REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
13-02-2008

2. REPORT TYPE
Conference Proceeding Paper

3. DATES COVERED *(From - To)*
19 Jan 08 – 24 Jan 08

4. TITLE AND SUBTITLE
Wafer-fused orientation-patterned GaAs

5a. CONTRACT NUMBER
IN-HOUSE

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
61102F

6. AUTHOR(S)
*Jin Li, **David B. Fenner, *Krongtip Termkoa, **Mark G. Allen, **Peter F. Moulton, Candace Lynch, David F. Bliss, *William D. Goodhue

5d. PROJECT NUMBER
2305

5e. TASK NUMBER
HC

5f. WORK UNIT NUMBER
01

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Electromagnetic Technology Branch, 80 Scott Drive, Hanscom AFB, MA 01731
*Photonics Center, University of Massachusetts at Lowell, Lowell, MA 01854
**Physical Sciences, Inc., 20 New England Business Ctr, Andover, MA 01810

8. PERFORMING ORGANIZATION REPORT

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Electromagnetics Technology Division Source Code: 437890
Sensors Directorate
Air Force Research Laboratory
80 Scott Drive
Hanscom AFB MA 01731-2909

10. SPONSOR/MONITOR'S ACRONYM(S)
AFRL/RYHC

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
AFRL-RY-HS-TP-2008-0008

12. DISTRIBUTION / AVAILABILITY STATEMENT
DISTRIBUTION A: APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED.

13. SUPPLEMENTARY NOTES
The U. S. Government is joint author of this work and has the right to use, modify, reproduce, release, perform, display, or disclose the work. Published in Proceedings of the SPIE, Volume 6875 68750H, 13 February 2008. Cleared for Public Release by ESC/PA number: ESC-08-0040

14. ABSTRACT
The fabrication of thick orientation-patterned GaAs (OP-GaAs) films is reported using a two-step process where an OP-GaAs template with the desired crystal domain pattern was prepared by wafer fusion bonding and then a thick film was grown over the template by low pressure hydride vapor phase epitaxy (HVPE). The OP template was fabricated using molecular beam epitaxy (MBE) followed by thermocompression wafer fusion, substrate removal, and lithographic patterning. On-axis (100) GaAs substrates were utilized for fabricating the template. An approximately 350 μm thick OP-GaAs film was grown on the template at an average rate of ~70 μm/hr by HVPE. The antiphase domain boundaries were observed to propagate vertically and with no defects visible by Nomarski microscopy in stain-etched cross sections. The optical loss at ~2 μm wavelength over an 8 mm long OP-GaAs grating was measured to be no more than that of the semi-insulating GaAs substrate. This template fabrication process can provide more flexibility in arranging the orientation of the crystal domains compared to the Ge growth process and is scalable to quasi-phase-matching (QPM) devices operating from the IR to terahertz frequencies utilizing existing industrial foundries.

15. SUBJECT TERMS
Orientation-patterned Gallium Arsenide, hydride vapor phase epitaxy, quasi-phase-matching, nonlinear frequency conversion

16. SECURITY CLASSIFICATION OF:			**17.LIMITATION OF ABSTRACT**	**18.NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON** David Bliss
a. REPORT Unclassified	**b. ABSTRACT** Unclassified	**c. THIS PAGE** Unclassified	SAR	9	**19b. TELEPHONE NUMBER** *(include area code)* N/A

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

Wafer-fused orientation-patterned GaAs

Jin Li*[a], David B. Fenner[b], Krongtip Termkoa[a], Mark G. Allen[b], Peter F. Moulton[b],
Candace Lynch[c], David F. Bliss[c], William D. Goodhue[a]

[a]Photonics Center, University of Massachusetts at Lowell, Lowell, MA 01854, USA;
[b]Physical Sciences, Inc., 20 New England Business Center, Andover, MA 01810, USA;
[c]Air Force Research Laboratory, Hanscom AFB, MA 01731, USA

