Sublattice reversal epitaxy: a novel technique for fabricating domain-inverted compound semiconductor structures

T. Kondo\(^a\)\(^*,\) S. Koh\(^b\), R. Ito\(^c\)

\(^a\)Department of Materials Science, Faculty of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
\(^b\)Research Center for Advanced Science and Technology, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8904, Japan
\(^c\)Department of Physics, Meiji University, 1-1-1 Higashi-Mita, Tama-ku Kawasaki 214-8571, Japan

Received 7 August 2000; accepted 4 September 2000

Abstract

Sublattice reversal in III–V compound semiconductors grown on group-IV epitaxial layers on III–V substrates has been proposed for fabricating nonlinear optical devices with domain-inverted compound semiconductor structures. Sublattice reversal epitaxy has been demonstrated in GaAs/Si/GaAs, GaP/Si/GaP, and GaAs/Ge/GaAs systems. Growth of sublattice-reversed epilayers is assisted by self-annihilation of antiphase domains. Periodically domain-inverted AlGaAs waveguides of satisfactory crystal quality have been successfully fabricated using sublattice reversal epitaxy of GaAs/Ge/GaAs (100) system combined with photolithography and regrowth techniques.

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Keywords: Nonlinear optics; Frequency conversion; Quasi phase matching; Domain inversion; Sublattice reversal; Antiphase domain; Compound semiconductor

1. Introduction

Quadratic nonlinear optical devices allow conversion and extension of the wavelengths of coherent light sources via second-harmonic generation (SHG), difference-frequency generation (DFG), sum-frequency generation (SFG), and optical parametric oscillation (OPO). Efficient wavelength conversion requires phase matching which has long been achieved only by using materials birefringence, and thus only a small number of nonlinear optical crystals have been used in practical devices. However, quasi phase matching (QPM) enables us to utilize nonlinear optical crystals incompatible with conventional birefringent phase matching [1]. Recent development of reliable electric-field poling technique in ferroelectric crystals has led to compact and efficient frequency conversion devices such as periodically-poled LiNbO\(_3\), LiTaO\(_3\), and KTP.

Compound semiconductors are promising nonlinear optical materials for frequency conversion because of their large optical nonlinearities; e.g. \(d_{30}(\text{GaAs}) = 170 \text{ pm/V}\) and \(d_{30}(\text{GaP}) = 71 \text{ pm/V}\), both at 1.064 \(\mu\text{m}\) [2]. Their facility for monolithic integration and sophisticated device fabrication technologies will lead to a new class of waveguiding coherent light sources. Furthermore, transparencies in the infrared region (down to about 15 \(\mu\text{m}\) for GaAs), high thermal conductivities and high optical damage thresholds are also their great advantages. Semiconductor QPM structures would allow efficient generation of arbitrary wavelength in the infrared and near-infrared wavelength region. Development of QPM technique is indispensable for semiconductors, which have no intrinsic birefringence. Since QPM requires spatial modulation of \(d\) coefficients, techniques for fabricating ‘domain-inverted’ semiconductor structures should be developed. QPM SHG of CO\(_2\) lasers (10.6 \(\mu\text{m}\) in wavelength) has been demonstrated in stacks of bulk plates of GaAs or CdTe [3–5]. Gordon et al. has developed a QPM device with diffusion-bonded GaAs stack of plates for SHG of a CO\(_2\) laser source [6]. Although such stacks of bulk plates are phase-matchable in long wavelength regions where domain periods required for QPM are long, microfabrication technologies should be introduced in order to develop wavelength conversion devices covering their entire transparency wavelength regions (see Fig. 1 for GaAs). Direct wafer bonding combined with microfabrication and regrowth techniques has been applied to fabricate periodically domain-inverted AlGaAs waveguides with domain periods as short as 3 \(\mu\text{m}\). This technique has been applied to quasi phase-matched SHG [7,8], SFG [9], DFG [10] devices, all operating at 1.5 \(\mu\text{m}\) wavelength region.
Wafer bonding techniques, however, require complicated fabrication processes and inevitable misorientation in the bonding process results in defects in the overgrown epitaxial layers. We have proposed and demonstrated an alternative and more versatile way based on a novel epitaxial growth technique, sublattice reversal epitaxy. In this paper, we report the demonstrated sublattice reversal epitaxy and its application to fabrication of QPM devices.

