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The goals of this AFOSR-supported program have been: 1) to investigate novel applications of non-linear gas phase photochemistry to the low temperature growth of semiconductor and metal films and 2) to develop new sources of stimulated emission at short wavelengths ($\lambda < 200$ nm). This work has resulted in several significant accomplishments: 1) epitaxial semiconductor (Ge) films have been grown on GaAs at temperatures as low as 285°C by laser photochemical vapor deposition (LPVD); 2) NH_3 has been demonstrated as a photosensitizer in the LPVD growth of films; 3) Ge/Si alloys have been grown by LPVD and analyzed; 4) the photochemical nature of laser-assisted MOCVD growth of GaAs on GaAs has been demonstrated; and 5) the excited state structure of Zn_2, Cd_2, Ar_2 and Ne_2 has been examined by laser spectroscopy.

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"NON-LINEAR OPTICAL TECHNIQUES FOR THIN FILM GROWTH AND VISIBLE AND ULTRAVIOLET LASERS"

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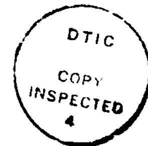

I. INTRODUCTION

Over the past three years, the Physics Division of AFOSR has supported a research program here at the University of Illinois for which the goals have been: 1) to investigate novel applications of non-linear gas phase photochemistry to the low temperature (T_S < 400°C) growth (or processing) of semiconductor or metal films and 2) to develop new sources of stimulated emission at short wavelengths ($\lambda < 200$ nm). This work has been quite productive as evidenced by the following accomplishments:

1) Epitaxial Ge films have been grown on [100] GaAs at temperatures as low as 285°C by laser photochemical vapor deposition (LPVD). This is at least 100°C below the lowest temperatures at which epitaxial Ge/GaAs heterointerfaces can be grown by conventional approaches (i.e., CVD).

2) The efficacy of NH_3 as a photosensitizer in the growth of semiconductor films by laser photochemical vapor deposition has been demonstrated.

3) Ge/Si alloys have been grown by LPVD in which the alloy composition is continuously variable.

4) The laser assisted MOCVD growth of GaAs on GaAs by photochemical processes has been demonstrated. Although heating of the GaAs substrate with a visible laser has been demonstrated previously, we are aware of no other example of the photochemical enhancement of the film growth rate and morphology improvement in an MOCVD reactor.

5) A time-of-flight (TOF) mass spectrometer has been built and is being used to study the fragmentation and ionization of metal alkyl and metal halide molecules (such as trimethylgallium or indium monoiodide, respectively) in an intense optical field (resonant

and non-resonant). The goal of this aspect of the program is to develop an inexpensive but high brightness metal ion source. Experiments producing Ga^{+} and In^{+} ions have been successful.

6) Laser spectroscopic experiments to observe the excited state structure of excimer molecules such as Zn_2, Cd_2 and the rare gas dimers have been successful. These molecules are being studied as candidates for an Anti-Stokes Raman Laser (ASRL) operating in the VUV.

This report will briefly describe the results that have been obtained under this AFOSR-supported program. In particular, the next section discusses each of the areas mentioned above. Also, the Appendices summarize the tangible results of this research effort: papers published, degrees granted and the patents that have been applied for or granted.

II. EXPERIMENTAL RESULTS OBTAINED UNDER AFOSR SUPPORT

This section describes in more detail the research accomplishments that were mentioned earlier. Particular emphasis will be placed on those results that were realized in the last year.

A. Laser Photochemical Vapor Deposition

One of the major goals of this research program has been to grow epitaxial semiconductor films at low substrate temperatures ($T < 400°C$) by invoking photochemical processes. After considerable effort over several years, these experiments have been successful.

1. Epitaxial Ge/GaAs Interfaces.

Experiments have been conducted in which epitaxial Ge films have been grown on [100] GaAs for T_S as low as 285°C by photodissociating GeH_4 (in He) at 193 nm (ArF laser). All experiments were conducted in parallel geometry (to avoid transient heating of the film and adlayer photolysis) and, in the absence of laser radiation, the films were (depending on T_S) amorphous or polycrystalline.

This is the first demonstration of the growth of epitaxial semiconductor films solely by laser photochemical vapor deposition (LPVD). That is, growth is clearly not attributable to transient heating of the substrate or adlayer photolysis but rather to a photochemically generated species which migrates to the substrate (or is collisionally transformed *en route* into a more stable species) and radically alters tne surface kinetics. These results demonstrate the ability to grow epitaxial films by laser photochemical vapor deposition (LPVD) under conditions in which growth is clearly not attributable to substrate heating but rather to species generated photochemically and in the gas phase. It

must be reiterated that we are aware of no other clear example in which photons have altered the gas phase chemistry of a reactor so as to make possible the growth of epi films at a surface which is itself not illuminated.

The experiments were carried out by passing the unfocussed beam from an ArF laser (193 nm) parallel to but above a [100] oriented GaAs substrate. The energy fluence typically available above the substrate at the beginning of a growth run was ~15 mJ-cm^{-2} (in a ~20 ns FWHM pulse) and under no circumstances exceeded 20 mJ/cm^2. For the gas pressures utilized in these experiments, the distance from any point in the gaseous region above the substrate (and illuminated by the beam) to the substrate corresponds to at least 10-60 mean free paths (MFPs) for a collision with GeH_4.

Convergent beam electron diffraction studies of both plan view and cross-sectional samples demonstrate that the Ge films (grown by LPVD) have the following epitaxial relationship with the substrate:

Ge [100] // GaAs [100]; Ge [010] // GaAs [010].

Part (a) of Fig. 1 is a convergent beam diffraction pattern (taken along GaAs [011] with a 150 Å electron probe) of a Ge film grown at 305°C. The absence of $\underset{\sim}{g}$ = {200} reflections confirms the identity of the film as being Ge ({200} reflections are kinematically forbidden for Ge but not GaAs). The pattern is that for [100] Ge and the lack of structural information within the discs is a result of the epilayer being thin (several hundred Å). A similar electron diffraction pattern for the GaAs substrate (near the Ge/GaAs interface) is shown in Fig. 1(b). As expected, the {200} reflections are now present.