ABSTRACT

The fabrication of thick orientation-patterned GaAs (OP-GaAs) films is reported using a two-step process where an OP-GaAs template with the desired crystal domain pattern was prepared by wafer fusion bonding and then a thick film was grown over the template by low pressure hydride vapor phase epitaxy (HVPE). The OP template was fabricated using molecular beam epitaxy (MBE) followed by thermocompression wafer fusion, substrate removal, and lithographic patterning. On-axis (100) GaAs substrates were utilized for fabricating the template. An approximately 350 μm thick OP-GaAs film was grown on the template at an average rate of ~70 μm/hr by HVPE. The antiphase domain boundaries were observed to propagate vertically and with no defects visible by Nomarski microscopy in stain-etched cross sections. The optical loss at ~2 μm wavelength over an 8 mm long OP-GaAs grating was measured to be no more than that of the semi-insulating GaAs substrate. This template fabrication process can provide more flexibility in arranging the orientation of the crystal domains compared to the Ge growth process and is scalable to quasi-phase-matching (QPM) devices operating from the IR to terahertz frequencies utilizing existing industrial foundries.

Keywords: Orientation-patterned Gallium Arsenide, hydride vapor phase epitaxy, quasi-phase-matching, nonlinear frequency conversion

1. INTRODUCTION

Quasi-phase-matching (QPM)[1] is an effective technique for monochromatic optical frequency generation at wavelengths not readily available using direct laser generation. Zinc-blende semiconductor compounds, such as GaAs, are excellent candidates for nonlinear optical frequency conversion in the infrared by QPM, if periodic crystal domain inversions are incorporated in those otherwise optically isotropic materials. The effective nonlinear optical coefficient of GaAs is higher than ferroelectric materials, such as periodically-polled $LiNbO_3$. GaAs is also attractive for its high thermal conductivity, high laser damage threshold, and transparency from 0.8 μm to 17 μm and in the very far infrared to terahertz. In addition, GaAs-based nonlinear devices can take advantage of existing technologies available to III-V compound semiconductor industries. Second harmonic generation (SHG) in a QPM GaAs was first demonstrated using a 10.6 μm laser in 1976.[2] Wavelength conversion by difference frequency generation (DFG) in QPM GaAs and AlGaAs was also realized for long-wavelength infrared (LWIR)[3] and short-wavelength infrared (SWIR),[4] respectively. Most recently, Vodopyanov *et al.* demonstrated room temperature terahertz generation in QPM GaAs using femtosecond laser pulses.[5]

Early orientation-patterned GaAs (OP-GaAs) was obtained by stacking[2] or wafer bonding[6,7] of GaAs wafers with alternating crystal orientations, resulting in changing the sign of the nonlinear optical coefficient periodically. Wafer fusion bonding of multiple wafers can produce OP crystals with large optical apertures and is attractive for LWIR and terahertz generation. The variation in individual wafer thickness and impurities and voids between the bond interfaces should be controlled for maximum efficiency. However, it remains challenging to fabricate and bond the thin crystal plates (<100 μm) required by the shorter grating periods needed for mid-wavelength (MWIR) applications. To overcome this problem, two-step processes where an orientation-patterned template is first prepared and then a thick GaAs layer with vertical domain boundaries is epitaxially grown have been developed. These types of techniques are easily scalable to produce QPM devices from SWIR to terahertz by simply varying the grating period patterned on the template. Low pressure hydride vapor phase epitaxy (HVPE) with a rapid growth rate well above 100 μm/hr is usually employed for GaAs growths up to 500 μm thick.[8] There are currently two types of approaches to prepare orientation-

Nonlinear Frequency Generation and Conversion: Materials, Devices, and Applications VII, edited by Peter E. Powers,
Proc. of SPIE Vol. 6875, 68750H, (2008) · 0277-786X/08/$18 · doi: 10.1117/12.762315

patterned templates. One approach is based on Molecular Beam Epitaxial (MBE) growth of antiphase GaAs films using GaAs/Ge/GaAs heteroepitaxy.[9,10,11] By inserting a thin layer of Ge (~ 3 nm) on a (100) GaAs substrate slightly misoriented (≤4°) towards a (111)B plane, an antiphase GaAs layer can be obtained under proper growth conditions. The other approach bonds two wafers that are carefully aligned with inverted phase domains. With this method an etch stop layer is generally used to facilitate the sacrificial substrate removal of the bonded wafer pair. Conventional photolithography followed by etching is used in both approaches to produce the grating pattern with inverted crystal orientations. In the former process, a second MBE growth of approximately 5 μm thick GaAs is typically employed as a preparation layer for subsequent HVPE growth. While both techniques have successfully produced OP-GaAs templates, wafer bonding techniques are more compatible with current III-V compound semiconductor industry standard processes and have greater potential for commercialization utilizing foundry services.

