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**RARE EARTH DOPED III-V SEMICONDUCTORS
FOR OPTOELECTRONICS**

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by

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1. Introduction

The overall goal of this Phase I project was to focus on developing procedures for the fabrication and evaluation of epitaxial layers of GaAs which are doped with rare earth (RE) ions of Erbium. The essential elements of the originally proposed approach have been demonstrated through the efforts on this Phase I project. Erbium was successfully incorporated in epitaxially grown Gallium Arsenide (GaAs) and Aluminum-Gallium Arsenide (AlGaAs) by using the Metal Organic Chemical Vapor Deposition (MOCVD) method and using Tris(n-butylcyclopentadienyl)erbium $[\text{Er}(\text{C}_4\text{H}_9\text{C}_5\text{H}_4)_3]$ as Er source material. Concentrations of Erbium as high as 10^{19}cm^{-3} were detected by Secondary Ion Mass Spectroscopy (SIMS). A substantial, though unknown, amount of the Erbium was incorporated in the form of trivalent ions; this was evident by the observation of the characteristic $\text{Er}(3+)$ light emission from photoluminescence spectra of our samples.

2. Phase I Technical Objectives and Accomplishments

2.1 Search for an Erbium source suitable for MOCVD

In the proposal an ideal metal-organic erbium source, i.e., one which is volatile and contains only Erbium, Carbon and Hydrogen, was identified: tris(methylcyclopentadienyl)erbium $[\text{Er}(\text{CH}_3\text{C}_5\text{H}_4)_3]$ also called Tris-m.c.p.-Erbium. Japanese had developed experimental quantities of this compound in their own laboratory and were able to obtain

workable vapor pressures at about 100° C.¹ The above identified compound had allowed them to fabricate the Er-doped GaAs LEDs.² Unfortunately, our expectation that Alpha Products CVD would make this product commercially available in the US was premature. During our investigations Weber et al. published results on Ytterbium doped InP using tris(isopropylcyclopentadienyl)ytterbium.³ Professor J. Cooper, Department of Chemistry of the University of Pittsburgh, encouraged by this publication agreed to synthesize the corresponding Erbium compound. The material resulting from several synthesis attempts, however, did not have the expected vapor pressure, such that we could use the compound at temperatures below 90 C, and there were other indications that the resulting synthesized material indeed was not the one they expected to synthesize; i.e., that their attempts had not been successful. Finally we were able to purchase 10 gram of Tris(n-butylcyclopentadienyl)erbium $[\text{Er}(\text{C}_4\text{H}_9\text{C}_5\text{H}_4)_3]$ also known as (n-butyl-Cp)₃-Erbium from the *Strem Chemicals, Inc.*⁴, which also provided us with the following vapor pressure data:

Table I: Vapor Pressure of $[\text{Er}(\text{C}_4\text{H}_9\text{C}_5\text{H}_4)_3]$

T [°C]	200	215	219	235	247	250
P [Torr]	0.1	2	4	6	10	boiling

The use of this precursor necessitated that we modified our MOCVD system such that the Erbium source and the vapor lines leading to the reactor could be heated to about 240 °C. Erbium incorporation in GaAs and AlGaAs epitaxial layers was achieved with Hydrogen flowing through the bubbler at various rates.

2.2 Epitaxial Growth using MOCVD

Numerous samples of GaAs:Er and a few samples of AlGaAs:Er were grown by MOCVD at atmospheric pressure in a vertical quartz reactor using Trimethylgallium (TMG) and Tertiarybutylarsine (TBA). See Figure 1 for a schematic of the MOCVD system at the University of Pittsburgh which performed the epitaxial growth under subcontract. Erbium was incorporated into GaAs using Tris(n-butylcyclopentadienyl)-erbium $[\text{Er}(\text{C}_4\text{H}_9\text{C}_5\text{H}_4)_3]$ as liquid source. The epitaxial layers were grown on (100)-oriented Si-doped or undoped GaAs substrates. Growth parameter, such as III-V ratio, substrate temperature and deposition rate were varied and their effect on the incorporation of Erbium as trivalent ion was qualitatively monitored by subsequent photoluminescence measurements. The epitaxial layer thickness (and thereby the deposition rate by staining a cleaved segment of the wafer; see Fig.2. The growth temperature was varied from 620°C to 680°C. While always good morphology can be obtained for growth of conventional GaAs at 680°C, the addition of Er-vapor caused a degradation of the morphology as shown in Fig. 3. However, with similar deposition conditions, but a substrate temperature reduced to 620°C, a mirror-like feature-less surface was obtained and luminescence showed the $\text{Er}(3+)$ incorporation. It is speculated, that at the higher growth temperature the Erbium is segregating toward the front surface, and, due to its larger atomic size, degrades the crystalline quality. The Er concentration in the layers was controlled by the Er source temperature and the H_2 flow through the Er bubbler ranging from 175°C to 225°C and from 50 SCCM to 210 SCCM, respectively. The typical growth rate was about 1-2 $\mu\text{m}/\text{h}$.

