Low-temperature growth of GaAs with high quality by metalorganic vapor phase epitaxy

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Abstract. Growth of GaAs by MOVPE (Metal-Organic Vapor-Phase Epitaxy) at a much lower temperature than conventional conditions of 650°C required to produce highly resistive buffer layers and molecular-layer-level abrupt heterojunctions and doped-layer interfaces. It has been widely recognized that growth at 550–600°C causes poor morphological surfaces on the grown layers. This paper describes a fundamental improvement of the low-temperature growth of GaAs, resulting in smooth surfaces with very low impurity concentrations. Excellent GaAs layers can be grown at 500°C by increasing partial pressure of AsH₃ during growth. The method has been applied to high quality epitaxial layers for electronic device production.

1. Introduction
High purity and highly resistive buffer layers and molecular-layer-level abrupt interfaces are key to recent improvement of compound semiconductor electronic devices. Although MOVPE is now recognized as the most suitable mass-production method of epitaxial layers for electronic and optical
devices, its growth temperature has usually been 650–850°C, which enhances thermal diffusion of lattice atoms at interfaces. When the growth temperature is reduced to 550–600°C, which is widely used in MBE, a result is poor morphological surfaces of the MOVPE GaAs layers. Therefore, there have been few reports on development of low temperature growth techniques using MOVPE.

It has been reported that the growth of GaAs by MOVPE is governed by mass transport of molecules at the range of 600–850°C and by kinetic movement of molecules on the surface at the range of 400–600°C[1]. This suggests that an unstable growth takes place at the transition temperature of the two ranges, which leads to the rough surface. Thus, if the growth is performed at fully kinetic conditions (below 500°C), mirror-like stable surfaces can be obtained again. This paper unveils our fundamental technology on the low temperature growth of GaAs with a smooth surface and high purity. The method has been applied to mass-production of the epitaxial layers for various GaAs-based devices.

2. Experimental

GaAs epitaxial layers were grown by MOVPE under an atmospheric pressure of H₂ using the material gases of TMG (Trimethyl gallium) and AsH₃. The flow rate of H₂ was 20 l/min. The substrate crystals were undoped LEC (Liquid Encapsulated Czochralski)-grown semi-insulating GaAs wafers with (100) surface. The growth temperature was changed in the range between 400 and 650°C. The measured items were (1) surface observation by an optical microscope, (2) electrical properties by the van der Pauw method, and (3) photoluminescence properties at liquid He temperature.

3. Results and Discussion

3.1. Low temperature growth of GaAs

The growth rate dependency on the growth temperature is shown in Figure 1. From the slope in the figure, the growth below 500°C was in the kinetic controlled region while above 600°C was in the mass transport limited region. The transition temperature was 550°C. The activation energy of the growth in the kinetic controlled region was 19.7 kcal/mol. This result agrees with that of D.H.Reep[1]. The layer grown below 400°C could not be observed. It is estimated that the growth rate at 400°C was 1/10 of that at 600°C. The reason must be little decomposition of TMG at that low temperature.

The photographs of the surface of the layers grown at the temperature range 450–600°C are shown in Figure 2. The thickness of the layers was 0.5–2µm. The layers grown at 600°C...
mass transport limited region) had smooth surfaces, while the layers grown at 550°C (transition region) had milky surfaces. At the lower temperature of 450–500°C (kinetic controlled region), the grown layers successfully had smooth surfaces, as expected. A few hillocks like oval defects on MBE-grown wafers were observed on the surface of the layers grown at 500°C. More and smaller hillocks were observed on the surface of layers grown at 450°C.

3.2. The characteristics of GaAs grown at low temperature

The carrier concentration of undoped layers grown between 450°C and 700°C are shown in Figure 3. Above 600°C, the layers had high resistivity. The layers grown between 500°C and 550°C became p-type and the hole concentration increased with decreasing growth temperature. These p-type GaAs layers have the high values of mobility 270–360 cm²/V·s. The layers grown at 450°C became highly resistive (or fully depleted). The photoluminescence spectra from undoped GaAs layers grown at various values of temperature are shown in Figure 4. The acceptor in the p-type GaAs layers grown at low temperature is identified as carbon from the photoluminescence spectra. The intensity of photoluminescence from the layer grown at 450°C is very weak. This means that the properties of the grown crystal layer must be poor.

3.3. The effect of AsH₃ in low temperature growth

From photoluminescence spectra, carbon was determined to be the acceptor of the p-type layer grown at 450–500°C. It is well known that in the higher temperature growth range the incorporation of carbon into the photoluminescence spectra. The intensity of photoluminescence from the layer grown at 450°C is very weak. This means that the properties of the grown crystal layer must be poor.

Figure 2. Surface of low-temperature growth GaAs.

Figure 3. Growth temperature dependence of carrier concentration for epitaxial layers on (100) GaAs with $P_{\text{TMG}}=10.1\text{ Pa and } P_{\text{AsH}_3}=1.01\times10^2\text{ Pa } ([\text{AsH}_3]/[\text{TMG}]=10)$. The values near the circle show the mobility of the layers $[\text{cm}^2/\text{V} \cdot \text{s}]$.

Figure 4. Low-temperature photoluminescence spectra of undoped GaAs epitaxial layers grown at various temperatures on (100) GaAs. $P_{\text{TMG}}=10.1\text{ Pa and } P_{\text{AsH}_3}=1.01\times10^2\text{ Pa } ([\text{AsH}_3]/[\text{TMG}]=10)$
MOVPE-grown GaAs crystals can be suppressed by increasing AsH₃ partial pressure P(AsH₃). An experimental study was added for the confirmation of the effect of P(AsH₃) at low temperature. The growth temperature was 500°C and P(AsH₃) was varied from 1.01 ×10² to 5.05×10² Pa. The carrier concentration of the undoped GaAs layers grown under various P(AsH₃) is shown in Figure 5. The hole concentration of GaAs decreases with increasing P(AsH₃) or molar ratio of AsH₃ to TMG ([AsH₃]/[TMG]), and the layers become semi-insulating at [AsH₃]/[TMG]=40 and 50. The photoluminescence spectra from these layers are shown in Figure 6. The intensity of the peak originated in carbon acceptor relatively decreases with increase of P(AsH₃) ([AsH₃]/[TMG]). The fine structures of the exciton peak can be observed in the photo-luminescence spectra from layers grown at [AsH₃]/[TMG]=50. This means that high purity GaAs crystals can be grown at high P(AsH₃) ([AsH₃]/[TMG]) through low temperature growth.

4. Summary
Low temperature growth of GaAs was studied, and very smooth surfaces were successfully found on the layers grown at 450~500°C by MOVPE. Undoped GaAs layers grown at 500~550°C are p-type and their hole concentration increased with decreasing growth temperature. The acceptor in these layers was identified as carbon from photoluminescence spectra at 4.2K. GaAs crystal layers with high purity were grown at 500°C by increasing the partial pressure of AsH₃ during growth.

References
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Figure 5. Effect of AsH₃ pressure ([AsH₃]/[TMG]) on the carrier concentration of undoped GaAs epitaxial layers grown at 500°C with P(TMG)=10.1Pa. The values near the circle show the mobility of the layers.

Figure 6. Low-temperature photoluminescence spectra from undoped GaAs epitaxial layers grown at 500°C with various AsH₃ pressures ([AsH₃]/[TMG]).