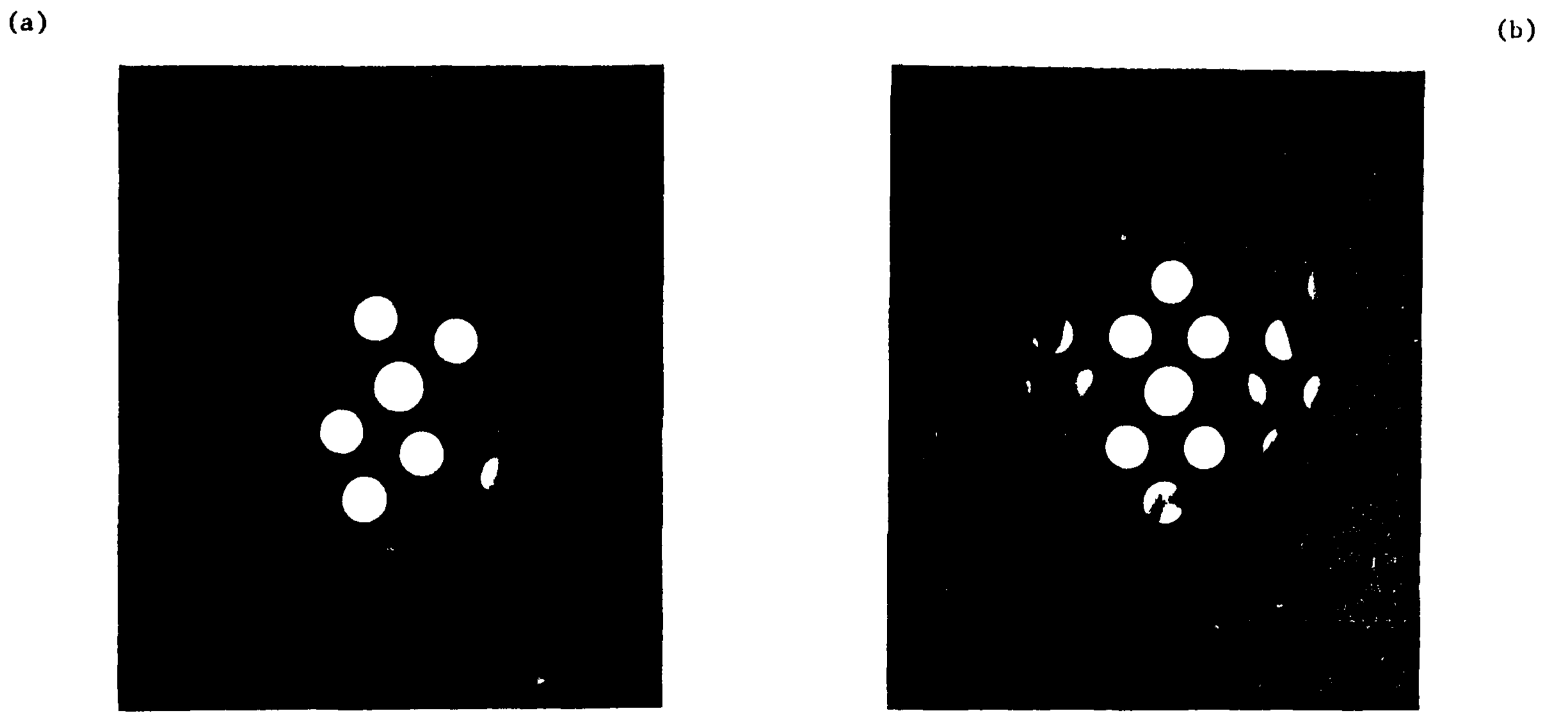

Fig. 1: (a) Convergent beam electron diffraction, taken along [011] GaAs with a 150 Å diameter electron probe, of a Ge film grown at 305°C by LPVD. The absence of $\underset{\sim}{g}$ = {200} reflections confirms that the film is indeed crystalline Ge; (b) same pattern as in (a) but of the GaAs substrate.

Energy dispersive X-ray (EDX) analysis of the LPVD grown films demonstrate that because the substrate temperature has been successfully reduced by $\gtrsim$ 100°C, autodoping of the epitaxial Ge films by the underlying substrate is negligible.

Further confirmation of the epitaxial nature of the Ge films is provided by lattice images of the GaAs/crystalline Ge interface (taken along [110] GaAs at 300 kV) which show two sets of {111} lattice fringes. These fringes run continuously from the GaAs substrate into the Ge crystalline layer, thus illustrating the epitaxy between the two crystals. To date, the lowest substrate temperature at which epitaxial Ge films have been grown is 285°C. Typically, the epi Ge layer grows at a rate of 4-6 nm/min (up to $\sim$1 Å - s^{-1}) until reaching an average thickness of 400-700 Å.

Failure to etch the substrate prior to film growth resulted only in amorphous Ge films. In the absence of UV radiation (i.e., conventional CVD), films grown at 300-310°C are completely amorphous while those grown at higher temperatures (415°C) are heavily defected (microtwinning, dislocations and stacking faults) polycrystalline.

Films grown on substrates having different orientations reveal adatom mobilities to be the greatest obstacle to further reductions in the growth temperature. Films grown on [111] substrates were completely amorphous while studies of [100] substrates tilted 3° towards [110] yielded epitaxial films of excellent morphology but thinner than those grown on untilted [100] substrates. The latter result is consistent with the high density of potential nucleation sites on tilted substrates. For these reasons, one of the emphases of future work will center on non-thermal approaches to increasing adatom mobilities.

Even more recent analysis of these Ge/GaAs films by SIMS indicates that carbon accumulation may be responsible for the amorphization of the Ge epitaxial layer. That is, the solid solubility of carbon is much lower for c-Ge than it is for amorphous material. It appears, therefore, that the carbon concentration at the c-Ge/gas interface rises

monotonically until reaching the point where the growth of crystalline material can no longer be supported. This is an encouraging result since it suggests that, with improvements in our vacuum system (we are currently evacuating the reactor with only a mechanical pump), it should be possible to grow high quality epi-Ge films of arbitrary thickness by LPVD.

Two papers on this work have been written. One was published earlier this year in Applied Physics Letters and a copy is attached. A second, longer version has been accepted by the Journal of Applied Physics and will be published in early 1989. Also, a patent application covering various aspects of these experiments was submitted in November of 1987 and the Patent Office has recently indicated that it will grant a patent.

2. NH_3 as a Photosensitizer.

Another highlight of our work in this area has been the demonstration of ammonia as a viable sensitizer for the growth of semiconductor films by LPVD. Of course, NH_3 has been around for a long time in this field but, to date, its usage has centered on acting as a precursor in the growth of stoichiometric Si_3N_4. That is, the focus has been on the amidogen radical, NH_2, which is produced when NH_3 is photodissociated at 193 nm.

What we have done is to shift the emphasis from NH_2 to the hydrogen atom that is also produced by photodissociation of NH_3. The chemical reactivity of the H atom is almost legendary and we have found it to be quite useful in dissociating hydrides that are difficult to pyrolyze. Figure 2 shows the dramatic enhancement in film growth rates that are observed when trace ($\lesssim$ 1 sccm) amounts of NH_3 are added to the gas flow stream. The most interesting point is that, despite the acceleration in growth rate, the film remains epitaxial with the substrate. The beneficial effect of the NH_3 is attributed to the dissociation of GeH_4 by H atoms produced by the laser. Consequently, we are convinced that these results will prove beneficial to other reactors and situations which deal with the

