

Characterization of epitaxially grown GaAs on Si substrates with III-V compounds intermediate layers by metalorganic chemical vapor deposition

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GaAs grown on Si substrate with AlP, AlGaP, GaP/GaAs_{0.5}P_{0.5} superlattice, and GaAs_{0.5}P_{0.5}/GaAs superlattice was investigated by varying the structure of the intermediate layers between GaAs and Si by metalorganic chemical vapor deposition. It was found that (1) the insertion of AlP and AlGaP layers makes the crystallinity and the surface morphology better, (2) PL (photoluminescence) intensity with two superlattice layers is about one order of magnitude stronger than that without these layers, (3) the crack formation in the GaAs surface layer can be avoided by the strained superlattice layers, (4) the PL intensity has a maximum at about 20 nm for each layer thickness in the superlattices, and (5) the PL intensity increases and the carrier concentration decreases while increasing the thickness of the surface GaAs and saturates over 3 μm . The PL intensity of GaAs on Si substrates is about 80% of that grown on GaAs substrates.

1. INTRODUCTION

High-performance devices using AlGaAs/GaAs heterojunctions, such as lasers,¹ solar cells,² FETs³ etc., have been fabricated on GaAs substrates by MOCVD (metal organic chemical vapor deposition). If these devices were grown on Si substrate, the new devices such as optoelectronic ICs that contain GaAs optical and Si electronic devices, GaAs IC on large-area Si substrate, GaAs high efficiency solar cell on cheap and lightweight Si substrate, and many other devices combining GaAs and Si would become realistic. But, in growing GaAs on Si substrates, there are problems such as the large lattice mismatch (about 4.1%), the large difference in the thermal expansion coefficients, and the formation of the antiphase domain. To overcome these difficulties, some attempts have been made, and GaAs was successfully grown on Si substrate with Ge⁴ and SiO₂/W/Ge⁵ as intermediate layers. But these methods have problems of Ge contamination because of its high vapor pressure and Ge diffusion into the grown epilayer. Moreover, another growth technique other than MOCVD such as ICB (ion cluster beam) or vacuum evaporation is indispensable to form Ge on Si. The method to grow GaAs on Si substrates directly without intermediate layers has also been investigated by MBE (molecular beam epitaxy),⁶ and more recently GaAs grown at low temperature is used as the intermediate layer.⁷ But there are still some questions about the crystal quality of these layers.

In the previous letter, we have proposed and demonstrated the new structure to use AlP, AlGaP, GaP/GaAs_{0.5}P_{0.5} superlattice (SL) and GaAs_{0.5}P_{0.5}/GaAs SL as intermediate layer between Si and GaAs by MOCVD.⁸ Figure 1 shows our structure to grow GaAs on Si and the lattice constants of the materials used in this structure. Among many III-V compounds GaP, AlGaP, and AlP have fortunately nearly the same lattice constant as Si, and the growth of AlP on Si is easier than that of GaP because of the strong

bond between Al and Si atoms. However, AlP and compounds including high Al content are not stable in an atmosphere, and the crystal quality of these materials becomes very sensitive to the residual water/oxygen vapor in the growth system. Thus, these layers should be as thin as possible. Finally, we followed a route Si→AlP→GaP to grow GaP on Si. Al_{0.5}Ga_{0.5}P is inserted between AlP and GaP to smoothly connect them. This layer brings about better surface of GaP. The large lattice mismatch between GaP and GaAs (about 3.7%) was relaxed by the two stages of strained layer superlattices of GaP/GaAs_{0.5}P_{0.5} and GaAs_{0.5}P_{0.5}/GaAs.⁹⁻¹¹ These two SL have equivalent lattice constants of 5.499 and 5.600 Å, respectively, according to the formula shown in Ref. 11.

The alternative structures such as Si→AlP→AlP/

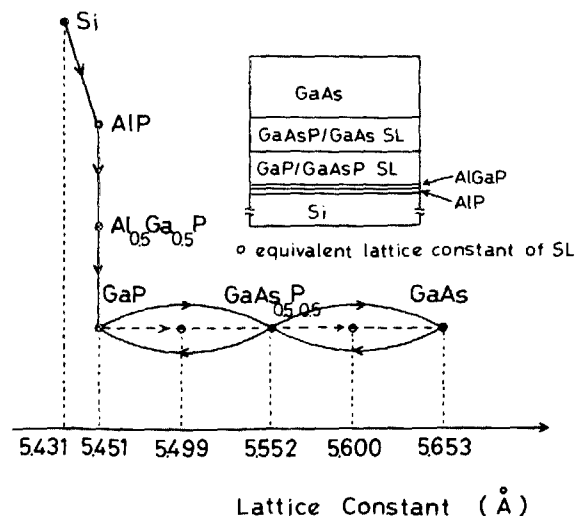


FIG. 1. Structure to grow GaAs on Si and lattice constants of semiconductors used in this structure.