The fabrication of OP-GaAs using wafer fusion bonding techniques is discussed in this paper. Two full 2-inch on-axis (100) wafers were diffusion bonded together at high temperature under high pressure. The sacrificial substrate was removed by mechanical thinning and chemical etching with the assistance of an etch stop layer previously grown with MBE. After lithographic patterning of grating structures along $[01\bar{1}]$ direction, a thick OP-GaAs film up to approximately 350 μm in thickness was grown on the template by low pressure HVPE. In contrast to the specific crystal orientation required by using GaAs/Ge/GaAs heteroepitaxy to obtain antiphase crystal domains, wafer bonding can be applied to wafers with a variety of crystal orientations. This freedom in choice of the orientation can be further explored for QPM and integrated device applications.

2. EXPERIMENT DETAILS

Wafers of industry standard (100) orientation are suitable for QPM in OP-GaAs if the beam propagates along [011] in plane and domains alternate with the [100] direction up and down.[3-8,11] From the refractive index measurements for GaAs at 25°C,[12] the calculated relationships between idler and signal wavelengths (λ) across a range of QPM periods and for three pump wavelengths are shown in Fig. 1. It is shown that a period in the range of 55 to 65 μm is suitable for MWIR generation. A grating period of 62 μm was selected. At high optical pumping levels, the high thermal conductivity and optical damage threshold (requiring high surface quality) of GaAs are advantageous. Still, the device damage threshold must be increased by expanding the pump beam at the entry facet which requires thick crystals. The thick film also allows easy pump laser coupling and avoids beam clipping. Thus, OP-GaAs films for QPM of up to 1-mm thick are highly desired.

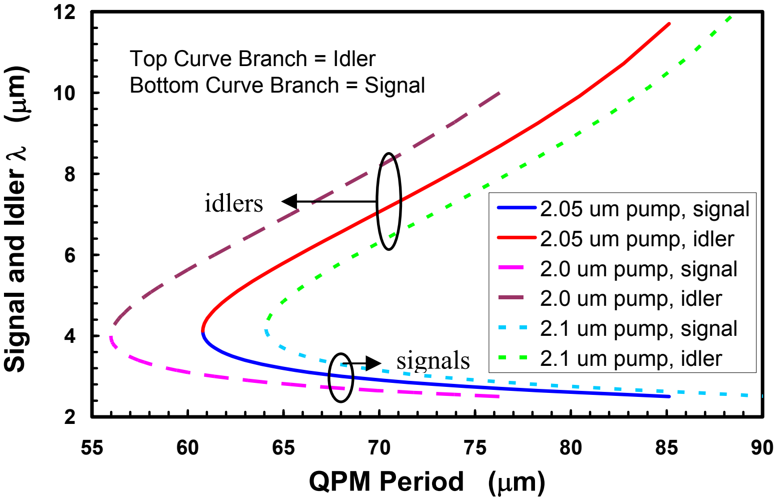


Fig. 1. Calculated quasi-phase-matched conditions for the pump laser wavelengths of 2.0 μm, 2.05 μm and 2.1 μm, respectively.

Orientation-patterned GaAs films were fabricated by wafer fusion bonding illustrated in Fig. 2. First, epitaxial layers of AlGaAs/GaAs with thicknesses of 0.6 μm and 3.8 μm, respectively, were grown on an on-axis (100) GaAs wafer by a Veeco GenII Molecular Beam Epitaxy system (Fig. 2(a)). The AlGaAs epitaxial layer has a high Al composition and is used to assist the sacrificial substrate removal after the wafer bonding. This wafer was next fusion bonded in a tube furnace to a supporting on-axis (100) GaAs wafer. The wafers were aligned with inverted crystal orientations (Fig. 2(b)). The sacrificial substrate was removed by mechanical lapping and selective chemical etching (Fig. 2(c)). After removing the AlGaAs etch stop layer, photoresist lithography and wet etching were used to create an orientation-patterned template (Fig. 2(d)). Finally, a thick GaAs film was grown on the template by low pressure HVPE (Fig. 2(e)). The process details are discussed below.

