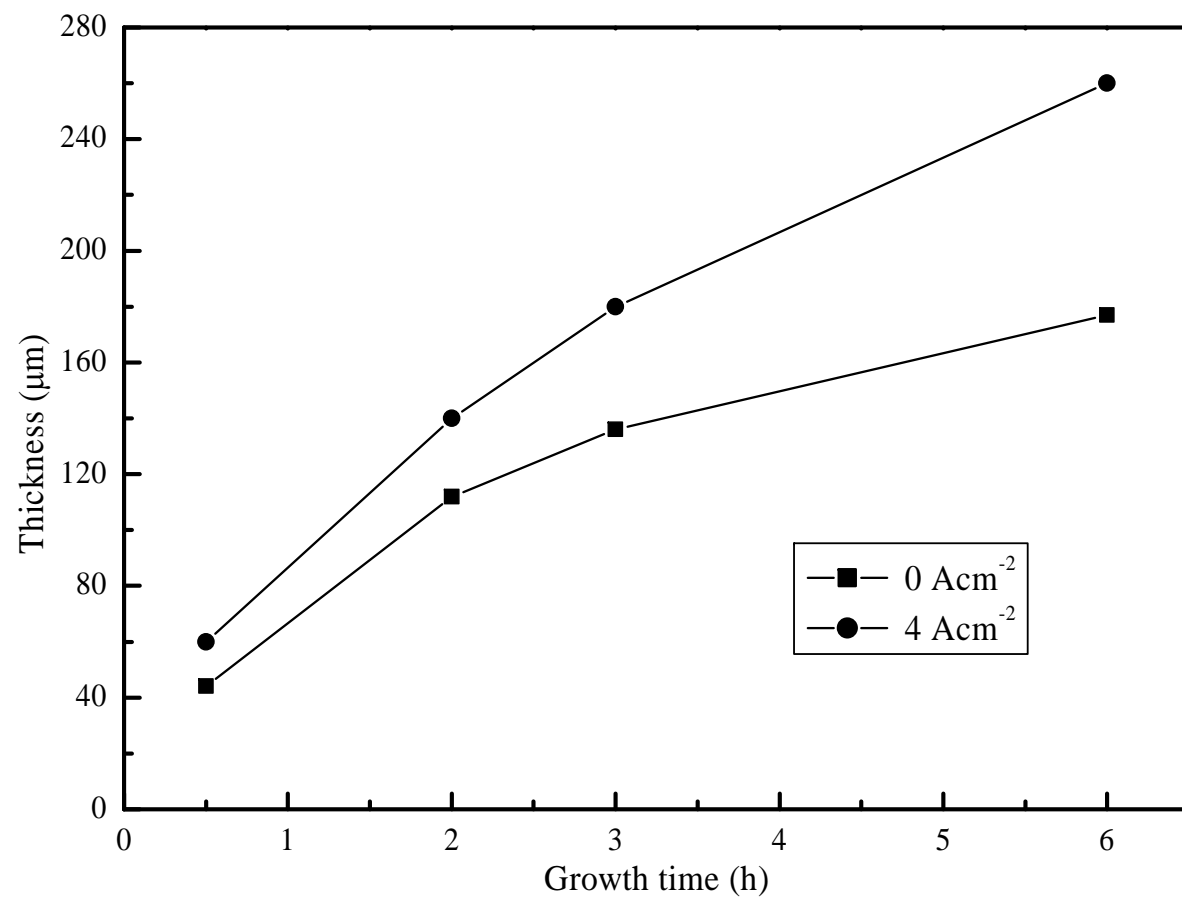


Figure 3
Mouleeswaran D et al.