AlGaAsP SL \rightarrow AlGaAsP/GaAs SL \rightarrow GaAs, etc., may be considered, but these structures are expected to be inferior to the present structure because these structures contain many high Al content layers in the intermediate layers.

We have already reported about the relationship between the PL (photoluminescence) intensity and the thickness of AlP + AlGaP.⁸ The insertion of thin AlP and AlGaP layers (~ 20 nm) have made the PL intensity stronger. But, in our structure, there are many other parameters to be optimized for obtaining a high quality epitaxial GaAs.

This paper describes the effects of the strained superlattice layers, AlP + AlGaP layers and the thickness of GaAs layer on the crystallinity, the PL intensity, and the carrier concentration.

II. EXPERIMENT

The MOCVD growth apparatus consists of a horizontal square (4.5×5.5 cm) reactor and an inductively heated graphite susceptor at atmospheric pressure. To increase the flow speed and to smooth the gas flow, a block of SiO₂ was inserted into the reactor as shown in Fig. 2. TMG (trimethylgallium), TMA (trimethylaluminum), AsH₃ (10% in hydrogen), and PH₃ (5% in hydrogen) were used as the source gases. There is no precracking system for PH₃ and AsH₃. The substrates are 2×2 cm², (100)-oriented, Sb-doped *n*-type and B-doped *p*-type Si cut from Czochralski-grown single crystals. The mole fractions of TMG and TMA to hydrogen in growing the intermediate layers were kept constant at 3.6 and 3.1×10^{-5} , respectively, and the V/III ratio (the ratio of group V atoms to group III atoms introduced into the reactor) was 84. The growth temperature T_g was 950°C for AlP and AlGaP and 830°C for the superlattice layers. The total hydrogen flow rate was 3.8 l/min. The growth rate was about 20 nm/min for the superlattice growth. The growth conditions of the surface undoped GaAs layer were the following; the growth temperature was 730°C , the V/III ratio was 40, the total hydrogen flow rate was 3.8 l/min, the mole fraction of TMG to hydrogen was 1.2×10^{-4} , and the growth rate was about 75 nm/min.

Si substrates are etched in HF:HNO₃:CH₃COOH = 1:2:4 solutions for 2 min, followed by the annealing at 1000°C in hydrogen atmosphere for 10 min to remove the oxidized layer at the surface.¹² The grown wafers

were evaluated by the photoluminescence at room temperature using a 5145 Å line of an Ar ion laser with an excitation intensity of 2.4 W/cm^2 . The carrier concentration was measured by van der Pauw and *C-V* methods.

III. RESULTS AND DISCUSSION

A. Crystallinity of GaAs on Si substrates

The effects of the intermediate layer structure on the crystallinity and the surface morphology were investigated for various structures. Figure 3 shows the x-ray diffraction curves from the (400) Bragg lines of GaAs for the following three samples; (A) GaAs ($2 \mu\text{m}$)/SLs($0.35 \mu\text{m}$)/Si, (B) GaAs($2 \mu\text{m}$)/GaP($0.1 \mu\text{m}$)/AlGaP(13 nm)/AlP(7 nm)/Si, (C) GaAs($2 \mu\text{m}$)/SLs($0.35 \mu\text{m}$)/AlGaP(13 nm)/AlP(7 nm)/Si. Figure 4 shows the surface morphology for the respective structures taken by the Nomarsky differential interference microscope. The intermediate layers of AlP + AlGaP + GaP bring about the narrow peak in the x-ray diffraction curve and the smooth surface [Sample (B), Fig. 4(b)] compared to the sample with only superlattices [sample (A), Fig. 4(a)]. But the cracks at the surface are observed for sample (B) [Fig. 4(b)]. On the other hand, the insertion of superlattices between GaAs and GaP together with AlP and AlGaP layers brings about the crack-free superior surface morphology and the narrower peak of the rocking curve. This means that the large lattice mismatch between GaAs and Si can be relaxed by two stages of strained layer superlattices. An example of reflection electron diffraction pattern for sample (C) is shown in Fig. 5, indicating the spot pattern with Kikuchi lines. This photograph shows that the good crystalline single crystal of GaAs could be obtained with AlP, AlGaP, and the strained superlattice layers.

