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MBE growth of antiphase GaAs films using GaAs/Ge/GaAs heteroepitaxy

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Abstract

Semiconductor films with periodic crystal orientation modulation have nonlinear properties useful for optical wave-mixing devices. We have developed an all-epitaxial technique for preparing orientation-patterned GaAs templates by GaAs/Ge/GaAs epitaxy and have used these to grow laterally orientation-patterned films. We have investigated the effects of substrate misorientation, substrate temperature, and prelayer to find conditions which will allow controlled MBE growth of antiphase GaAs using thin Ge interlayers. After fabricating templates from these films using lithography and etching techniques, we have regrown GaAs films with antiphase crystal orientation modulation in the plane of the film. The template-induced antiphase boundaries were observed to propagate vertically under all conditions examined. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Research into the Ge/GaAs heteroepitaxial system has primarily focused on growing material suitable for electronic applications, such as HBTs, solar cells using inexpensive and lightweight Ge substrates, and $\text{Si}_x\text{Ge}_{1-x}$ buffer layers for Si/GaAs integration [1,2]. Two major difficulties are usually encountered: cross-contamination resulting in unintentional doping between the two materials (i.e. Ge doping of GaAs), and problems arising from growing a polar material (GaAs) on a nonpolar one (Ge) [3]. Because of the reduced symmetry of the GaAs zincblende crystal lattice, two possible GaAs

orientations (or phases) can nucleate on the Ge diamond lattice. Since the preference for one orientation over the other on a nominally (1 0 0) surface is slight, both orientations will typically nucleate simultaneously, resulting in antiphase boundaries (APBs) and antiphase domains (APDs). Since an APB consists of charged As-As or Ga-Ga bonds, they are expected to act as mid-level traps and hence degrade device performance [3]. By growing on substrates slightly misoriented ($\leq 4^\circ$) towards a $\langle 111 \rangle$ plane, though, the antiphase problem can be controlled resulting in the growth of single-domain GaAs on Ge films and substrates [4].

Because the electronic properties of the two competing GaAs phases are identical, there was little reason to try and control which phase of GaAs

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(either with respect to an underlying GaAs substrate, or to the Ge substrate misorientation) nucleates and grows on top of the Ge, as long as the resulting material was single-domain. The two phase do differ, however, in their sign of $\chi^{(2)}$, the second-order nonlinear optical coefficient. The ability to grow epitaxial GaAs on a (1 0 0) surface that is antiphase to the substrate could open up new nonlinear optical applications for semiconductor materials, such as wavelength shifting or difference-frequency generation of infrared light. GaAs has many properties that make it an attractive material for nonlinear optical applications, specifically its high effective nonlinear coefficient, transparency in a region of technological interest, high damage threshold, well established epitaxial techniques for waveguide and thick film growth, a mature materials processing technology, and the potential for direct integration with semiconductor laser diode sources [5]. To be efficient, however, a nonlinear optical process needs to be phasematched, in order to avoid the effects of material dispersion which induces a phase velocity mismatch between the polarization wave and the radiation wave. Birefringent phasematching cannot be employed due to the isotropic nature of GaAs, but quasiphasematching (QPM) can be used, provided there is a method of periodically modulating $\chi^{(2)}$ in the direction of wave propagation every coherence length ($L_c = \lambda/4(n_1 - n_2)$). Although orientation-patterned GaAs waveguides have been grown using templates fabricated through wafer bonding techniques, high losses result due to the large corrugation induced by the template [6]. An all-epitaxially fabricated template could potentially reduce this initial corrugation and ultimately lead to lower loss devices as well as eliminate the wafer bonding step. In order to do this, however, the capability to grow single domain GaAs, *antiphase to the substrate*, on thin Ge interlayers, must be developed. As such, growth studies were undertaken in order to determine the necessary growth conditions.

