

AOARD REPORT

Chemical Beam Epitaxy, Japan

July 21-23, 1993
H. Seki
IBM-Almaden

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This report summarizes the 4th International Conference on Chemical Beam Epitaxy and Related Growth Techniques, held in Nara, Japan, 21-23 Jul. 93. The report also assesses CBE technology in Japan, and gives a brief overview of the government, academic and industry players.

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A Report on the 4th International Conference on
CHEMICAL BEAM EPITAXY AND RELATED GROWTH TECHNIQUES
 Nara, Japan, July 21-23, 1993

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INTRODUCTION

The Fourth International Conference on Chemical Beam Epitaxy and Related Growth Techniques (ICCB-4) was held in the Shin-Kohkaido (New Public Hall), Nara, Japan, on July 21-23 1993. The related growth techniques includes the two techniques of molecular beam epitaxy (MBE) and metalorganic chemical vapor deposition (MOCVD) from which CBE has evolved. The total attendance was 160 compared to about 180 for the last ICCBE-3 held at University of Oxford, UK, in September, 1991 reflecting the generally depressed business climate. Although this was an international conference the attendance from abroad (outside Japan) was not very high, 36, or 22%. Also noticeable was that US participation was less than from Europe, i.e., 14 vs 17. The US activity in this area tended to be oriented towards the military application so this in itself may not mean reduced commitment. Nevertheless it is an index that should be of some concern and examined to see if there is any correlation with other statistics.

The technologies covered by this conference, highly controlled epitaxial growth of thin films primarily of III-V and II-VI type compound semiconductors, are at the heart of device fabrication for the coming optoelectronic technical revolution. How soon and in which specific areas this revolution will reach its peak may be open to debate, but that it has already started is unquestioned. It will have broad impact in many areas, long range communications, local area networks, switching, high speed circuitry, optical storage, computers, displays, smart systems, just to name a few. Thus having a technical community that is up to date and competent in this area is vital to any major industrial nation.

It is probably appropriate to present here a brief discussion of the technology covered in this conference. (A list of the most commonly used acronyms in this area is provided at the end). The most widely used epitaxial growth technique for compound semiconductors in the industry at present and considered to be the most cost effective is MOCVD or MOVPE. (These terms seem to be used interchangeably). This is due

most likely to its close relation to the doping process used widely in the well established Si semiconductor industry and the fact that the requirements seemed not to be stringent at first (the process does not require ultra-high vacuum and is done in the range of a few torrs to atmospheric pressure) and is easily scaled up for manufacturing. The techniques preceding this were liquid phase epitaxy (LPE) and vapor phase epitaxy (VPE) both of which are equilibrium processes and don't have the control for monolayer accuracy. The early reactor was made of a quartz tube inside a conventional cylindrical furnace and there are still many quartz reactors in use today. The feedstock for this process are generally gases, typically metalorganics typically trimethyl gallium (TMG), triethyl gallium (TEG), trimethyl aluminum (TMA) or hydrides such as arsine (AsH_3) and phosphine (PH_3). These gases are transported by carrier gases to the substrates which are heated to cause the feedstocks to undergo thermal decomposition and deposition of the desired atoms. The technique generally involves chemistry in the gas phase and walls as well as on the substrate and the flow pattern of the gases is not simple. Thus the process is complex and not amenable to simple analysis. Until recently there was no technique to monitor the deposition process in-situ for MOCVD. However the reflectance difference spectroscopy (RDS), an optical technique, is now available to distinguish between As-terminated and Al- or Ga-terminated surfaces of GaAs or AlAs layer. MOCVD is the main technique used by multilayered wafer suppliers. Compared to MBE and CBE, to be described, MOCVD's consumption of the feedstock is quite high. This becomes important not only from the cost of the feedstocks but also from safety and environmental considerations when using highly toxic gases such as arsine and phosphine.

MBE is a technique that evolved almost parallel to MOCVD. It started out more as a research tool but soon became very important in the manufacture of GaAs/GaAlAs lasers. The deposition chamber is an ultra-high vacuum (UHV) system and the deposition sources consist of vapor from pure solids of the elements generated thermally or by electron beams. The source temperature is computer controlled by feedback from a rate monitor. Since the process is in UHV it can be monitored *in situ* by reflection high energy electron diffraction (RHEED) and RDS, so very precise heterojunctions and superlattices can be made. It is significant that recent MBE machines made for the manufacture of GaAs/GaAlAs devices are production scale multiwafer types with which very high level of uniformity in composition and thickness is consistently being achieved. However there are some elements for which MBE has difficulty maintaining good control, e.g., the vapor pressure of P is dependent on its allotropic form which will vary depending on the thermal history of the solid.