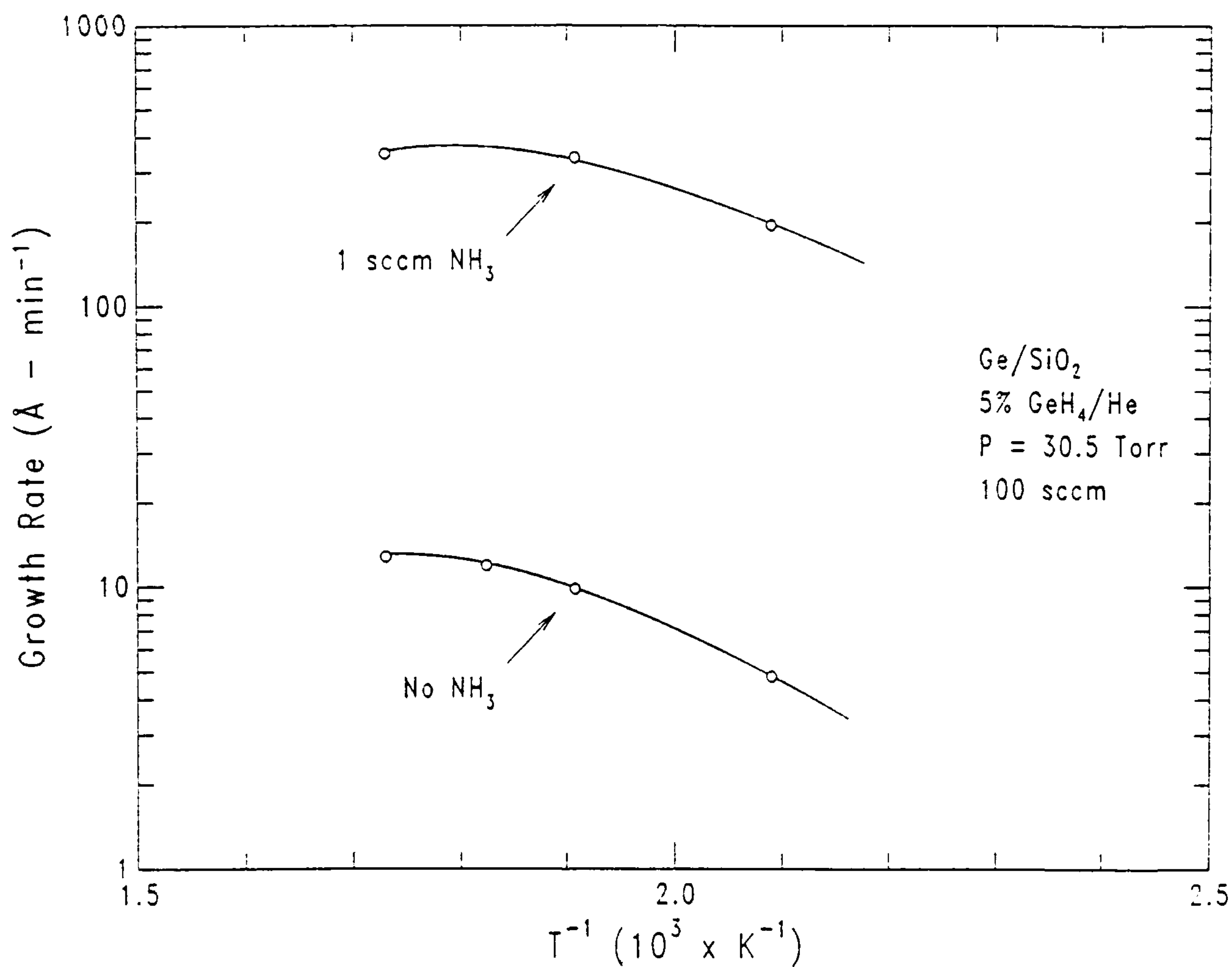

Fig. 2: Rates for the growth of epi-Ge by LPVD with (top trace) and without NH_3 added to the GeH_4/He gas flow stream. The difference in growth rates exceeds a factor of 30 at all temperatures investigated.

pyrolysis of Column V hydrides such as MOCVD. We expect to explore this in detail in the coming year. A paper on this subject has been written and submitted to Applied Physics Letters.

3. Ge/Si Alloys.

Since LPVD enables one to grow semiconductor or metal films under conditions considerably more favorable than those under which conventional CVD deposition techniques must operate (as far as temperature, toxicity of precursors, etc., are concerned), we have explored the LPVD growth of other materials and structures. Specifically, LPVD is currently being utilized for growing $Ge_x Si_{1-x}$ alloy films. The ultimate goal of this effort is the growth of compositionally and doping modulated superlattice structures. The latter is particularly difficult to obtain at conventional processing temperatures. One advantage of LPVD is that adjusting the composition of the alloy is straightforward by varying the relative partial pressures of the precursor molecules.

This work is being conducted in collaboration with Prof. Irving Herman of Columbia University. During the past nine months, several families of films (for which the alloy composition has been systematically varied) have been grown and Prof. Herman's group is presently studying the structure of these films by Raman spectroscopy. This initial result of this work has been presented at the AVS meeting (Atlanta, October 1988) and we expect to be able to write it up for publication in the near future.

B. Laser-Assisted MOCVD of GaAs on GaAs

A set of experiments is also being conducted in cooperation with Prof. J. J. Coleman in which an MOCVD reactor has been coupled to an excimer laser. Our initial efforts have concentrated on the growth of GaAs on GaAs and excimer laser pulses

(10-20 mJ - cm^{-2}) are being directed above or onto the substrate. The laser repetition rate and pulse energy are both being kept sufficiently small in the perpendicular configuration to ensure that substrate transient heating effects are negligible.

In our first experiments, the reactor vessel that is normally used by Prof. Coleman (for non-laser experiments) was involved. With a KrF laser (λ = 248 nm) operating at a PRF $\leq$ 60 Hz, it was found that high quality GaAs films could be grown at temperatures as low as T_S = 450°C. At higher temperatures (550-650°C), scanning electron micrographs of the grown films showed dramatic improvements in morphology when the UV radiation was present.

More importantly, we have found that at low temperatures (~450°C), KrF radiation significantly enhances the film growth rate. This wavelength was chosen specifically to photodissociate TMGa but not affect AsH_3 which is transparent at 248 nm. Identical experiments carried out at 351 nm showed no such effect which clearly demonstrates that the effect is photochemical in origin. While other groups (Bell Labs, SMU) have irradiated a substrate with excimer laser beams during the MOCVD growth of III-V films, their laser fluences were at least an order of magnitude higher and all effects observed were thermally initiated. To our knowledge, this is the first demonstration of a purely photochemical improvement. Therefore, our results to date show that UV lasers will, indeed, be effective in enhancing the flexibility of existing MOCVD or VPE reactors, allowing them to operate at considerably reduced temperatures and with precursors of lower toxicity (i.e., alkyls or halides, rather than hydrides). A manuscript describing these results is in preparation and we plan to extend our experiments to even lower temperatures in the near future.

C. Multiphoton Ionization of Metal Alkyl and Metal Halide Vapors

One of the most promising applications of laser physics and technology that has received little attention is the generation of high brightness, pulsed beams of singly charged metal ions. For such a technique to be practical, however, will require that the fragmentation pathways of the precursor molecule be better understood.

