

Chapter 4. Chemical Beam Epitaxy of Compound Semiconductors

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4.1 Facility for the Gas Source Epitaxy of Compound Semiconductors

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The new laboratory for the growth of both II-VI and III-V compound semiconductor heterostructures, using gas source epitaxy techniques, has received all hardware necessary to complete the multichamber system. The epitaxy system consists of six interconnected ultrahigh vacuum chambers: two introduction chambers, a transfer chamber, a II-VI-dedicated reactor, a III-V-dedicated reactor, and an analytical/metalization chamber. The analytical/metalization chamber is now attached to the transfer chamber; figure 1 shows a photograph

of the new chamber. In situ analytical tools which are available include Auger electron spectroscopy, reflection high energy electron diffraction (RHEED), additional ports for laser illumination of the sample, and a three-source electron beam evaporator for metals. The ultrahigh vacuum interconnection to both of the growth systems allows surface analysis of the many II-VI, III-V, and II-VI/III-V heterostructures which are envisioned, immediately following fabrication, without concern of contamination from atmospheric gases. The analysis chamber is expected to provide additional insight into the effect of both electron and photon beams on the surface of films grown using metalorganic molecular beam epitaxy. Metal evaporators will enable us to probe the initial stages of ohmic contact formation specifically with regard to the difficulties experienced in forming an ohmic contact to p-type ZnSe. The presence or absence of mixed interfacial layers in multilayered II-VI/III-V heterostructures may also be detected (in some instances) in the analytical chamber.

The final addition was the connection of a gas source molecular beam epitaxy (GSMBE) reactor to a small buffer chamber attached to the transfer chamber. The new reactor, shown in figure 2, was purchased from Instruments S.A., Riber Division, and is now in the final stages of installation. The gas source reactor has solid elemental sources of Ga, In, Al, Si, and Be, and gaseous hydride sources of arsenic and phosphorus. The purpose

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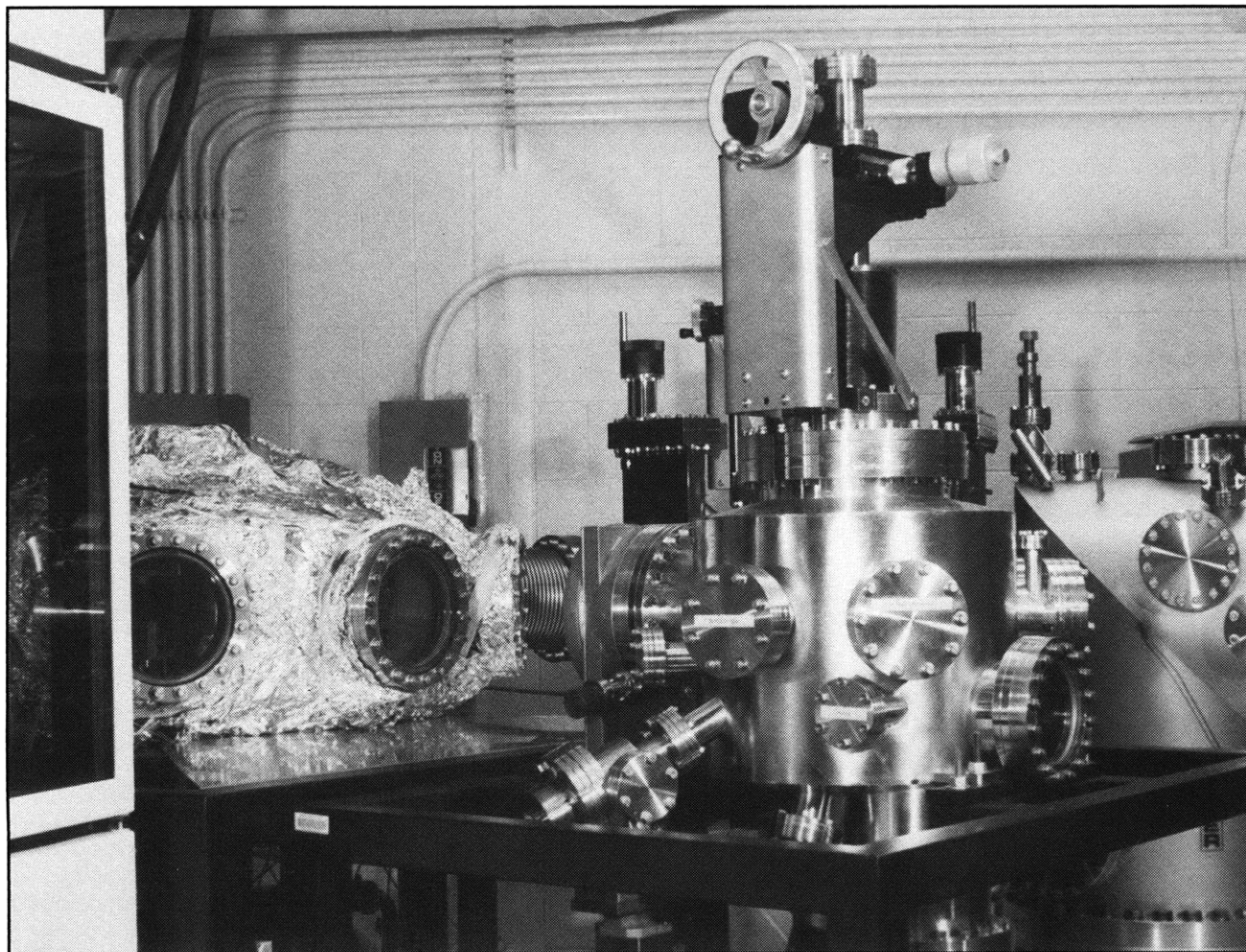