Schematic Diagram of MOCVD System

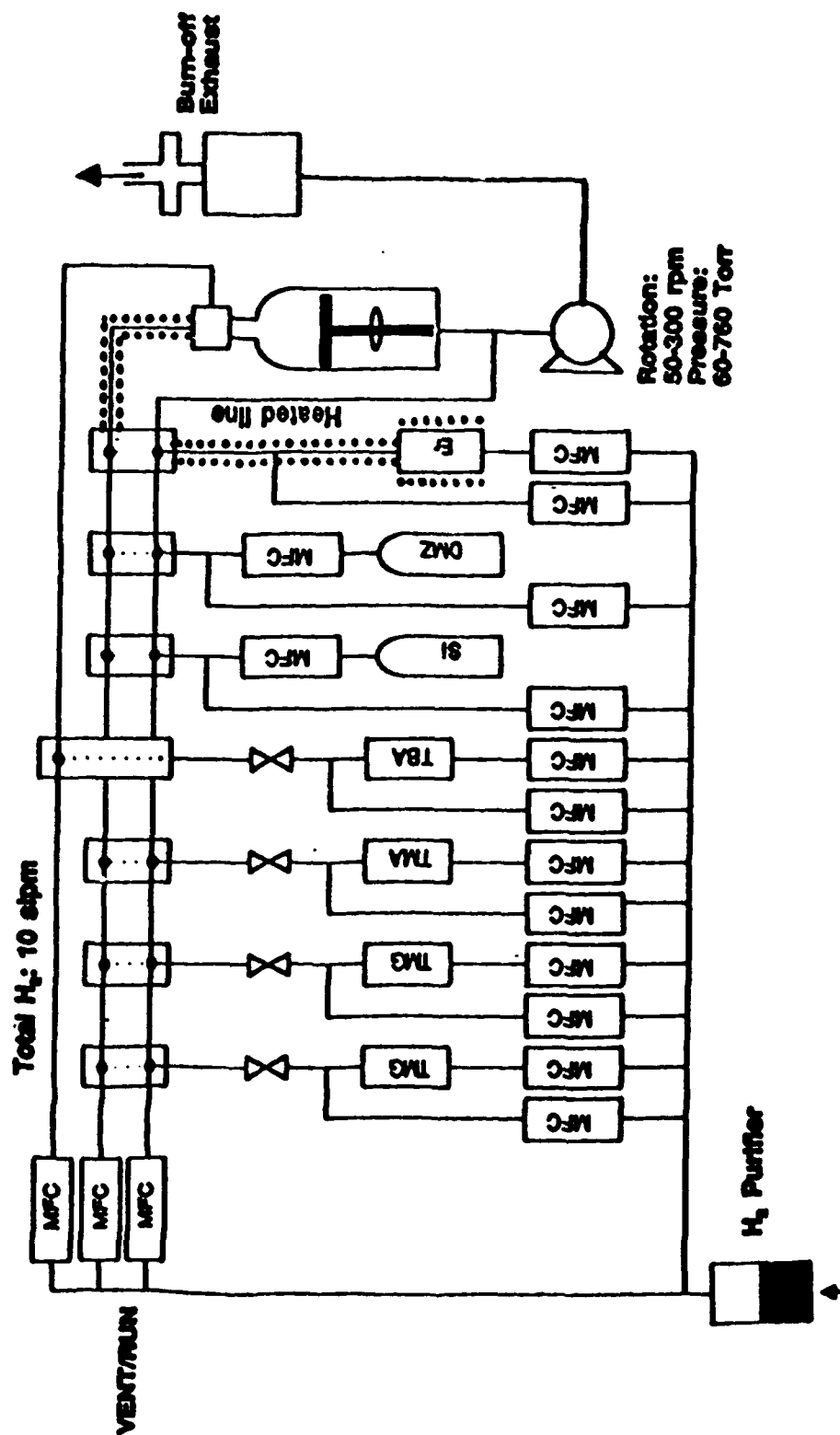


Fig. 1 A schematic of the Metal Organic Chemical Vapor Deposition system used for the growth of epitaxial III-V compound semiconductors.