2. Sublattice reversal epitaxy

Let us consider III–V semiconductors of the zinc-blende structure. Spatial inversion operation in zinc-blende type crystals is equivalent to a 90° rotation around the [100] directions owing to the existence of four-fold inversion axes parallel to the [100] axes. Because the zinc-blende structure consists of two mutually penetrating face-centered-cubic sublattices, one occupied with group-III atoms and the other with group-V atoms, a reversal of the sublattice occupation also results in spatial inversion. Usual epitaxy, however, does not allow such sublattice reversal because of the considerable difference in the valence characteristics of the group-III and group-V atoms. In order to achieve sublattice reversal in epitaxial growth processes, we have to trick the atoms into forgetting which sublattice they should occupy. Fig. 2 illustrates the basic scheme of the sublattice reversal epitaxy on (100) substrates. By inserting a thin intermediate epitaxial layer of group-IV atoms, we would be able to reverse the sublattice occupation in the overgrown III–V epitaxial layer under certain conditions. This type of heteroepitaxy has been studied in conjunction with polar-on-nonpolar epitaxy. Although sublattice reversal has been observed GaAs/Si/GaAs and GaAs/Ge/GaAs [11,12] systems and considered to be a peculiar phenomenon, we have studied III–V/IV/III–V heteroepitaxy with a firm objective, for the first time, and achieved reproducible sublattice reversal. We have investigated GaAs/Si/GaAs, GaP/Si/GaP, and GaAs/Ge/GaAs systems. Lattice constants and thermal expansion coefficients of GaAs, GaP, Si, and Ge are summarized in Table 1.

2.1. GaAs/Si/GaAs sublattice reversal epitaxy

In order to demonstrate sublattice reversal epitaxy, we have grown GaAs on GaAs (100) substrates with an Si intermediate layer (GaAs/Si/GaAs) [13] using a solid source molecular beam epitaxy (MBE) system equipped with a high-temperature K cell for Si effusion. The substrates used were (100) GaAs wafers misoriented by 4° toward [011]. After thermal cleaning of the substrates at 600°C for 10 min, 3000 Å-thick GaAs buffer layers were grown at 580°C. Then the substrates were cooled down to 500°C and the As source shutter was closed. A 10 Å-thick Si intermediate layer was grown on the GaAs buffer layer at 500°C. After the Si growth, the As shutter was opened and the Si surface was exposed to As4 flux to establish an As prelayer. GaAs epitaxial layer was grown in two steps: first, a 300 Å-thick initial GaAs layer was deposited at low-temperatures (300 or 450°C) after which an 8000 Å-thick final GaAs layer was grown at 580°C. The typical growth rate was 8000 and 14 Å/h for GaAs and Si, respectively.

| Lattice constants and thermal expansion coefficients of GaAs, GaP, Si, and Ge |
|---|---|---|---|
| Lattice constant (Å) | 5.653 | 5.451 | 5.429 | 5.657 |
| Thermal expansion coefficient (10⁻⁶/K) | 6.86 | 5.3 | 2.6 | 7 |
Table 2
RHEED patterns observed in GaAs/Si/GaAs epitaxy

| GaAs initial growth temperature | GaAs buffer | 10 Å Si | 8000 Å GaAs |
|---------------------------------|-------------|--------|-------------|
| 300°C                           | (2 x 4)     | (2 x 2)| (2 x 4)     |
| 450°C                           | (2 x 4)     | (2 x 2)| (4 x 2)     |

Reflection high energy electron diffraction (RHEED) patterns of the GaAs buffer layers, Si intermediate layers, and epitaxial GaAs layers were observed under Ar ion flux, and summarized in Table 2. The (4 x 2) structure observed in GaAs epitaxial layer with the higher-temperature (450°C) initial growth shows that the grown final GaAs epilayer is rotated by 90° with respect to the GaAs substrate; i.e. the final GaAs layer is actually sublattice-reversed. By contrast, the (2 x 4) structure observed in the GaAs epilayer with lower-temperature (300°C) initial growth shows that the epilayer is not reversed.