2. Single-domain antiphase material

As reported in the literature, APD-free GaAs could be reliably grown on Ge films grown on

GaAs substrates misoriented towards $\langle 111 \rangle_A$, such that the epilayer was in phase with the substrate [1]. Like the substrate, this GaAs layer also has A-type steps exposed, or equivalently is misoriented towards its $\langle 111 \rangle_A$ plane. A GaAs substrate misorientation towards $\langle 111 \rangle_B$ should produce the same step structure in the Ge film, and hence the same phase of GaAs (misoriented towards its $\langle 111 \rangle_A$ plane) should grow on top. As a result, the epilayer GaAs will be antiphase to the substrate. It can likewise be seen that any growth conditions that yield antiphase films on substrates misoriented towards $\langle 111 \rangle_A$ should yield in-phase films on substrates misoriented towards $\langle 111 \rangle_B$ and vice versa.

Growth studies were performed to determine the necessary conditions for growth single-domain films on misoriented substrates. The MBE chamber consisted of a modified Gen II machine equipped with Ga, Ge, and Al furnaces and a valved cracker for the As source. The test structure used was based on the work of Ting et al. [2], and consisted of a 1000 Å GaAs buffer layer, 100 Å Ge layer deposited at 350°C, a 15 min anneal at 640°C, 10 ML migration enhanced epitaxy (1.2 ML of Ga at ~ 1 ML/10 s at 350–500°C), 1000 Å GaAs at 500°C, and 9000 Å GaAs at 620°C. The substrates used were misoriented 4° towards $\langle 111 \rangle_A$, unless noted. Samples were grown both with and without an As₂ flux during the Ge anneal, and also with both As and Ga prelayers in the MEE cycle. (All temperatures reported are thermocouple temperatures.)

During growth, the RHEED patterns could be observed to indicate whether or not the top GaAs epilayer was antiphase by noting the position of the $2 \times$ and $4 \times$ patterns with respect to the horizon caused by the misorientation. (For substrates misoriented towards $\langle 111 \rangle_A$, the $2 \times$ pattern appears above/below the horizon, while $4 \times$ pattern appears on the horizon.) In addition, after growth, ridges were lithographically defined in both the $[110]$ and $[1\bar{1}0]$ directions and preferentially etched using 1 : 1 : 6 NH₄OH : H₂O₂ : H₂O in order to confirm the orientation of the epilayer GaAs. By comparing the angle of the sidewalls before and after etching through the thin Ge layer, the phase of the film with respect to the substrate could be

determined. In addition, a qualitative measure of the APD density could be determined by examining the sidewall roughness of the film after etching.

3. Results

The phase of the GaAs epilayer depends on several parameters, summarized in Table 1. For samples annealed under an As₂ flux, it was found that the critical temperature for determining the phase of the material was approximately 400°C. Samples nucleated above this temperature were misoriented towards $\langle 111 \rangle_A$ (i.e. in-phase with a substrate misoriented towards $\langle 111 \rangle_A$). Fig. 1 shows SEM micrographs illustrating films nucleated at 350, 397, and 500°C on the Ge interlayer, and anisotropically etched to highlight film orientation and quality. (The As₂ flux was supplied up until the first Ga ML deposition of the MEE cycle.) Films grown on substrates misoriented towards $\langle 111 \rangle_B$ under similar conditions show similar behavior, such that films nucleated at 350°C are in phase with the substrate and films nucleated at 500°C are antiphase to the substrate. In both cases, the epitaxial GaAs $[1\bar{1}0]$ direction is perpendicular to the misorientation-induced steps for low temperature nucleation, while for high temperature nucleation the $[11\bar{0}]$ direction is parallel to the steps. This implies that the factors that determine the final phase of the epilayer are inherent in a Ge surface misoriented