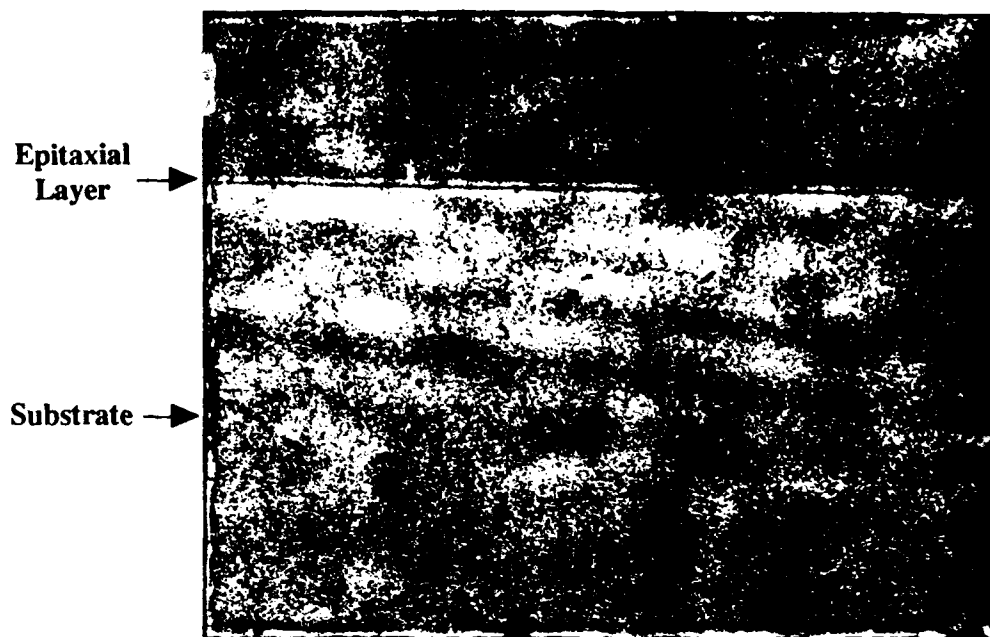


Fig. 2 Cross-sectional view of an $\sim 1\mu\text{m}$ thick, epitaxially grown layer of GaAs:Er on a GaAs substrate.

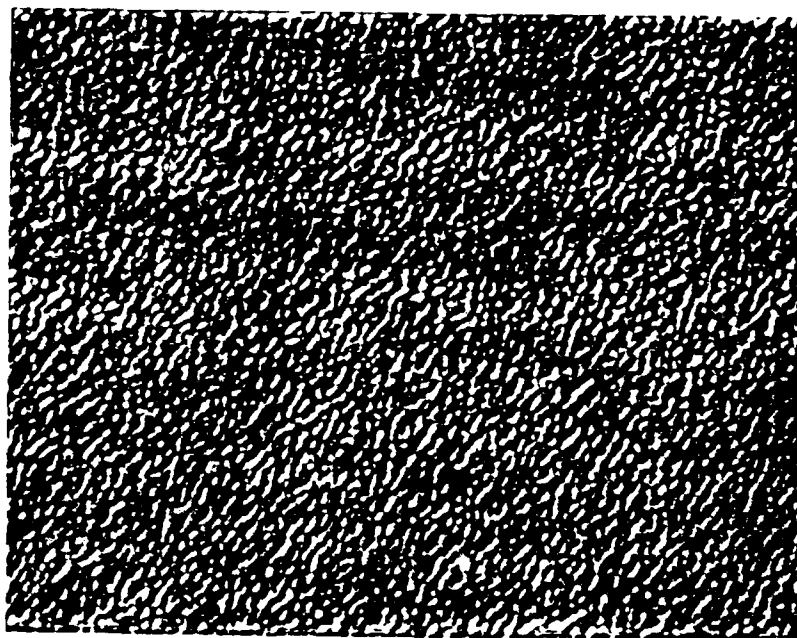


Fig. 3 Micrograph (800x) of the surface of "bad" epilayer, the combination of substrate temperature and Er flow rate was too high. In contrast, a micrograph of a "good" surface is absolutely without features.

As mentioned, the morphology of Er-doped GaAs epitaxial layers was found to depend noticeably on the growth temperature, the Er source temperature and the H₂ flow through the Er bubbler. At the growth temperature of 680°C, the morphology became cloudy as the Er source temperature and the H₂ flow through the Er bubbler increased in the range from 190°C to 225°C and from 110 SCCM to 210 SCCM, respectively. This is likely due to the formation of precipitates with high Er concentrations, as previously reported.⁵ The photoluminescence (PL) measurements indicated that all these samples with cloudy surface presented nearly the same PL intensities around 1.54μm despite the differences in Er source temperatures and H₂ flow rates. Good morphology was obtained on those samples grown with the Er source temperature and the H₂ flow through the Er bubbler lower than 190°C and 110 SCCM respectively. However, they did not show perceptible emissions from Er 4f electrons around 1.54μm. Reducing the growth temperature generally improved the morphology even with those growth parameters which resulted in the growth of the samples with cloudy surface. The optimum morphology was attained with the growth temperature of around 620°C.

The Er concentration was characterized by secondary ion mass spectroscopy, courtesy of the University of Dayton Research Institute, Dr. J. Solomon. The dependence of Er concentration on Er source temperature was obtained with the H₂ flow rate fixed at 210 SCCM as shown in Fig. 4. The dependence of Er concentration on growth temperature was investigated with the H₂ flow rate and the Er source temperature maintained at 210 SCCM and 200°C, respectively, as shown in Fig. 5.