Sublattice reversal was also confirmed by orientation-dependent preferential etching [14]. Profiles of (100) GaAs etched in an H2SO4:H2O2:H2O (8:1:1) solution through photoresist mask stripes are dependent on the stripe direction as shown in Fig. 3; mesa shape in [011] stripe and inverted-mesa shape in [001] stripe. Etched profiles of GaAs epilayers are shown in Fig. 4. GaAs epilayers etched through photoresist mask stripes running along the [011] direction of the substrates exhibited inverted-mesa shape for the GaAs grown with the higher-temperature initial growth, whereas mesa shape was seen in that grown with the lower-temperature initial growth, confirming the sublattice reversal for the epilayer grown with the higher-temperature initial growth. The roughness of the surface and etched side wall readily seen in Fig. 4 indicates relatively low crystal quality probably due to large lattice mismatch.

The quality of the sublattice-reversed GaAs epilayer was investigated using cross-sectional transmission electron microscopy (XTEM). XTEM observation revealed that the sublattice-reversed GaAs epilayers on Si intermediate layer contain misfit dislocations due to the considerable lattice mismatch between GaAs and Si (~4%, see Table 1) as seen in Fig. 5. In addition, the contrast reversal between two images with different reflection vectors shows the existence of antiphase domains (APDs) in the initial GaAs epilayer [15,16]. After the APDs are self-annihilated, sublattice-reversed domain survives and single-domain growth proceeds. This shows the mechanism of the present sublattice reversal is quite different from the simple scheme shown in Fig. 1, and that the sublattice reversal is assisted by self-annihilation of APDs.

2.2. GaP/Si/GaP sublattice reversal epitaxy

Sublattice reversal of GaP has been achieved in GaP/Si/GaP system where the lattice mismatch is relatively small (~0.4%). Si and GaP layers were grown on GaP (100) substrates using a gas-source MBE system. The substrates used were (100) wafers misoriented by 4° toward [011] and (100) wafers misoriented by 4° toward [011]. After thermal cleaning of the substrates, 2000 Å-thick GaP buffer layers were grown at 615°C. Then the substrates were cooled down to 350°C and the P source shutter was closed. A 25 Å-thick Si intermediate layer was grown on the GaP buffer layer at 350°C. After the Si growth, the P shutter was opened and GaP epitaxial layers were grown in the following two steps: first, 500 Å-thick initial GaP layers were deposited at 450°C, and then 4000 Å-thick final GaP layers were grown at 615°C. The typical growth rate was 4000 and 10 Å/h for GaP and Si, respectively.

Sublattice ordering in the GaP epilayers has been identified by in-situ RHEED observation and preferential etching. Sublattice reversal has been reproducibly achieved on both substrates irrespective of the misorientation direction. Sublattice reversal in the GaP/Si/GaP system seems to be assisted by the self-annihilation of APDs as in the case of the GaAs/Si/GaAs system.

2.3. GaAs/Ge/GaAs sublattice reversal epitaxy

Sublattice reversal with satisfactory crystal quality has been achieved in GaAs/Ge/GaAs system [17,18] where Ge is almost lattice-matched with GaAs (mismatch ~0.1%) and the thermal expansion coefficient of Ge is also very close to that of GaAs as shown in Table 1. We have grown GaAs on GaAs (100) substrates with a Ge intermediate layer using a solid source MBE system. The substrates we examined were nominally (100) GaAs wafers, (100) wafers misoriented by 4° towards [011], and (100) wafers misoriented by 4° towards [011]. After thermal cleaning of the substrates at 600°C for 10 min, 2500 Å-thick GaAs buffer layers were grown at 580°C. Then the substrates were cooled down to 450°C and the As source shutter was closed. A 30 Å-thick Ge intermediate layer was grown on the GaAs buffer layer at 450°C. Then the As shutter was opened to establish an As prelayer. A 8000 Å-thick GaAs layer was grown at 580°C. The typical growth rate was 8000 and 250 Å/h for GaAs and Ge, respectively.

The RHEED patterns reproducibly observed are summarized in Table 3. The same surface reconstruction was observed for the GaAs buffer layers and 30 Å Ge layers, irrespective of the surface orientation. The RHEED pattern for the GaAs epilayers, however, depended on the orientation. The GaAs epilayer showed clear single-phase reconstruction for the misoriented substrates: a (2 x 4) structure for substrates misoriented towards [011] and a (4 x 2)
structure for substrates misoriented towards [0\text{1\text{1}}] indicating that sublattice reversal occurred on the latter substrates. The (4\times4) structure observed for the nominally (100) GaAs epilayers is a mixture of (2\times4) and (4\times2) structures, which implies that the epilayers consist of reversed and non-reversed domains. Although misorientation dependence of the sublattice ordering in the grown GaAs epilayers was also reported by Strite et al. [11] and Saito et al. [12], they observed sublattice reversal on the (100) substrates misoriented towards [0\text{1\text{1}}] in contrast with our present result. This discrepancy is probably due to a subtle difference in the growth conditions.

