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# Chemical Beam Epitaxy of III-V Semiconductors

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Chemical beam epitaxy (CBE) is the newest development in epitaxial growth technology. It combines many important advantages of molecular beam epitaxy (MBE) and organo-metallic chemical vapor deposition (OM-CVD). Our results undisputedly established CBE as a superior technique for producing extremely high quality multi-layer heterostructures and advanced the epitaxial growth technology beyond both MBE and OM-CVD.

## 1. Introduction

Chemical beam epitaxy (CBE)[1] is the newest development in epitaxial growth technology. It combines many important advantages of molecular beam epitaxy (MBE)[2] and organo-metallic chemical vapor deposition (OM-CVD),[3] both of which were first developed in 1968, and advances the epitaxial technology beyond both techniques. In CBE, unlike MBE which employs atomic beams (e.g. Al, Ga, and In) evaporated at high temperature from elemental sources, all the sources are gaseous at room temperature. The Al, Ga and In are derived by the pyrolysis of their organo-metallic compounds, e.g. trimethylaluminium, triethylgallium and trimethylindium, at the heated substrate surface. The $As_2$ and $P_2$ are obtained by the thermal decomposition of their hydrides passing through a heated baffled cell. Unlike OM-CVD, in which the chemicals reach the substrate surface by diffusing through a stagnant carrier gas boundary layer above the substrate, the chemicals in CBE are admitted into the high vacuum growth chamber in the form of a beam. Therefore, comparing with MBE, the main advantages include: (1) The use of room-temperature gaseous group-III organo-metallic sources that simplifies multi-wafer scale-up; (2) Semi-infinite source supply and precision electronic flow control with instant flux response, (which is suitable for the production environment); (3) A single group-III beam that guarantees material composition uniformity; (4) No oval defects even at high growth rates, (important for integrated circuit applications) and (5) High growth rates if desired. Comparing with OM-CVD, these include: (1) No flow pattern problem encountered in multi-wafer scale-up; (2) Beam nature produces very abrupt hetero-interfaces and ultra-thin layers conveniently; (3) Clean growth environment; (4) Easy implementation of in-situ diagnostic instrumentations e.g. RHEED and RGA; (5) Compatible with other high vacuum thin-film processings e.g. metal evaporation, ion beam milling, and ion-implantation.

## 2. Growth Kinetics of CBE

A gas handling system similar to that employed in organo-metallic chemical vapor deposition (OM-CVD) with precision electronic mass flow controllers was used for controlling the flow rates of the various gases admitted into the growth chamber as shown in Fig. 1.

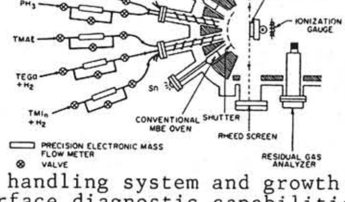


Fig. 1 Gas handling system and growth chamber with in-situ surface diagnostic capabilities incorporated in a CBE system.

Hydrogen was used as the carrier gas for transporting the low vapor-pressure group III alkyls. Separate gas inlets were used for group III organo-metallics and group V hydrides. A low-pressure arsine ($AsH_3$) and phosphine ($PH_3$) cracker[4,5] with a reduced input pressure of ~200 torr was maintained on the high-pressure side of the electronic mass flow controller was used. The cracking temperature was ~920° C. Complete decomposition of arsine and phosphine into arsenic, phosphorous, and hydrogen was routinely achieved as observed by the absence of arsine and phosphine peaks inside the growth chamber with an in-situ residue gas analyzer.

Triethylgallium (TEGa) maintained at 30°C, trimethylindium (TMIn) at 37°C, and trimethylaluminum (TMAl) at 25°C were used. The TEGa, TMIn and TMAl flows were combined to form a single emerging beam impinging line-of-sight onto the heated substrate surface. This automatically guarantees composition uniformity[6]. The typical growth rates were 2-3 μm/h for GaAs, 4-6 μm/h for AlGaAs 3.65 μm for GaInAs and 1.5-2.5 μm for InP although even higher rates have been achieved. Such growth rates are higher than those typically used in MBE.