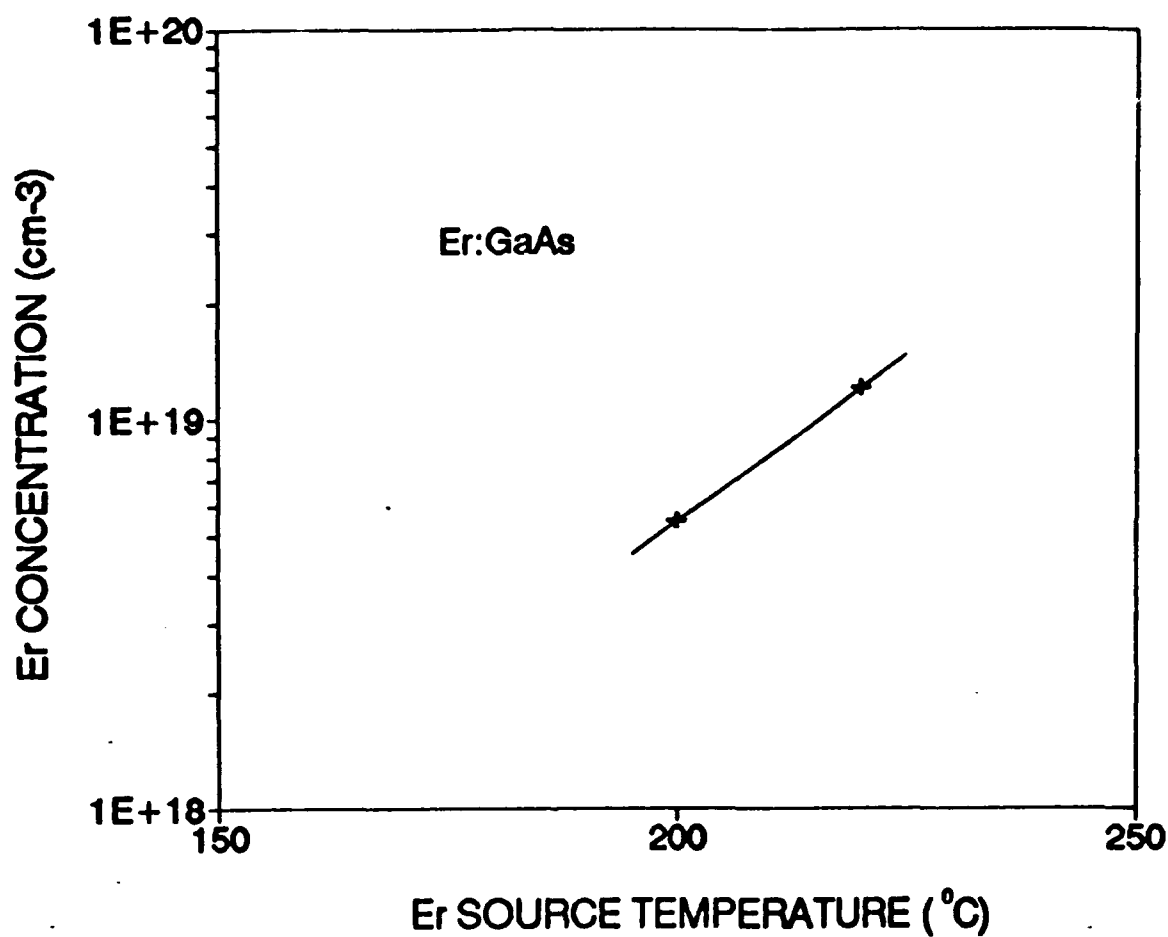


Fig. 4 Dependence of Er concentration in GaAs on the $\text{Er}(\text{C}_4\text{H}_9\text{C}_5\text{H}_4)_3$ source temperature. GaAs epilayers were grown at 620°C with the H_2 flow rate through the Er bubbler of 210 SCCM and V/III ratio of 13.5:1, respectively.