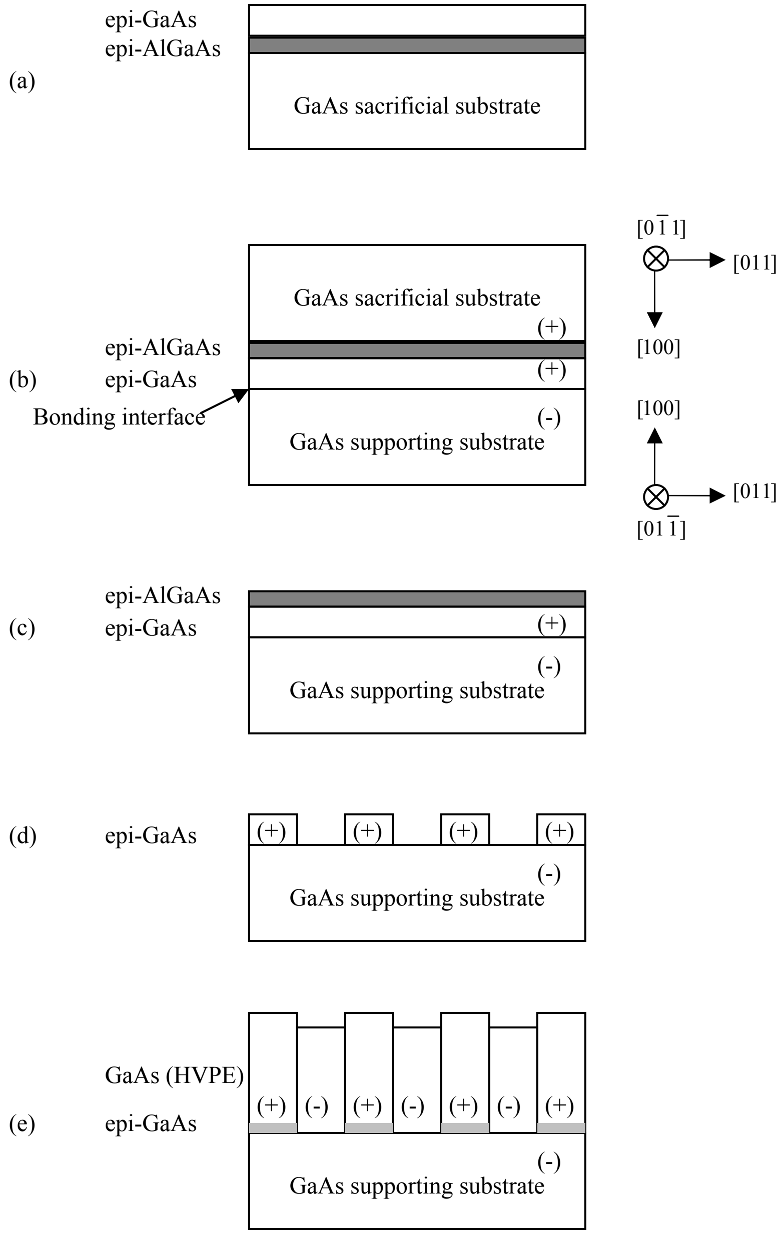
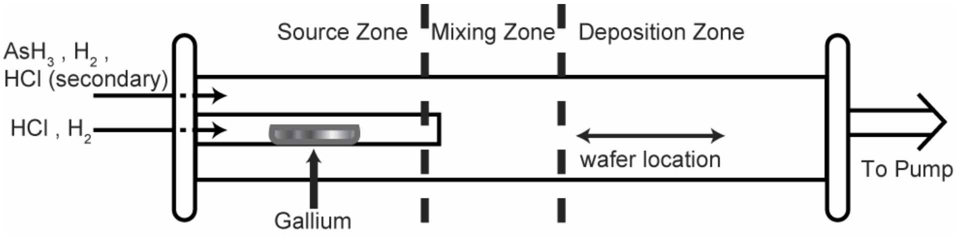


