Second-Harmonic Generation in Heteroepitaxially Grown, Orientation-Patterned, Ternary GaAsP Periodic Structures

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Orientation-patterned GaAs$_{0.85}$P$_{0.15}$ is grown by hydride vapor phase heteroepitaxy on an orientation-patterned GaAs template and second-harmonic generation is demonstrated for this ternary periodic structure using ultrashort pulses with an internal conversion efficiency exceeding 19%.

1. Introduction

Compact, high-power, tunable laser sources for the midinfrared (mid-IR) part of the spectrum above 5 μm are in great demand for a wide range of applications starting with robust military or security equipment for IR countermeasures, enhanced laser radar and long-range IR telecommunications or remote sensing of chemical and biological species, to fine medical and scientific applications like breath analysis and ultrafast spectroscopy of chemical reaction dynamics. As the available direct laser sources in this spectral range do not satisfy requirements for power and tunability, frequency downconversion via quasiphase matching (QPM) in periodic structures with alternating crystal polarity has been developed as a viable solution free of spatial walk-off.[1] The most successful among all studied to date nonferroelectric noncentrosymmetric cubic materials that are transparent in this spectral range has been the orientation-patterned GaAs (OP-GaAs).[2] This binary semiconductor material combines superior second-order nonlinearity and thermal conductivity with transparency up to 18 μm but suffers from strong two-photon absorption (TPA) up to 1.7 μm and for this reason cannot be pumped by pulsed laser sources between 1 and 1.7 μm.[3] Compared to GaAs, the isostructural GaP not only has a negligible TPA in the same spectral range but shows some additional advantages such as higher laser damage threshold, lower refractive index (strictly correlated with the nonlinear figure of merit and the domain width), and higher thermal conductivity at lower thermal expansion—most of them as a consequence of the increased bandgap. This, however, comes at the expense, again due to the increased bandgap, of somewhat lower nonlinearity and lower transparency upper limit in the mid-IR. In spite of all the progress subsequently achieved with OP-GaP,[4–6] the low quality of the commercially available GaP wafers, their 5–6 times higher price and extremely narrow market present a huge technological hurdle. Heteroepitaxy, i.e., the growth of one material on another, can be used not only to grow GaP on the cheaper, robust, and higher quality GaAs substrates, notwithstanding the relatively large lattice mismatch (3.6%)[7–9] but also offers a unique opportunity to grow mixed GaAsP on GaAs with engineering properties and at reduced lattice mismatch. Here, we demonstrate for the first time to our knowledge nonlinear frequency conversion (second-harmonic generation, SHG) in such a ternary OP-GaAsP structure with a nominal P content of 15%, i.e., GaAs$_{0.85}$P$_{0.15}$, grown on an OP-GaAs template. The thickness of ≈600 μm is the largest achieved so far for such a ternary QPM structure.

2. Fabrication of OP-GaAsP

OP-GaAsP layers were fabricated by low-pressure hydride vapor phase epitaxy (LP-HVPE) on OP-GaAs templates, performed in a horizontal quartz tube reactor.[10] During the growth process the reactor pressure was kept under 10 Torr, the substrate temperature was about 726 °C, and the total gas flow was under 200 sccm. Molten Ga overflown by HCl diluted with hydrogen (H$_2$) to form GaCl was used as a group-III precursor, while a mixture of AsH$_3$ + PH$_3$ diluted with H$_2$ was used as a group-V precursor. Taking into account the higher volatility of P compared to As, the PH$_3$ flow was chosen to be three times higher than the AsH$_3$ flow in order to obtain 15% P content in the GaAsP layer.[10,11]