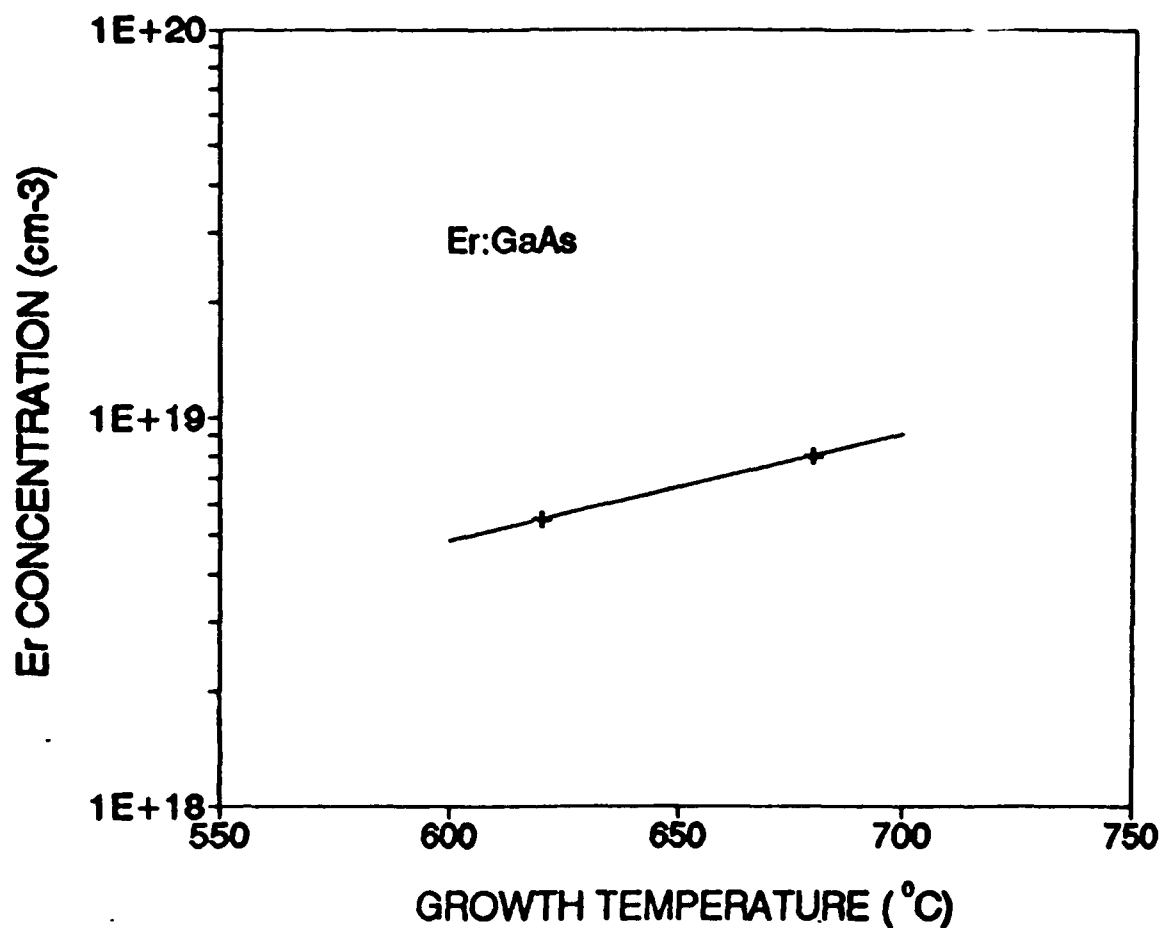


Fig. 5 Dependence of Er concentration in GaAs on the growth temperature. GaAs epilayers were grown with the $\text{Er}(\text{C}_4\text{H}_9\text{C}_3\text{H}_4)_3$ source temperature, the H_2 flow rate through the Er bubbler and V/III ratio maintained at 200°C, 210 SCCM and 13.5:1, respectively.

2.3 Erbium Doping by Diffusion

Several attempts were made to dope bulk and epitaxial GaAs by diffusion. GaAs with evaporated Erbium metal placed in a forming gas environment inside quartz ampuls. Heating cycles, up to 610 °C and up to 10 hours, did not produce any Erbium related PL emission.

2.4 Material Characterization

Photoluminescence measurements were performed using the 488.5 nm or 514.5 nm line of an argon-ion laser, a 0.275 m Jarrell-Ash monochromator, a room-temperature InGaAs photodetector and an ORTEC Brookdeal 9503 lock-in amplifier. Samples were mounted on the cold finger of a liquid-helium cryostat with temperatures ranging from 4.2K to 300K.

Fig. 6 shows a typical PL spectrum of Er-doped GaAs epitaxial layers obtained at 5.5K. The samples used for these PL measurements were all grown at 620°C with a V/III ratio of 13.5:1. Several crystal-field-split zero phonon lines related to emissions from Er 4f electrons were clearly seen at around 1.54μm. Two distinct peaks, labeled as A and B, were dominant around 1.54μm. In addition to these two peaks, another two relatively weak structures, C and D, were also denoted. These results are similar to the previously reported ones achieved with MOCVD using different Erbium sources.^{6,7} As shown in Fig. 6, the intensities of emissions in other spectral regions due to deep level defects such as EL2 or unintentionally doped impurities are very weak. The PL spectra of Er-doped GaAs epitaxial layers were found to depend on the V/III ratio. Changing