Figure 1. Photograph of the analytical/metalization chamber. Connection to the ultrahigh vacuum transfer chamber is yet to be completed.

of the III-V chamber is two-fold: (1) layers containing P and As will be crucial for utilizing lattice-matched buffer layers for the II-VI-based quantum well structures which are under investigation, and (2) III-V-based optical and electronic devices will be explored including quantum-effect electronic devices (in collaboration with Professors Dimitri A. Antoniadis and Henry I. Smith), and channel dropping filters and waveguide structures (in collaboration with Professor Hermann A. Haus). In addition, the III-V chamber will be employed for fabrication of II-VI/III-V multilayered heterostructures which contain III-V layers having substantial thickness. The II-VI reactor, which has gaseous sources for In, Ga, and As, will only be used for the growth of very thin III-V layers on the order of hundreds of angstroms or less.

4.2 Metalorganic Molecular Beam Epitaxy (MOMBE) of ZnSe

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Optical sources operating in the blue portion of the visible light spectrum have many potential commercial and military applications in, for example, optical information storage systems,

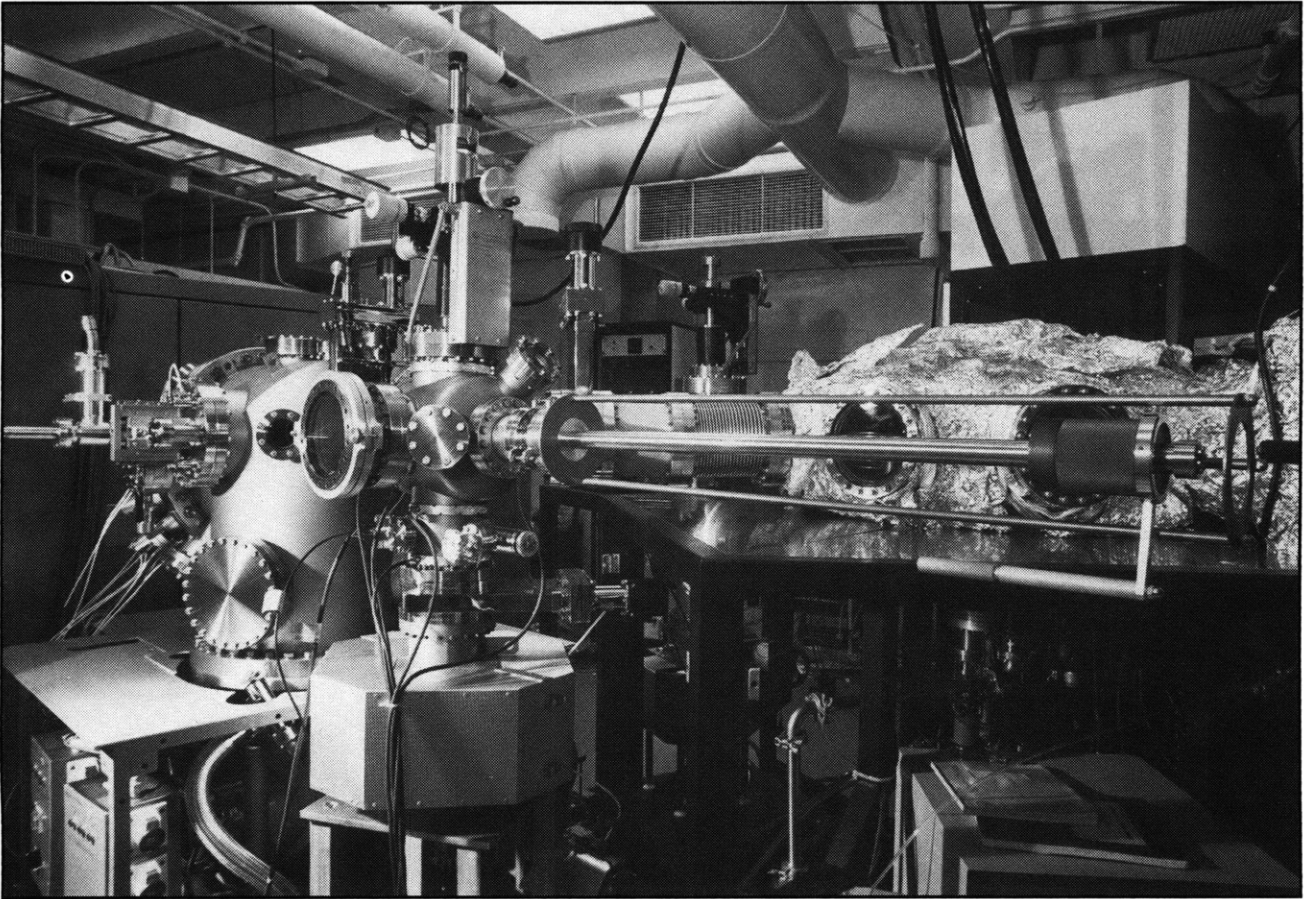


Figure 2. Photograph of the new III-V-dedicated GSMBE (which is attached to the small loadlock/buffer chamber). Final connection to the hemispherical ultrahigh vacuum transfer chamber can be seen.

medical imaging systems, electroluminescent flat panel displays, and color laser printers.

Although there are a variety of material systems, such as SiC, frequency doubled III-V-based lasers, and GaN, which can potentially offer a source of blue light, each of these systems has some limitations relative to integration and/or fabrication. The II-VI family of semiconductors (specifically the Zn chalcogenides) offers a solution to the problem of integration, and impressive recent gains have been achieved in fabrication technology. II-VI-based quantum well structures exhibiting excellent crystal quality are routinely fabricated on technologically important III-V substrates, suggesting that future integration needs will be straightforward. However, some substantial problems still remain to be solved.