In this growth technique, the growth kinetic is completely different from that of conventional MBE and in some respect also quite different from OM-CVD as depicted in Fig. 2.

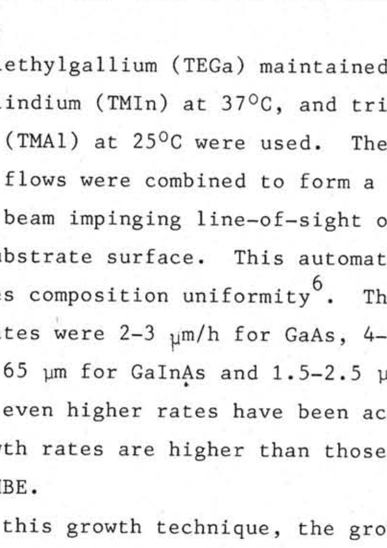


Fig. 2 (a), (b), and (c) depict the growth kinetics involved in conventional MBE, OM-CVD and CBE, respectively.

In conventional MBE, the atomic group III beams impinge on the heated substrate surface, migrate into the appropriate lattice sites, and deposit epitaxially in the presence of excess impinging group V molecular beams, usually dimers or tetramers. Since the sticking coefficient of the group III atoms on the substrate surface at the usual growth temperatures is practically unity, the growth rate is determined by the arrival rate of the group III atomic beams. No chemical reaction is involved in deriving the group III atoms at the substrate surface as they are generated by thermal evaporation from solid elemental sources. The same growth kinetics occurs in the group V gas source MBE demonstrated by Morris and Fukui[4], Calawa[5], and Panish[7], in which they derive the group V dimer and possibly even monomer species by thermally cracking the group V hydrides instead of the usual thermalization from an elemental condensed phase source.

In atmospheric or low-pressure OM-CVD[8,9], the group III alkyls in the gas stream of $H_2$ and $N_2$, Ar or He are already partially dissociated. They then diffuse through a stagnant boundary layer above the heated substrate, further dissociation yield the atomic group III elements. These then migrate into the appropriate lattice sites and deposit epitaxially by capturing a group V atom derived as a result of thermal dissociation of the hydrides either at the heated substrate surface or, by thermal precracking upstream. For the usual growth temperature employed, the growth rate is limited by the diffusion rate of the group III alkyls, which can be partially or completely dissociated, through the boundary layer.

In CBE, the beam of group III alkyl molecules impinges directly line-of-sight onto the heated substrate surface as in conventional MBE process. There is no boundary layer in front of the substrate surface nor are there space-flight molecular collisions on the path because of the long mean-free-path of the molecules at the pressure of $<5\times10^{-4}$ Torr. Thus, after a group III alkyl molecule strikes at the substrate surface, it can either acquire enough thermal energy from the heated substrate and dissociate all its three alkyl radicals leaving the elemental group III atom on the surface or reevaporate undissociated or partially dissociated. The probability of whichever process occurs depends on the substrate temperature and arrival date of the organo-metallics. Thus, at a high enough substrate temperature the growth rate is determined by the arrival rate of the group III alkyls, while at lower substrate temperature the growth rate is limited by the surface pyrolysis rate.

3. Extremely High Quality $Ga_{0.47}In_{0.53}As$ by CBE

GaInAs lattice matched to InP has emerged as a very important semiconductor material. High electron mobility and peak velocity are attractive for ultra-high speed devices. The band gap of 0.74eV (1.65 μm) is ideal for photodetectors in optical communication systems in the optimum wavelength range of 1.3 - 1.6 μm. Thus, it is very important to demonstrate here that very high quality InGaAs can be grown by CBE. Full widths at half-maximum intensity of the (004) Bragg reflection peak as small as 24 arcs were obtained from InGaAs epilayers 4-6 m thick. Such linewidth is the narrowest reported thus far for an InGaAs epilayer grown by any vapor phase technique reported in literature. Such extreme composition uniformity was also supported by results from Auger depth profiles and 2K photoluminescence (PL) measurements. Very intense efficient luminescence peaks due to excitonic transitions with linewidths (FWHM) as narrow as 1.2 meV were obtained as shown in Fig. 3.