Our initial experiments have centered on $A\ell^+$ or Ga^+ ions produced by the multiphoton ionization of precursors such a trimethylaluminum (TMA). Little is known of the processes involved and, although the $A\ell^+$ production rate is dramatically enhanced in the vicinity of a three photon resonance in atomic aluminum, the products of and mechanisms responsible for ionization off-resonance are poorly understood. Similar comments hold for the production of Column IIIA ions by dissociative ionization of metal halides in the VUV (such as In^+ from InI).

To more closely investigate this process, we have recently constructed a time-of-flight (TOF) mass spectrometer and have carried out several experiments involving the fragmentation of $Ga(CH_3)_3$ by tunable blue dye laser radiation. The apparatus is shown schematically in Fig. 3. Representative time-of-flight (TOF) spectra that have been obtained with this system are presented in Figs. 4 and 5 demonstrate that the system resolution is sufficiently high to resolve peaks associated with the two most abundant isotopes of gallium. It is a simple matter to select a particular mass peak for study and preliminary experimental results show that the spectral dependences for the Ga^+ peaks differ considerably from those for the other fragments. In particular, the atomic ion spectra display strong resonant structure whereas the other fragments yield essentially continua. These experiments are continuing with the goal of elucidating fragmentation patterns for the molecule, both on and off a gallium 2 + 1 resonance.

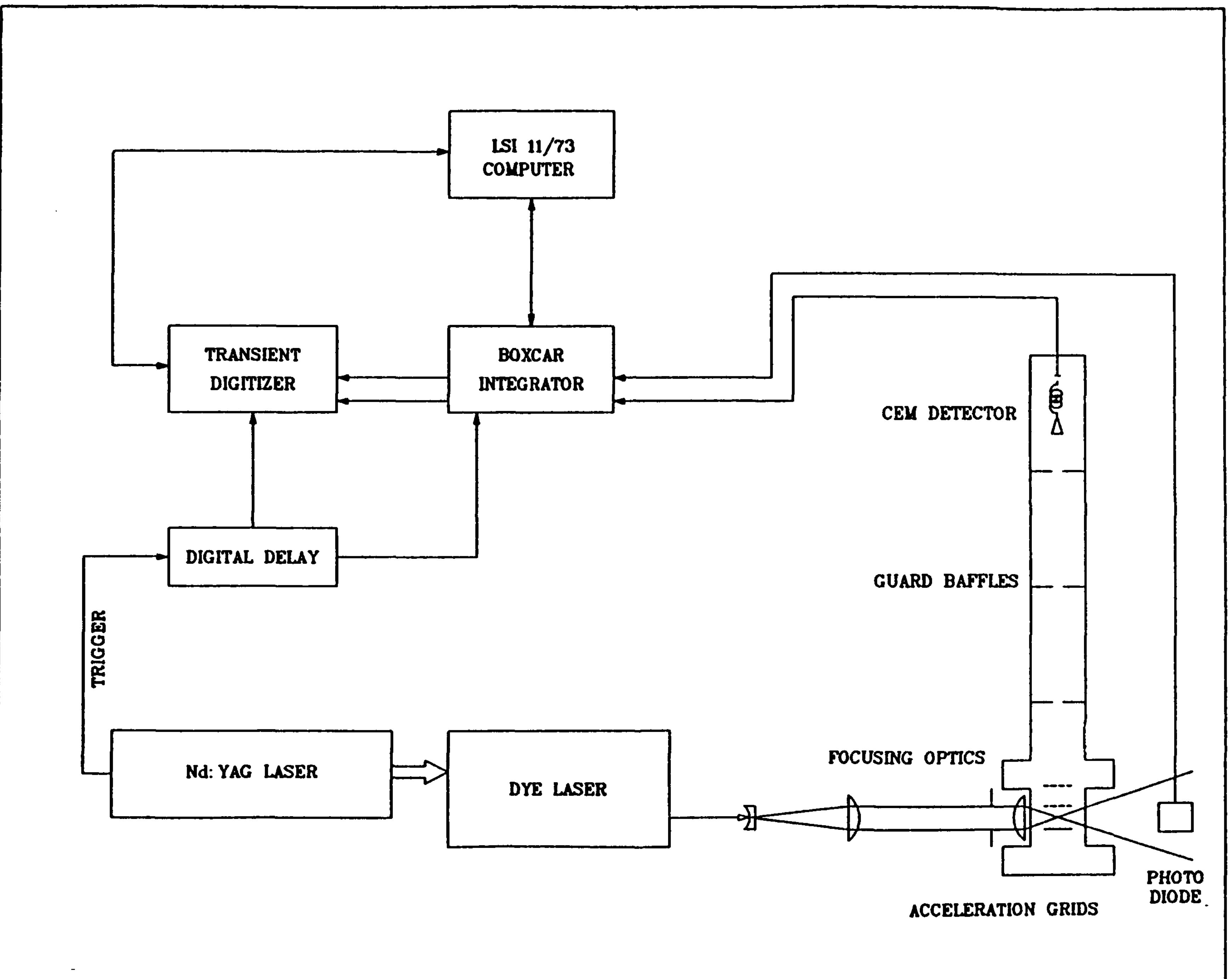

Fig. 3: Schematic diagram of the apparatus used in studying the photofragmentation of trimethylgallium by time-of-flight mass spectrometry.