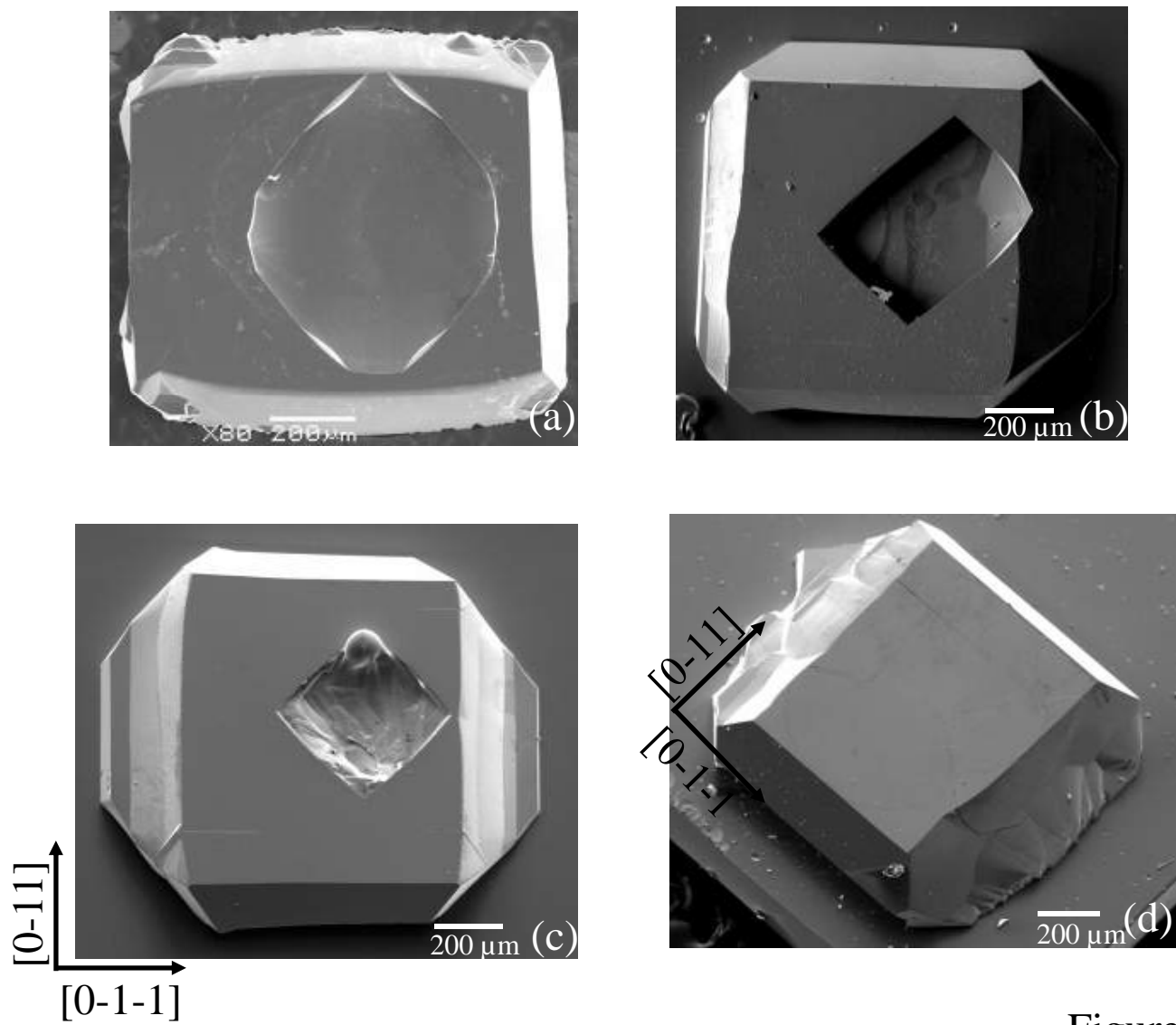


Figure 4
Mouleeswaran D et al.