CBE, which is the principal topic of this conference, evolved to overcome the shortcomings of the above two techniques and combine their strengths. During its

development other terms such as gas source MBE (GSMBE) and metalorganic MBE (MOMBE) have been used and though some may make distinctions they are often used interchangeably. The important point is that these terms all imply that the deposition is carried out under molecular flow conditions, i.e., at pressures $< 10^{-3}$ Torr and it is possible to have various combinations of gas and solid sources. Thus the reaction chamber is essentially similar to the MBE systems and is consistent with UHV requirements. Ideally all the feedstocks are gaseous and introduced from feedthroughs located near each other or preferably from one feedthrough at low temperature. Chemistry in the gas phase or on the chamber walls is negligible and only takes place at the substrate. The result would be a simpler, cleaner system with better control of the deposition process providing uniform deposition over large areas. In reality this ideal has not yet been achieved, e.g., some of the feedstocks require precracking at specially designed heated cells or the chemical interaction occurs at places other than the substrate, etc. Many papers in this conference are directed to the achievement of this ideal.

It is significant that the investigators of CBE usually have been or continue to be active in the other related epitaxial techniques so they are conscious of the relative merits of the different approaches. Experience gained in one area is quickly applied to the other areas and in this respect CBE is particularly useful in providing fundamental understanding to processes in MOCVD because of the available *in-situ* analytical capability and the relative simplicity of the chemistry. In some circles CBE, MOMBE, GSMBE are considered a subset of MBE as in the International Conference on MBE. In such cases the traditional MBE is referred as solid source MBE (SSMBE) to distinguish it from the other MBE techniques.

ASSESSMENT OF CBE TECHNOLOGY IN JAPAN

It is quite evident that Japan is actively involved in every important aspect of the CBE technology as it pertains to potential application in optoelectronics and high speed circuitry. The surface emitting (SE) laser in the 1.3-5 μ range is considered to be a critical device for use with low loss fluoride optical fiber and papers V-1 from the Precision and Intelligence Laboratory of Tokyo Institute of Technology, V-5 and VII-2 from the NTT Opto-electronics Lab indicate very good work along this line. Another important area is the blue green emitting diodes which have application potential in flat panel, sharp red green blue (RGB) displays and optical discs, and here the Japanese have had a long history in II-VI materials. This has been put to good use in the pursuit of the blue green diode laser as seen in the activity of M. Kobayashi of Chiba University although this did not appear explicitly in this conference. Besides the work on the II-VI type materials work relevant to the blue diodes using SiGe/Si heterojunctions or blue diodes using the

GaN systems are seen in papers VI-2 and IX-1, respectively. In the exploration of new CBE precursors the work done at Hiroshima University has been extensive and relevant as seen in II-3 and IV-9. Thus over a relatively wide range the quality of the work is generally quite good.

This is the result of these areas being recognized by the government, i.e., Ministry of International Trade and Industry and the Ministry of Education, Science and Culture to be of importance to the future economic well being of Japan. The facility required to carry out investigations in CBE alone is quite costly, since it involves UHV compatible equipment, a number of surface analytical instrumentation, sophisticated control electronics and handling of toxic gases. These requirements exceed what is needed to enter into minimal hi T_c superconductor or fullerene research. Furthermore besides having the capability to do CBE it must usually be supported by some equipment for characterization of the deposited film but ideally it is desirable to have a level of semiconductor device fabrication capability, i.e., clean rooms, laminar flow hoods, lithographic facilities etc., and with this kind of capital investment a minimal staff is required to maintain the facility. Thus the establishment of CBE research is an expensive proposition and cannot be entered without considerable financial commitment which is being provided by the government. The analogue of this in the US are the grants from NSF, DARPA, DOE and DOD.

Based on the papers presented in this conference alone it is possible to identify a number of key Japanese laboratories active in CBE. The list below are some of the main laboratories associated with academic institutions with the professor in charge.

Center for Integrated Systems (CIS)
Hiroshima University, Professor Z. Hirose

Institute of Scientific and Industrial Research (ISIR)
Osaka University, Professor S. Gonda

Precision and Intelligence Laboratory (PII.)
Tokyo Institute of Technology, Professor K. Iga

Research Center for Advanced Science and Technology (RCAST)
The University of Tokyo Professor Y. Shiraki

Research Center for Interface Quantum Electronics (RCIQE)
Hokkaido University, Professor H. Hasegawa

Research Institute of Electrical Communication (RIEC)
Tohoku University, Professors Ohmi and Nishizawa

Department of Electrical and Electronics Engineering
Chiba University, Professor A. Yoshikawa

The top six are equipped to engage in general semiconductor research starting from material preparation to device fabrication and testing. They are all engaged in CBE to some extent and usually have one or two of the MOCVD, OMVPE and MBE capabilities. These facilities are mostly established by Grant-in-Aid for Scientific Research on Priority Area issued by the Ministry of Education, Science and Culture. Among these the top 4 are currently very productive but the rest are growing quite rapidly. Of these the RCIQE at Hokkaido University is probably the newest. I. Suemune, who was active at CIS of Hiroshima University, has just gotten a professorship there and was describing the clean room which is larger than the one in Tohoku University. The EEE department of Chiba University is also listed here since they have been quite active using CBE in the development of the II-VI type blue-green diodes and lasers in close collaboration with New Japan Radio Corporation in Tokyo. For a technique like CBE whose significance is closely coupled to device fabrication it seems that it is important that there are a number of facilities which allows all the interrelated technologies to operate in concert to fabricate a meaningful device. Without this type of collaborative activity and the feedback it provides an isolated step by itself in spite of the excellence that may exist has a hard time developing to be utilized on a production scale on its own.