B. Optical and electrical properties of GaAs on Si substrates

To investigate the effects of the intermediate layers on the PL intensity and the carrier concentration of the surface GaAs, the layer number in SL layers, the thickness in SL, and the GaAs layer thickness were changed while keeping the same growth conditions. All the grown GaAs layers were *n* type, and the thickness was $2 \mu\text{m}$ unless mentioned.

Figure 6 shows the PL intensity normalized by the car-

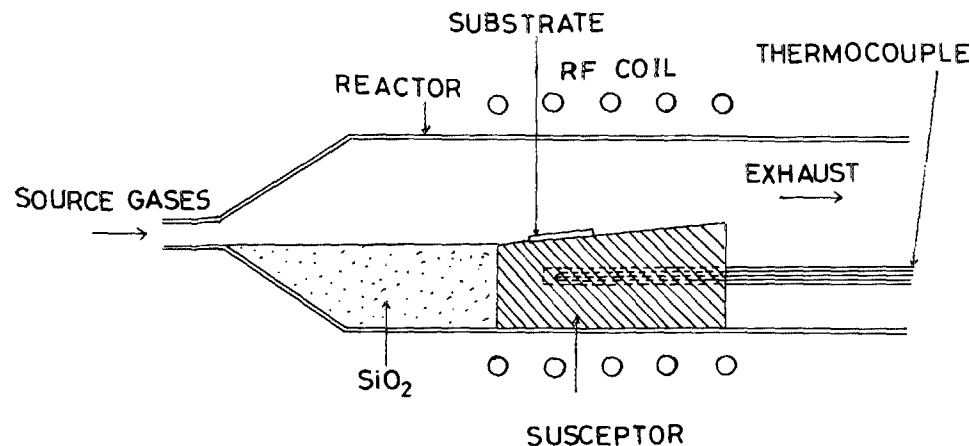


FIG. 2. Schematic view of the MOCVD reactor.

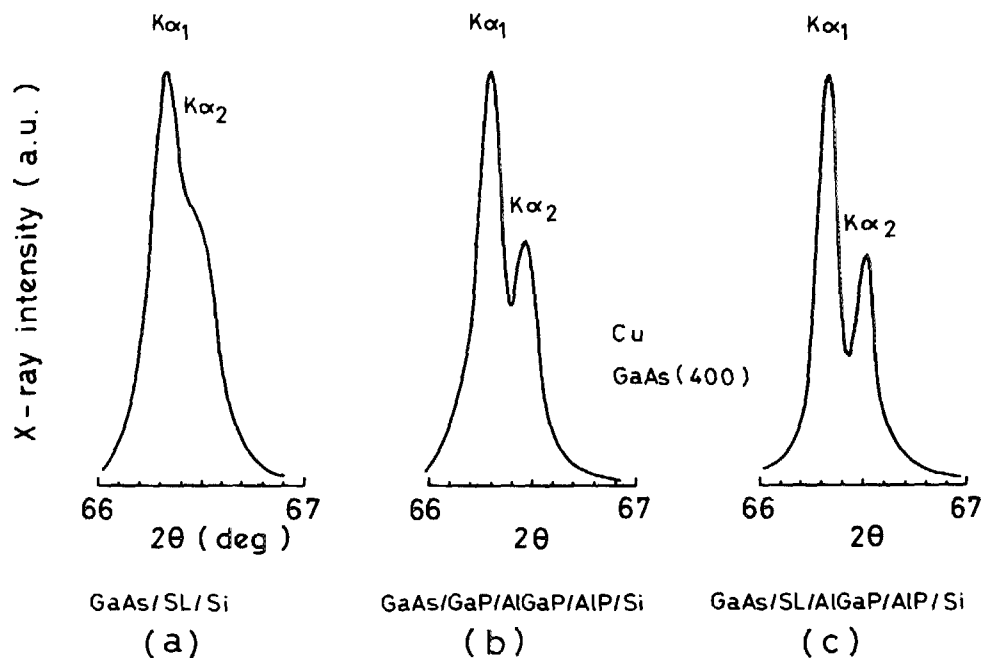


FIG. 3. X-ray rocking curves for various structures: (a) GaAs/SLs/Si, (b) GaAs/GaP/AlGaP/AIP/Si, and (c) GaAs/SLs/AlGaP/AIP/Si. The layer number in one SL is 10, and the one layer thickness in SL is 16.5 nm. The layer numbers for two SLs are the same.