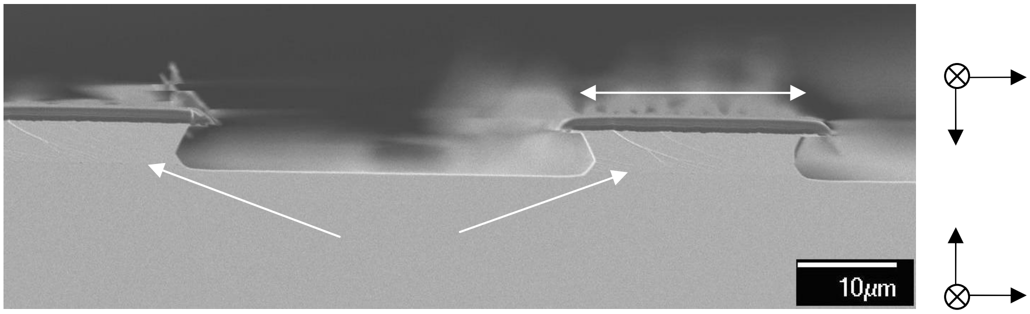
Fig. 2. Schematic diagrams of the fabrication process of QPM GaAs films: (a) MBE growth of epitaxial AlGaAs/GaAs layers; (b) wafer fusion bonding; (c) sacrificial substrate removal; (d) etch stop layer removal and OP-GaAs template patterning; and (e) HVPE growth of thick GaAs films.

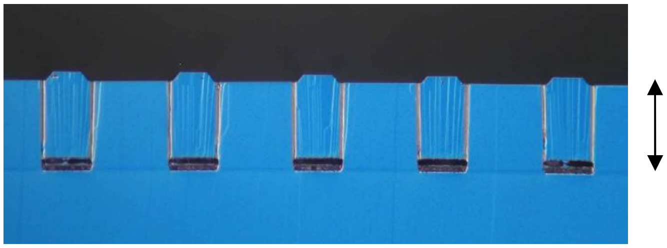
Direct wafer bonding of GaAs to GaAs was accomplished by mass transport wafer fusion.[13] This is simpler than the atomic rearrangement bonding assisted by intermediate $In_{0.5}Ga_{0.5}P$ layers on both wafers reported in Ref. 14. Commercial 2-inch epi-ready semi-insulating GaAs wafers with on-axis (100) orientation were used. After growing AlGaAs/GaAs layers on one of the wafers, both wafers were cleaned and immediately put face to face together with inverted crystal orientations as illustrated in Fig. 2(b). The wafer pair was then inserted in a close fit graphite quartz apparatus similar to the one described in Ref. 13. Graphite shims with different thicknesses were used to adjust the spacing between the graphite and quartz tube. The entire assembly was then loaded into a quartz tube furnace. After an initial baking at 110°C with continuous purified N_2 flow, the tube furnace temperature was raised to 700°C gradually and kept at the elevated temperature for one hour. When the tube furnace is heated, a strong compression is induced on the wafer pair, due to the large difference in the thermal expansion coefficients of graphite (9×10^{-6} K^{-1}) and quartz (0.5×10^{-6} K^{-1}). Crystallites in contact can fuse together at elevated temperatures under high pressure because of surface-energy-induced migration. Finally, the temperature of the furnace was returned to the room temperature. Purified N_2 flow was kept throughout the whole process. One of the common problems associated with wafer bonding is the occurrence of unbonded interface areas caused by wafer surface contamination prior to the bonding step. Therefore, a thorough cleaning of wafers with solvents is critical. The wafers were also chemically etched in HCl before insertion into the graphite assembly. Full 2-inch bonded wafer pairs were successfully obtained routinely using this technique. The bonding was very strong and the bonded wafer pair can be cleaved, mechanically lapped and patterned in the subsequent processing steps. The graphite is also believed to help wafers to conform to each other under high temperature and high pressure, producing a uniform bonding interface across large areas. Wafer fusion bonding of full 2-inch wafer pairs at a lower temperature of 600°C was also obtained.