Although the following laboratories are now corporations their origin lies with the MITI and still have considerable relationship with the government. They have indicated notable activity in CBE in this conference.

Optoelectronics Technology Research Laboratory
Optoelectronics Technology Research Corporation

Opto-electronics Laboratory, Basic Research Laboratory
NTT, Atsugi

The NTT laboratories are considered to be the Japanese counter part of Bell Labs and their motivation in the field of communication can be expected to be similar. Besides these there are also the Electro Technical Laboratory, Tsukuba sponsored by MITI, but so far they have not been very committed to CBE. The industrial laboratories, where one would expect the most interest in CBE, appear to be watching the development of CBE very carefully but still not fully committed. The bulk of their activity still is with the traditional deposition techniques of MOCVD, MBE and MOVPE and this situation can be expected to continue until the economic situation improves or competitive pressures arise from some technical breakthroughs. They have a few people working in

the field ready to scale up whenever necessary. The following are some of the major industrial labs where the knowhow is being prepared.

Hitachi Central Research Center

Fujitsu Laboratories Ltd.,

Materials and Devices Research Laboratories
Toshiba Corporation, Research and Development Center

Central Research Laboratory
Mitsubishi Electric Corporation

Microelectronics Laboratorys
NEC Corporation

The major academic laboratories mentioned above are generally very well equipped but suffer from shortage of good manpower and expense money. This creates an opportunity for industry to send their young technical people on joint studies enabling them to train their personnel and keep up to date in areas they are not yet ready to committ themselves. For this they contribute funding to the laboratories and this arrangement is particularly beneficial for small and medium size companies. Examples of this type of collaboration can be seen in the poster papers, e.g., IV-9, IV-11, VI-2.

There is a general interest and effort in Japan to become more "kokusaiteki" (cosmopolitan) and in the process gain some of the spontaneity and creativity of the western culture. The presence of a number of young foreign (non-Japanese) scientists or engineers working in Japanese laboratories was noticeable at this conference. Just as an illustration, Dr. Philippe Bove had completed his PhD program in France and not being able to find a suitable job in Europe or the US, he chose to take a temporary position about a year ago at the Fujitsu Laboratory. His rational was to learn about a different culture, the "secret" of the Japanese hi-tech business and continue working at some level of technology while earning a reasonable wage. At the lab he is very conscious that he is being watched, so he tries to live up to the expectations of the Japanese, going out of his way to do things in a creative way. He is also studying Japanese and does a reasonably good job of speaking and making astute observation of the Japanese. He knows that he is not being exposed to the most sensitive technology and the work is not to his ideal. Nevertheless he has given a paper at this conference and finds the overall experience worthwhile. Besides it beats being unemployed. He wants to go to the US when the opportunity arises and does not hold much hope for the Common Market. There are probably no average or typical case for foreign scientists in Japan, but Philippe may give the reader an indication that working conditions in

Japan are about on the par with the rest of the free world, technical jobs are still available inspite of the economic slow down.

The development of CBE like technology is also dependent on various support industry. In this respect although the first class laboratories preferred foreign CBE and MBE equipment such as RIBER, there are a number of Japanese suppliers such as Anleva, Nippon Sanso Corp, and ULVAC. There also are a number of chemical company ready to supply precursor compounds such as TRI Chemical Laboratory inc., Sumitomo Electric and Osaka Asahi. The industrial display area was on the slightly sparce side again reflecting the depressed economy. If one could make a guess the moral among the Japanese participants of the conference appeared to be slightly up beat with expectation of progress. With the government committed to spiking the economy by increased spending the laboratories dependent on Government funding are probably faring better than the industrial laboratories.

