

# Effects of annealing and substrate orientation on epitaxial growth of GaAs on Si

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(Received 6 September 2009; accepted 22 September 2009; published online 23 October 2009)

GaAs thin films grown on Si (100) and (111) substrates by metal-organic chemical vapor deposition were investigated by electron microscopy. It was found that the growth rate of the GaAs epitaxial layers on Si (100) was faster than that on Si (111) due to a lower Si (111) surface energy. The morphologies and internal crystal structure quality of GaAs films grown on Si (111) were better than those grown on Si (100). It was also found that postannealing at high temperature can improve the morphology of the epitaxial layer surface and reduce lattice defects in the thin films. © 2009 American Institute of Physics. [doi:10.1063/1.3248372]

## I. INTRODUCTION

The III–V compound semiconductor thin films epitaxially grown on Si substrates have been investigated extensively due to their unique electronic and optoelectronic properties.<sup>1,2</sup> Recent studies have shown that III–V nanostructures on Si, especially the GaAs/Si system, can be used to build lasing devices with unique features,<sup>3,4</sup> high efficiency solar cells,<sup>1,5–7</sup> and advanced electronic devices.<sup>8</sup> It has been well documented that the performance of these nanostructural-based devices relies heavily on their morphologies and the qualities of their crystal structures. As a consequence, high quality thin films such as GaAs with a low density of lattice defects or even defect free are critical for constructing such functional devices. However, the large lattice mismatch and thermal expansion coefficient difference between GaAs and Si make it difficult to attain high quality GaAs thin films. For this reason, numerous approaches have been devoted to growing GaAs epitaxial layers on Si substrates in the past two decades, including the two-step growth,<sup>9–11</sup> the post-thermal annealing,<sup>12</sup> strained-layer superlattices,<sup>13–16</sup> strained short-period superlattices,<sup>17,18</sup> and graded InGaAs single interlayers.<sup>19</sup> Dislocation-free GaAs epitaxial layers have been successfully achieved by using a special growth technique of epitaxial lateral overgrowth combining molecular beam epitaxy or metal-organic vapor phase epitaxy with liquid-phase epitaxy.<sup>20,21</sup> Nevertheless, it should be noted that all of the techniques introduced above were dealing with GaAs thin films grown on Si (100) or slightly tilted Si (100) substrates. GaAs grown on Si (111) has been seldom studied. Since Si (111) surface has a lower surface energy than Si (100) surface,<sup>22</sup> a better quality GaAs single-crystal epitaxial layer may be expected.

In this paper, GaAs thin films were grown on Si (100) and (111) substrates by metal-organic chemical vapor deposition (MOCVD) and the quality of the GaAs thin films were investigated using electron microscopy. Based on the experimental results, the fundamental reason of the microstructures of the obtained GaAs thin films is explored.

## II. EXPERIMENTS

In this experiment, the two-temperature growth and annealing methods were designed to improve the GaAs thin films. The low temperature step with low V/III ratio (i.e., the flow rate of total group V precursors over that of total group III precursors) was essential to overcome the large lattice mismatch between GaAs and Si (~4%).<sup>23</sup> After the GaAs layer is initialized through the low temperature growth (can be considered as a nucleation step), the high temperature growth with high V/III ratio would improve the quality of the film.<sup>9–11</sup> Annealing process was also used in this study to improve both the surface morphologies and the internal crystal structure of the grown films.<sup>12</sup>

GaAs thin films were epitaxially grown on Si (100) and (111) substrates by MOCVD using trimethylgallium and arsine (AsH<sub>3</sub>) as group III and group V sources, respectively. Si substrates were first cleaned in solvent to remove the organic contaminants and then etched in buffered HF solution for 5 min to remove the native oxide. The substrate was immediately transferred into the MOCVD reactor after etching and the first GaAs layer was grown at a low temperature of 400 °C for 60 min with a V/III ratio of 15.4; then without any interruptions GaAs was further grown at a high temperature of 700 °C for 10 min with a V/III ratio of 154.3. Without taking out from the reactor, the samples were additionally annealed at 750 °C for 15 min under AsH<sub>3</sub> atmosphere. As a reference, another growth was carried out with the same parameters but without additional annealing. For the simplicity hereafter, we use AG0 and AG1 to represent the as-grown