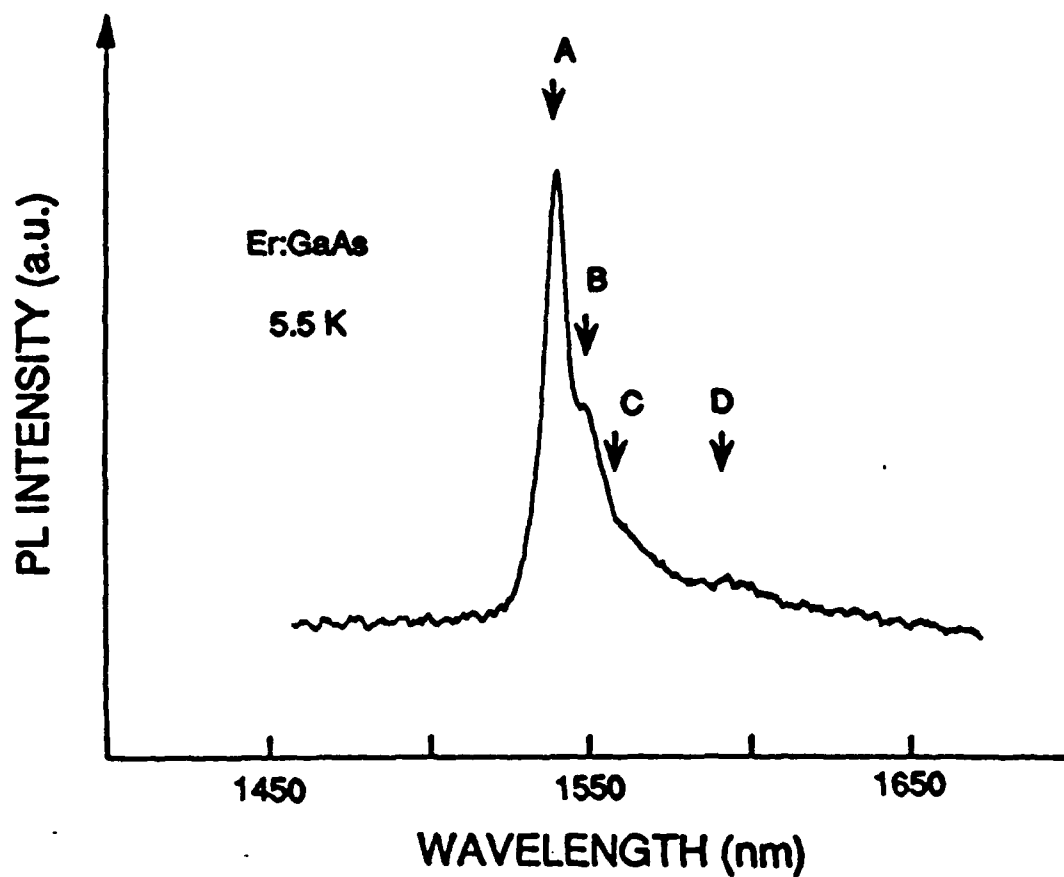


Fig. 6 Photoluminescence spectrum at 5.5K for an Er-doped GaAs grown at 620°C with $\text{Er}(\text{C}_4\text{H}_9\text{C}_3\text{H}_4)_3$.

the V/III ratio from the value of 13.5:1, either larger or smaller, while keeping the other growth parameters same as those which resulted in the growth of the samples with PL spectra of Fig. 6, we obtained the results which showed that the Er-related peak A around $1.54\ \mu\text{m}$ was superimposed on a broad emission band which might be due to the incorporation of deep level defects such as EL2 associated with the inappropriately chosen V/III ratio.⁸

The spectrum at 77K for the same sample is shown in Fig. 7. By comparing Fig. 6 and Fig. 7, it can be seen that the two dominant lines A and B shift to shorter wavelengths by $\sim 2\text{nm}$ as the temperature is increased from 5.5K to 77K. We also observed the Er 4f emission at 300K, which is shown in Fig. 8. The dominant peak A is located at $1538 \pm 1\ \text{nm}$, shifting by less than 1 nm from that at 77K. Fig. 9 shows the temperature dependence of the PL intensity of the intense Er-related emission line A. Note that the PL intensity of the emission line A is essentially inversely proportional to the sample temperature, in contrast to the rapidly change in band-edge emissions with temperature.

Relatively little effort was spent on the obtaining optimal growth parameter for AlGaAs:Er. The spectrum of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ shows the broader, crystalline field related Er emission; however the sharp line structure is absent. Other samples, grown with different Aluminum concentrations and at different substrate temperatures showed no luminescence at all.