GROWTH MECHANISMS AND CHEMICAL PRECURSORS

The issues discussed in the sessions on growth mechanisms and chemical precursors were often quite interrelated. Trevor Martin of DRA Malvern, UK, gave a nice review, I-1, of recent developments in the understanding of growth mechanism touching on growth parameter windows, selective area growth, radiation assistance and mechanisms associated with the higher alkyl precursors. As an example he described the series of trialkyl Ga, TMG, TEG, tri-isopropyl gallium (TIPG), tri-isobutyl gallium (TIBG) and tris-tributyl gallium (TTBG) and their effect on C incorporation and their ability to provide larger parameter windows. The paper, I-2, by B. Junno, G. Paulsson, M. Miller and L. Samuelson, Department of Solid State Physics, Lund University dicussed the growth of InGaAs using trimethyl indium (TMI), TEG and tributyl aluminum (TBA) as precursors which did not use precracking. The deposition was monitored *in-situ* by RD and RHEED. A poster paper, IV-6 and IV-7, by S-J. Park et al., of the Electronics and Telecommunications Research Insitute, Korea introduced monoethylarsine (MEAs) as a novel precursor for As deposition. GaAs growth was possible without precracking the MEAs with TMGa or TEGa with substrate temperatures in the range of 540-660°C. The growth rate is very dependent on the IV/III ratio and the majority carrier type is dependent on on the substrate temperature. Higher growth rate and lower substrate temperature is possible with TEGa. The carbon incorporation was claimed to be much lower than in the case using arsine.

The paper, I-3, by Y. Okuno, H. Asahi and S. Gonda, Institute of Scientific and Industrial Research, Osaka University, was of particular interest since they examined the possibility of using computational chemistry to analyze the growth mechanism of III-V semiconductors in CBE. *Ab-initio* molecular orbital calculations of some of the

representative precursor molecules as well as calculations on simple cluster models of the semiconductor surfaces of the type $\text{II}_3\text{III-VII}_3$ were carried out using the semi-empirical technique of MNDO-PM3 provided in MOPAC Ver.6.0. The fact that they were able to obtain results which were consistent with a number of observed trends in CBE is very significant. For example, it was shown that the Al-C bond strength weakens as the number of carbon increases in the alkyl group of the organo-Al precursors and this is consistent with the fact that the C-incorporation during CBE growth using organo-Al precursors. Along this line there was a Poster paper IV-1, by Y.S. Hiraoka and Mashita, Research and Development Center, Toshiba Corp., which reports on *ab-initio* investigation comparing the thermal decomposition of TMGa into a methyl radical and $\text{Ga}(\text{CH}_3)_2$ and the reaction of a hydrogen molecule with TMGa to form methane and $\text{GaH}(\text{CH}_3)_2$. Calculations were done at the HF/MIDI-4* level along a reaction path where the Ga-C distance was varied. The results indicate how the hydrogen carrier gas may be aiding the decomposition process. It has been expected that the availability of cheaper and greater computational power from work stations and the development of user friendly software will bring the tools of computational chemistry closer to the "bench chemist". These papers are indications that this is happening and this will result in better understanding of the chemical processes by the investigators shortening the time to discovery of important trends and new precursors.

The paper I-4, by M. Yoshimoto, T. Hashimoto, Pablo Vaccaro and H. Matsunami, Department of Electrical Engineering, Kyoto University described a laser enhanced process for the growth of GaP in which UV photons aid the decomposition of the TEGa adsorbed on the substrate. Operating at a substrate temperature at which the growth rate of GaP becomes very small without laser irradiation, they supply both TEG and phosphine, and control growth with a combination of N_2 laser pulses (337nm, 10nsec, 2mJ) and the TEGa flow rate. The phosphine is precracked and no carrier gas is used. This technique not only gives monolayer by monolayer control but also enables selective area growth (SAE) controlled by a laser pattern instead of using patterned films of insulators in the conventional method. So far they have not fabricated any device structures which would enable them to determine the electrical properties of the grown layer.

Dave Bohling gave an invited paper II-1, by D. Bohling, C. Apenathy, K.F. Jensen, representing the joint work of Air Products Chemical and AT&T on the development of novel precursors for CBE. He used the arsine substitutes as examples to demonstrate the considerations that go into the selection of precursor. The principle materials he elaborated on were tertiary butyl arsine (TBAs), phenyl arsine (PhAs) and trisdimethylamino arsenic (DMAAs). DMAAs is particularly interesting in that there are no As-C bonds so that incorporation of C in the GaAs or GaAlAs is very low. A

number of other exotic precursors were also mentioned but the main significance that comes out of this paper is the fact that a great deal of work has been done where knowledgeable researchers from both a chemical firm and from the more device oriented company worked in close collaboration. The development of new precursors is a highly interdisciplinary activity and is not possible without reliable input from a number of areas simultaneously. It is not enough to just synthesize the new precursors in useable quantity, but it must also be done with a high level purity to be characterized properly. It must then be fabricated to some minimal device configuration to be fully characterized both electrically and optically. On the whole most of the precursors presented had already been reported on previously.

Trevor Martin did an excellent job of chairing the Romp Session on new precursors for CBE/MOMBE/GSMBE. He briefly reviewed some of the newer precursors and their faults and played the devil's advocate. Dave Bohling, appropriately took the opportunity to mention a series of exotic precursors and possibilities. Although the attendance was quite good and more comments began to dribble out, with the imbibing of liquid refreshments, there was relatively little that was really new that came out.