In order to meet the requirements for room temperature, blue optical sources, the II-VI materials will require greater concentrations of sulfur to increase the bandgap. However, the alloying of ZnSe with sulfur results in a contraction of the lattice parameter and, therefore, an increase in the lattice mismatch with binary compounds such as GaAs. This problem is eliminated by utilizing lattice-matched

alloy buffer layers such as InGaP and GaAsP. The attached III-V gas source molecular beam epitaxy reactor will be the source of any III-V-based lattice-matched buffer layer. Although the lattice mismatch difficulty is circumvented here, we are also fabricating "epilayer-on-epilayer" structures. These epilayer-on-epilayer structures are necessary to provide the minimum possible number of defects created at the heterovalent interface and ultimately within the active region of the II-VI optical device. In addition, a key advantage offered by gas source epitaxy techniques is the ability to control, via mass flow controllers, the flux of species which exhibit very high vapor pressures as a function of temperature. Sulfur and phosphorus containing materials are excellent candidates for fabrication utilizing gas source epitaxy techniques with impressive successes reported.

The objectives of the research described here revolve around the growth of various II-VI-based heterostructures using gaseous source epitaxy including metalorganic molecular beam epitaxy (MOMBE), chemical beam epitaxy (CBE), and gas source molecular beam epitaxy (GSMBE). The various techniques utilize combinations of gaseous

sources such as metalorganics and hydrides, as well as solid elemental sources. Thus far we have explored the MOMBE of ZnSe using diethylzinc and diethylselenium.

A large number of films have been grown with the details of the growth parameters described below. ZnSe epilayers were normally grown on carbon-controlled semi-insulating (001) GaAs wafers, although n-type, p-type and 2°-off n-type GaAs were also used. Typical growth temperatures ranged from 250°C to 425°C, with the majority of the film growths performed near 320°C. The VI/II flow ratio was varied from 0.2 to 5.0, with diethylzinc (DEZn) and diethylselenium (DESe) gas flows ranging from 0.5 to 2.5 sccm. Reactor pressure during growth was typically 1×10^{-4} Torr. In nearly all cases the DEZn cracker was set at 50°C, and the DESe was thermally decomposed at 800°C. Cracking experiments with the quadrupole mass spectrometer (QMS) indicated that DESe decomposed at 800°C, while DEZn thermally dissociated at temperatures above 300°C.

Preliminary microstructural and optical characterization of the ZnSe suggests that the thin films are of good quality. A typical RHEED pattern observed following growth shows the presence of narrow streaks and readily apparent Kikuchi bands suggesting the existence of single crystalline films with smooth surface morphology. Secondary ion mass spectroscopy (SIMS) results indicate very low levels of carbon incorporation which is near the detectability limit of our instrument (VG-Fisons Instruments Model IX70S SIMSLAB). X-ray diffraction rocking curve analysis confirms the pseudomorphic nature of thin 1000Å films of ZnSe on GaAs. Typical full width at half maximum measurements for the (400) reflection is around 220 arc seconds. Optical characterization from photoluminescence measurements indicates the presence of bandedge excitonic features which are shifted to higher energy reflecting the presence of strain, in addition to features originating from deep level defects. We speculate that the presence of these particular deep level features is due to stoichiometry such as Zn vacancies, and we are therefore investigating growth with various flux ratios.

The growth rate using DEZn and DESe has continued to be very low. Although the actual species at the surface front are not known, we expect to find ethyl species of Zn and Se, in addition to dimers of Se from the thermal decomposition of the metalorganic. The growth temperatures inves-

tigated and the cracking data suggest that there is sufficient thermal energy to decompose the Zn molecules. (The RHEED patterns exhibit reconstructions of a Zn-stabilized surface.) In addition, the nearly constant growth rate observed for a wide variety of growth conditions (flow ratio and rate, substrate temperature, and with and without hydrogen) suggests that the growth is surface kinetics limited. Similar to metalorganic vapor phase epitaxy (MOVPE), although lacking the gas phase reactions, the MOMBE growth technique is expected to exhibit complex surface chemical reactions. We speculate that at the necessary low growth temperatures employed here, lattice sites for incorporation of Zn and Se are being blocked by alkyl radicals. The alkyl radicals are a copious byproduct of the surface pyrolysis of DEZn and thermal decomposition of the DESe. At higher growth temperatures ($\geq 425^\circ\text{C}$), where one might expect the alkyl radicals to desorb, competing desorption of Zn and Se limits the growth rate. Previous work² reported using these metalorganic sources show growth rates approximately an order of magnitude greater under similar growth conditions. Differences which may exist include (1) pressure during growth, (2) use of hydrogen carrier gas, or (3) the actual design of the gas crackers.