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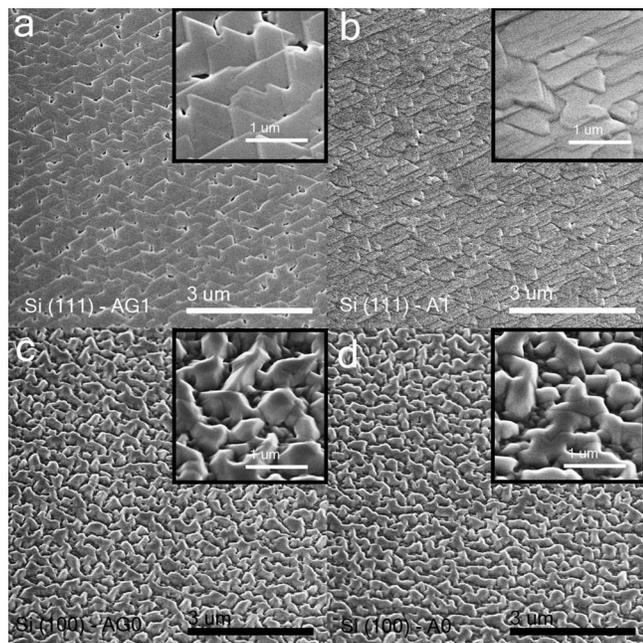


FIG. 1. SEM images of GaAs epitaxial layers grown at various substrates with different techniques and growth temperatures. (a) Two-temperature grown film on Si(111), AG1, (b) two-temperature grown then postannealed film on Si(111), A1, (c) two-temperature grown film on Si(100), AG0, and (d) two-temperature grown then postannealed film on Si(100), A0. Inserted images are higher magnification illustrations of the corresponding images.

samples on Si (100) and Si (111), respectively, and A0 and A1 to represent the annealed samples on Si (100) and Si (111), respectively.

The structural quality and morphology of the GaAs films were investigated by scanning electron microscopy (SEM) using either a Hitachi S4500 or a Zeiss Ultraplus operated at an accelerating voltage of 5 kV and cross-sectional transmission electron microscopy (XTEM) using a FEI Tecnai F20. XTEM specimens were prepared by polishing the specimen first using a tripod technique and final thinning using a Gatan precision ion polishing system.<sup>24</sup>

### III. RESULTS AND DISCUSSION

Figure 1 presents the typical SEM images of the GaAs films on (111) and (100) Si substrates with magnified images in the insets, showing their surface morphologies. As can be seen, the GaAs films grown on Si (111) have generally flatter surfaces than those grown on Si (100) substrates. After annealing, the films form a continuous layer over the substrates and became flatter and smoother especially for sample A1 [GaAs grown on Si (111)]. It is of interest to note from Fig. 1(a) that the film grown on Si (111) shows a layer-by-layer growth, while island growth can be clearly identified for those grown on Si (100) [Fig. 1(c)]. Since island growth is generally faster than the layer-by-layer growth,<sup>25</sup> the GaAs films grown on Si (111) are expected to be thinner than those on Si (100).

In order to confirm the above results, XTEM was carried out. Figure 2 shows the XTEM images taken from the as-grown (AG0 and AG1) and annealed (A0 and A1) samples. For the as-grown GaAs films [Figs. 2(a) and 2(c)], the thick-