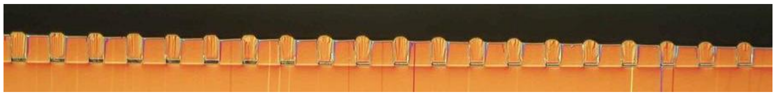
After the wafer bonding, the bonded wafer pair was cleaved into approximately 2×2 cm^2 pieces. The sacrificial GaAs substrate was mechanically lapped down to approximately 150 μm in thickness. Great care was taken to minimize the crystal damage introduced by the lapping and to maintain the parallelism of the substrate. With the backside of the supporting GaAs substrate protected by the photoresist, the sample was etched in a H_2O_2:NH_4OH solution until the AlGaAs etch stop layer was reached. This etch solution has a high etch selectivity between GaAs and AlGaAs with an Al composition above 30%.[15] The etch rate of GaAs was measured to be approximately 3 μm/hr for the freshly prepared solution. The wafer surface discolors when the AlGaAs etch stop layer is exposed to air due to the fast oxidation of Al. The fully exposed AlGaAs layer was then removed by using 1:1 HCl:H_2O solution, indicated by the grey metallic surface of GaAs epitaxial layer. A final quick dipped in H_2O_2 followed by 1:1 HCl:H_2O was used to eliminate aluminum-containing residues.[16,11] Using high selectivity wet etch solution with the AlGaAs etch stop layer prevents crystal damage generated during lapping from propagating into the GaAs epitaxial layer. After removing the protective photoresist on the backside of the supporting GaAs substrate, photoresist lithography was employed to pattern the grating structure on the epitaxial GaAs layer. The grating lines were aligned in the $[01\bar{1}]$ direction. A citric acid/hydrogen peroxide solution was used to etch the grating pattern down to the bottom GaAs substrate, generating the grating structure with alternating crystal domains from the supporting GaAs substrate and the GaAs epitaxial layer from the removed sacrificial substrate. The citric acid/H_2O_2 solution etches GaAs at a rate of approximately 0.25 μm/min. The resulting crystal domains of the template are illustrated in Fig. 1(e). After photoresist mask removal, the sample was ready for the thick film GaAs growth.

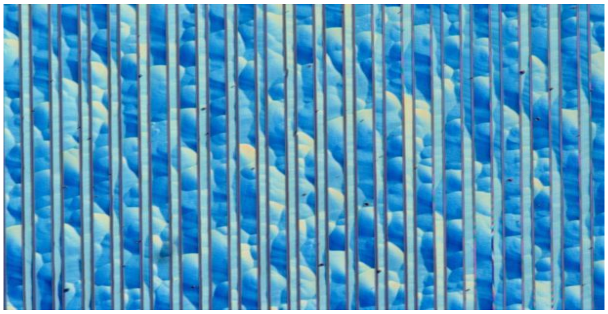
A thick OP-GaAs film (up to 1 mm in height) with defect-free vertical domain walls is required for effective frequency conversion. The benefit of low pressure HVPE over other methods of epitaxial growth is the capability for growth of very thick layers in a reasonable time period. Thicknesses on the order of 1 mm have been achieved in single 10 hour growth runs. Thick regrowth of GaAs on patterned templates was conducted via low pressure HVPE in a custom-built reactor at the Air Force Hanscom Research Site.[8] The system consists of a horizontal quartz tube, heated by a three-zone furnace and sealed to allow low pressure operation in the range of 1 to 5 Torr, illustrated in Fig. 3. HCl vapor passing over a liquid Ga source reacts to form GaCl, which is transported to the substrate with a hydrogen carrier gas. Arsenic is supplied in the form of arsine (AsH_3). Both the Ga source and the substrate are heated to temperatures in the range of 650 to 750˚C; the temperature gradient along the tube drives GaCl formation at the source and GaAs deposition on the substrate. The growth rate can be controlled by varying the vapor supersaturation – i.e., increasing or decreasing the partial pressures of the reactants with respect to their equilibrium values alters the tendency toward growth or etching of GaAs. In this HVPE reactor, GaAs growth rates of up to 200 microns per hour are achievable; however, careful control over the gas supersaturation and furnace temperature profile is necessary to maintain this growth rate for many hours, while minimizing parasitic GaAs deposition on the reactor walls upstream of the sample.