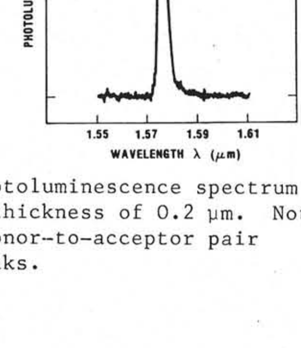


Fig. 3 The 2K photoluminescence spectrum for an epilayer with a thickness of 0.2 μm. Note the absence of the donor-to-acceptor pair recombination peaks.

This again represents the narrowest linewidth ever reported for InGaAs grown by any technique.[10] In fact, such a linewidth represents the narrowest linewidth ever measured for any alloy semiconductor. Further, the photoluminescence spectra reveal that donor-to-acceptor pair recombination was nearly absent. This indicates that the InGaAs is of very high purity. Hall measurements of 2-5 μm 4 thick epilayers grown directly on InP substrates have mobilities of 10,000-12,000 and 40,000-57,000 $cm^2/Vs$ at 300 and 77K with $n=5X10^{14}-5X10^{15} cm^{-3}$. These values are among the highest of all the results for GaInAs grown by other techniques[9,11-13] as compared in Fig. 4.

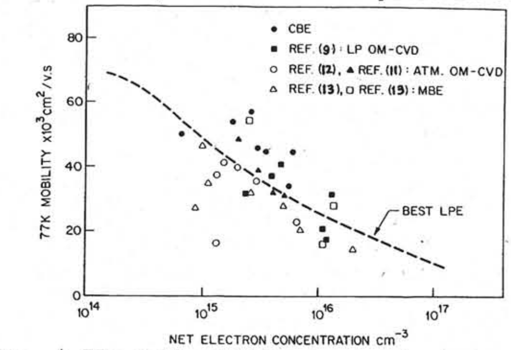


Fig. 4 77K Hall mobility versus background net electron concentration for closely lattice-matched InGaAs epilayers without two-dimensional electron gas effect.

4. Quantum Well Heterostructures by CBE

One extreme way of testing the technique is to evaluate the qualities of the quantum well (QW) heterostructures grown by it. High quality QW's should have smooth and abrupt ("squareness" of the QW) interfaces, few background impurities, and a high PL efficiency. Quantum wells of $GaAs/Al_xGa_{1-x}As$ and $Ga_{0.47}In_{0.53}As/InP$ have been grown by CBE and characterized by low temperature PL and excitation spectroscopy techniques.

For $GaAs/Al_xGa_{1-x}As$ single and multiquantum well heterostructures, studies using low temperature photoluminescence and excitation spectroscopy techniques show that on the average the samples are similar in quality to similar structures grown by MBE and in certain characteristics superior to the MBE ones. Further, in some important respects, they are also superior to those grown by OM-CVD. The very small red shifts observed between emission and $E_{1h}$ with continuous growth shows that the emission is dominated by $E_{1h}$ excitons. An interface roughness of $L \lesssim \pm a/2$ and very square wells (undistorted) even with continuous growth are inferred from the excitation spectra. Unusually sharp exciton transition peaks up to $E_{3h}$ including forbidden transitions were obtained as shown in Fig. 5.

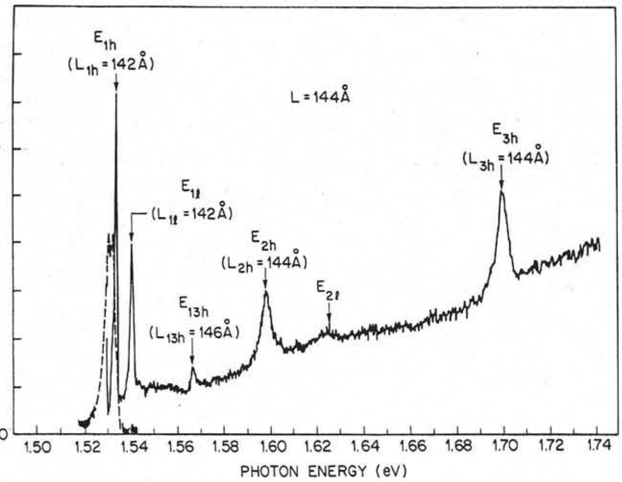


Fig. 5 Photoluminescence (dashed) and excitation (solid) spectra at 6K from a single GaAs/$Al_{0.5}Ga_{0.5}As$ quantum well, L = 144 Å, grown by CBE. The excitation spectrum was obtained with detector set at 1.53 eV. Note the unusually sharp and intense exciton transition peaks even up to $E_{3h}$. Both spectra were taken with 0.23W/$cm^2$ of incident pump power. For other details see text.

