J Mater Sci (2019) 54:7028–7034

Electronic materials

Dissolution of antiphase domain boundaries in GaAs on Si(001) via post-growth annealing

C. S. C. Barrett[1], A. Atassi[1,*], E. L. Kennon[1], Z. Weinrich[1], K. Haynes[1], X.-Y. Bao[2], P. Martin[2], and K. S. Jones[1]

[1] *Department of Materials Science and Engineering, University of Florida, Gainesville, FL 32607, USA*
[2] *Applied Materials, 3050 Bowers Avenue, Santa Clara, CA 95054, USA*

Received: 12 October 2018
Accepted: 12 January 2019
Published online:
24 January 2019

ABSTRACT

GaAs-on-Si epitaxial crystal quality has historically been limited by a number of growth-related defects. In particular, antiphase domain boundaries (APBs) can nucleate at the GaAs/Si interface and propagate throughout the entire GaAs layer. Still little is known about how thermal processing can affect the APB density in GaAs. In this study, GaAs was grown on nominally on-axis Si(001) by metal–organic chemical vapor deposition. The effect of ex situ post-growth annealing was evaluated for a temperature range of 550–700 °C. It was found that upon annealing the APB density was decreased significantly. The rate of APB density decrease was found to be temperature dependent. At annealing temperatures of 650 °C and above, the APB density was reduced from 0.10 μm^{-1} to approximately 0.010 μm^{-1} in less than 10 min. The activation energy for APB dissolution was determined to be 3.8 eV. The mechanism of APB dissolution is discussed.

Introduction

High-quality GaAs-on-Si epitaxy is a critical step for the integration of III–V compound semiconductors in future transistor technologies. The higher electron mobilities that are characteristic of III–V compounds could theoretically solve the recent slowdown of performance gains with Si-based device scaling, i.e., Dennard scaling [1]. GaAs, while having a greater electron mobility than Si, will likely be incorporated in these future technologies as a buffer layer material for other III-Vs such as InGaAs [2, 3].

While much research has been conducted on the epitaxial growth of GaAs on Si over time, many of the same issues that plagued early development are still relevant. In particular, the presence of defects such as antiphase domain boundaries (APBs) in the GaAs films remains a significant challenge. APBs nucleate at single steps on the (001) Si surface as a consequence of the polar-on-nonpolar growth [4]. Like atoms become bonded together in the layer forming planes of antisite defects, i.e., Ga–Ga and As–As bonds. Classic strategies for avoiding APB nucleation include using off-cut Si wafers [5–8] and annealing the wafers above 1000 °C to induce a double-step

---

Address correspondence to E-mail: ama3100@ufl.edu

Springer

https://doi.org/10.1007/s10853-019-03353-7

reconstruction of the Si surface prior to GaAs growth [9, 10]. However, current industrial process flows are based on wafers with no intentional off-cut and restricted thermal budgets rendering these solutions largely impractical. It is also possible to suppress APBs by simply growing the GaAs layers to several microns in thickness [11, 12]. Later work demonstrated that APBs have a tendency to self-annihilate during growth with increasing film thickness [13]. In practice, epitaxial film thickness should be minimized to save cost and time. Thick GaAs-on-Si films also have the potential to crack upon cooldown due to thermal stresses [14, 15]. Thus, other methods must be explored to reduce the density of APBs in submicron epitaxial GaAs layers on nominally on-axis Si(001) wafers.

Post-growth annealing of GaAs layers grown on Si has been investigated as a method of reducing the density of threading dislocations (TDs) that arise during growth from the lattice mismatch [16–18]. Yamaguchi et al. [17] and Ayers et al. [18] found corresponding activation energies for dislocation annihilation during annealing of 1.35 eV and 1.91 eV, respectively. However, the effect of annealing treatments on APBs in GaAs-on-Si layers has not been as well studied. Chu et al. [19] showed a reduction in APB density after a single anneal condition of 2 h at 800 °C. APB evolution under anneal was examined recently for GaP-on-Si, but the effect of anneal temperature on APB density was not quantified [20, 21]. In order to better understand the effect of post-growth annealing on the process of APB annihilation in III-V films, a systematic study was conducted for GaAs grown on Si(001) by metal–organic chemical vapor deposition (MOCVD). It is shown that APB density can be reduced with post-growth thermal treatments. An activation energy for APB annihilation during annealing is extracted from an Arrhenius relationship, and a plausible mechanism for the underlying process is proposed.