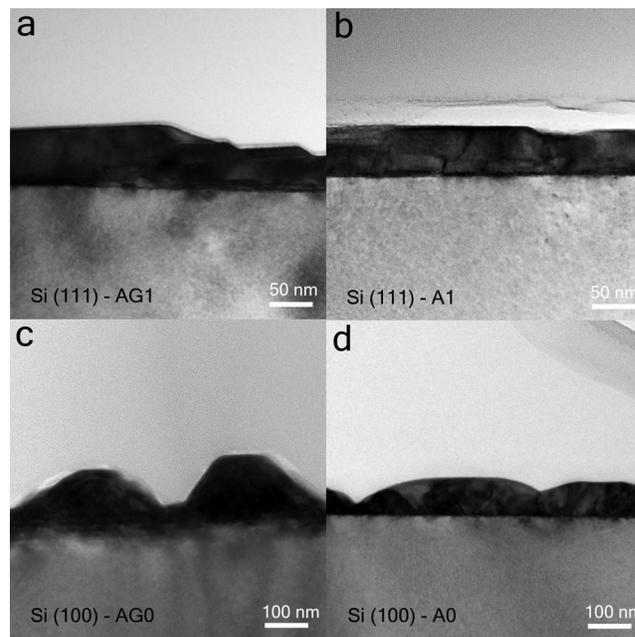


FIG. 2. XTEM image of GaAs epitaxial layer grown on various Si substrates using different techniques. (a) Two-temperature grown film on Si(111) AG1, (b) two-temperature grown then postannealed film on Si(111), A1, (c) two-temperature grown film on Si(100), AG0, and (d) two-temperature grown then postannealed film on Si(100), A0.

nesses were measured to be up to 190 nm for AG0 and  $65 \pm 10$  nm for AG1, respectively. As expected, the GaAs film grown on Si (100) is thicker and shows island growth. However, for those on Si (111) substrate, the GaAs film is rather smooth, suggesting significant layer-by-layer growth. After the annealing process, the films became  $85 \pm 5$  nm thick for A0 and  $60 \pm 5$  nm for A1 [Figs. 2(b) and 2(d), respectively]. Island structures found in AG0 have decreased in quantity. However, the overall surface morphology of the GaAs film grown on Si (111) was still found to be better than that on Si (100) after annealing.

Taking all the above results from Figs. 1 and 2 into account, one can conclude that (1) GaAs film grown on Si (111) substrate is generally thinner than that grown on Si (100) substrate; and (2) the surface of the GaAs film grown on Si (111) is generally smoother and covers the substrate more evenly than that grown on Si (100). It has been reported that GaAs epitaxial layer prefers to grow on substrates that have higher surface energy.<sup>26</sup> Substrates with lower surface energy are more stable due to the lower number of dangling bonds, which makes it more difficult for adatoms to be attached to. For this reason, it is reasonable to observe a thicker GaAs layer grown on the Si (100) substrate. GaAs islands were found on the Si (100) substrate when the two-temperature growth method is used [Fig. 2(c)]. It is well understood that islands commonly form during the initial stages of epitaxial growth of most semiconductors that have a lattice mismatch of more than  $\sim 2\%$  with their substrates.<sup>25</sup> Generally speaking, both the lattice strain and surface and interfacial energies of the system play an important role in determining whether an epitaxial film undergoes a layer-by-layer growth (Frank–Van der Merwe), a direct islanding (Volmer–Weber), or a layer-by-layer growth followed by is-

TABLE I. Energy balance of GaAs layer grown on Si (100) and Si (111). (The data were obtained from Refs. 28 and 29; the unit is mJ/m<sup>2</sup>.)

| Crystal orientation | $\gamma_s$<br>(Si) | $\gamma_f$<br>(GaAs) | $\gamma_i$<br>(GaAs/Si) | $\Delta\gamma = \gamma_f + \gamma_i - \gamma_s$ |
|---------------------|--------------------|----------------------|-------------------------|---|
| (100)               | 2512               | 2953                 | 1000                    | 1441  |
| (111)               | 1467               | 1697                 | 900                     | 1130  |