Such quality lineshape has not been obtained with and MBE- or OM-CVD-grown quantum wells so far[14]. The excitation spectra also show no evidence of band filling due to holes or electrons from the $Al_xGa_{1-x}As$ layers which is a common problem with the OM-CVD technique[15]. From this study we also conclude that the GaAs and $Al_xGa_{1-x}As$ materials are of very high purity.

Extremely high quality $Ga_{0.47}In_{0.53}As$/InP quantum wells with thickness as thin as 6 Å have also been prepared by chemical beam epitaxy[16]. Emission as short as 1.09 μm at 2K (1.14 μm at 300K) was obtained. Very sharp intense efficient luminescence peaks due to excitonic transitions were obtained from all quantum wells as shown by an example in Fig. 6.

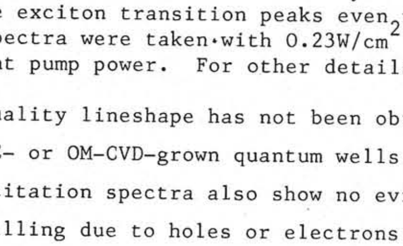


Fig. 6 A typical photoluminescence spectrum from a stack of quantum wells with different thicknesses separated by 700 Å InP barriers at 2K. The pumping power is 1 μW and pumping area is ~50 μm diameter.

The PL linewidths at 2K were the narrowest that have been ever reported for $Ga_{0.47}In_{0.53}As$ quantum wells grown by any technique[17-23] as compared in Fig. 7.

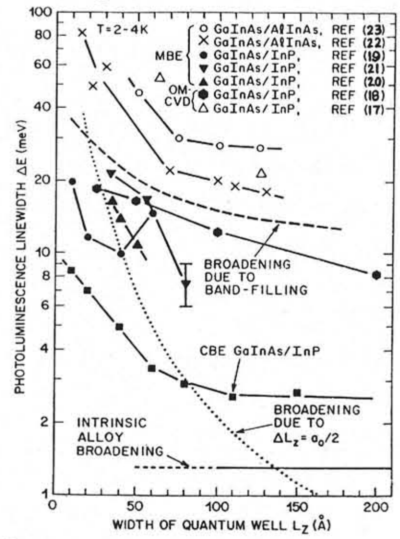


Fig. 7 Represents a compilation of PL linewidths (FWHM) as a function of well thickness for all published $Ga_{0.47}In_{0.53}As/Al_{0.48}In_{0.52}As$ quantum wells grown by OM-CVD and MBE together with present results by CBE. The dashed curve was calculated broadening due to band-filling from impurities. A sheet carrier density of $2X10^{11}$ $cm^{-2}$ was used. The dotted curve was calculated broadening due to "effective" interface roughness, $L_z$, of $a_o/2$ assuming finite-height barriers.

In fact, such narrow linewidths for $Ga_{0.47}In_{0.53}As$ quantum wells are, for the first time, at least equal to the narrowest linewidths ever reported for the perfected GaAs/AlAs and GaAs/$Al_xGa_{1-x}As$ quantum wells. These linewidths indicate the "effective" interface roughness to be 0.12 lattice constant, which can be interpreted as that the quantum well was largely consisting of a big domain of the same thickness $L_z$ perforated with small domains of $(L_z + a_o/2)$, where $a_o$ (=5.86 Å) is the lattice constant. No broadening due to band filling from impurities was found. Alloy broadening in $Ga_{0.47}In_{0.53}As$ was limited to the intrinsic value of 1.3 meV. Also, for the first time in $Ga_{0.47}In_{0.53}As$ quantum wells, the measured PL energy upshifts were in excellent agreement with theoretical values. We believe such superior quantum wells were possible by CBE due to different growth chemistries occuring in CBE when compared with MBE and quick composition transition and cleaner environment in CBE then in OM-CVD.