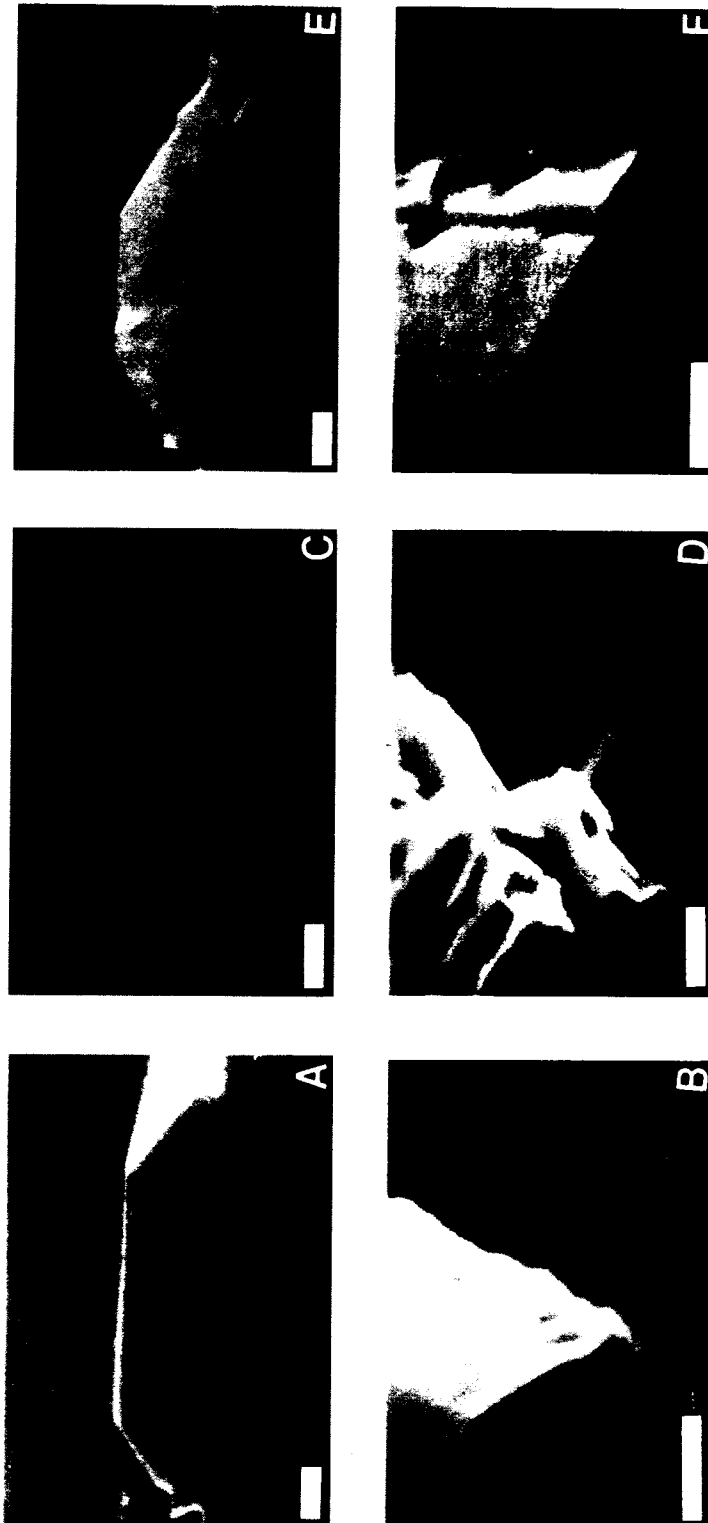
towards $\langle 111 \rangle$ (no A or B planes in Ge). No appreciable difference in material quality due to the difference in substrate misorientation was observed.

Furthermore, we have grown an A-B-A structure consisting of alternating phases of GaAs on thin Ge interlayers, simply by changing the GaAs nucleation temperature. (Unfortunately, such a structure does not have useful nonlinear properties for a collinear waveguide device due to the symmetry of the $\chi_{xyz}^{(2)}$ tensor since normal-incidence interactions would lack the necessary z-component.)

For samples annealed without an As₂ flux and growth initiated with a Ga prelayer, the same phase of GaAs resulted for samples nucleated at both 350 and 500°C. It should be noted, though, that etching studies revealed a high density of large APDs for the sample nucleated at 500°C, but not at 350°C. (The As shutter and value were closed for approximately 40 min during the Ge growth and anneal.) In both cases, the $[1\bar{1}0]$ direction for the GaAs was parallel to the steps, or the GaAs surface was misoriented towards $\langle 111 \rangle_A$. For samples annealed without an As₂ flux and growth initiated with an As prelayer, the results are the same as those annealed under an As₂ flux: the sample nucleated at 350°C was misoriented towards $\langle 111 \rangle_B$ while the sample nucleated at 500°C was misoriented towards $\langle 111 \rangle_A$. In all films we see evidence of small APDs near the GaAs/Ge interface, but these should have little or no impact on