4.3 Photo-Assisted MOMBE of Wide Bandgap II-VI Compound Semiconductors

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Photo-assisted heteroepitaxial growth of ZnSe on GaAs by MOMBE is currently under intense investigation. MOMBE has several potential advantages when compared to other epitaxial growth techniques such as metalorganic vapor phase epitaxy (MOVPE) and molecular beam epitaxy (MBE). The advantages include: (1) The flux ratio of gaseous metalorganics can be precisely controlled using mass flow controllers; (2) in-situ analysis techniques such as reflection high-energy electron diffraction (RHEED) and quadrupole mass

² H. Ando, A. Taïke, R. Kimura, M. Konagai, and K. Takahashi, "Metalorganic Molecular Beam Epitaxial Growth of ZnSe Using Diethylzinc and Diethylselenide," *Japanese J. Appl. Phys.* 25(4): L279-L281 (1986).

spectroscopy (QMS) are available; and (3) surface chemistry allows for fine tuning of the growth conditions. Photo-assisted MOMBE adds an extra degree of versatility because both selective deposition of material and modification of the surface chemistry are possible.

Photo-assisted growth was performed by selectively illuminating a portion of the wafer's surface. Radiation from a 5 Watt Ar ion laser (Spectra-Physics, Model 2025) was introduced at a 45° angle to the substrate normal. The laser spot on the wafer was typically an ellipse with major and minor axes of 1.4 and 1.0 cm. The effect of wavelength on growth has been studied by using laser radiation ranging from 780 nm to 350 nm. To produce the 780 nm line, a Ti:sapphire crystal was pumped with all lines of the argon ion laser. The power density was kept low at approximately 180 mW/cm², thus allowing thermal heating effects to be neglected.

As mentioned in Section 4.2, under the growth conditions described here, the growth rate during MOMBE of ZnSe has consistently remained very low. The growth rate without laser illumination is typically 250 to 375 Å/hour. As a function of calibrated growth temperature, the unilluminated growth rate shows a remarkable temperature insensitivity over the temperature range of 250-425°C. This is quite unexpected since MOMBE has typically demonstrated a strong temperature dependence.³ Laser illumination, however, has been found to ameliorate the low growth rate. For the portion of the film grown with photo-assistance, a significant temperature dependence is observed which is more typical of MOMBE growth.

Figure 3 shows the ratio of illuminated to unilluminated growth rates (enhancement ratio) as a function of laser wavelength. At a growth temperature of 320°C the bandgap energy of ZnSe corresponds to a photon energy of ~520 nm.⁴ The 780 nm radiation was found to produce no growth rate enhancement, while the higher energy photons produced significant growth rate enhancement. Furthermore, the growth rate enhancement was found to be directly proportional to the laser intensity (see insert of figure 3). When the TEM₀₀ mode of the argon ion laser was used, the