Materials and methods

Samples for this study were taken from a single GaAs-on-Si wafer to ensure that all had experienced similar growth conditions prior to annealing. The substrate was a commercially available 300 mm Si(001) wafer with no intentional off-cut. Before being transferred into the growth chamber, the native oxide was removed from the Si substrate in a selective process that has been discussed previously [22, 23]. This pre-clean procedure can greatly reduce the density of nucleated APBs [23]. The substrate was then transferred under vacuum to an industrial III-V MOCVD reactor for the GaAs film growth. The precursors used for Ga and As were trimethylgallium (TMGa) and tertiarybutylarsine (TBAs), respectively. The V/III ratio was within the standard MOCVD process range, and the chamber was maintained at typical reduced pressure ambient during film growth. An initial layer of 200 nm of GaAs was grown at a low temperature (< 550 °C) followed by an additional 200 nm of GaAs grown at a higher temperature (> 600 °C, < 650 °C). This two-step process is commonly employed in GaAs-on-Si epitaxy to improve crystal quality [11, 24]. Higher bulk growth temperatures also have the effect of accelerating APB annihilation in GaAs-on-Si [25].

Prior to annealing, samples were encapsulated with 20 nm of Al_2O_3 deposited at 200 °C by atomic layer deposition (ALD) to prevent surface degradation. Samples were annealed at temperatures of 550, 600, 650, and 700 °C over a range of times. Longer anneals (> 5 min) were performed in a tube furnace with Ar ambient, and shorter anneals (< 5 min) were performed in a rapid thermal anneal (RTA) system with Ar ambient. Test anneals with overlapping times were done to ensure consistency between the furnace and RTA. After annealing, the Al_2O_3 caps were removed by dipping the samples in pure HF(49%) for 30 s.

APBs in the as-grown and annealed samples were revealed using an APB-selective etchant of $HF(49\%):HNO_3(69\%):H_2O$ (20:1:7). Samples were etched for 10 s. Images of the sample surfaces in various areas were then taken with a scanning electron microscope (SEM) and APB features were traced in ImageJ software [26]. The APB density was quantified as the total APB line length measured over the total observed surface area, giving units of μm^{-1}. For depth profiling of APB density, groups of samples were annealed side by side for each given anneal condition. Subsequently, a non-selective etchant of $CH_3OH:H_3PO_4(85\%):H_2O_2(30\%)$ (10:1:1) was used to etch the GaAs layer in the samples down to different thicknesses. The remaining GaAs film thickness was measured with a JA Woollam M88 ellipsometer, and then the selective HF/HNO_3 etchant was used to delineate the APBs.

Results

Annealing treatments had a noticeable effect on the density of APBs at the surface of the GaAs layer. Figure 1 shows representative plan view SEM images of the GaAs surface after etching with the APB-selective HF/HNO_3 solution for an as-grown sample (a) and a 650 °C, 7.5 min furnace annealed sample (b). The APB density is reduced from 0.10 to 0.014 μm^{-1} after annealing, and there is also a clear decrease in the number of antiphase domains present in a given area. The corresponding histograms of domain size, i.e., APB loop length for a domain, for all domains counted in the as-grown sample and the sample annealed at 650 °C for 7.5 min are shown in (c) and (d), respectively. There is a significant decrease in the average domain size after annealing. It can then be inferred that the APBs must be mobile during the anneal and that the net motion is toward their centers of curvature. This motion eventually leads to self-annihilation.