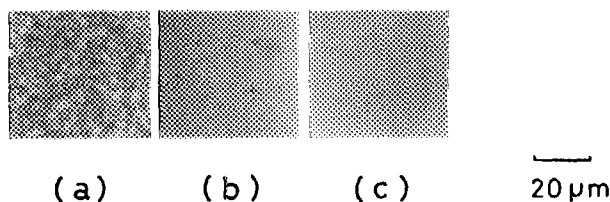


FIG. 4. Surface morphology for various structures: (a) GaAs/SLs/Si (b) GaAs/GaP/AlGaP/AIP/Si, and (c) GaAs/SLs/AlGaP/AIP/Si.



FIG. 5. Reflection electron diffraction pattern for GaAs (GaAs/SLs/AlGaP/AIP/Si).

rier concentration PL/n and the carrier concentration n determined by van der Pauw method as a function of the number of layers in one superlattice when the thickness of AIP + AlGaP is 20 nm. The numbers of layers in two superlattice layers are the same. When there is no superlattice, the PL intensity is about one order of magnitude smaller than that with superlattice layers. PL/n has a small maximum at about ten layers. On the other hand, the carrier concentration slightly increases while increasing the layer number. The total intermediate layer thickness is less than $0.7 \mu\text{m}$. Figure 7 shows the PL intensity and the carrier concentra-

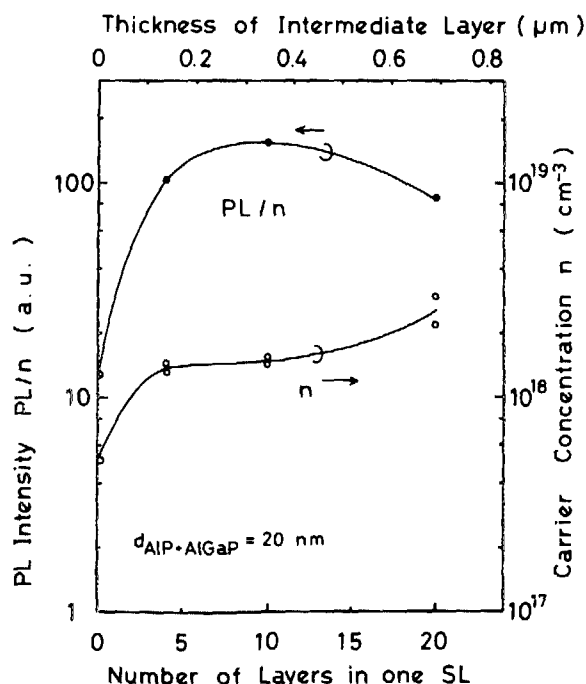


FIG. 6. PL intensity and carrier concentration vs layer number in one superlattice. The one layer thickness in SL is 16.5 nm, and the number for two superlattice layers is the same.

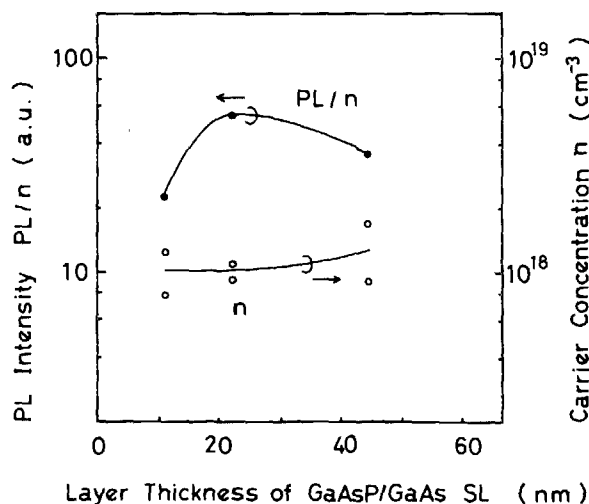


FIG. 7. PL intensity and carrier concentration vs layer thickness in SLs. The thickness of AlP + AlGaP is 20 nm.

tion versus each layer thickness in the superlattices. The layer number in one superlattice is 10. PL/n has a maximum at around 20 nm for each layer thickness while the carrier concentration is unchanged.