5. Opto-Electronic Device Applications

To further demonstrate the capability of CBE as a growth technique for preparing high optical quality multilayer heterostructures, both photodiodes and current injection lasers were fabricated for evaluation.

a. $Ga_{0.47}In_{0.53}As/InP$ p-i-n Photodiodes with Very Low Leakage Current

Two types of mesa-type InGaAs/InP p-i-n photodiodes have been fabricated from wafers grown by CBE[24]: (1) a conventional diffused In GaAs homojunction and (2) a novel InP/In GaAs/InP double heterojunction. Both types of devices have exhibited very low dark current, good quantum efficiency of 70% (without anti-reflection coatings) and transit-time-limited pulse response. The lowest dark currents, less than 1 nA at -10V bias, have been achieved with the double heterojunction devices in spite of the fact that the p-n junction is coincident with a heterojunction interface as shown in Fig. 8.

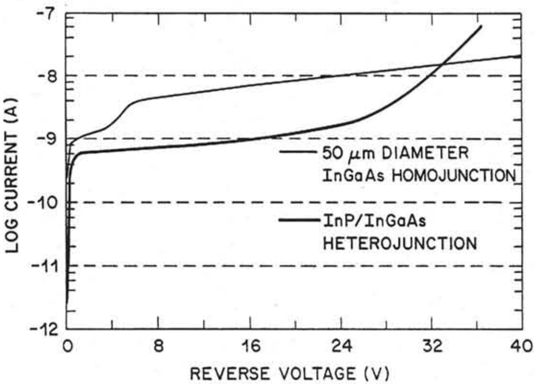


Fig. 8 Typical dark current versus voltage of Type I and Type II photodiodes grown by CBE.

This attests to the excellent quality of heterojunction interfaces grown by CBE. Such results are among the best p-i-n photodiodes grown by other techniques.

b. High Performance $Ga_{0.47}In_{0.53}As$ Photoconductive Detectors

Highly sensitive, planar, interdigited photoconductive detectors on undoped $Ga_{0.47}In_{0.53}As$ lattice-matched on a semi-insulating InP substrate was grown by CBE.[25] The devices exhibit intensity dependent gains as high as 7000, gain-bandwidth products of 20 GHz, detectivities as large as $10^2$ cm $Hz^{1/2}W^{-1}$ at 300°K, and responsitivites close to 3000 A/W at ~ = 1.3 μm. These results are similar to the highest performance characteristics obtained with $Ga_{0.47}In_{0.53}As$ photoconductive detectors that are grown by well established techniques.

c. Very Low Threshold $GaAs/Al_xGa_{1-x}As$ Double-Heterostructure Lasers

Chemical beam epitaxially grown DH lasers[26] have achieved current threshold densities as low as the best MBE-grown lasers[27] and those of OM-CVD and liquid-phase epitaxy (LPE) as compared in Fig. 9.

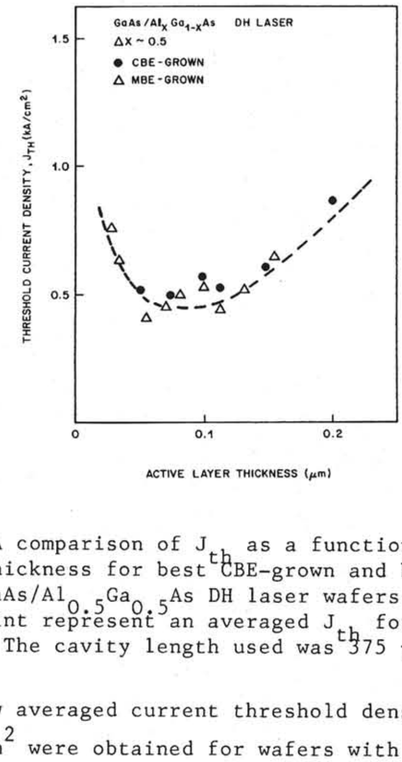


Fig. 9 A comparison of $J_{th}$ as a function of active layer thickness for best CBE-grown and best MBE-grown $GaAs/Al_{0.5}Ga_{0.5}As$ DH laser wafers. Each data point represent an averaged $J_{th}$ for each wafer. The cavity length used was 375 μm in all cases.