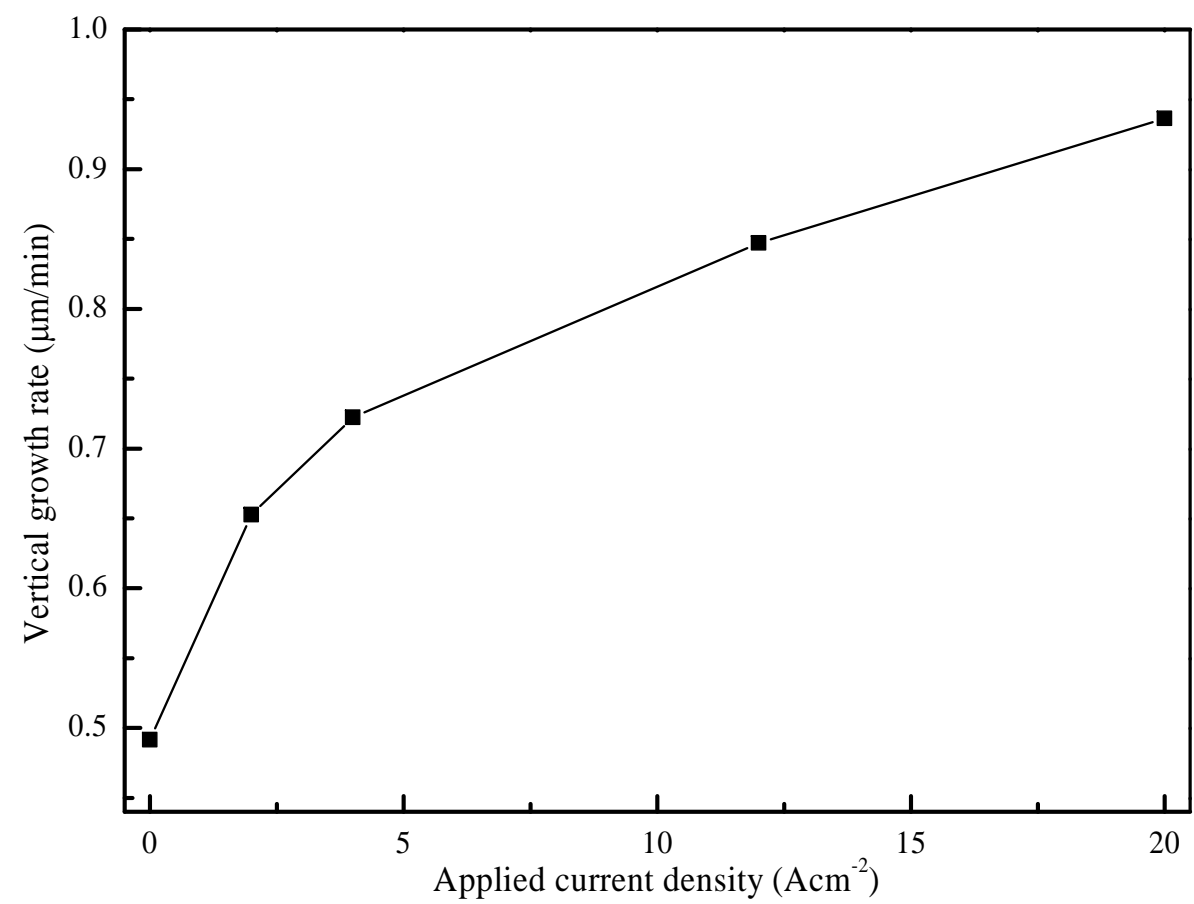


Figure 5
Mouleeswaran D et al.