landing [Stranski–Krastanov (SK)].<sup>27</sup> The tendency for SK growth mode is usually attributed to variations in the surface and interfacial energies of the system, including the surface energies for the thin film and the substrate, as well as their interfacial energy.<sup>25</sup> In the case of GaAs grown on Si substrate, the  $\sim 4\%$  lattice mismatch between GaAs and Si (100) (Ref. 23) is well above the  $\sim 2\%$  limit.<sup>25</sup> Nevertheless, our observation suggests the layer-by-layer growth is the dominant growth mode when GaAs thin film is grown on Si (111). To understand this, we note that, on one hand, the growth mode of the GaAs epitaxial layer on Si depends upon the energy criterion  $\gamma_s \geq \gamma_f + \gamma_i$ , where  $\gamma_s$  and  $\gamma_f$  are the respective surface energies for the substrate and the thin film and  $\gamma_i$  is the interfacial energy between the thin film and the substrate. When the energy criterion  $\gamma_s \geq \gamma_f + \gamma_i$  is satisfied, the growth mode would tend to be layer by layer.<sup>28</sup> The values of  $\gamma_s$ ,  $\gamma_f$ , and  $\gamma_i$  for the GaAs/Si system can be obtained from Refs. 28 and 29 and are listed in Table I. From Table I,  $\gamma_s < \gamma_f + \gamma_i$  for both (100) and (111) surfaces, indicating that island growth should dominate when the GaAs epilayer is grown on both the Si (100) and the Si (111) surfaces. However, the SK growth mode requires initial layer-by-layer growth, after which the island growth takes over when a critical thickness is reached.<sup>27,30</sup> Furthermore, the onset of island growth can be prolonged if the growth is conducted at a relatively low growth temperature.<sup>21</sup> Taken all these facts into account, we believe that the onset of the island growth is complicated. Careful analysis of Table I shows that the  $\Delta\gamma_{100} (\gamma_f + \gamma_i - \gamma_s)_{100} > \Delta\gamma_{111} (\gamma_f + \gamma_i - \gamma_s)_{111}$ , meaning that GaAs grown on the Si (100) substrate would experience island growth more than that on Si (111) substrate. Using this argument, our observation that the surface of GaAs grown on Si (111) being much smoother than on Si (100) suggests the island formation of the GaAs film on Si (111) has been prolonged which in turn suggests that the GaAs film grown on Si (111) has a larger critical thickness. Therefore, we conclude that the critical thickness for a given material system may vary with the orientation of the substrate surface. With decreasing  $\Delta\gamma$ , the critical thickness of the epilayer may increase. Ideal layer-by-layer growth mode could be achieved when the value of  $\Delta\gamma (\gamma_f + \gamma_i - \gamma_s)$  is less than zero. However, in actual growth, a number of factors such as strain in the epilayer, growth temperature, and growth rate also play an important role in determining the morphology of epitaxial layers grown on a lattice mismatched substrate.

It is well understood that lattice defects can deteriorate the device performance, so that it is necessary to evaluate the nature of defects in the GaAs films grown on different Si substrates. To do this, high resolution XTEM was performed. As can be seen in Fig. 3(a), the film grown on (111) Si shows

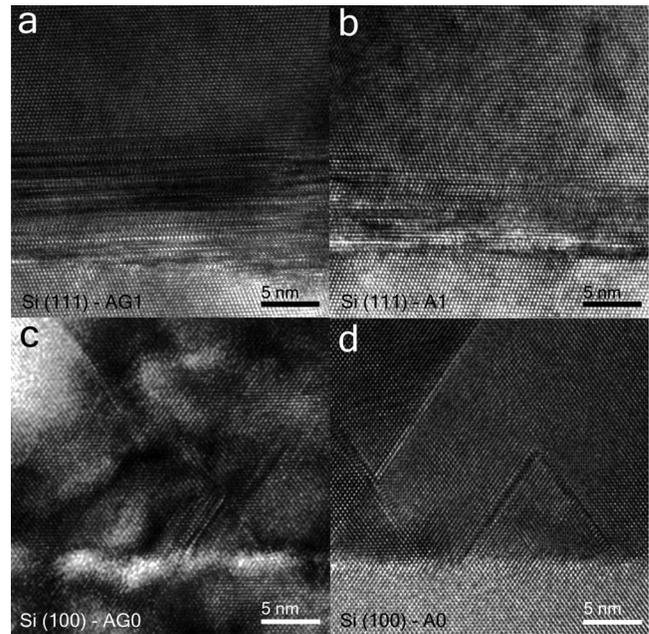


FIG. 3. Cross-sectional HRTEM images of GaAs epitaxial layer grown on various Si substrates using different techniques. (a) two-temperature grown film on Si(111), AG1, (b) two-temperature grown then postannealed film on Si(111), A1, (c) two-temperature grown film on Si(100), AG0, and (d) two-temperature grown then postannealed film on Si(100), A0.