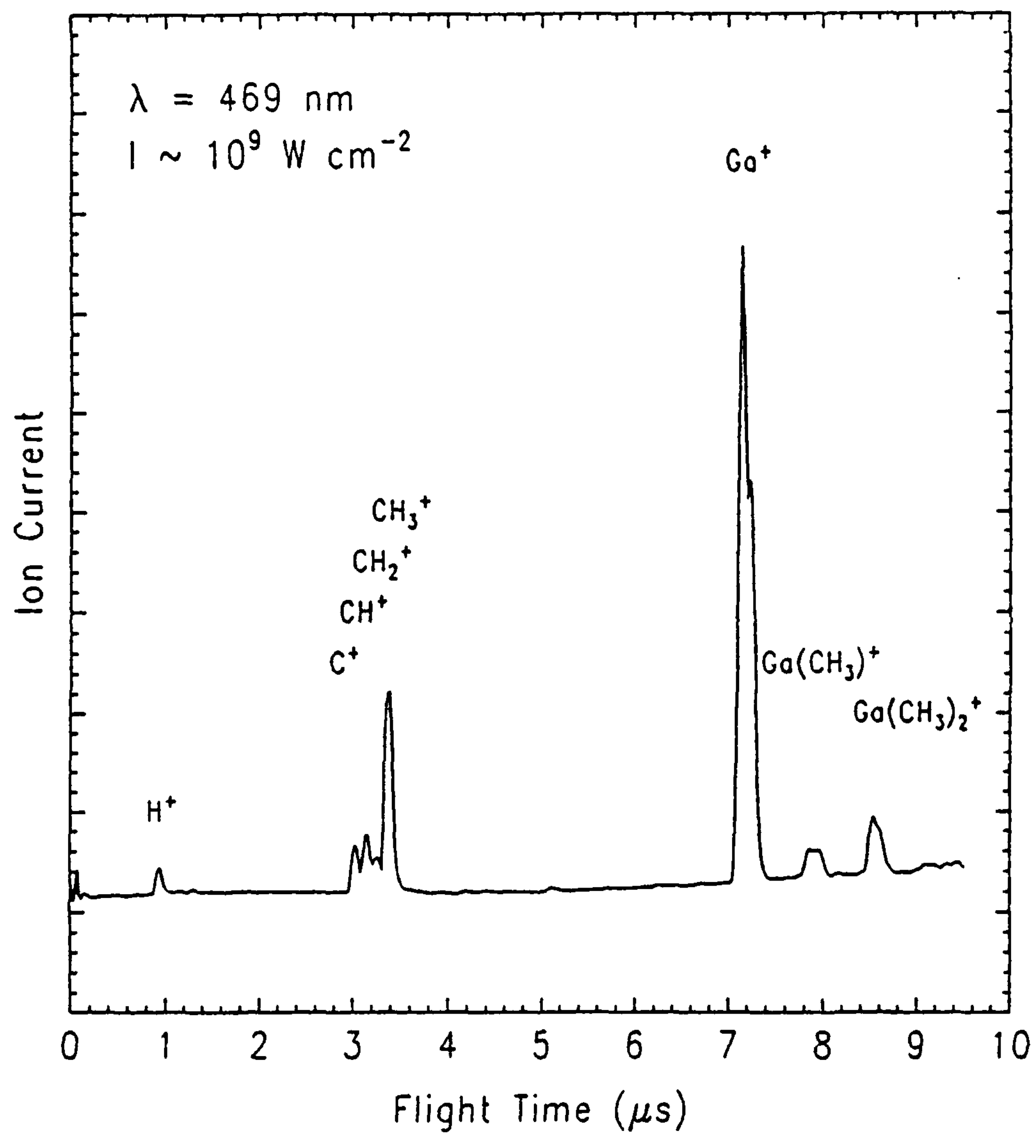

Fig. 4: Low resolution time-of-flight spectrum for TMGa at 469 nm.

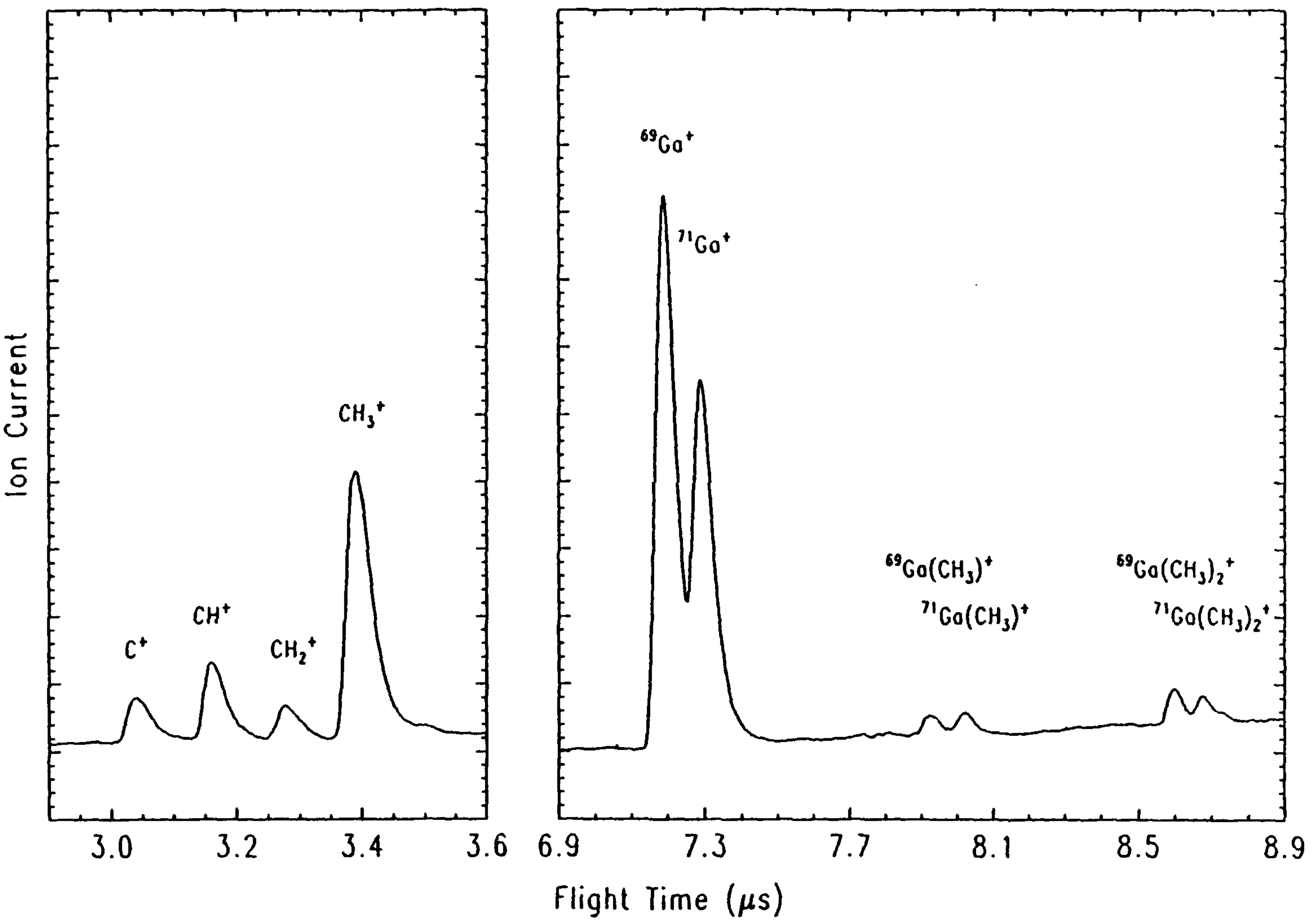

Fig. 5: Expanded views of selected segments of the TOF spectrum of Fig. 4 showing isotopically-resolved peaks.

A set of parallel experiments in this area is being cond ucted with InI in which we are exploring the feasibility of selectively producing In^+ ions by dissociative excitation of the molecule. Resonantly-enhanced multiphoton ionization (REMPI) spectra for the molecule have been obtained in the visible (cf. Fig. 6) and several new states of the molecule have been observed. We are currently in the process of constructing an energy level diagram for the molecule and expect to be able to propose a scheme whereby untuned (i.e., broadband) visible or UV lasers can be used to produce only In^+ positive ions by REMPI processes. The production of only one positive ion will eliminate the need for bulky (and expensive) mass selection equipment which is based on generating intense magnetic fields.

