論 文

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溶液Ga에서 成長된 高純度 積層 GaAs의 製造와 그의 性質

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要 約

GaAs의 單結晶은 Ga의 溶液으로부터 epitaxial 方法으로 成長시키는데 300°K에서는 carrier concentration $10^{14}/cm^3$에서 electron-mobility 7,500～9,300cm^2/V-sec. 程度의 것이 얻어지며 77°K에서는 electron-mobility 50,000～95,000cm^2/V-sec. 의 것이 얻어진다.

mobility—溫度 關係曲線의 理論的인 것과 實驗的인 것을 比較해 보면 77°K에서 430°K의 溫度範圍內에서 ion化한 不純物과 phonon이 主要한 scattering mechanism이라는 것을 나타 낸다.

이것은 epitaxial層이 mobility를 制限하는 다른 결함을 별로 내포하지 않는다는 것을 의미한다.

epitaxial層의 photoluminescence spectra는 深部에 存在하는 결함의 準位에 依한 放出을 나타내지 않는다.

ABSTRACT

GaAs single crystals were grown epitaxially from Ga solution with carrier concentrations in the $10^{14}cm^{-3}$range and electron mobilities between 7,500 and 9,300cm^2/V-sec. at 300°K, and 50,000 and 95,000 cm^2/V-sec. at 77°K. A comparison of the theoretical and experimental curves for the mobility vs. temperature indicates that the significant scattering mechanisms are ionized impurities and phonons in the temperature range of 77°K to 430°K. This indicates that the epitaxial layers do not contain other mobility limiting imperfections to a significant degree. Photoluminescence spectra of the epitaxial layers did not show any emission due to deep lying imperfection levels.

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THE PREPARATION AND PROPERTIES OF HIGH—PURITY EPITAXIAL GaAs GROWN FROM Ga SOLUTION

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There have been several reports on the growth of GaAs from Ga solution (1,2,3,4). However, no successful effort has been reported in growing GaAs with properties comparable to the best results obtained by vapor phase epitaxial technique. For example Eddolls(5) et al. have reported electron mobilities as high as 103,000cm²/V-sec. at 52°K in GaAs grown by the vapor phase epitaxial technique while Bolger and co-workers(6) have measured mobilities up to 101,000cm²/V-sec. at 77°K in GaAs grown by the same technique. We have been able to grow reproducible GaAs epitaxially from Ga solution with carrier concentrations in the 10^{14}cm^{-3} range and electron mobilites between 7,500 and 9,300cm²/V-sec. at 300°K and between 50,000 and 95,000cm²/V-sec. at 77°K.

The tilt tube technique initiated by Nelson(3) was modified some what for the liquid epitaxial growth. Undoped polycrystalline GaAs* with a carrier concentration of approximately 3×10^{16}cm^{-3} was dissolved in Ga of 7N purity** at 850°C for two hours under a flowing palladium-purified H_2 atmosphere. The GaAs-saturated Ga was then poured over the chemically polished Cr-doped semi-insulating GaAs substrate. The Ga solution was then cooled to a 200°C/hr. cooling rate. GaAs single crystal layers of 50 to 100μm thickness were grown on the $(\bar{1}\bar{1}\bar{1})$ face of the substrate. The interface between the substrate and the epitaxial layer revealed by cleaning or angle lapping was straight and could be seen only by chemical staining. A graphite boat was used for the growth experiments. The boat was vacuum-baked at 1,400°C for several hours prior to the experiment.

Hall effect measurements were carried out on rectangular shaped samples etched out from the grown layers. Six indium contacts were soldered to the periphery of the samples and heat treated at 850°C to provide ohmic contacts. Measurements at 5KG at temperatures ranging from 77°K to 42°K were taken in a conventional liquid nitrogen cryostat using an automatic data acquisition system(7).

The results of the Hall effect measurements on several samples are plotted in Fig. 1. Sample TD61 showed the highest mobility at 77°K and the lowest carrier concentration,

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* Obtained from the Monsanto Co.

** Obtained from the Eagle-Picher Industries, Inc.

which was lower than the carrier concentration in the source material by more than two orders of magnitude.

The temperature dependence of the carrier concentration indicates that the donor levels are shallow enough to be nearly completely ionized at 77°K.