Figure 2 shows the surface APB densities of the GaAs-on-Si samples for all annealing conditions. There is a clear and consistent trend of decreasing APB density with increasing anneal time and temperature. For the higher temperature anneals at 650 °C and 700 °C the APB density decreases very rapidly but plateaus at a nonzero value. These low densities represent an average of one to two antiphase domains present in a given SEM image of approximately 200 μm^2. The presence of domains even after relatively long and high temperature anneals may be explained by the energetics of APB habit planes. APBs tend to facet along planes that are

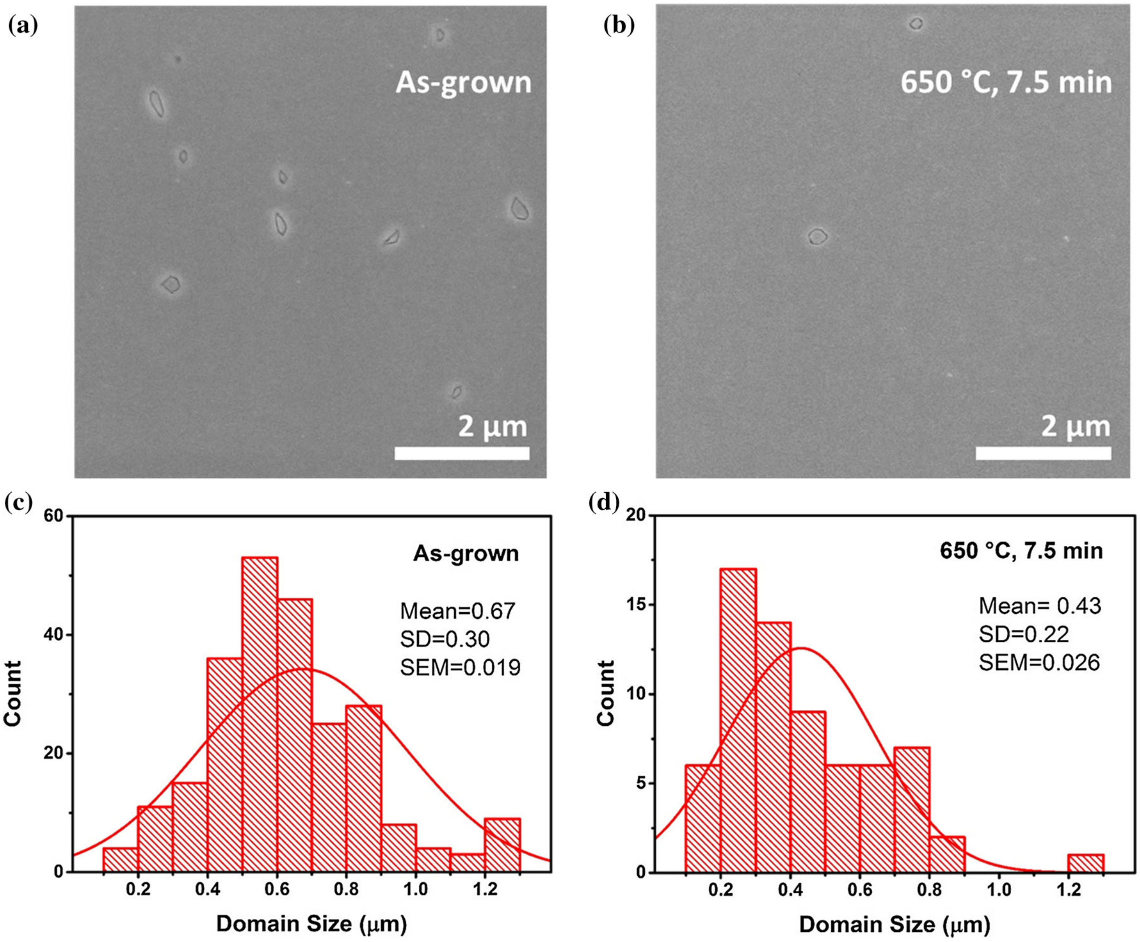

Figure 1 Plan view SEM images of GaAs-on-Si surface after etching in APB-selective HF/HNO_3 solution for samples as-grown (**a**) and after a 650 °C, 7.5 min furnace anneal (**b**). The APB densities before and after annealing are 0.10–0.014 μm^{-1}, respectively. The corresponding histograms of domain size for all counted domains are shown in **c** for the as-grown sample and in **d** for the 650 °C, 7.5 min anneal sample.