D. Spectroscopy of Ar_2 and Ne_2: Potential Raman Lasers in the VUV

For more than a year, we have become increasingly interested in developing sources of coherent radiation in the VUV that are more efficient, tunable and (hopefully) less complex than those currently available. The Conference on Future Prospects and Applications for UV and VUV Lasers (Santa Barbara, February, 1987) concluded that: "Higher intensity sources in the 50-150 nm region are particularly needed." Existing sources generally rely on nonlinear optical processes (such as four wave mixing) to generate the desired wavelength and, although this approach yields tunable radiation, the conversion efficiencies (and, hence, the peak output power) are terribly low ($\eta \sim 10^{-5} - 10^{-3}$).

One potential solution to this problem is the Anti-Stokes Raman Laser (ASRL). Consequently, we have initiated experiments to assess the feasibility of a molecular ASRL in the rare gas or Column IIB metal dimers. Several considerations suggest that this is a particularly intriguing possibility. The lowest excited states of the Rg_2 excimers [ns $^3\Sigma_u{}^+(1_u, 0_u^-)$ n = 2 - 6] are metastable (since ground has the configuration

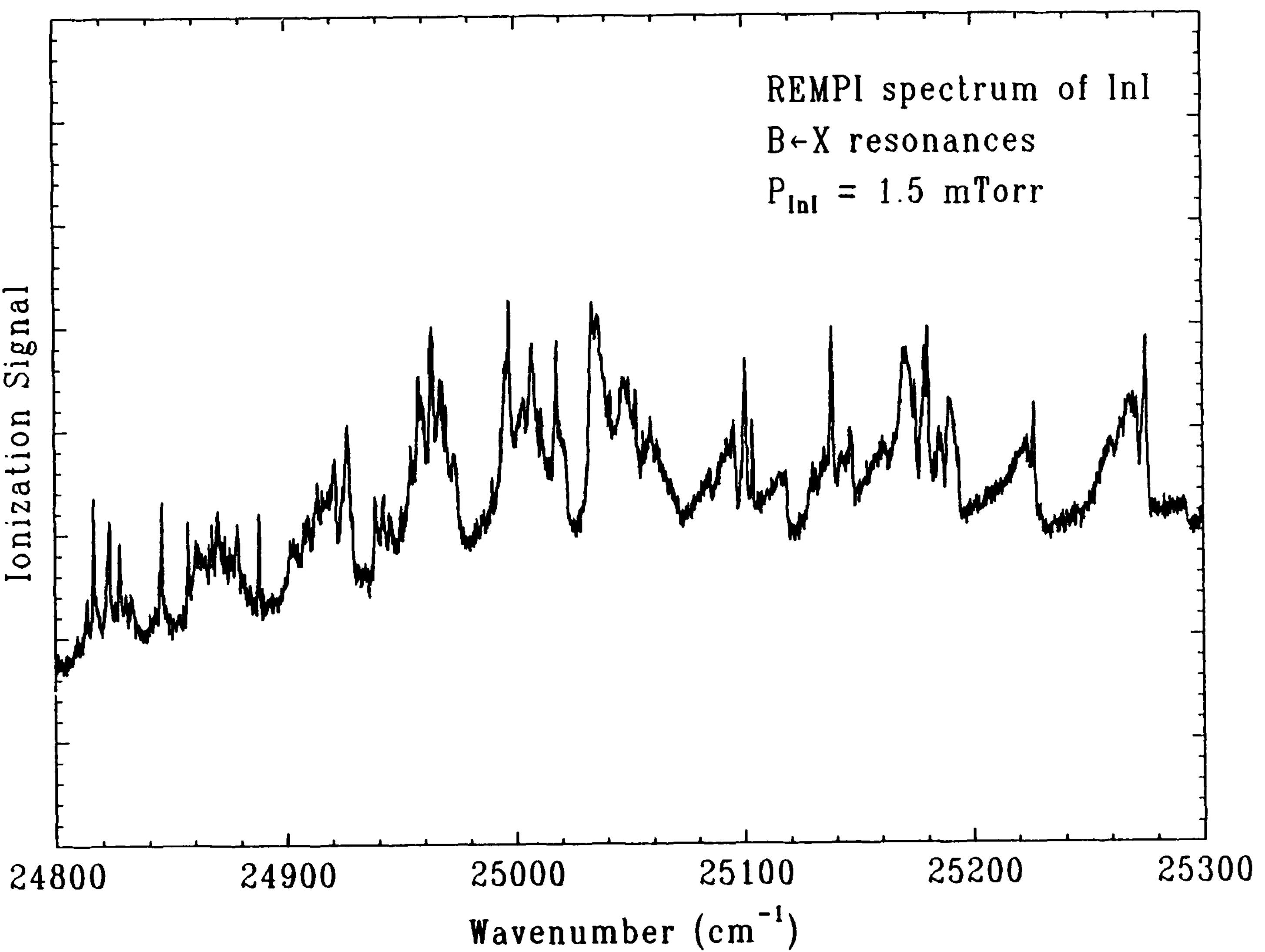

Fig. 6: REMPI spectrum of indium monoiodide in the violet ($24800 \leq \tilde{\nu} \leq 25300$ cm^{-1}). The resonances in this region are associated with B ← X (single photon) transitions.

$X\ ^1\Sigma_g^+ (0_g^+)$ and the production of these excited species by relativistic electron beams (e-beams) was well studied in the 1970's in connection with the development of the Ar_2, Kr_2 and Xe_2 VUV lasers. The conversion of absorbed e-beam energy into the metastable dimer state is known to be efficient at high energy loadings. In Xe_2, for example, $\sim 10^{16}$ cm^{-3} of 6s $^3\Sigma_u^+ (1_u, 0_u^-)$ molecules can be produced with e-beam deposited energy to excimer production efficiencies exceeding 20%. Since the lowest Rg_2 metastable state $(1_u, 0_u^-)$ has the opposite parity of ground (0_g^+), a molecular ASRL in the rare gas dimers will require a gerade molecular upper Raman state.

Therefore, it is not difficult to envision a tunable VUV or XUV laser in which the energy stored in these metastable levels is "switched out" by anti-Stokes Raman transitions induced by a visible laser.

To work towards this goal, we have undertaken a study of the inter-Rydberg spectroscopy of Ar_2, Ne_2, Zn_2 and Cd_2. The purpose of this work is to identify the intermediate molecular levels required for an anti-Stokes laser to work. A great deal of progress has been made and can be summarized as follows:

1) The inter-Rydberg spectra of Ar_2 and Ne_2 have been recorded in the visible and near-UV. Both have been done in absorption by e-beam pumping and by laser excitation spectroscopy in the afterglow of a pulsed discharge. The latter is slow but gives us rotationally-resolved spectra. Note that these experiments map out for us the gerade Rydberg states of both dimers.

2) Experiments are underway to measure the absorption spectra of Ar_2 in the infrared. These will give us the lowest principal quantum number transitions which also have the largest oscillator strengths.

3) Two photon measurements designed to access the ungerade states are almost completed. When they are finished, we expect to be able to identify the final Raman laser state necessary for our scheme.

4) Similar experiments with Zn_2 and Cd_2 have worked well. We have observed the excited state absorption spectra for both molecules in the visible and UV and, by laser excitation spectroscopy, have begun to identify the states responsible.