some twining and stacking faults parallel to the GaAs/Si interface. Those lattice defects were possibly generated in the initial growth stage at 400 °C with a lower V/III ratio of 15.4. The subsequent GaAs layers grown at 700 °C with a higher V/III ratio of 154 is almost defect free. Although the interface between GaAs grown at 400 °C and the one grown at 700 °C is hard to identify, it is believed that the growth at 700 °C with V/III ratio of 154 is more favorable for growing high quality GaAs epitaxial layer on Si. Since there are less planar defects found parallel to the GaAs/Si interface for the annealed sample [refer to Fig. 3(b)], annealing must have provided sufficient thermal energy to remove these lattice defects as these defects would not relieve any misfit strain.<sup>31</sup> In this regard, annealing at 750 °C has not only reduced surface roughness but also improved the quality of the grown epitaxial layer.

On the other hand, the GaAs layer grown on Si (100) shows island structures, with planar defects lying along the {111} atomic planes. The planar defects may have originally been generated at 400 °C growth and elongated further along {111} planes after the temperature was raised to 700 °C. Similar to the case in GaAs/Si (111) system, less planar defects are seen from the annealed sample [Fig. 3(d)], suggesting that the annealing process has also improved the crystal structures of GaAs films on Si (100). The reduction in lattice defects during the annealing is attributed to dislocation movement under high thermal stress and temperature.<sup>12</sup>

#### IV. CONCLUSION

We have shown that GaAs thin films grown on Si (111) have a better surface morphology and higher internal crystalline quality than those grown on Si (100) under the same

growth condition. Islands are found in GaAs grown on Si (100), while layer-by-layer growth mode dominates GaAs grown on Si (111) suggesting that Si (111) substrate is more suitable for growing high quality GaAs epilayers. Free surface energy of the substrates is the dominating factor causing the difference in the growth rate, surface morphology, and internal structural quality of the GaAs films. It was also shown that post annealing technique can improve the surface morphologies and reduce the stacking faults for both GaAs/Si (100) and GaAs/Si (111) systems.

## ACKNOWLEDGMENTS

The Australian Research Council is acknowledged for its financial support. The Australian National Fabrication Facility established under the Australian Government's National Collaborative Research Infrastructure Strategy is gratefully acknowledged for access to the facilities used in this work.