Table 1
GaAs orientation dependence on growth conditions

Substrate misorientation	As during anneal?	Nucleation temperature (°C)	Prelayer	Phase
4° → $\langle 111 \rangle_A$	Yes	350	-	→ $\langle 111 \rangle_B$ (antiphase)
4° → $\langle 111 \rangle_B$	Yes	350	-	→ $\langle 111 \rangle_B$ (in phase)
4° → $\langle 111 \rangle_A$	Yes	397	-	Mixed
4° → $\langle 111 \rangle_A$	Yes	500	-	→ $\langle 111 \rangle_A$ (in phase)
4° → $\langle 111 \rangle_B$	Yes	500	-	→ $\langle 111 \rangle_A$ (antiphase)
4° → $\langle 111 \rangle_A$	No	350	Ga	→ $\langle 111 \rangle_A$ (in phase)
4° → $\langle 111 \rangle_A$	No	500	Ga	→ $\langle 111 \rangle_A$ (in phase)
4° → $\langle 111 \rangle_A$	No	350	As	→ $\langle 111 \rangle_B$ (antiphase)
4° → $\langle 111 \rangle_A$	No	500	As	→ $\langle 111 \rangle_A$ (in phase)



nonlinear optical applications provided they annihilate early in growth.

4. Discussion of antiphase growth

Temperature-dependence of the phase of GaAs growth on Ge has been observed and reported before [7] while other researchers have observed a dependence on either prelayer type (As versus Ga) [1] or As species (As_2 versus As_4) [8]. Li et al. explained temperature-dependence of the phase through a competing mechanism of terrace-dominated versus step-dominated nucleation. Nucleation occurs on both the steps and terraces simultaneously, but with competing domains. For high temperature growth (or large misorientation angle) the step-nucleated islands have time to coalesce, thus resulting in single-domain material. For lower temperatures (or smaller misorientation angle) the step-nucleated islands and terrace-nucleated islands do not have time to coalesce, but rather the terrace-nuclei overgrow the step-nuclei, resulting in single-domain material that is of opposite phase as the high temperature scenario.

5. Orientation-patterned growth

For regrowth of orientation-patterned films, template structures were first grown consisting of 200 Å of GaAs antiphase to the substrate, surrounded by two $Al_{0.8}Ga_{0.2}As$ etch stops, as shown in Fig. 2. Alternating regions of phase and antiphase regions (with respect to the substrate) were then exposed using selective etching, followed by removal of the etch stop layers before regrowth. The initial corrugation (height difference between the phase and antiphase regions) was approximately 600 Å. After growth of a 1 µm thick

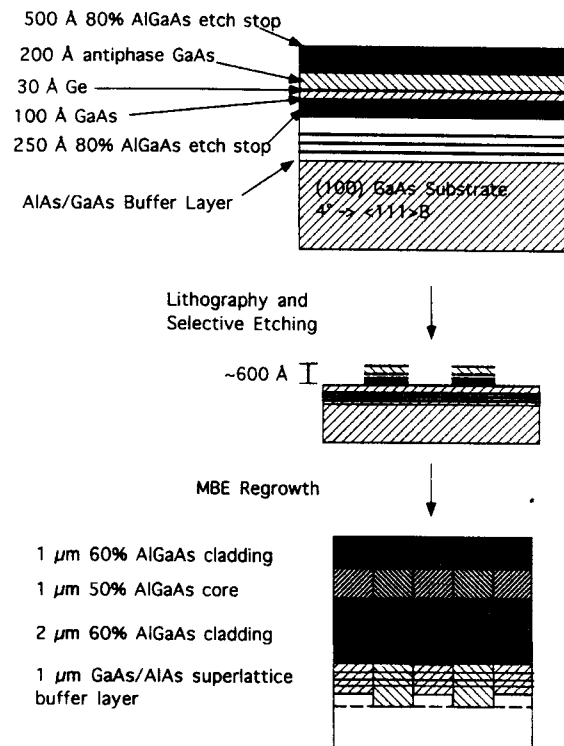


Fig. 2. Process diagram for fabrication of orientation-patterned thin films.