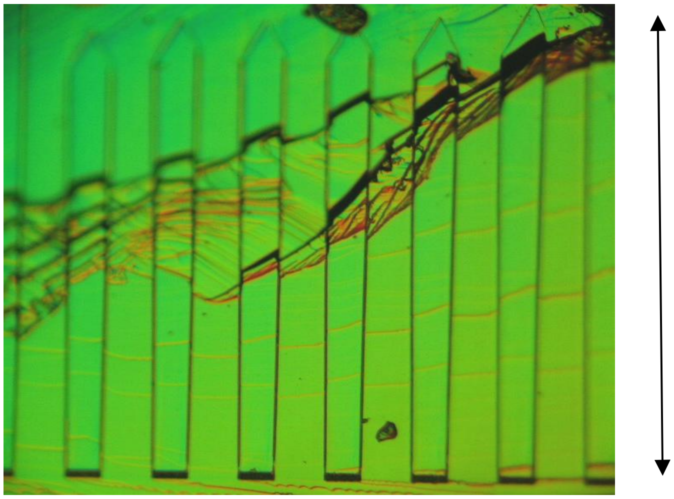

Source Zone
Mixing Zone
Deposition Zone
AsH$_3$, H$_2$,
HCl (secondary)
HCl , H$_2$
wafer location
To Pump
Gallium


10μm









facet was also formed. The top view (Fig. 5(c)) reveals that domain walls are parallel and straight along the sample surface. Interfaces between streets and gratings are clear and no apparent overgrowth or loss of grating structure was observed after the ½ hour growth. The growth rate was estimated to be approximately 80 µm/hr. The second sample was grown for a longer period of 5 hours. A 350 µm thick OP-GaAs film was achieved with a single HVPE growth run. The average growth rate was approximately 70 µm/hr. The domain walls propagate vertically and show good domain quality (Fig. 5(d)). These results show similar crystal quality to OP-GaAs films obtained from templates with offcut (100) substrate and domain walls on (011) planes.[8,11] However, the growth rate on templates with on-axis (100) substrate was higher than expected.[8] The previous study by Bliss *et al.*[8] shows that the thick film growth rate on OP-GaAs templates fabricated using a Ge layer depends on the offcut angle of the substrate. The growth rate on wafers with the (100) substrate oriented 4° toward the <111>B is approximately twice the growth rate on wafers with a 2° offcut, i.e., 110 µm/hr vs. 55 µm/hr. The fact that a rapid growth rate for HVPE growth can be obtained with on-axis wafer-fused templates offers flexibility in selecting substrate orientation and crystal domain orientation. For example, vertical domain walls in $(01\overline{1})$ planes may be obtained with OP-GaAs templates prepared by wafer fusion bonding of on-axis (100) wafers, which was difficult with templates prepared using GaAs/Ge/GaAs heteroepitaxy due to the offcut angle from the substrate normal.[8,11]

The OP-GaAs material was characterized by measuring the IR optical loss at 2 µm wavelength. End facets were lightly polished to mirror finishes on the 350 µm thick OP-GaAs film. A single-mode fiber pigtailed laser diode was focused and aligned onto an entry facet and the transmitted beam intensity was measured. Translation of the OP-GaAs film provided the relative intensity for beams passing through gratings, streets, and semi-insulating substrate regions. The loss observed in the grating regions over an 8-mm path length was no greater than that of the substrate within instrumental precision of ~3%, indicating low loss antiphase domain interfaces.

4. CONCLUSIONS

We have demonstrated the production of thick orientation-patterned GaAs films based on the wafer fusion bonding technique. High growth rates were achieved for HVPE growth on templates fabricated using on-axis (100) GaAs substrates. This provides more flexibility for OP-GaAs template design than the conventional Ge-based process. In addition, this OP-GaAs template fabrication process is more compatible with the existing III-V compound semiconductor industry. It may offer a practical approach to the volume production of orientation-patterned GaAs films for nonlinear optical applications.

ACKNOWLEDGEMENTS

This work was supported by AF Contract FA9550-06-C-0053 under contract monitor Dr. Howard Schlossberg.

REFERENCES

[1] M. M. Fejer, G. A. Magel, D. H. Jundt, and R. L. Byer, “Quasi-phase-matched second harmonic generation: tuning and tolerances,” IEEE Journal of Quantum Electronics, **38(11)**, 2631-2654 (1992).

[2] A. Szilagyi, A. Hordvik, and H. Schlossberg, “A quasi-phase-matching technique for efficient optical mixing and frequency doubling,” Journal of Applied Physics, **47(5)**, 2025-2032 (1976).