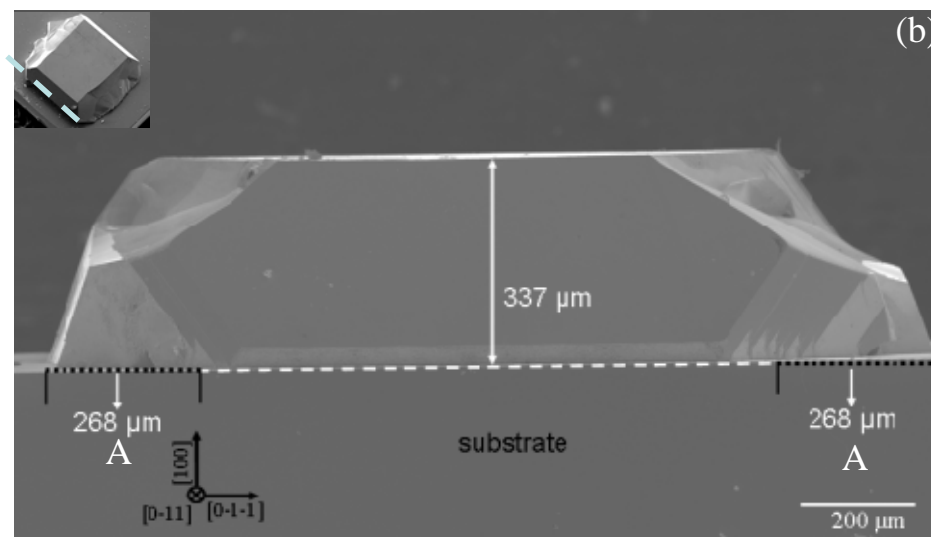
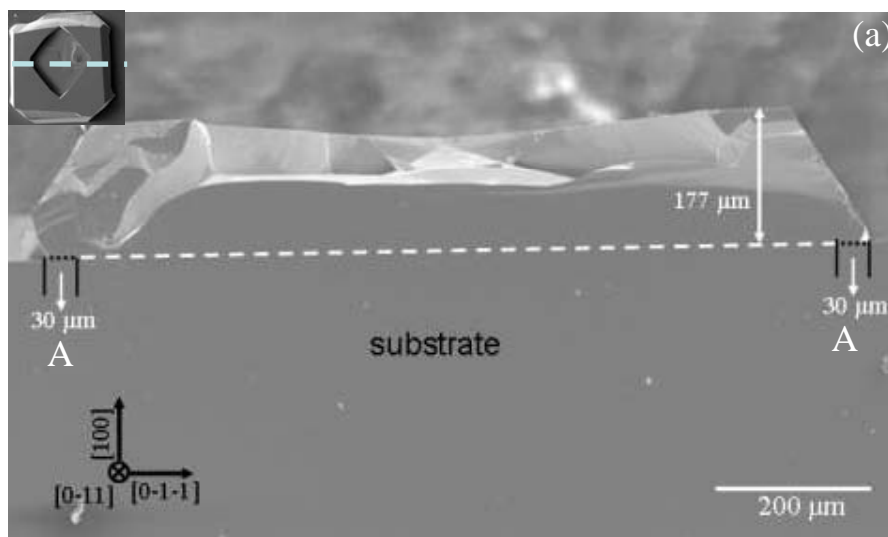


Figure 6
Mouleeswaran D et al.

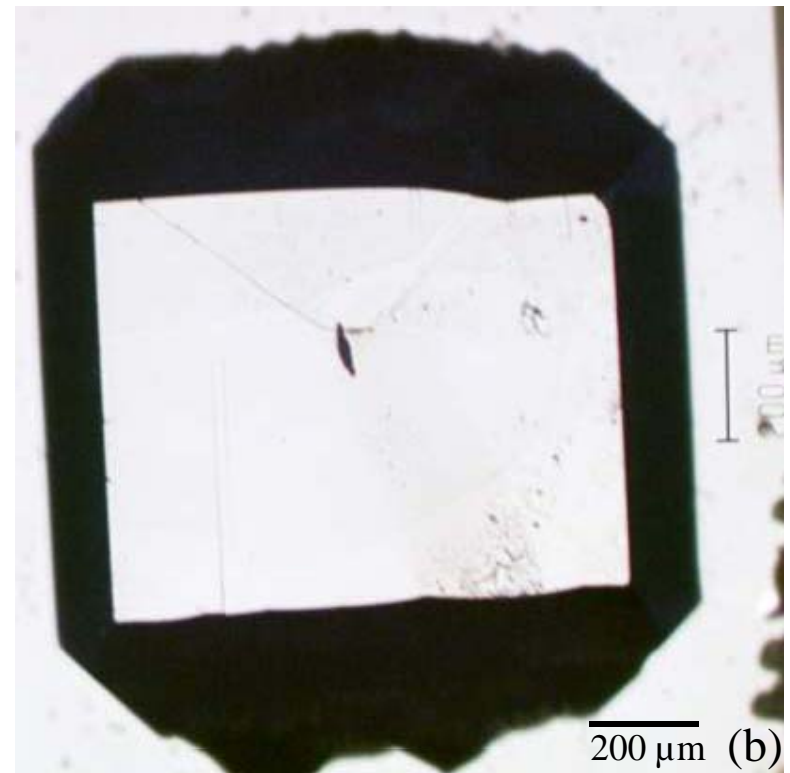
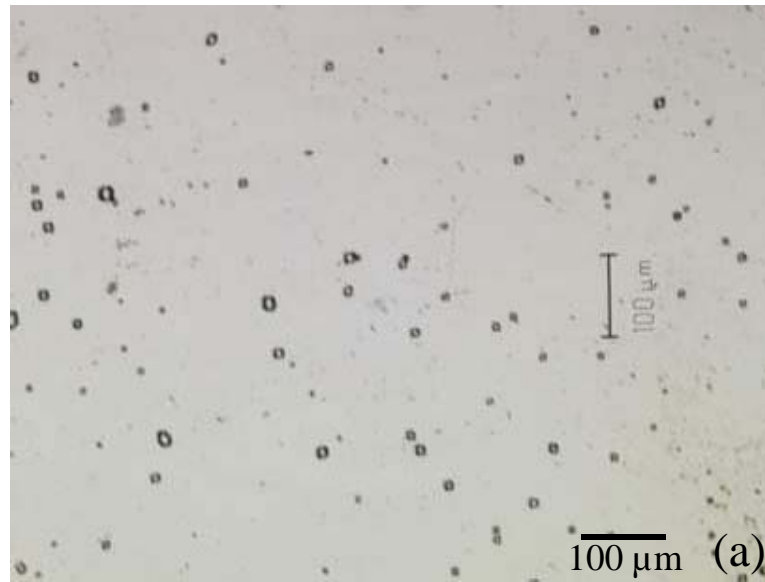