CAN CBE SURPASS MBE AND MOCVD IN WHICH AREAS?

There was a mini-symposium with this question as its title. Most of the papers described some aspect of CBE that could be considered to be its strength, thus implicitly advocating the CBE process rather than addressing this issue directly. The comparison with MBE is perhaps somewhat meaningless since the basic feature of depositing in the molecular flow regime is common to both. The interesting question is between CBE and MOCVD for the large scale manufacture of III-V and II-VI compound semiconductor devices.

E. Beam reported that the team at Texas Instrument have successfully manufactured devices including single- and double-heterojunction bipolar transistors, in the InGaP/GaAs and InGaAs/InP materials system using TBA and TBP as substitute for arsine and phosphine in CBE. The rapid fire presentation by C. Abernathy of Bell Labs covered a lot of ground in S-2, and complimented Bohling's earlier talk by discussing the use of the more novel precursors in terms of the performance of the fabricated HBT's. She made a conscientious effort to address the question of the symposium, coming out clearly in favor of CBE for its ability to achieve uniformity and reproducibility and its ability for regrowth of contact layers using selective epitaxy.

W.T. Tsang of Bell Labs in S-2, W. Tsang, R. Kapre and P. Sciortino, and in the last paper of the conference X-I-9, W. Tsang, T. Chiu and R. Kapre, presented their recent work on *in-situ* dry etching by reactive chemical beam etching (RCBE) and

regrowth in the CBE chamber. As was pointed out by Abernathy, this is, at present, only possible by CBE for InP and GaAs layers and is important in the fabrication of advanced optoelectronic devices. In the case of GaAs etching with AsCl_3 mono-layer chemical beam etching (ML-CBE), in which etching is carried out monolayer at a time, was observed by RHEED.

Selective area epitaxy (SAE) of the III-V materials in CBE was reviewed in S-3 by H. Heinecke, University of Ulm. The selected areas are defined by patterned insulating films of SiO_2 or Si_3N_4 and selectivity is achieved by the fact that the sticking probability of the group III alkyl on the insulator is very low. The fact that gas flow dynamics are nonexistent in CBE allows well defined edges to develop at the growth area boundaries. by optimizing the growth parameters. The presentation by S. Yoshida of the work at the Optoelectronics Technology Research Laboratory described selective-area epitaxy using a GaN film as the mask for defining the growth area. An attractive feature of this technique is that the GaN film, deposited on a GaAs substrate at 630°C using catalytically cracked ammonia, is patterned by electron beam. This means that, in principle, the patterning can be done *in-situ* and does not require lithographic etching. They had confirmed by quadrupole mass spectrometry that the TMG does not decompose on the GaN surface at 450°C while it does on the GaAs surface exposed by the electron beam irradiation and epitaxial growth of GaAs could be observed. The paper V-2 which was presented at the III-V Device session by T.S. Rao reported on SAE of InP on InP substrates using SiO_2 and Si_3N_4 films as masks.

M. Yamaguchi of NTT Opto-electronics Labs gave a paper S-4, "CBE as a breakthrough technology for PV solar energy applications", M. Yamaguchi, T. Warabisako and H. Sugiura. Although the objective of the talk was commendable what was presented did not reflect a very thorough job. Nevertheless there were some interesting information, e.g. whereas most solar cells used as satellite power source are single or double heterojunction GaAs/AlGaAs solar cells with up to 25-7% conversion efficiency the Japanese satellites are using InP based solar cells of comparable conversion efficiency. The significance of this is that these are estimated to be about five times more radiation resistant than their GaAs counterparts. This is particularly significant if the satellite orbit encounters regions of high radiation such as the van Allen belt. However almost all of these solar cells were prepared using the MOCVD technique. It was only speculated that with the control possible using CBE the efficiency of the cell could be raised further by utilizing multi-heterojunction structures. The fabrication cost reduction was estimated to be appreciable due to the more efficient use, by at least a factor of 10, of the feed stock and the resulting lower safety requirements.

There was almost a unanimous agreement that CBE is a very effective R and D technique to further the understanding of epitaxial growth and to fabricate complex