Fig. 1. (a) and (b) Profile and side view of wafer #175 (350° nucleation). Change in sidewall angle indicates epilayer GaAs is antiphase to substrate. (c) and (d) Profile and side view of wafer #296 ($397^\circ C$ nucleation). Top surface and edge roughness is indication of large APDs. (e) and (f) Profile and side view of wafer #257 ($500^\circ C$ nucleation). Epilayer GaAs is in phase with the substrate. White bar equals 1 µm in each picture.

GaAs/AlAs superlattice buffer layer, waveguide structures were then grown consisting of a 2 µm $Al_{0.6}Ga_{0.4}As$ lower cladding layer, 1 µm $Al_{0.5}Ga_{0.5}As$ core, and 1 µm $Al_{0.6}Ga_{0.4}As$ top cladding layer. The 3.5 µm period of the orientation patterning and waveguide structure were designed for second harmonic generation with a 1550 nm pump wavelength. After stain-etching this sample, we see that the template-induced APBs propagate vertically through the subsequent epilayers, preserving the orientation pattern throughout the growth (Fig. 3). The APB boundaries were observed to propagate vertically under all conditions examined: substrate temperatures of 500–600°C and AlGaAs compositions from 0 to 60%. Anisotropic etching confirms that the alternating orientations of the underlying template are indeed preserved, and that the vertical boundaries are not corrugation-induced artifacts. Our observed propagation of the large intentional APBs

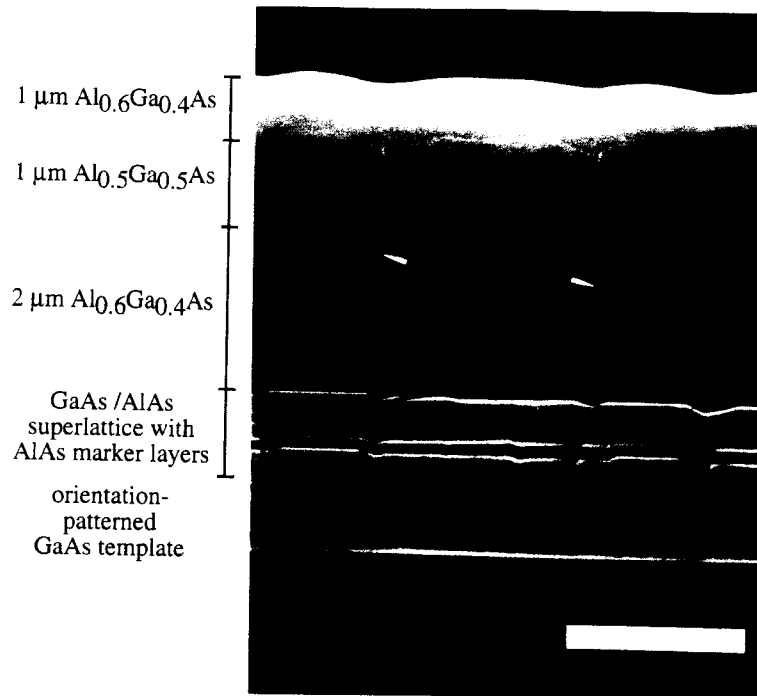


Fig. 3. Cross-section SEM view of stain-etched orientation-patterned GaAs film. Arrows mark locations of vertically propagating APBS. White bar is 2 μm .

primarily along $\{1\ 1\ 0\}$ is consistent with the observation of stable $\{1\ 1\ 0\}$ APB propagation by Li and Gilling [9] using MOVPE at growth temperatures of 700°C. Domain ratios of up to 10:1 have been observed, with 0.5 μm domains propagating through 5 μm of epitaxial growth without significant variation in domain width. These domain dimensions and aspect ratios are sufficient to quasiphase-match any collinear frequency conversion process within the entire transparency region of AlGaAs. Unfortunately, some corrugation of the waveguide core is observed, which will increase optical scattering losses in these waveguides. Research is ongoing to minimize the amplitude of these APD-induced corrugations and reduce associated optical waveguide losses.

6. Conclusion

We have successfully explored conditions which enable us to grow epitaxial GaAs layers that are

antiphase to the original GaAs substrate through the use of thin Ge interlayers and the proper growing conditions. Utilizing this capability, we have fabricated laterally orientation-patterned templates and regrown waveguide device structures for non-linear optical applications.

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