[3] D. Zheng, L. A. Gordon, Y. S. Wu, R. S. Feigelson, M. M. Fejer, R. L. Byer, and K. L. Vodopyanov, “16-µm infrared generation by difference-frequency mixing in diffusion-bonded-stacked GaAs,” Optics Letters, **23(13)**, 1010-1012 (1998).

[4] S. J. B. Yoo, C. Caneau, R. Bhat, M. A. Koza, A. Rajhel, and N. Antoniades, “Wavelength conversion by difference frequency generation in AlGaAs waveguides with periodic domain inversion achieved by wafer bonding,” Applied Physics Letters, **68(19)**, 2609-2611 (1996).

[5] K. L. Vodopyanov, M. M. Fejer, X. Yu, J. S. Harris, Y.-S. Lee, W. C. Hurlbut, V. G. Kozlov, D. Bliss and C. Lynch, “Terahertz-wave generation in quasi-phase-matched GaAs,” Applied Physics Letters, **89(14)**, 141119, (2006).

[6] D. Zheng, L. A. Gordon, Y. S. Wu, R. K. Route, M. M. Fejer, R. L Byer, and R. S. Feigelson, “Diffusion bonding of GaAs wafers for nonlinear optics applications,” J. Electrochem. Soc., **144(4)**, 1439-1441, (1997).

[7] E. Lallier, M. Brevignon, and J. Lehoux, “Efficient second-harmonic generation of a CO_2 laser with a quasi-phase-matched GaAs crystal,” Optics Letters, **23(19)**, 1511-1513, (1998).

[8] D. F. Bliss, C. Lynch, D. Weyburne, K. O’Hearn, J. S. Bailey, “Epitaxial growth of thick GaAs on orientation-patterned wafers for nonlinear optical applications,” J. of Crystal Growth, 287, 673-678, (2006).

[9] S. Strite, D. Biswas, N. S. Kumar, M. Fradkin, and H. Morkoc, “Antiphase domain free growth of GaAs on Ge in GaAs/Ge/GaAs heterostructures,” Applied Physics Letters, **56(3)**, 244-246, (1990).

[10] C. B. Ebert, L. A. Eyres, M. M. Fejer, J. S. Harris Jr., “MBE growth of antiphase GaAs films using GaAs/Ge/GaAs heteroepitaxy,” J. Crystal Growth, **201/202**, 187-193, (1999).

[11] L. A. Eyres, P. J. Tourreau, T. J. Pinguet, C. B. Ebert, J. S. Harris, M. M. Fejer, L. Becouarn, B. Gerard, and E. Lallier, “All-epitaxial fabrication of thick, orientation-patterned GaAs films for nonlinear optical frequency conversion,” Appl. Phys. Lett., **79(7)**, 904-906, (2001).

[12] T. Skauli, P. S. Kuo, K. L. Vodopyanov, T. J. Pinguet, O. Levi, L. A. Eyres, J. S. Harris, M. M. Fejer, B. Gerard, L. Becouarn, E. Lallier, “Improved dispersion relations for GaAs and applications to nonlinear optics,” J. Appl. Phys. **94(10)**, 6447-6455, (2003).

[13] Z. L. Liau, and D.E. Mull, “Wafer fusion: a novel technique for optoelectronic fabrication and monolithic integration,” Applied Physics Letters, **56(8)**, 737-739 (1990).

[14] S. J. B. Yoo, R. Bhat, C. Caneau, and M. A. Koza, “Quasi-phase-matched second-harmonic generation in AlGaAs waveguides with periodic domain inversion achieved by wafer-bonding,” Applied Physics Letters, **66(25)**, 3410-3412, (1995).

[15] Y. Uenishi, H. Tanaka, and H. Ukita, “Characterization of AlGaAs microstructure fabricated by AlGaAs/GaAs micromachining,” IEEE Transactions on Electron Devices, **41(10)**, 1778-1783, (1994).

[16] L. Becouarn, B. Gerard, M. Brevignon, J. Lehoux, Y. Gourdel, and E. Lallier, “Second harmonic generation of CO_2 laser using thick quasi-phase-matched GaAs layer grown by hydride vapour phase epitaxy,” Electronics Letters, **34(25)**, 2409-2410, (1998).