exploratory devices. But whether the technique was suitable for large scale manufacture was open to debate. Professor Iga of Tokyo Institute of Technology was of the opinion that once the device fabrication process is developed that the cost effectiveness of the MOCVD would take over. On the other hand Professor Kolodziejki of MIT felt that there was no intrinsic reason why CBE couldn't be scaled up for multiwafer processing as has been done for MBE without excessive costs. A great deal depends on the final end product and the availability, cost and quality of the precursor feedstock. This was well illustrated in the poster paper IV-12 by G. Munns, W. Chen, M. Sherwin, D. Knightly, G. Haddad, L. Davis, and P. Bhattacharya, Center for High Frequency Micro-Electronics, University of Michigan on the influence of hydride purity on InP and InAlAs growth. The report V-3, by J. Shirakashi, R. Yoshioka, M. Konagai and K. Takahashi, Department of Electrical and Electronic Engineering, Tokyo Institute of Technology, is interesting since it reports that by combining elemental Ga flux to the conventional CBE growth sources of InGaAs they could get increased growth rate as well as avoid carbon contamination while maintaining high hole concentration. This illustrates that it is somewhat academic to be hung up too much on terminology or definitions. Although there was much concern regarding the safety and environmental factors, it seems that all the issues have yet to be completely thought out. Just from the quantity required in MOCVD the problem is greater for this technology.

III-V DEVICES AND RELATED STRUCTURES

Papers on III-V devices and related structures were given in sessions III, V and VII. The paper III-1 by Y. Houng, M. Tan, B. Liang, S. Wang, L. Yang and D. Mars, Hewlett-Packard Lab. was interesting in that they used what they called an "in-situ IR pyrometric measurement" to monitor the growth of the epitaxial layer. This is a misnomer since although an optical pyrometer is used what is measured is the apparent temperature fluctuation due interference effects to monitor the thickness of the growing layer. Very high accuracy and reproducibility of the structure was achieved in the fabrication of a InGaAs/GaAs vertical cavity surface emitting lasers (VCSEL) which was claimed to have an external quantum efficiency higher than 40%. W.T. Tsang substituted as the speaker for a Bell Labs paper III-3, Y. Chen, R. Kapre, W. Tsang and L. Fan, reporting on a carbon-doped InGaP/GaAs/InGaP DHPT made by CBE. The transistor with a large area non-alloyed base contact showed a collector breakdown voltage and an extremely low 1/f current noise which was attributed to the absence of burst noise from deep level impurities. With a base doping density of $2 \times 10^{19} \text{cm}^{-3}$ a very high current gain of 120 was achieved.

Paper III-2, "One step growth of buried heterostructures by CBE over patterned InP substrates" by A. Rudra, H. Sugiura, J. Carlin, J. Ling, J. Ganiere and M. Hegems, takes clever advantage of the fact that InP and GaInAs do not grow on the

(111)B sidewall planes in a to form and bury the heterostructure on a ridge and valley patterned (100)-oriented InP substrate. The ridges are oriented along [011] direction with (111)B side walls and TMIIn molecules migrate down the (111)B side wall to join the InP growth in the valley, thus burying the whole ridge complex and making a structure similar to the buried heterostructure of a separate confinement heterostructure (SCH) quantum well laser. It is interesting that this paper of Institute for micro- and optoelectronics, Ecole Polytechnique Federale de Lausanne in Switzerland includes H. Sugiura of NTT Optoelectronics Laboratories, Japan as joint author, indicating the collaborative activity between the two institutions. The paper V-5 on the work done at the NTT Optoelectronics was also on the CBE growth of InP and related compounds. It claimed to report for the first time the fabrication of SCH-MQW lasers on (110)InP substrate which operate at 1.52- μm with a threshold current density of 0.83 kA/cm².

K. Iga and T. Uchida of Precision and Intelligence Laboratory, Tokyo Institute of Technology gave a very comprehensive paper, V-1, on the complete fabrication of a surface emitting (SE) laser of GaInAsP/InP layers. This type of laser with emission wavelength suited for low loss fluoride optical fiber, low divergence circular beam and consequent potential for high density array is expected to be critical in areas such as optical interconnection and communication. The laser consisted of Si/SiO₂ multilayer reflector, 8.5 pair distributed Bragg reflector (DBR), and a 1 μ thick active layer. The CBE was carried out in the RIBER CBE-32 system. CW lasing at 1.55 μ was observed at 77K with a threshold current as low as 320A/cm². They are optimistic that room temperature operation should be possible soon. The work described in this paper reflects the impressive capability of the P & I Laboratory of fabricating a complete optimized SE laser. Two poster papers, VIII-17 by Y. Inaba, T. Uchida, N. Yokouchi, T. Miyamoto, K. Mori, F. Koyama and Iga and VIII-18 by N. Yokouchi, Y. Inaba, T. Uchida, T. Miyamoto, K. Mori, F. Koyama and K. Iga, from the same laboratory supplemented Iga's presentation. VIII-17 described some of the details on the growth of the MQB layer and its optimization as a barrier. The determination of the Ga content in the the GaInAs region in the MQW super-lattice was described in VIII-18. This was determined by taking the x-ray diffraction pattern of the MQW with its x-ray satellite peaks and simulating the pattern for various Ga content. Although the gas flow rates were controlled to achieve Ga_{0.47}In_{0.53}As, the stoichiometry for lattice matching, they found that the Ga content decreased for thinner layers. This was explained to be due to substrate temperature fluctuations which occurs as a result of the decomposition of the group III metalorganics and methods of avoiding this was described.