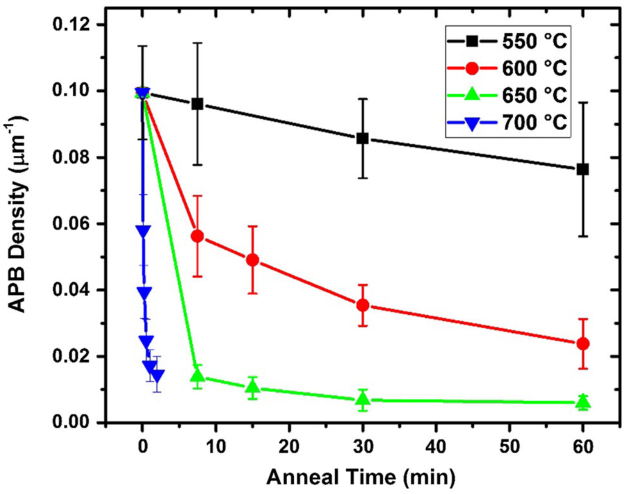

Figure 2 Plot of surface APB densities in the GaAs layer for different annealing conditions. All samples were capped with Al_2O_3 during the anneals. APB density consistently decreases with increasing anneal time and temperature.

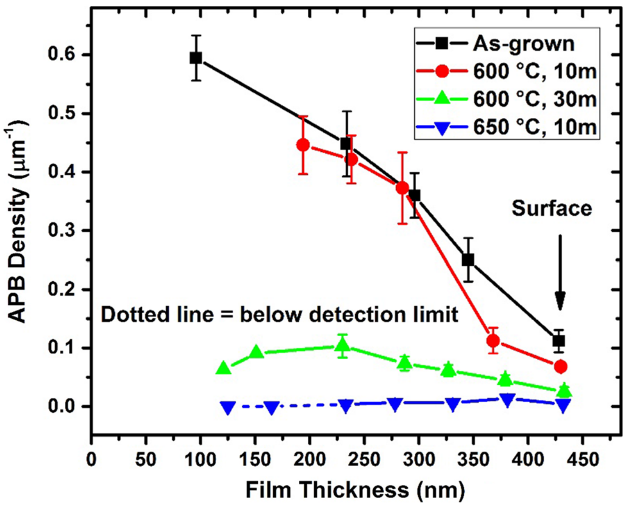

Figure 3 Plot of APB density versus GaAs film thickness for different anneal times and temperatures, including as-grown. The APB density decreases toward the surface of the GaAs layer after a 600 °C 10 min anneal. After increasing the annealing time to 30 min or increasing the temperature to 650 °C, the APB density is reduced throughout the rest of the GaAs layer.

stoichiometric and thus the lowest energy cost [27] and are commonly observed on {110} type planes [28, 29]. Thus, the plane of propagation for an APB greatly impacts the boundary energy [30]. It is feasible that the conditions of few antiphase domains, such as the initial size and APB habit plane, are such that the energy cost to facilitate annihilation during annealing is too great for the conditions observed here. Regardless, annealing shows a significant impact on antiphase domains in GaAs-on-Si as over 90% of domains at the surface are eliminated and the APB density is reduced by an order of magnitude.

In order to gain further insight on the evolution of APBs during post-growth anneals, depth profiles of the APB density in GaAs-on-Si samples were obtained for selected anneal conditions of varying time and temperature. Figure 3 shows the APB density depth profiles for these annealed samples along with an as-grown sample. In the as-grown sample, the APB density starts very high near the GaAs/Si interface but then drops significantly with the onset of the higher temperature bulk growth layer. This decrease is consistent with the tendency of APBs to kink over from vertical {110} type planes to inclined higher-index planes, e.g., {111} or {112}, and self-annihilate at higher growth temperatures [25, 31]. The inverse relationship of APB density with film thickness also demonstrates that APBs are energetically unstable. After annealing at 600 °C for 10 min, it is observed that the APB density closer to the surface of the GaAs layer begins to decrease relative to the as-grown sample. In the middle of the GaAs layer, the APB density remains approximately the same. Thus, it is hypothesized that APBs begin self-annihilating from the surface down during annealing. Annealing for longer time (30 min) or at a higher temperature (650 °C) leads to an enhanced reduction in APB density throughout the GaAs layer. With an anneal of at least 650 °C for 10 min, the APB density for this sample is reduced to nearly undetectable limits for the majority of the GaAs film. It is unclear when increasing anneal time at 600 °C from 10 min to 30 min why the APB density in the bulk decreases much more than the APB density at or near the surface. It is possible that there are surface effects that are a factor in APB migration and annihilation and thus the annihilation rate in the bulk cannot be directly compared to that at the surface. The scope of this work will focus on APB annihilation rate at the surface of the GaAs-on-Si film.