As a reference, binary GaAs with a similar layer thickness was grown under nearly identical conditions, again on an OP-GaAs template. At an average rate of 54 μm h$^{-1}$, the growth of a 435 μm-thick layer of OP-GaAs took 8 h. At a similar average
growth rate of 50 μm h⁻¹ for OP-GaAsP, a thicker layer of 571 μm with 15% P content was obtained for 11.5 h. In both cases, the growth rate declined gradually with time due to the unavoidable parasitic nucleation and growth on the inner reactor surfaces. This parasitic growth competes with the growth on the substrate and often deteriorates layer quality.⁹ The OP-GaAs templates used were fabricated by the molecular beam epitaxy (MBE)-assisted polarity inversion technique on 650 μm-thick standard (001) GaAs wafers with a 4° miscut toward the [111]B direction. The domain walls are on (110) surfaces.¹² This OP template preparation technique typically requires a follow-on MBE regrowth after patterning of the inverted layer (obtained in the initial MBE growth) to confirm and secure the propagation of domains in the growth direction. Such a fully processed template, i.e., with an encapsulating MBE layer, was indeed used for the growth of the OP-GaAs HVPE layer. However, the preparation of the OP template used for the growth of the GaAsP layer was simplified by omitting the encapsulating MBE growth step. Instead, after patterning the inverted GaAs layer to reveal both crystallographic orientations (such samples were purchased from BAE Systems and we used 1/4 of a 3 in. wafer), the following HVPE growth was performed directly. The motive for omitting the encapsulating layer growth was that the rougher periodically patterned surface of the OP template offers more sites for the atoms approaching the surface to adhere and thus contributes to a more uniform initial layer nucleation. In other words, an OP template without an encapsulating layer could be a better start for the HVPE growth which turned out to be indeed the case. As can be seen in Figure 1, the achieved domain fidelity using such templates was excellent. Last but not least, omitting the MBE regrowth significantly reduces the wafer preparation time, cuts the template price by half, and offers the freedom of changing the pattern design from template to template with at least comparable, if not better, layer quality. As a matter of fact, growth on patterned templates, especially for large lattice mismatch with the substrate, is a well-known approach in heteroepitaxial growth.¹³ which we successfully utilized for the growth of GaAsP on OP-GaAs templates.

The crystalline quality of the grown ternary GaAsP (without encapsulating layer) and binary GaAs (with encapsulating layer) was previously compared and the homogeneity of the composition of the ternary layers was verified (variations within 1% of P) using different methods and unpatterned samples.¹⁴ In addition, the performed energy dispersive X-ray spectroscopy indicated that the layer composition is not orientation dependent, i.e., it is about the same in two neighboring oppositely oriented domains.

3. SHG

The period of the heteroepitaxial ternary OP-GaAsP structure (λ = 124 μm) corresponds to a fundamental wavelength of ≈5450 nm for SHG at room temperature. This estimation is based on averaging the refractive index and the thermal expansion coefficient according to the specific composition using data for pure GaAs and GaP.¹⁵,¹⁶ For the SHG experiments we employed a commercial laser source (Carmina, APE, Berlin, Germany) based on difference-frequency generation (DFG) between the signal and idler of an optical parametric oscillator, synchronously pumped by a femtosecond Yb-fiber laser at a repetition rate of 40 MHz. This source is not only tunable in wavelength but offers two modes in terms of spectral width (pulse duration). In the narrowband mode we measured a spectral bandwidth of 22.6 cm⁻¹ corresponding to Fourier-limited pulse duration of 650 fs assuming Gaussian shapes. In the broadband mode, the spectral bandwidth was 177.5 cm⁻¹ corresponding to Fourier-limited pulses of 83 fs duration. The actual pulse durations, measured independently, were roughly 700 and 100 fs, respectively. The beam was focused by a 50 mm CaF₂ lens and the measured waist diameters (e⁻² metric) in the position of the OP-GaAs₀.₈₅P₀.₁₅ sample were 0.22 mm (H) × 0.34 mm (V) in the narrowband mode and 0.15 mm (H) × 0.32 mm (V) in the broadband mode. Here, H (horizontal) means along the 9.8 mm width of the sample aperture while V (vertical) means along the sample total thickness of ≈1.2 mm (with about 50% in the upper part corresponding to the OP-GaAs₀.₈₅P₀.₁₅ structure and the rest to the GaAs substrate). The sample length (along the beam propagation) amounted to 5.03 mm. This is much shorter than the available length of about 30 mm in order to satisfy the spectral acceptance condition. The fundamental beam was polarized in the horizontal plane. Then the effective nonlinearity for QPM is given by d_eff = (2/π) d₄₄ for second harmonic (SH) polarized in the perpendicular (i.e., vertical) direction. For the SHG measurements, the input beam was attenuated with the help of a broadband MgF₂ waveplate and a thallium bromoiodide grid polarizer. The residual fundamental behind the sample was blocked by a 2 mm-thick Infrasil plate with 90% transmission at the SH. At the maximum average powers near 5450 nm (41 mW in the narrowband and 57 mW in the broadband mode), the peak on-axis intensity incident on the sample amounted to 5 and 75 MW cm⁻², respectively.