The paper VII-1, by H. Asahi, M. Enokida, K Asami, J. Kim, T. Watanabe, R. Soni and S. Gonda, Institute of Scientific and Industrial Research, Osaka University reported the preparation of of short period super-lattices of GaP/AlP. The goal of this

work is the fabrication of green to yellow light emitting optical devices making use of the zone-folding and band mixing effects which should enable the structure to exhibit direct band gap behavior even though the two component semiconductors each have indirect band gaps. The short period SLs were prepared on either (001) GaP or GaP substrates to which they are lattice matched. In the process they found that short-range roughness at the GaP/AIP interface could be decreased by employing migration enhanced epitaxy (MEE) developed by Horikoshi et al., recently. The emission wavelength of the short period SL depends on the monolayer numbers of the two semiconductors in a single period of the SL. Spectra were presented showing the low temperature photoluminescence band for 3 SLs, $(\text{GaP})_{11}(\text{AIP})_{\text{sub.3}}$, $(\text{GaP})_9(\text{AIP})_{\text{sub.5}}$, and $(\text{GaP})_7(\text{AIP})_{\text{sub.7}}$ to be at about 555, 570 and 577nm, respectively. The optical absorption of the short period SL were smaller than those of normal direct band semiconductors as expected from the calculated oscillator strengths. But the fact that the confined modes of the GaP and AIP LO phonons were clearly observed is very encouraging.

In the following paper VII-2, R. Iga, T. Yamada and H. Sugiura, NTT Opto-electronics Labs reported on a new laser assisted technique for depositing SLs with InAsP as the well layer and InGaAsP as the barrier layer. An Ar laser beam is irradiated for 5 to 30 seconds with a constant 30 second off interval on a 10mm x 0.4mm area of (100) InP substrate at 510°C while a steady flow of feedstock was maintained. TMIn, TEGa, thermally cracked arsine and phosphine were used as sources. The PL peak wavelength of the SL could be controlled between 1.3 and 1.48 μ by the switch on time of the Ar laser from 0 to 30 seconds and the corresponding layer thickness varied from 2 to 12nm. The technique could be important in the fabrication of devices requiring precision in the layer thickness in SLs.

SI-BASED MATERIALS

One of the interesting areas in the CBE of Si based materials is the possibility for monolithic integration of optoelectronic devices into the silicon technology. This is due to the enhanced radiative recombination rates by the zone folding effect in SLs or carrier confinement in heterostructures such as QW. S. Fukatsu, N. Usami, Y. Kato, H. Sunamura, Y. Shiraki, H. Oku, T. Ohnishi, Y. Ohmori and K. Okumura, Research Center for Advanced Science and Technology, The University of Tokyo, in paper VI-2 described their work on strained $\text{Si}_{1-x}\text{Ge}_x/\text{Si}$ single and multiple QWs which were grown on a variety of substrates, (100), (110), (111) and vicinal surfaces. They were successful in reproducibly varying the Ge content from 0.09 to 0.73. The substrate temperature during growth of the QW and the effects of annealing were investigated and optimized based on PL characteristics. Comparison of measured and calculated PL energy

indicated they had achieved atomic scale abrupt interfaces. Based on these results they fabricated an EL device which was described in a poster paper VIII-14 by Y. Kato, S. Fukatsu, N. Usami and Y. Shiraki, from the same laboratory. The device was prepared in two separate chambers, a GSMBE chamber using disilane and germane to prepare the SQW and a solid source MBE chamber in which an n-type Si contact was regrown on the air exposed SQW. The use of two separate chambers reduced the possibility of contaminating the SQW part of the device and the demonstration that this could be done may prove very useful for manufacturing purposes. The Ge content used was 0.177 and the well width was 34.2Å. The device was cleaved into rectangular pieces after which gold electrodes were deposited. The EL was collected from one of the cleaved surfaces. The EL spectra and the PL spectra were presented for comparison and showed that they were essentially identical, signifying the high quality of the device.

II-VI MATERIALS

One of the most exciting development for this type material is the blue green ZnSe QW diode lasers. Although this conference did not witness any major breakthroughs, the presented papers indicate that investigations that pave the way are well underway. As pointed out by a Late News Session paper IX-1-1 by E. Hō et al., presented by L. Kolodziejski there are a number of difficult technical problems that must be overcome before a commercially viable room temperature CW blue green diode laser can be produced. The results to date indicate that to achieve low ohmic contacts, especially to the p-type layer and reduce threshold current density MQW structures involving ternary and quaternary compounds will be used and these structures are most likely to be deposited successfully by the CBE technique. The group led by Kolodziejski have investigated this possibility in a number interesting cases, e.g., they found that the abnormally low growth rate of ZnSe, seen when diethyl zinc (DEZn) and diethyl selenium (DESe) are used is due to the blockage of the surface sites by ethyl radicals and/or ethyl species. Using a tunable laser source they showed that this could be overcome by illuminating the substrate with photons with greater than band gap energy to get a factor of up to a factor of 20 enhancement in the growth rate. The explanation is that electron-hole pairs are generated which enabled the desorption of the surface alkyls or their radicals.