The thermally activated motion and subsequent annihilation of APBs observed for GaAs-on-Si in this study is similar to the motion of APBs that has been investigated in metals and metal oxides. According to the theory established by Allen and Cahn [32], APBs in binary alloys evolve to reduce their curvature and the density of APBs changes with annealing time as $t^{-1/2}$. This time dependence of APB density with annealing has been observed experimentally for epitaxial Fe_3O_4 films grown on MgO [33] and for bulk Cu–Pd alloys [34]. A similar treatment of the APB density evolution data in this study is applied to determine the activation energy of APB motion in GaAs-on-Si. For simplicity, the inverse square of the surface APB density (see Fig. 2) is plotted against the annealing time. The rate constant for APB motion, k, for the Arrhenius equation $k = k_0 * \exp(- E_a/k_B T)$ is extracted from the slope and has units of $\mu m^2\ s^{-1}$. Figure 4a shows this procedure for the APB density versus annealing time data at 700 °C. This procedure was repeated for the surface APB density data for all other annealing temperatures. Figure 4b is the Arrhenius plot of the natural log of the extracted rate constants versus inverse annealing temperature. From the slope of this curve, the activation energy for the motion of APBs at the surface of the GaAs film during annealing is determined to be 3.8 eV.

Discussion

While it is not immediately clear what atomic exchange process facilitates the movement of an APB during annealing, a plausible mechanism can be proposed. The requirements for APB motion involve the breaking of the original antisite bond, either Ga–Ga or As–As, and then the diffusion of the Ga or As atom to an adjacent antisite. This process must also occur nearly simultaneously for numerous antisite bonds for the entire APB plane to move. The activation energy of 3.8 eV determined in this study is very close to the activation energy that has been reported for Ga self-diffusion via Ga vacancies in GaAs of ~ 4 eV [35–37]. The self-diffusion of As in GaAs is not as well studied, but is also believed to occur via vacancies [38]. Correspondingly, there is a greater thermal equilibrium concentration of vacancies at elevated temperatures. It follows that the motion of an APB during annealing is likely enabled by the presence of nearby vacancies and that the rate limiting step is the diffusion of Ga atoms. The APBs will have a tendency to migrate toward their centers of curvature in order to reduce the total APB interfacial area in the GaAs layer and consequently lower the overall free energy of the system.

It should also be noted that this activation energy for APB diffusion in GaAs-on-Si is much higher than the activation energy previously determined for APB kinking during growth of 1.1 eV [25]. Thus, the reduction in APB density during film growth is expected to be dominated by APB kinking from adatoms aligning along higher-index planes, rather than the diffusive motion of existing APBs. Both processes have a large energetic driving force to reduce the APB interfacial area and decrease the proportion of antiphase to main phase in the GaAs layer.

The activation energy found for APB migration during annealing in this study is again only valid for