Figure 8 shows the PL intensity and the carrier concentration as a function of the surface GaAs layer thickness. The PL intensity increases while increasing the thickness of GaAs and saturates over $3 \mu\text{m}$. The increase in PL intensity while increasing the layer thickness is not caused by the increased absorption of the exciting light because the minimum GaAs layer thickness ($\sim 0.6 \mu\text{m}$) is much larger than the absorption length of the exciting light ($\sim 0.1 \mu\text{m}$). This saturated value of the PL intensity is about 80% of that of GaAs grown on GaAs substrate. Figure 9 shows the in-depth profile of the carrier concentration measured by the C-V method using an electrochemical cell. The carrier concentration increases drastically while approaching the intermediate layer, and n^+ -Si layer is formed by the diffusion of P or As into Si substrate. The slightly larger carrier concentration compared to that on GaAs substrate seems to be caused by the auto doping of Si during the growth and will

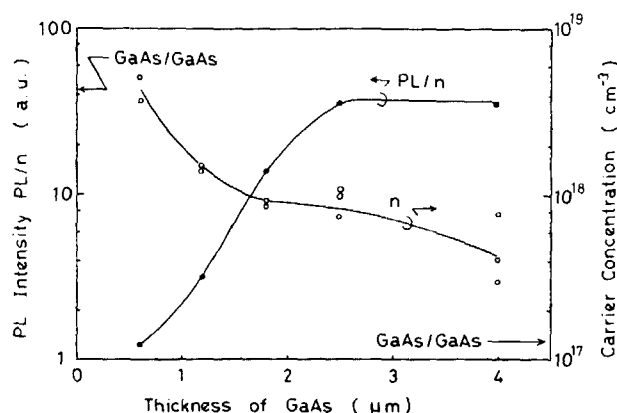


FIG. 8. PL intensity and carrier concentration vs thickness of GaAs surface layers. The structure of the intermediate layer is the same as sample (c) in Fig. 3.

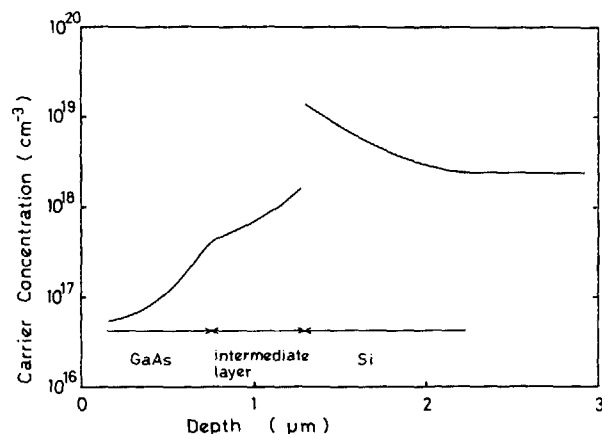


FIG. 9. In-depth carrier profile of GaAs on Si substrate. The structure of the intermediate layer is the same as sample (c) in Fig. 3.

be improved by the SiO_2 coating to the back side of the Si substrates. These results indicate that GaAs grown thicker than $3 \mu\text{m}$ on Si substrate is hardly affected by the Si substrates and the intermediate layers, and the optical and electrical properties are comparable to that grown on GaAs substrates.

IV. CONCLUSIONS

In this paper we have described GaAs grown on Si substrate with the intermediate layers of AlP, AlGaP, GaP/GaAsP superlattice and GaAsP/GaAs superlattice. The relationships between the intermediate layer structure and the optical and electrical properties were investigated. The high-quality single-crystalline GaAs was reproducibly obtained, and the PL intensity and the carrier concentration were almost the same as that grown on GaAs substrates. The obtained results can be summarized as follows: (1) The layers of AlP and AlGaP bring about the superior surface morphology and the good crystallinity. (2) The two stages of GaP/GaAs_{0.5}P_{0.5} and GaAs_{0.5}P_{0.5}/GaAs superlattices relax the large lattice mismatch between GaAs and Si, and they make the PL intensity strong and prevent the crack formation in the epitaxial layer. (3) The PL intensity becomes maximum when each superlattice layer thickness is 20 nm. (4) The PL intensity increases with increasing GaAs layer thickness until $3 \mu\text{m}$ up to about 80% of that grown on GaAs substrate.

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