Fig. 6 shows a scanning electron microscope (SEM) image of the etching profile of a GaAs epitaxial wafer in which one half was GaAs grown on a Ge intermediate layer and the other half was GaAs directly grown on GaAs (100) substrate misoriented towards [0\text{1\text{1}}]. GaAs was etched through mask stripes running along the [0\text{1\text{1}}] direction of the substrate using H_2SO_4:H_2O_2:H_2O (8:1:1) at 38 C. The inverted-mesa shape seen in the GaAs epilayer grown on the Ge intermediate layer is a clear evidence of the sublattice reversal. Smooth surface and the etched side walls in the sublattice-reversed GaAs shows that the crystal quality is much better than that of sublattice-reversed GaAs in the GaAs/Si/GaAs system (compare with Fig. 4). No misfit dislocation can actually be seen in the sublattice-reversed GaAs as shown in an XTEM dark-field image (Fig. 7) supporting much improved crystal quality (compare with Fig. 5). An X-ray diffraction study has also confirmed that the crystal quality of the sublattice-reversed GaAs epilayer is satisfactorily high [19].

The contrast indicating planar defects is observed in the sublattice-reversed GaAs layer. This type of defects has been observed in a Ge–GaAs superlattice and identified as APDs [20]. Since lattice images of these planer defects in the sublattice-reversed GaAs showed perfect lattice ordering, the observed contrast corresponds to APDs. The observed APDs are self-annihilated after about 1000 Å-thick GaAs growth. The formation of APDs on the GaAs/Ge interface is reasonable because the (2\times2) RHEED pattern observed for the Ge layers resulting from the coexistence of the (2\times1) and (1\times2) structures shows the surfaces of the Ge layers have single atomic height steps that cause APD generation in the GaAs epilayer growth.

| Substrate | GaAs buffer | 30 Å Gi | 8000 Å GaAs |
|-----------|-------------|--------|-------------|
| Nominally (100) | (2\times4) | (2\times2) | (4\times4) |
| (100) misoriented towards [0\text{1\text{1}}] | (2\times4) | (2\times2) | (2\times4) |
| (100) misoriented towards [0\text{1\text{1}}] | (2\times4) | (2\times2) | (4\times2) |
Again, sublattice reversal in GaAs/Ge/GaAs system is assisted by the self-annihilation of the APDs.

2.4. Mechanism of sublattice reversal epitaxy

As described above, sublattice-reversed epilayers contain APDs at the III–V/IV interfaces in all the GaAs/Si/GaAs, GaP/Si/GaP, and GaAs/Ge/GaAs systems. Although growth conditions (growth temperature, substrate misorientation, etc.) needed to achieve sublattice reversal are different, the self-annihilation of the APDs seems to assist the growth of the sublattice-reversed epilayers irrespective of the difference in the combination of the epicrystal and intermediate layer. Mechanism of sublattice reversal is presented in this section for GaAs/Ge/GaAs system for which we have succeeded in high-quality growth and thus obtained ample experimental data.

Antiphase boundaries (APBs) generated at step edges on the Ge surface are composed of Ga–Ga bond planes or As–As bond planes. These APBs propagate on inclined (111) planes and encounter each other, resulting in their self-annihilation [21]. Therefore, step formation on the Ge surface and the character of APBs are responsible for sublattice ordering of GaAs epilayers. For the misoriented GaAs (100) substrates, misorientation-induced steps run perpendicular to the misorientation directions. For nominally (100) substrates, however, the surface has both types of steps due to non-deliberate misorientation. If As–As bond planes ((111)B) are assumed to be dominant in our growth condition, self-annihilation of APBs will lead to the survival of sublattice-reversed domain on GaAs (100) substrates misoriented toward [011] (Fig. 8(a)). On the other hand, non-reversed domain will survive on GaAs (100) substrates misoriented toward [011] (Fig. 8(b)). For nominally (100) GaAs substrates, APBs cannot be completely annihilated due to the coexistence of two orthogonal steps and, thus, will survive all through the GaAs overgrowth process resulting in the multi-domain growth.