In order to identify the scattering mechanisms operating in the epitaxial layers, a comparison of the theoretical(8) and the experimental dependence of mobility on the temperature was made in **Fig. 1.** The upper solid curve is Ehrenreich's theoretical curve for the case of optical phonon scattering alone. The experimental dependence of mobility on temperature follows that of the theoretical curve in the range of approximately 150°K to 300°K. Similar behavior was reported by Bolger et al.(6) for GaAs grown by the vapor phase epitaxial technique.

Note that the measured Hall mobility of TE61 has reached the theoretical limit of mobility predicted by the calculation of Ehrenreich in the range of 150°K. The deviation of the measured mobility from the upper theoretical curve at lower and higher temperatures may be attributed to the importance of ionized impurity scattering and acoustical phonon scattering respectively at these temperatures(5).

It was interesting to note that the samples with higher carrier concentrations tended to have higher mobilities in the high temperature region above 300°K. This behavior may be attributed to the increased screening of polar scattering with an increase in the free electron concentration(9). A similar behavior has been observed for InP(10).

The result of the mobility measurements indicates the high degree of purity and the structural perfection of the crystals grown by the liquid epitaxy.

The total concentration of ionized impurities was calculated using the Brooks-Herring(11) relation and the result is shown in **Table I.** The mobility due to the ionized impurity scattering used in the calculation was estimated from the measured mobility and the lattice mobility of 200,000cm^2/V-sec.(6) at 77°K. The dielectric costant of GaAs was taken to be 11.6 and the effective electron mass to be 0.072m$_0$ for the calculation.

The shallow donor may be silicon which was always present in the spectrographic analysis of the gallium used for the epitaxial growth. The main compensating acceptor may also be silicon, since silicon is known to be an amphoteric impurity in GaAs(12) especially when there is a low arsenic activity in the growth environment(13).

The photoluminescent spectra were measured at 300°K and at 77°K with a Perkin-Elmer Model 13 spectrophotometer. A mercury lamp with a Corning 7-59 filter and Cu$_2$SO$_4$ solution filter was used for the excitation. The spectra were corrected for the photomultiplier spectral sensitivity (S-1 response). The surfaces of the crystals were etched in H_2O_2:H_2SO_4:H_2O(1:3:1) prior to the measurement.

Typical photoluminescence spectra are shown in **Fig. 2.** The photoluminescence spectrum of the n-type GaAs used for the source material with 3×10^{16}cm^{-3} carriers and that of the epitaxial GaAs are compared at 77°K. No emission due to deep lying defect states was observed from the epitaxial layers where as two emission peaks arising from the deep levels were observed from the source material. This indicates a significant reduction in the concentration of the related imperfections during the growth process. The energy of the sharp emission peak is at 1.506 eV which is approximately 3 meV lower than the GaAs band gap energy (1.509 eV) at 77°K(14). This peak is probably due to a direct band-to-band electron transition(15). An emission peak involving a shallow level approximately 30 meV from the band edge was observed in all of the epitaxial. A similar peak was observed by Williams and Blacknall(15) at 20°K. This peak may have been caused by the transition of electrons from the conduction band to the shallow silicon acceptor level as suggested by Williams and Blacknall. The emission spectra of our epitaxial layers did not change with carrier concentrations in 10^{14} to 10^{15}cm^{-3} range in agreement with the previous studies of Panish(4). This seems to indicate that the low growth temperature and the excess Ga in the growth environment decrease the solubilities of defects and impurities which create deep lying levels.

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Table I. Ionized Impurity Concentraton at 77°K

Sample	N_D+N_A (cm^{-3})	N_D-N_A (cm^{-3})	N_D (cm^{-3})	N_A (cm^{-3})	μ_H 300°K (cm^2/V-sec)	μ_H 77°K (cm^2/V-sec)	μ_I *77°K (cm^2/V-sec)
TE 61	6.84×10^{14}	1.20×10^{14}	4.02×10^{14}	2.82×10^{14}	9,300	95,000	181,000
TE 64	1.65×10^{15}	4.00×10^{14}	1.03×10^{15}	6.24×10^{14}	8,200	62,500	91,000
TE 80	2.21×10^{15}	1.10×10^{15}	1.66×10^{15}	5.5×10^{14}	7,500	53,200	72,500

* Impurity mobility, μ_I was calculated assuming the lattice mobility to be 200,000 at 77°K(6).

Figure Captions

Fig. 1

Variation of carrier concentration and Hall mobility with temperature.

Fig. 2

Comparison of photoluminescence at 77°K for liquid epitaxially grown GaAs layer and the source GaAs of 3×10^{16}cm^{-3} carrier concentration used for the growth process.

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