Very low averaged current threshold densities of ~500A/cm$^2$ were obtained for wafers with active layer thicknesses of ~500-1000Å and confinement layers of $Al_{0.5}Ga_{0.5}As$.

d. Very Low Threshold $Ga_{0.47}In_{0.53}As/InP$ Double-Heterostructure and Multi-quantum Well Lasers

$Ga_{0.47}In_{0.53}As/InP$ DH and MQW lasers emitting at 1.47-1.72 μm have also been successfully prepared by CBE[28]. Fig. 10 shows the light output versus pulsed injection current for a broad-area ~375 μm x 200 μm MQW laser at different heat-sink temperatures. The very low threshold current densities of 1.3 kA/cm$^2$ and 1.5 kA/cm$^2$ obtained for DH and MQW laser wafers, respectively,

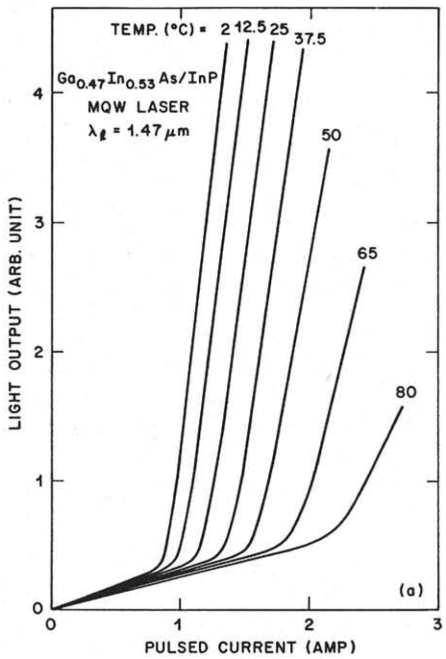


Fig. 10 The light output versus pulsed current amplitude for a typical $Ga_{0.47}In_{0.53}As/InP$ MQW laser at different heat-sink temperatures. This wafer has 8 quantum wells of 70 Å separated by 150 Å InP barriers.

suggest that the present materials and heterointerfaces are superior to those obtained previously by other techniques. In fact, these $J_{th}$'s are the lowest obtained thus far for such lasers. Such results are consistent with recent measurements on $Ga_{0.47}In_{0.53}As$ epilayers and $Ga_{0.47}In_{0.53}As/InP$ quantum well structures. Differential quantum efficiency of ~18% per facet was obtained for both DH and MQW lasers. Further, as shown in Fig. 11 we were also able to show that there was a definite improvement in $T_o$ from ~35–45 K for DH laser wafers to ~65–80 K for MQW laser wafers in contrast to previous experimental results. This, we believe, is due to the improvement in both material and heterointerface qualities of the present layer structures.