There were three other papers investigating the CBE of ZnSe but their results were not very conclusive. The paper IX-3, by Y. Kawakami, T. Toyoda, S. Fujita and S. Fujita, Dept. of Electrical Engineering, Kyoto University, reported on the effect of irradiation during growth using dimethyl zinc (DMZn) and dimethylselenide (DMSe). A high-pressure mercury lamp was used and comparisons were made for when irradiation was during DMZn only, during DMSe only and during the entire deposition.

Irradiation during DMZn deposition seemed to be most helpful in decreasing the deep acceptor states. A paper IX-2, by M. Imaizumi, Y. Endoh, K. Ohtsuka and T. Tsu, of the Mitsubishi Electric Corporation reported on their work looking into the CBE deposition of ZnSe using metal Zn and hydrogen selenide (H_2Se) which was cracked at $900^\circ C$. Reasonably smooth films were obtained at substrate temperature between $250-300^\circ C$ so long as the growth was limited by the H_2Se flow. The n-type dopant was Ga and p-type doping was from a N plasma. A poster paper VIII-9, was presented by S. Tokita, M. Kobayashi and A. Yoshikawa, Department of Electrical and Electronics Engineering, Chiba University of an *in-situ* technique of probing the ZnSe growth process. The method is called surface photo-interference (SPI) and appears to be sensitive to the surface species during the growth process. It was claimed that this measurement should yield details about the growth process. However the underlying principle was not clear and it is at the moment difficult to assess the generality of this approach.

The first paper in this session IX-I, by H. Okumura, S. Misawa, T. Okahisa and S. Yoshida was on epitaxial growth of GaN by CBE and was most likely given in this session because of the recent announcement that a blue light emitting diode consisting of a GaN/InGaN/GaN double heterostructure had been successfully made to operate at room temperature. The main message from this paper was that by using a microwave plasma of nitrogen in stead of dimethylhydrazine they were able to deposit higher quality GaN on both GaAs and SiC substrates. Cubic GaN was grown on (001) substrates and hexagonal GaN was grown on (111) substrates for both GaAs and SiC. The quality of GaAs was better on the SiC because of closer lattice matching.

ACRONYMS

ALE	Atomic layer epitaxy
BR	Bragg reflector
CBE	Chemical beam epitaxy
CL	Cathodoluminescence
DBR	Double Bragg reflector
DEGa	Diethyl gallium
DMAAs	Tris-Dimethylamino arsenic
DHBT	Double heterojunction bipolar transistor
FME	Flow-rate modulation epitaxy
GRINSCH	Graded index separate confinement hetero-structure
GSMBE	Gas source molecular beam epitaxy
HBT	Heterojunction bipolar transistor
HEMT	High electron mobility transistor

HREELS	High resolution electron energy loss spectroscopy
MBE	Molecular beam epitaxy
MBMS	Modulated beam mass spectroscopy
MEAs	Monoethyl arsine
MEE	Migration enhanced epitaxy
ML-CBET	Monolayer Chemical Beam Etching
MOCVD	Metalorganic chemical vapor deposition
MOMBE	Metalorganic molecular beam epitaxy
MOVPE	Metalorganic vapor phase epitaxy
MQB	Multi-quantum barrier
MQW	Multi-quantum well
OMVPE	Organometalic vapor phase epitaxy
PhAs	Phenyl arsine
QW	Quantum well
RCBE	Reactive chemical beam etching
RDS	Reflectance difference spectroscopy
RHEED	Reflection high energy electron diffraction
RTBT	Resonant tunneling bipolar transistor
SAE	Selective area epitaxy
SCH	Separate confinement heterostructure
SELD	Surface emitting laser diode
SEM	Scanning electron microscope
SHBT	Single heterojunction bipolar transistors
SIMS	Secondary ion mass spectroscopy
SL	Strained layer
SQW	Single quantum well
SSMBE	Solid source molecular beam epitaxy
TBAAs	Tertiarybutylarsine Liquid
TBP	Tertiarybutylphosphine Liquid
TEGa	Tri-ethyl gallium
TIBGa	Tri-isobutyl gallium
TIPGa	Tri-isopropyl gallium
TMAI	Tri-methyl aluminum
TMAAI	Tri-methylamine alane
TMGa	Tri-methyl gallium
TMI	Tri-methyl indium
TTBGa	Tris-tributyl gallium
UHV	Ultra-high vacuum
VCSEL	Vertical cavity surface emitting laser