3. Fabrication of QPM waveguides

Although epilayers grown by present sublattice reversal epitaxy contain APDs at the III–V/IV interfaces, we are still able to fabricate QPM devices with domain-inverted AlGaAs free of APD using lithography and regrowth techniques. We have fabricated QPM AlGaAs waveguides for SHG and DFG of 1.5 μm wavelength sources. The fabrication procedure is as follows: a 500 Å-thick sublattice-reversed GaAs was grown on a 70 Å-thick Ge intermediate layer using a GaAs (100) substrate misoriented towards [011] as shown in Fig. 9(a). By using photolithography technique, we prepared a periodically patterned template in which the sublattice-reversed GaAs and (non-reversed) GaAs substrate are alternately etched (Fig. 9(b)). It should be noted that the surface of the sublattice-reversed GaAs is free from APD. A 2 μm-thick GaAs buffer layer was then grown on the patterned template followed by the growth of an AlGaAs optical waveguide. The AlGaAs waveguide with 5 μm-wide ridge consists of a 1.7 μm-thick Al0.5Ga0.5As guiding layer and 2 μm-thick Al0.5Ga0.5As cladding layers (Fig. 9(c)). The overgrown AlGaAs follows the sublattice ordering of the template resulting in the periodical domain inversion in the waveguide. The QPM grating has a half period of 3 μm running along the [011] direction that corresponds to the third-order QPM-SHG condition at the fundamental wavelength of 1.54 μm.

Fig. 10(a) shows a SEM top image of the fabricated ridge waveguides. The duty ratio of inverted domain to

![Fig. 6](image-url) Etching profile of a GaAs epitaxial wafer grown on GaAs (100) substrate misoriented toward [011]. The upper half is GaAs grown on a Ge intermediate layer and the lower half is GaAs directly grown on GaAs substrate.

![Fig. 7](image-url) XTEM dark-field image of the (011) cross-section of a sublattice-reversed GaAs grown on a Ge/GaAs (100) substrate misoriented towards [011] (g = (200)).
The non-inverted domain estimated from surface corrugation on the ridge is smaller than that of the template. This indicates that the domain boundaries propagate in a direction slightly inclined from the surface normal. Since the propagation direction of the domain boundaries depend on the growth condition, we have to establish an optimized condition in order to fabricate highly efficient devices. Fig. 10(b) shows a SEM image of the cross section of the AlGaAs waveguide. It should be noted that no boundary between inverted and non-inverted domains can be seen, indicating that the fabricated AlGaAs waveguide is of high quality. Results of optical characterization including device performances will be reported elsewhere soon.

Fig. 8. (a) Self-annihilation of APBs in the GaAs epilayers grown on the Ge/GaAs (100) substrate misoriented towards [011] and (b) that misoriented towards [011].

Fig. 10. (a) Top-view and (b) cross-sectional SEM images of an AlGaAs QPM waveguide.

Fig. 9. Fabrication process of AlGaAs QPM waveguides.
4. Summary

We have achieved reproducible sublattice reversal of GaAs and GaP in GaAs/Si/GaAs, GaP/Si/GaP, and GaAs/Ge/GaAs systems. At the present stage of our investigation, growth of sublattice-reversed epilayers is assisted by self-annihilation of antiphase domains. Surface treatment of group-IV intermediate layers will be needed in order to obtain single-domain surfaces possibly leading to APD-free sublattice reversal. Periodically-domain-inverted AlGaAs waveguides of satisfactory crystal quality have been successfully fabricated using sublattice reversal epitaxy of GaAs/Ge/GaAs (100) system combined with photolithography and regrowth techniques.

Acknowledgements

The authors would like to thank Professors Yasuhiro Shiraki, Hideki Ichinose, and Toshio Takahashi of the University of Tokyo and Professor Hiroyuki Yaguchi of the Saitama University for help in crystal growth and characterization. This work was supported in part by Iketani Science and Technology Foundation and the Grant-in-Aid for Scientific Research form the Ministry of Education, Science, Sports, and Culture of Japan.

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