- <sup>1</sup>M. Bosi and C. Pelosi, *Prog. Photovoltaics* **15**, 51 (2007).
- <sup>2</sup>R. N. Hall, R. O. Carlson, T. J. Soltys, G. E. Fenner, and J. D. Kingsley, *Phys. Rev. Lett.* **9**, 366 (1962).
- <sup>3</sup>P. Bhattacharya, Z. Mi, J. Yang, D. Basu, and D. Saha, *J. Cryst. Growth* **311**, 1625 (2009).
- <sup>4</sup>Z. T. Mi, J. Yang, P. Bhattacharya, G. X. Qin, and Z. Q. Ma, *Proc. IEEE* **97**, 1239 (2009).
- <sup>5</sup>M. Yamaguchi, *Present Status and Future Prospects of Superhigh Efficiency III-V Compound Solar Cells* (Pergamon-Elsevier Science Ltd, Denver, 1996), p. 354.
- <sup>6</sup>M. Yamaguchi, *Sol. Energy Mater. Sol. Cells* **75**, 261 (2003).
- <sup>7</sup>M. Yamaguchi, T. Warabisako, and H. Sugiura, *Chemical Beam Epitaxy as a Breakthrough Technology for Photovoltaic Solar-Energy Applications* (Elsevier Science Bv, Nara, 1993), p. 29.
- <sup>8</sup>J. Kwo and M. Hong, *J. Cryst. Growth* **311**, 1944 (2009).
- <sup>9</sup>M. Akiyama, Y. Kawarada, and K. Kaminishi, *Jpn. J. Appl. Phys., Part 2* **23**, L843 (1984).
- <sup>10</sup>N. Gopalakrishnan, K. Baskar, H. Kawanami, and I. Sakata, *Effects of the Low Temperature-Grown Buffer Layer Thickness on the Growth of GaAs on Si by MBE* (Elsevier Science Bv, Seattle, 2002), p. 29.
- <sup>11</sup>M. Akiyama, Y. Kawarada, T. Ueda, S. Nishi, and K. Kaminishi, *J. Cryst. Growth* **77**, 490 (1986).
- <sup>12</sup>M. Yamaguchi, M. Tachikawa, Y. Itoh, M. Sugo, and S. Kondo, *J. Appl. Phys.* **68**, 4518 (1990).
- <sup>13</sup>N. A. Elmasry, J. C. Tarn, and N. H. Karam, *J. Appl. Phys.* **64**, 3672 (1988).
- <sup>14</sup>R. Fischer, H. Morkoc, D. A. Neumann, H. Zabel, C. Choi, N. Otsuka, M. Longerbone, and L. P. Erickson, *J. Appl. Phys.* **60**, 1640 (1986).
- <sup>15</sup>T. Soga, S. Hattori, S. Sakai, and M. Umeno, *J. Cryst. Growth* **77**, 498 (1986).
- <sup>16</sup>T. Soga, T. Imori, M. Umeno, and S. Hattori, *Jpn. J. Appl. Phys., Part 2* **26**, L536 (1987).
- <sup>17</sup>Y. Takagi, H. Yonezu, T. Kawai, K. Hayashida, K. Samonji, N. Ohshima, and K. Pak, *Suppression of Threading Dislocation Generation in GaAs-on-Si with Strained Short-Period Superlattices* (Elsevier Science Bv, Toyonaka, 1994), p. 677.
- <sup>18</sup>K. Samonji, H. Yonezu, Y. Takagi, K. Iwaki, N. Ohshima, J. K. Shin, and K. Pak, *Appl. Phys. Lett.* **69**, 100 (1996).
- <sup>19</sup>Y. Takano, M. Hisaka, N. Fujii, K. Suzuki, K. Kuwahara, and S. Fuke, *Appl. Phys. Lett.* **73**, 2917 (1998).
- <sup>20</sup>Z. R. Zytewicz and J. Domagala, *Appl. Phys. Lett.* **75**, 2749 (1999).
- <sup>21</sup>Y. S. Chang, S. Naritsuka, and T. Nishinaga, *Effect of Growth Temperature on Epitaxial Lateral Overgrowth of GaAs on Si Substrate* (Elsevier Science Bv, Toyonaka, 1996), p. 630.
- <sup>22</sup>R. Hull, *Properties of Crystalline Silicon*, 1st ed. (Institution of Engineering and Technology, London, 1999).
- <sup>23</sup>M. Kaya and Y. Atici, *Superlattices Microstruct.* **35**, 35 (2004).
- <sup>24</sup>J. B. Liu, B. M. Tracy, and R. Gronsky, *Microsc. Res. Tech.* **26**, 162 (1993).
- <sup>25</sup>R. V. Kukta and L. B. Freund, *J. Mech. Phys. Solids* **45**, 1835 (1997).
- <sup>26</sup>G. B. Stringfellow, *Organometallic Vapor-Phase Epitaxy: Theory and Practice*, 2nd ed. (Academic, San Diego, 1999).
- <sup>27</sup>M. Copel, M. C. Reuter, E. Kaxiras, and R. M. Tromp, *Phys. Rev. Lett.* **63**, 632 (1989).
- <sup>28</sup>A. Zdyb, J. M. Olchowik, and M. Mucha, *Mater. Sci. (Poland)* **24**, 1109 (2006).
- <sup>29</sup>A. Zdyb, J. M. Olchowik, D. Szymczuk, J. Mucha, K. Zabielski, M. Mucha, and W. Sadowski, *Cryst. Res. Technol.* **37**, 875 (2002).
- <sup>30</sup>J. H. Vandermerwe, *J. Appl. Phys.* **34**, 123 (1963).
- <sup>31</sup>J. Zou and D. J. H. Cockayne, *J. Appl. Phys.* **79**, 7632 (1996).