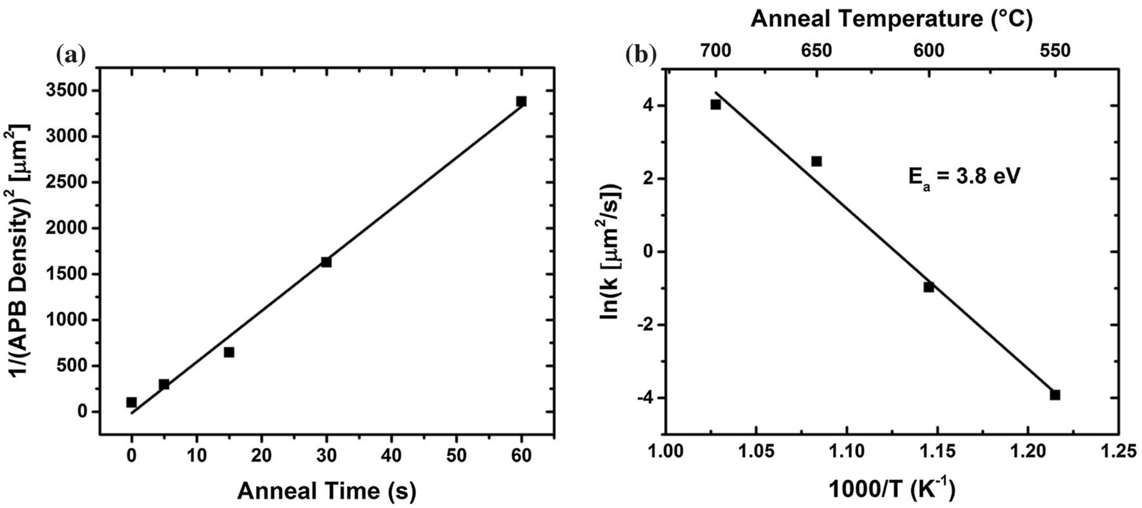

Figure 4 Linear fit of inverse square of surface APB density versus anneal time at 700 °C consistent with Allen–Cahn theory [32] is shown in **a**. Rate constant, k, for APB migration is extracted from the slope. Arrhenius plot of extracted rate constants for all annealing temperatures is shown in **b**. The activation energy for APB migration is determined to be 3.8 eV.

APBs at the surface of GaAs. The depth profiles of APB density in Fig. 3 for different annealing conditions indicate that other kinetic factors may govern the diffusive motion of APBs in the bulk of GaAs. Overall, these findings illustrate the need for additional computational and experimental analysis of APB systems in GaAs and other III-V materials. Future work should also investigate the effect of in situ annealing with an As overpressure and whether a similar reduction in APB density would occur.

Conclusions

In summary, it was shown that APBs in GaAs grown on planar Si(001) can be removed by ex situ post-growth annealing. APB evolution at the surface of the GaAs layer followed the $t^{-1/2}$ time dependence established by Allen and Cahn [32]. At annealing temperatures of 650 °C and above, the surface APB density was decreased by an order of magnitude in less than 10 min. The activation energy for APB migration at the surface during annealing was determined to be 3.8 eV. The motion of APBs is believed to be limited by Ga diffusion via vacancies. Depth profiles of APB density for annealed samples confirmed that the dissolution process initiates at the surface and that the APBs were being removed throughout the GaAs layer. The energetic driving force for the migration of APBs can be understood by a reduction in the total APB interfacial area. Since it is difficult to prevent the nucleation of APBs on Si(001) wafers with no intentional off-cut or high temperature pre-growth treatments, the ability to greatly reduce the grown-in APB density with relatively little additional processing is advantageous.

Acknowledgements

This work is funded through a research grant by Applied Materials. The Research Service Centers at the University of Florida is acknowledged for the use of its sample characterization and preparation facilities. Authors C. S. C. Barrett, E. L. Kennon, Z. Weinrich, K. Haynes, and K. S. Jones have received research grants from Applied Materials, Inc., and K. S. Jones has consulted for Applied Materials.

Compliance with ethical standards

Conflicts of interest The authors declare that they have no conflicts of interest.