Figure 7
Mouleeswaran D et al.

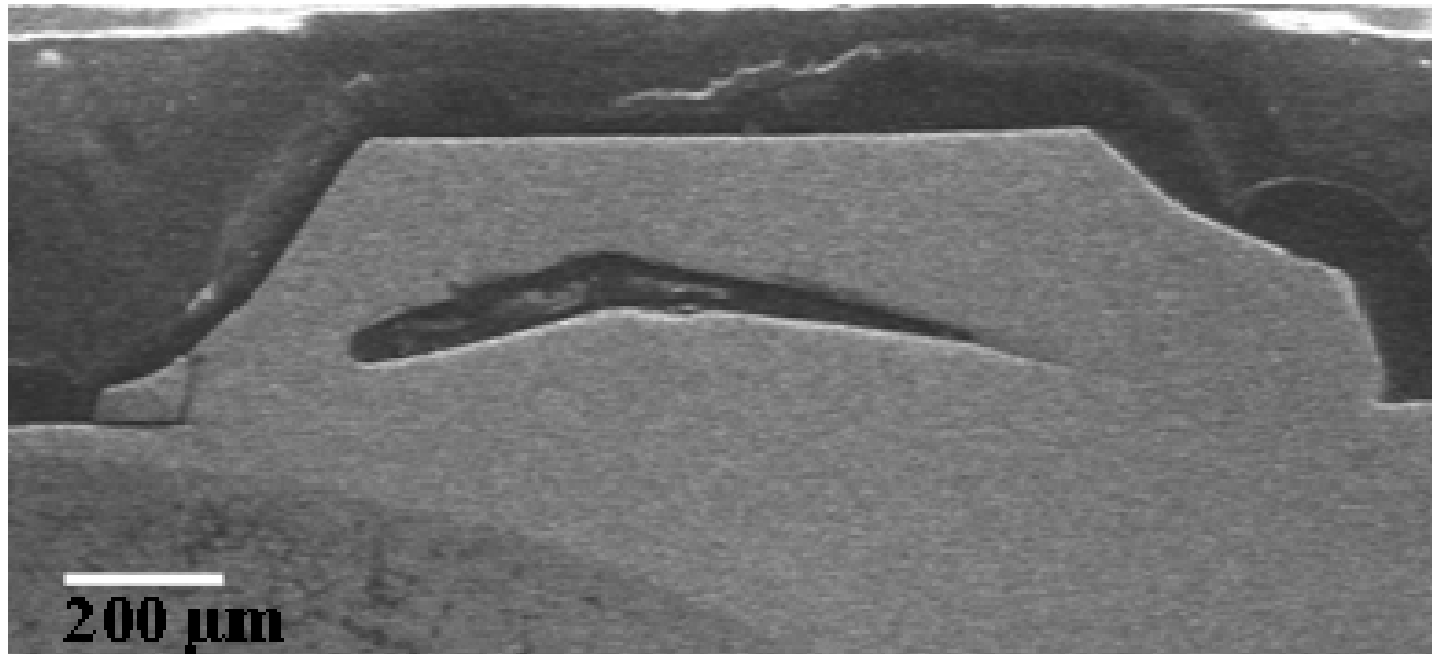


Figure 8
Mouleeswaran D et al.