In short, these spectroscopic experiments have been very productive and, within the next 6 months to one year, we expect to be able to identify a promising molecule/energy level scheme with which to proceed towards the demonstration of an ASRL.

III. SUMMARY

The work of the past three years has been multi-faceted and has included work in the application of UV/visible lasers to thin film growth as well as development of the lasers themselves. As attested to by the discussion of Section II, this work has (we believe) been quite fruitful and we hope that AFOSR concurs. We expect the next year or two to continue these efforts with increasing emphasis on the MOCVD and ASRL areas.

APPENDICES

PAPERS PUBLISHED THUS FAR UNDER AFOSR F49620-85-C-0141

1. V. Tavitian, C. J. Kiely, D. B. Geohegan and J. G. Eden, "Epitaxial growth of Ge on GaAs (285-320°C) by laser photochemical vapor deposition," Appl. Phys. Lett. 52, pp. 1710-1712 (1988).

2. C. J. Kiely, V. Tavitian and J. G. Eden, "Microstructural characterization of epitaxial Ge films grown on [100] GaAs by laser photochemical vapor deposition," (submitted to J. Appl. Phys.).

3. S. A. Piette, C. J. Kiely and J. G. Eden, "A TEM study of the structure of polycrystalline Si films on (111) Si substrates grown by low pressure chemical vapor deposition," Proc. Mat. Res. Soc. 106, pp. 15-20 (1988).

4. V. Tavitian, C. J. Kiely and J. G. Eden, "Epitaxial growth of thin Ge films on [001] GaAs by laser photochemical vapor deposition from GeH_4," Proc. Mat. Res. Soc. 101, pp. 349-353 (1988).

5. J. G. Eden, J. H. Schloss, D. J. Kane, D. C. Shannon, C. C. Abele and A. W. McCown, "Spectroscopy of absorbers in rare gas-halide laser plasmas," Proc. SPIE 894, pp. 54-58 (1988).

6. D. C. Shannon, K. P. Killeen and J. G. Eden, "Br_2 ion pair state formation by electron beam excitation," J. Chem. Phys. 88, p. 1719 (1988).

7. K. K. King, V. Tavitian, D. B. Geohegan, E. A. P. Cheng, S. A. Piette, F. J. Scheltens and J. G. Eden, "Laser photochemical vapor deposition of Ge films ($300 \leq T \leq 873$ K) from GeH_4: Roles of Ge_2H_6 and Ge," Mat. Res. Soc. Symp. Proc. 75, p. 189 (1987).

8. J. G. Eden, K. K. King, E. A. P. Cheng, S. A. Piette and D. B. Geohegan, "Laser photochemical vapor deposition," Proc. SPIE 710, pp. 43-45 (1987).

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10. D. E. Johnson and J. G. Eden, "High temperature, alkali rare gas optical cell," Rev. Sci. Instrum. 57, p. 2976 (1986).

11. D. B. Geohegan, A. W. McCown and J. G. Eden, "XeCℓ laser power enhancement with an external ultraviolet laser," IEEE J. Quant. Electron. QE-SS, pp. 501-504 (1986).

12. J. G. Eden, "Photochemical processing of semiconductors: New applications for visible and ultraviolet lasers," IEEE Circuits and Devices, pp. 18-24 (January 1986).

DEGREES GRANTED

1. D. B. Geohegan, Ph.D. in Physics, 1986, thesis on photoionization of rare gases and spectroscopy of Kr_2F. Postdoctoral work on LPVD growth of films. Present position: Solid State Div., Oak Ridge National Laboratory.

2. Emily Cheng, M.S. in Electrical Engineering, September 1987, thesis on laser-induced breakdown spectroscopy of impurities in semiconductor gases. Present position: Lightwave Electronics, Mtn. View, CA.

3. G. Rodriguez, M.S. in Electrical Engineering, 1987, thesis on spectroscopy of metal-halide molecules and PbI, in particular.

4. V. Tavitian, M.S. in Electrical Engineering, 1987, thesis on LPVD growth of Ge on GaAs.

5. C. J. Zietkiewicz, M.S. in Electrical Engineering, 1987, thesis on the physics of metal halide molecules and HgBr, in particular.

6. K. K. King will receive the Ph.D. degree in Physics in the spring of 1989 for his work on the multiphoton ionization of the Column IIIA metal alkyls and the halides.

7. D. J. Kane will receive the Ph.D. degree in Physics in February 1989 for his work on the inter-Rydberg spectra of Ne_2 and Ar_2.

PATENTS APPLIED FOR (OR GRANTED)

1. J. G. Eden, K. K. King and V. Tavitian, "Semiconductor processing by a combination of photolytic, pyrolytic and catalytic processes," U.S. Patent Application S.N. 07/126,891, filed Nov. 30, 1987; notice of allowance granted.

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Epitaxial Growth of Thin Ge Films on [001] GaAs By Laser Photochemical Vapor Deposition From GeH_4

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EPITAXIAL GROWTH OF THIN Ge FILMS ON [001] GaAs BY LASER PHOTOCHEMICAL VAPOR DEPOSITION FROM GeH_4

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ABSTRACT

Epitaxial Ge films have been grown on [001] GaAs for substrate temperatures (T_s) as low as 285°C by photodissociating GeH_4 at 193 nm in parallel geometry. For a laser fluence of ~15 mJ - cm^{-2}, the film growth rate varies from 0.6 to ~5 nm - min^{-1}, depending upon T_s and gas pressure. Plan and cross-sectional TEM studies of the Ge/GaAs bicrystal demonstrate that the 400-700 Å thick Ge films are single crystal and epitaxial with the substrate. The present limitation on epitaxial film thickness appears to be imposed by reduced adatom mobility at the temperatures investigated.

INTRODUCTION

Laser photochemical vapor deposition (LPVD) is especially attractive as a growth technique for those semiconductor (or metal) films whose electrical and structural properties are strongly dependent upon the surface temperature (T_s). This is certainly true for the III-V compound semiconductors for which the volatility of the column V constituent (As or P) poses increasing difficulties as the processing temperature rises. For this reason, several groups have pursued the growth of InP, GaAs, AlAs and [Ga,Al]As films by laser-assisted growth techniques [1-8]. In virtually all of these experiments, however, heating of the substrate and growing film by the incident visible or UV radiation played a significant or dominant role in the film growth process. In at least one case [6], obtaining crystalline material depended specifically on heating the substrate with laser pulses of $\Phi \gtrsim 100$ mJ - cm^{-2}. The heteroepitaxial Ge/GaAs is another example of a temperature sensitive system. Although epitaxial Ge films have been grown on GaAs by a variety of methods, autodoping of the Ge often occurs since T_s is typically > 400°C (cf. ref. 9).

This paper describes experiments in which epitaxial Ge films have been grown on [001] GaAs by LPVD at substrate temperatures as low as 285°C. The approach involved photodissociating GeH_4 (in He) at 193 nm in parallel geometry. Plan and cross-sectional view transmission electron microscopy (TEM) studies of the films clearly show them to be epitaxial with the substrate.