References

[1] Dennard RH, Gaensslen FH, Rideout VL, Bassous E, LeBlanc AR (1974) Design of ion-implanted MOSFET's with very small physical dimensions. IEEE J Solid-State Circuits 9:256–268

[2] Cipro R, Baron T, Martin M, Moeyaert J, David S, Gorbenko V, Bassani F, Bogumilowicz Y, Barnes JP, Rochat N, Loup V, Vizioz C, Allouti N, Chauvin N, Bao XY, Ye Z, Pin JB, Sanchez E (2014) Low defect InGaAs quantum well selectively grown by metal organic chemical vapor deposition on Si(100) 300 mm wafers for next generation non planar devices. Appl Phys Lett 104:262103-1–262103-15

[3] Wood B, Hatem C, Bao X, Zhou H, Zhang M, Jin M, Chen H, Cai MP, Munnangi SS, Okazaki M, Sanchez E, Brand A (2015) International symposium on VLSI technology, systems and application, pp 1–2

[4] Fang SF, Adomi K, Iyer S, Morkoç H, Zabel H, Choi C, Otsuka N (1990) Gallium arsenide and other compound semiconductors on silicon. J Appl Phys 68:R31–R58

[5] Kawabe M, Ueda T (1987) Self-annihilation of antiphase boundary in GaAs on Si(100) grown by molecular beam epitaxy. Jpn J Appl Phys 26:L944–L946

[6] Grundmann M, Krost A, Bimberg D (1998) Observation of the first-order phase transition from single to double stepped Si(001) in metalorganic chemical vapor deposition of InP on Si. J Vac Sci Technol B Microelectron Nanometer Struct 9:2158–2166

[7] Mori H, Tachikawa M, Sugo M, Itoh Y (1993) GaAs heteroepitaxy on an epitaxial Si surface with a low-temperature process. Appl Phys Lett 63:1963–1965

[8] Bogumilowicz Y, Hartmann JM, Cipro R, Alcotte R, Martin M, Bassani F, Moeyaert J, Baron T, Pin JB, Bao X, Ye Z, Sanchez E (2015) Anti-phase boundaries–Free GaAs epilayers on "quasi-nominal" Ge-buffered silicon substrates. Appl Phys Lett 107:212105-1–212105-4

[9] Sakamoto T, Hashiguchi G (1986) Si(001)-2 × 1 single-domain structure obtained by high temperature annealing. Jpn J Appl Phys 25:L78–L80

[10] Aspnes DE, Ihm J (1986) Biatomic steps on (001) silicon surfaces. Phys Rev Lett 57:3054–3057

[11] Akiyama M, Kawarada Y, Ueda T, Nishi S, Kaminishi K (1986) Growth of high quality GaAs layers on Si substrates by MOCVD. J Cryst Growth 77:490–497

[12] Ueda O, Soga T, Jimbo T, Umeno M (1989) Direct evidence for self-annihilation of antiphase domains in GaAs/Si heterostructures. Appl Phys Lett 55:445

[13] Georgakilas A, Stoemenos J, Tsagaraki K, Komninou P, Flevaris N, Panayotatos P, Christou A (1993) Generation and annihilation of antiphase domain boundaries in GaAs on Si grown by molecular beam epitaxy. J Mater Res 8:1908–1921

[14] Alberts V, Neethling JH, Leitch AW (1994) Correlation between structural, optical, and electrical properties of GaAs grown on (001) Si. J Appl Phys 75:7258–7265

[15] Yang VK, Groenert M, Leitz CW, Pitera AJ, Currie MT, Fitzgerald EA (2003) Crack formation in GaAs heteroepitaxial films on Si and SiGe virtual substrates. J Appl Phys 93:3859–3865

[16] Choi C, Otsuka N, Munns G, Houdre R, Morkoç H, Zhang SL, Levi D, Klein MV (1987) Effect of in situ and ex situ annealing on dislocations in GaAs on Si substrates. Appl Phys Lett 50:992–994

[17] Yamaguchi M, Tachikawa M, Itoh Y, Sugo M, Kondo S (1990) Thermal annealing effects of defect reduction in GaAs on Si substrates. J Appl Phys 68:4518–4522

[18] Ayers JE, Schowalter LJ, Ghandhi SK (1992) Post-growth thermal annealing of GaAs on Si(001) grown by organometallic vapor phase epitaxy. J Cryst Growth 125:329–335

[19] Chu SNG, Nakahara S, Pearton SJ, Boone T, Vernon SM (1988) Antiphase domains in GaAs grown by metalorganic chemical vapor deposition on silicon-on-insulator. J Appl Phys 64:2981–2989