The spectral acceptance measured by tuning the fundamental wavelength in the narrowband mode as shown in Figure 2 corresponds to a full width at half maximum of 30.7 cm⁻¹, larger than the calculated one of 20.2 cm⁻¹ but almost equal to the convolution of the calculated spectral acceptance and the

![Figure 1](https://www.advancedsciencenews.com/)
fundamental bandwidth which gives 30.3 cm\(^{-1}\). The QPM fundamental wavelength was measured by a calibrated spectrometer to be 5447 nm in the narrowband mode (see Figure 3a), almost coinciding with the one predicted by the calculation (\(\approx 5450\) nm).

The central fundamental wavelength for maximum SHG efficiency in the narrowband mode for the OP-GaAs sample (\(\Lambda = 123\ \mu\text{m}\) was 5415 nm, slightly longer than the calculated \(\approx 5400\) nm. The spectral acceptance measured with this 3.1 mm long sample (chosen to be shorter in order to compensate for the higher nonlinearity of GaAs) was almost the same which confirms the effect of the relatively large fundamental bandwidth in such measurements.

The SH average power dependence recorded for the OP-GaAsP sample at \(\approx 5450\) nm is shown Figure 4a,b by red symbols and fits for the narrowband and broadband cases, respectively. These data were corrected only for the Infrasil plate while the input power was measured after the focusing lens. The maximum SH powers achieved were 0.82 and 5.6 mW, respectively. If group-velocity mismatch and higher order dispersion are ignored, the expected ratio of the SH powers (pulse energies) in the absence of saturation and at equal fundamental pulse energy would be \(\approx 11\) (assuming plane waves this factor is just the ratio of the fundamental peak intensities). At a fundamental power of 41 mW, from Figure 4, this ratio equals 3.75, i.e., the spectral acceptance plays a significant role in the broadband SHG. As a matter of fact, a minor effect is expected even in the narrowband mode where the calculated temporal walk-off length is comparable but still slightly shorter than the sample length. The measured SH spectral bandwidth amounted to 17 and 43.4 cm\(^{-1}\) (see Figure 3) for the narrowband and broadband mode, respectively. The second value corresponds to the acceptance bandwidth at the SH which amounts to 40.4 cm\(^{-1}\) (twice the calculated acceptance bandwidth at the fundamental).

The performance of the reference OP-GaAs sample is also shown in Figure 4 at the corresponding optimum fundamental wavelength. The ratio of achieved maximum output powers (OP-GaAsP:OP-GaAs) amounts to 1.91 in the narrowband and 1.66 in the broadband mode. These values are lower compared...
to a rough estimation based on the different sample lengths which gives 2.63. This is partly due to the decreasing nonlinearity with the P content and the larger spectral acceptance of the OP-GaAs sample. The lower value in the broadband case is an evidence for the latter. However, some effect from the different surface optical quality cannot be ruled out for the present hand-polished samples.

Correcting for the Fresnel reflections at the uncoated input and exit faces of the OP-GaAsP sample (roughly 28% per surface), we obtained for the maximum internal SHG conversion efficiency 3.9% in the narrowband and 19.1% for the broadband case.

4. Conclusion

In conclusion, high domain fidelity OP-GaAsP with 15% P content was successfully fabricated by heteroepitaxial growth on an OP-GaAs substrate and SHG has been demonstrated for the first time. The performance of the present ternary OP-GaAsP sample grown by heteroepitaxy was not inferior compared to a reference OP-GaAs sample grown by homoepitaxy with a QPM period corresponding to SHG in the same wavelength range. SHG was studied with narrowband radiation (700 fs pulses) and broadband 100 fs pulses at 40 MHz. The SHG conversion efficiency with 100 fs pulse duration was much higher notwithstanding the severe bandwidth limitation.

Next steps of this research will include investigation of higher P content, improved surface polishing, and antirefection (AR) coating of the OP-GaAsP structures. Future work will be extended to frequency downconversion, e.g., synchronously pumped optical parametric oscillators (SPOPOs) by ultrafast Er-fiber lasers near 1.6 μm for which the already achieved layer thickness and sample length are sufficient both in the picosecond and in the femtosecond regime. While ternary structures with a P content as high as 50% have been already grown, a P content of about 30% will be more than sufficient to avoid TPA at 1.6 μm and still achieve idler wavelengths exceeding the upper transmission limit of GaP.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

Keywords

GaAsP, heteroepitaxy, orientation-patterned growth, second-harmonic generation

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