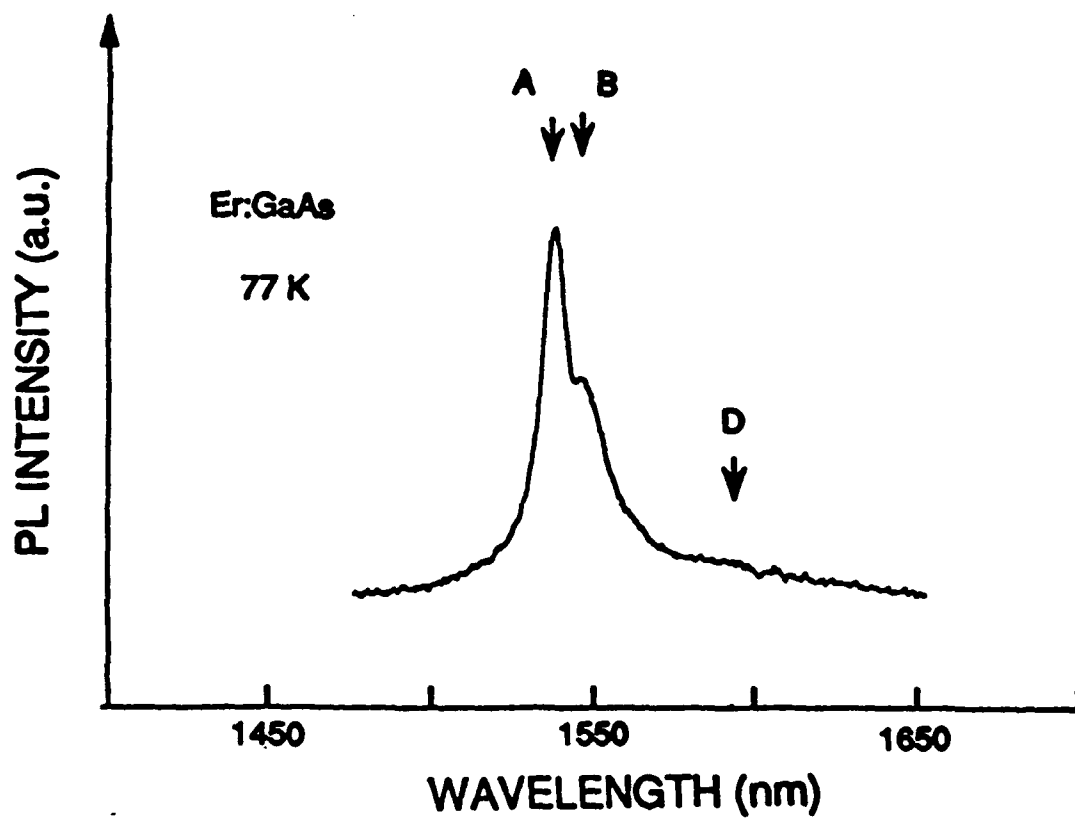


Fig. 7 Photoluminescence spectrum at 77K for an Er-doped GaAs grown at 620°C with $\text{Er}(\text{C}_4\text{H}_9\text{C}_3\text{H}_4)_3$.

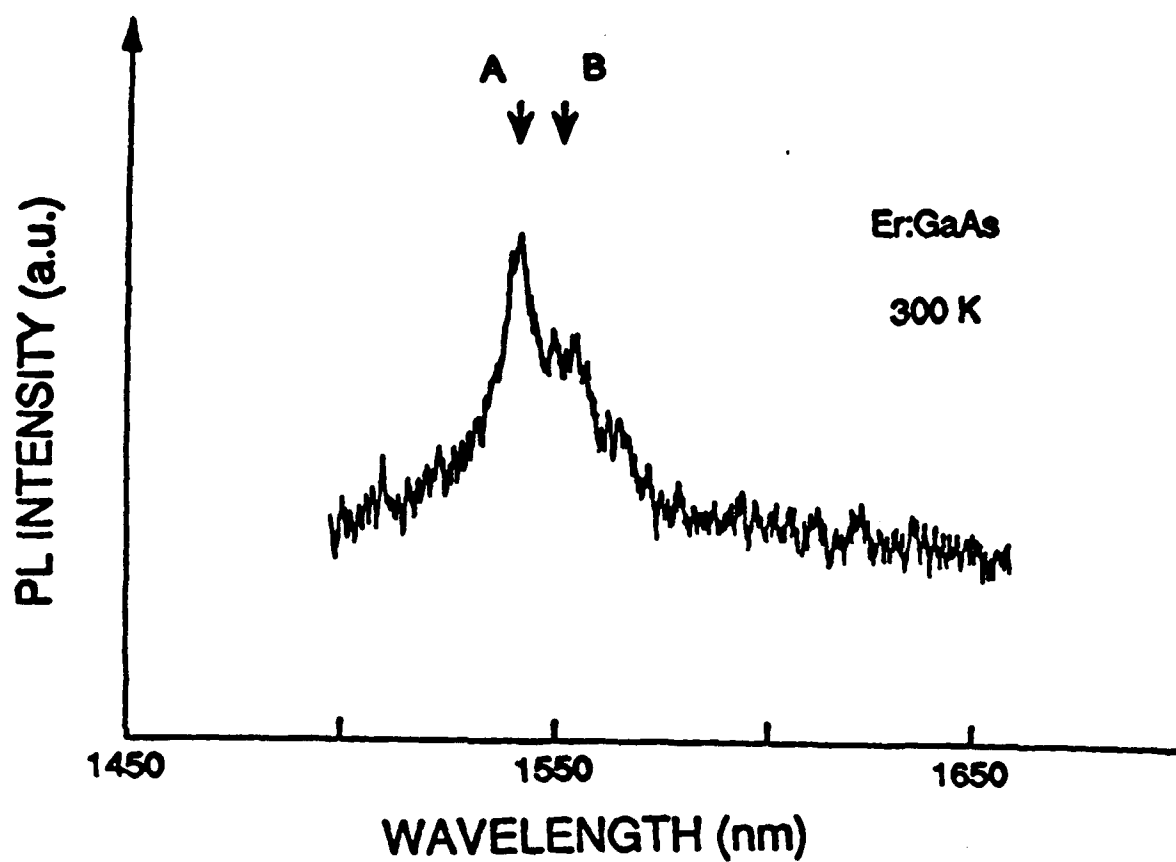


Fig. 8 Room temperature photoluminescence spectrum for an Er-doped GaAs grown at 620°C with $\text{Er}(\text{C}_4\text{H}_9\text{C}_3\text{H}_4)_3$.