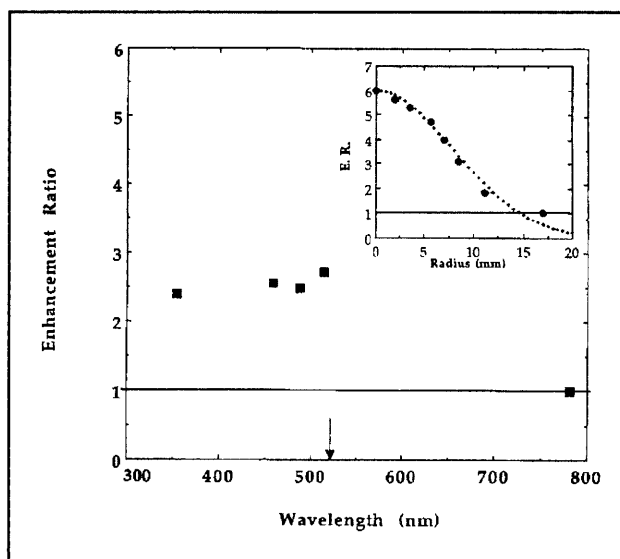


Figure 3. Growth rate enhancement ratio (ER) as a function of laser wavelength. The DESe and DEZn flow rates are both 0.5 sccm, and the substrate temperature is ~320°C (arrow indicates ZnSe bandgap). The insert shows the growth rate enhancement ratio of the illuminated region (457.9 nm laser line) as a function of spot radius (mm). The dotted curve is a Gaussian fit to the data suggesting a direct correlation between growth rate enhancement and power density.

enhancement ratio (solid circles) across the illuminated growth region was found to correlate well with the Gaussian intensity profile of the laser. The largest enhancement in the growth rate has been a factor of 9, although we have not yet attempted to optimize the various growth parameters to maximize the growth rate.

Thus far our data suggest that the creation of electron/hole pairs are required for the growth rate to be enhanced during photo-assisted growth. Photons having energies above the bandgap of ZnSe (at the growth temperature) resulted in growth rate enhancement, while photons with longer wavelengths do not increase the growth rate. Similar dependencies have been observed by Yoshikawa et al⁴ for growth of ZnSe by photo-assisted MOVPE. For the metalorganic molecules utilized here, gas phase absorption⁵ is expected to occur at wavelengths much shorter (248 nm for DEZn) than investigated here. Although a more

³ H. Ando, A. Taike, R. Kimura, M. Konagai, and K. Takahashi, "Metalorganic Molecular Beam Epitaxial Growth of ZnSe Using Diethylzinc and Diethylselenide," *Japanese J. Appl. Phys.* 25(4): L279-L281 (1986).

⁴ A. Yoshikawa, T. Okamoto, T. Fujimoto, K. Onoue, S. Yamaga, and H. Kasai, "Ar-Ion Laser-Assisted MOVPE of ZnSe Using DMZn and DMSe as Reactants," *Japanese J. Appl. Phys.* 29(2): L225-L228 (1990).

⁵ H. Hou, Z. Zhang, U. Ray, and M. Vernon, "A Crossed-Laser Beam Study of the Photodissociation Dynamics of Zn(C₂H₅)₂ and (Zn(C₂H₅)₂)₂ at 248 nm and 193 nm," *J. Chem. Phys.* 92(3): 1728-1746 (1990).

detailed investigation is required, we speculate that a potential mechanism is that a photo-generated carrier (we suspect holes) eliminates an ethyl-metal bond at the surface leading to a higher growth rate. Preliminary data (not shown here) provide evidence that there is a dependence of the growth rate enhancement on the gas flow ratio; this suggests that the growth rate enhancement is not due to liberation of surface alkyls which are blocking lattice sites by photo-generated carriers. The photo-assisted growth experiments currently underway are expected to aid our understanding of the dominant surface chemistry and growth mechanisms. By adjusting conditions such that growth

will only occur in regions irradiated by the laser, selective area epitaxy of ZnSe will be possible.

4.4 Publications

Coronado, C.A., E. Ho, L.A. Kolodziejski, and C.A. Huber. "Photo-Assisted Molecular Beam Epitaxy of ZnSe." Submitted to *Appl. Phys. Lett.*

Kolodziejski, L.A. "Chemical Beam Epitaxy of II-VI Semiconductors." Invited paper presented at the American Vacuum Society Meeting, Seattle, Washington, November, 1991.