[20] Létoublon A, Guo W, Cornet C, Boulle A, Véron M, Bondi A, Durand O, Rohel T, Dehaese O, Chevalier N, Bertru N, Le Corre A (2011) X-ray study of antiphase domains and their stability in MBE grown GaP on Si. J Cryst Growth 323:409–412

[21] Guo W, Bondi A, Cornet C, Létoublon A, Durand O, Rohel T, Boyer-Richard S, Bertru N, Loualiche S, Even J, Le Corre A (2012) Thermodynamic evolution of antiphase boundaries in GaP/Si epilayers evidenced by advanced X-ray scattering. Appl Surf Sci 258:2808–2815

[22] Yang R, Su N, Bonfanti P, Nie J, Ning J, Li TT (2010) Advanced in situ pre-Ni silicide (Siconi) cleaning at 65 nm to resolve defects in NiSix modules. J Vac Sci Technol B 28:56–61

[23] Barrett CSC, Lind AG, Bao X, Ye Z, Ban KY, Martin P, Sanchez E, Xin Y, Jones KS (2015) Quantitative correlation of interfacial contamination and antiphase domain boundary density in GaAs on Si(100). J Mater Sci 51:449–456. https://doi.org/10.1007/s10853-015-9334-0

[24] Biegelsen DK, Ponce FA, Smith AJ, Tramontana JC (1987) Initial stages of epitaxial growth of GaAs on (100) silicon. J Appl Phys 61:1856–1859

[25] Barrett CSC, Martin TP, Bao X-Y, Kennon EL, Gutierrez L, Martin P, Sanchez E, Jones KS (2016) Effect of bulk growth temperature on antiphase domain boundary annihilation rate in MOCVD-grown GaAs on Si(001). J Cryst Growth 450:39–44

[26] Schneider CA, Rasband WS, Eliceiri KW (2012) NIH Image to ImageJ: 25 years of image analysis. Nat Methods 9:671–675

[27] Cho N-H, Carter CB (2001) Formation, faceting, and interaction behaviors of antiphase boundaries in GaAs thin films. J Mater Sci 36:4209–4222. https://doi.org/10.1023/A:1017981324721

[28] Cho N-H, Cooman BCD, Carter CB, Fletcher R, Wagner DK (1985) Antiphase boundaries in GaAs. Appl Phys Lett 47:879–881

[29] Cohen D, Carter CB (2002) Structure of the (110) antiphase boundary in gallium phosphide. J Microsc 208:84–99

[30] Rubel O, Baranovskii SD (2009) Formation energies of antiphase boundaries in GaAs and GaP: an ab initio study. Int J Mol Sci 10:5104–5114

[31] Volz K, Beyer A, Witte W, Ohlmann J, Németh I, Kunert B, Stolz W (2011) GaP-nucleation on exact Si(001) substrates for III/V device integration. J Cryst Growth 315:37–47

[32] Allen SM, Cahn JW (1979) A microscopic theory for antiphase boundary motion and its application to antiphase domain coarsening. Acta Metall 27:1085–1095

[33] Eerenstein W, Palstra TTM, Hibma T, Celotto S (2003) Diffusive motion of antiphase domain boundaries in Fe_3O_4 films. Phys Rev B 68:14428-1–14428-7

[34] Goapper S, Barbier L, Salanon B, Loiseau A, Torrelles X (1998) Observation of domain structure and coarsening at Cu-Pd alloy vicinal surfaces. Phys Rev B 57:12497–12500

[35] Wager JF (1991) Energetics of self-diffusion in GaAs. J Appl Phys 69:3022–3031

[36] Wang L, Hsu L, Haller EE, Erickson JW, Fischer A, Eberl K, Cardona M (1996) Ga self-diffusion in GaAs isotope heterostructures. Phys Rev Lett 76:2342–2345

[37] Gösele UM, Tan TY, Schultz M, Egger U, Werner P, Scholz R, Breitenstein O (1997) Diffusion in GaAs and related compounds: recent developments. Defect Diffus Forum 143–147:1079–1094

[38] Palfrey HD, Brown M, Willoughby AFW (1983) Self-diffusion in gallium arsenide. J Electron Mater 12:863–877