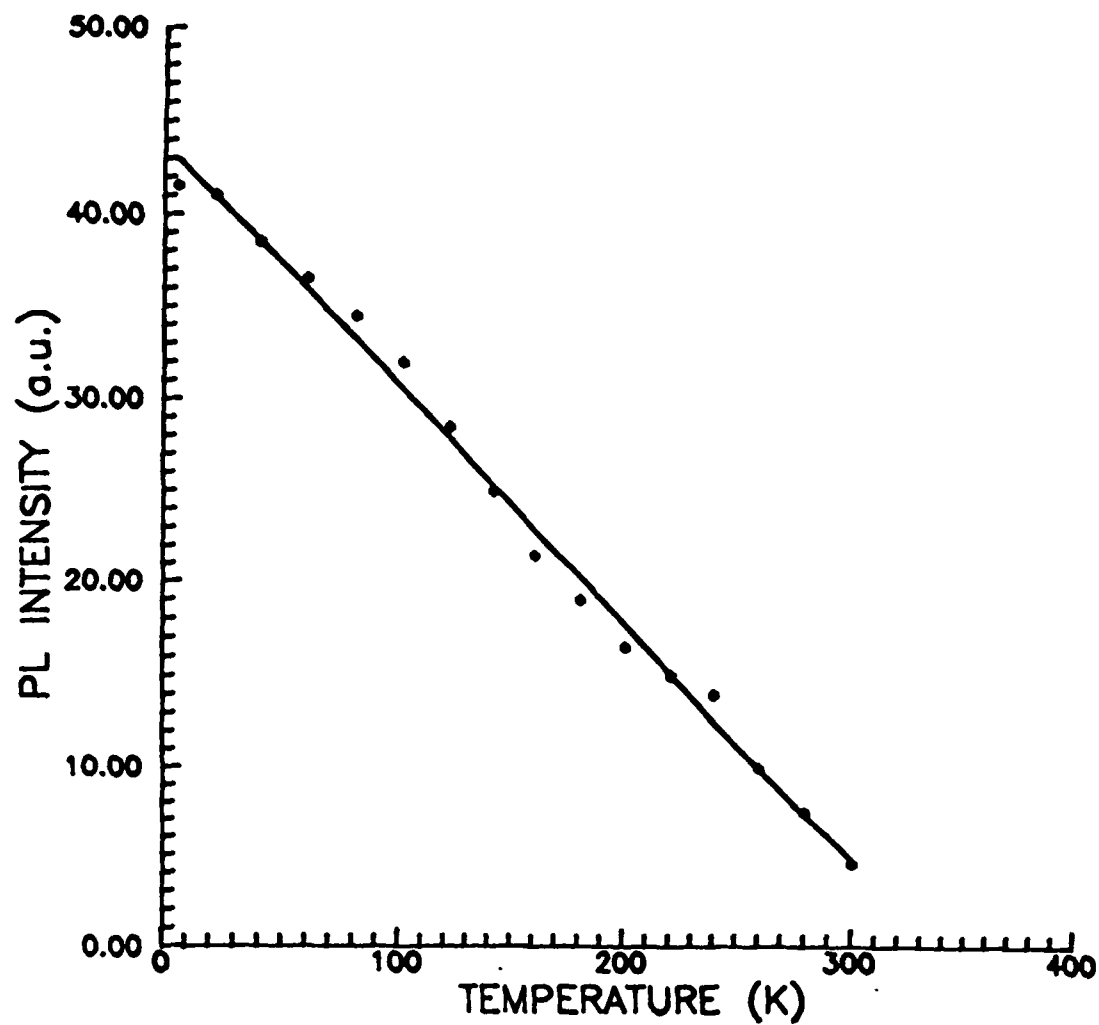


Fig. 9 Temperature dependence of the PL intensity of the intense Er-related emission line A for a GaAs grown at 620°C with V/III ratio of 13.5:1.

3. Summary and Conclusion

Photoluminescence and Secondary Ion Mass Spectroscopy measurements showed that epitaxial layers of Erbium doped Gallium Arsenide and Erbium doped Aluminum Gallium Arsenide were grown during this effort by the Metal Organic Vapor Deposition method. The light emission at $1.54\mu\text{m}$, characteristic for intra-atomic transitions in the $\text{Er}(3+)$ ion was studied in GaAs:Er . Growth parameter were optimized for highest quantitative emission efficiency. The temperature dependence of the emission was studied and it agreed with previously reported trends. The fact that we succeeded in growing these layers by MOCVD is significant because this growth method is the method of choice for a future large scale exploitation of the unique features of Erbium related light emission. *The results of the described work are to be presented at the Materials Research Society Meeting, San Francisco, April 1993, in paper E1.2.*

4. Suggestions for Future Work

Several options exist for future research and development for the ultimate purpose of manufacturing temperature independent, light emission or amplification devices with ultr-narrow spectral band width. *Microtronics Associates, Inc.* continues its effort toward this goal. and seeks funding for the following options: 1) Increasing the Erbium related emission by codoping with other elements, including Oxygen. 2) Growth of double-heterostructures of GaAs/AlGaAs for efficient light emission caused by current injection. 3) Investigation of other Rare Earth ions for higher efficiency light emission.

4) Using Silicon or SiO₂ as host for the RE ions. 5) Placement of the optical active (RE doped) material in a dielectric cavity for achieving gain and directivity of the emitted light.

5. Personnel

The effort was carried out under the leadership of Dr. Victoria Coon, PI. Senior Investigator at *Microtronics Associates, Inc.* was Dr. Xiao Ming Fang; he was assisted part time by Dr. V. Shadrin and technicians. Work under subcontract to the University of Pittsburgh was performed in the Department of Electrical Engineering by Professor H. K. Kim and his students. Furthermore, the collaboration of Professor D. W. Langer was enlisted by a separate consultation agreement.

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