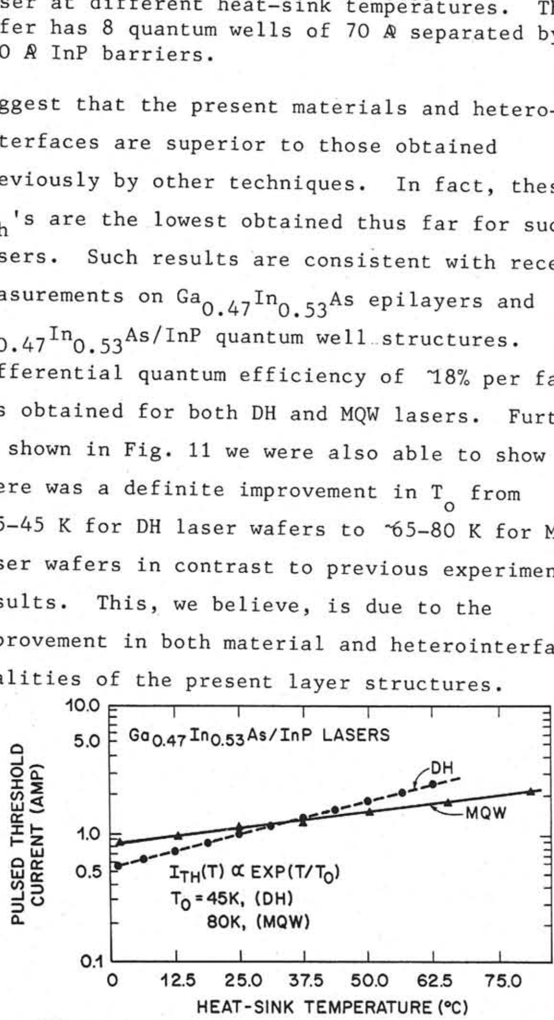


Fig. 11 A comparison of the threshold-temperature dependence of a $Ga_{0.47}In_{0.53}As/InP$ DH and a MQW laser.

e. High-Mobility Two-Dimensional Electron Gas at $Ga_{0.47}In_{0.53}As/InP$ Hetero-interface

Shubnikov-de Haas, quantum Hall effect, and cyclotron resonance measurements revealed the existence of a high mobility, two-dimensional electron gas at the $Ga_{0.47}In_{0.53}As/InP$ heterointerface grown by CBE[29]. An example is given in Fig. 12. Enhanced electron mobilities were as high as ~$130X10^3 cm^2/Vs$ at 4.2K.

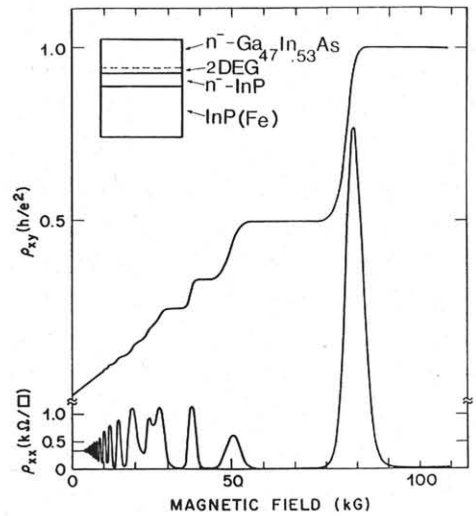


Fig. 12 The longitudinal resistivity, $\rho_{xx}$, and Hall resistivity, $\rho_{xy}$, as a function of magnetic field from 0 to 120 kG. The temperature is around 350 mK. In $_{xx}$, Shubnikov-de Haas oscillations are observed above ~2 kG, with zero resistance states, associated with the quantized Hall effect, in the vicinity of 67 kG and 120 kG. In Lxy, Hall plateaus are observed near 33 kG, 42 kG, 67 kG, and 120 kG, corresponding to Landau level filling factors, i, of around 4, 3, 2, and 1. The i=1, 2, and 3 plateaus are quantized to $h/e^2$, $h/2e^2$, $h/3e^2$, respectively, to better than 0.5%. The inset shows the layer structure.

Figure 13 gives a comparison with previous results[30-36]. Shubnikov-de Haas oscillations were observable up to a Landau level filling factor of around 50, corresponding to a Landau level index of 25 indicating that the sample is of high quality.

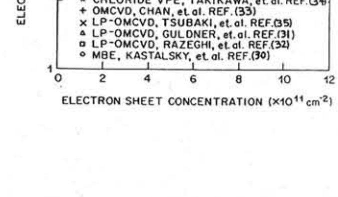

Fig. 13 A comparison of 2DEG mobilities for $Ga_{0.47}In_{0.53}As/InP$ grown by various techniques as a function of electron sheet concentration. The solid curve is the calculated mobility limited by alloy scattering versus electron sheet concentration in the channel as obtained by Basu and Nag, Ref. (36).

6. Conclusion

Our results have undisputedly established CBE as a superior epitaxial technique for producing extremely high quality multi-layer heterostructures for opto-electronic applications. It advances the epitaxial technology beyond both MBE and OM-CVD.

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