EXPERIMENTAL DETAILS

The experimental apparatus has been described previously [10] and will only be reviewed briefly here. The reactor was constructed of square quartz tubing and is ~30 cm in length. The beam from an ArF excimer laser (193 nm) is spatially filtered (0.5 × 2.0 cm^2 rectangular slit) and enters the reactor through one quartz wall (transverse to gas flow) and passes ~2 mm above the substrate. The UV fluence above the GaAs substrate is typically 15 mJ - cm^{-2} which is considerably smaller than that generally used in parallel geometry LPVD experiments. The rate of growth of the Ge film was measured *in situ* by recording the interference fringes produced by infrared blackbody radiation from the GaAs substrate propagating through the growing Ge film.

After being chemically cleaned, the [001] oriented, Si or Cr-doped GaAs substrates were placed in the reactor and prebaked at ~510°C for 30 minutes, followed by dry etching at the growth temperature (285 - 410°C) by flowing a 5% HCl/He mixture for 5 minutes. Subsequently, with a 5% GeH_4/He mixture flowing through the reactor (P_{TOTAL} = 5.6 - 30.4 Torr, 100 sccm mass flow rate), the UV laser was pulsed at 40 Hz for 40 - 50 minutes. Film growth rates varied from 0.6 to 5 nm/min, depending upon T_s and gas pressure.

Plan view and cross-sectional samples of the LPVD grown Ge/GaAs interfaces were examined by TEM in a Philips EM430 microscope operating between 150 and 300 kV. Figure 1 is a selected area diffraction pattern (SADP) observed along the substrate normal direction of a Ge film grown at 305°C and P_{TOTAL} = 30.2 Torr. The electron diffraction pattern is that for crystalline ([001]) Ge and we note that $\underset{\sim}{g}$ = {200} reflections, which are kinematically forbidden for Ge (but not for GaAs), are conspicuous by their absence. However, the diffuse rings indicate that an amorphous layer is also present along with the crystalline film. An SADP of the Ge/GaAs bicrystal is shown in Figure 2. The $\underset{\sim}{g}$ = {200} reflections are now evident (confirming that GaAs is now also being observed) but the pattern is otherwise identical to Figure 1, demonstrating that crystalline Ge has been grown on GaAs.

Cross-sectional TEM images of the sample studied in Figures 1 and 2 (as well as samples grown at other temperatures) confirm the supposition that the Ge film initially grows epitaxially but subsequently switches to amorphous material. The thickness of the crystalline film varies from ~250 to 700 Å, depending upon the growth temperature, and the morphology is rough. The electron micrographs suggest that the Ge initially nucleates on the substrate as crystalline islands which grow and eventually coalesce to form a film. For each sample studied, the switch from epitaxial to amorphous material occurs immediately upon coalescence. We attribute this to the limited adatom mobility which is characteristic of the substrate temperatures employed in these experiments. The successful demonstration of nonthermal approaches to increasing atomic surface mobilities would dramatically reduce the temperatures at which one could grow smooth epitaxial semiconductor films.

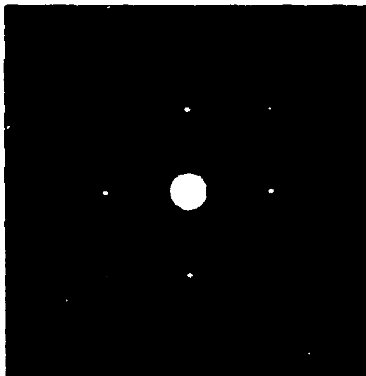

Figure 1. Selected area diffraction pattern (SADP) of a Ge film grown by LPVD on [001] GaAs at T_s = 305°C. The pattern is characteristic of that for a crystalline ([001]) Ge film and an amorphous layer.

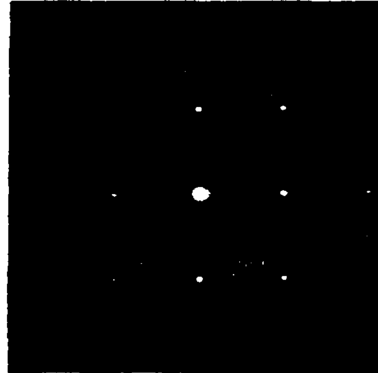

Figure 2. SADP of the Ge/GaAs bicrystal, revealing the expected g = {200} reflections that are characteristic of GaAs. Otherwise, the pattern is virtually identical to Figure 1.

Convergent beam electron diffraction studies of both plan view and cross-sectional samples demonstrate that the thin Ge films reported here are not only crystalline but have the following epitaxial relationship with the substrate:

Ge[001] // GaAs[001]; Ge[010] // GaAs[010].

Furthermore, lattice images of cross-sectional samples, taken along [011] GaAs at 300 kV, clearly show two sets of {111} fringes running continuously from the substrate, across the interface and into the Ge film. Figure 3 shows such a lattice image for an epitaxial Ge film, also grown at a substrate temperature of ~300°C. Note that the characteristic spacing of the {111} fringes is ~3.3 Å and that they are inclined with respect to the interfacial plane by ~55°.

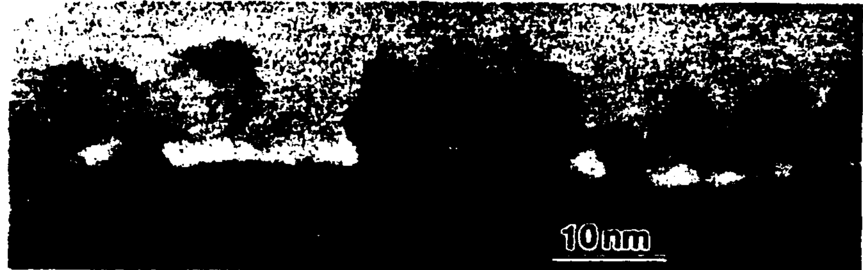

Figure 3. Lattice image of LPVD Ge film grown at ~300°C showing the continuity of {111} fringes across the Ge/GaAs interface.

Consequently, the TEM studies demonstrate that the Ge films grown by LPVD are indeed epitaxial.

RESULTS

The TEM results discussed briefly above are representative of those obtained for other samples grown at various temperatures. To date, epitaxial Ge films have been grown on GaAs for T_s as low as 285°C. Typically, the film growth rates lie in the range 0.6 - 5 nm - min^{-1} and in situ pre-etching of the substrate with the 5% HCl/He mixture was found to be essential for obtaining epitaxial Ge films.

Without the ArF laser radiation (i.e., conventional CVD), the Ge film quality deteriorates significantly. In the 285 - 310°C temperature range, the films are completely amorphous while those grown at higher temperatures (~410°C) in our apparatus are heavily-defected polycrystalline (microtwinning, stacking faults, dislocations).

In summary, epitaxial Ge films have been grown on [001] GaAs for substrate temperatures as low as 285°C by photodissociating GeH_4 at 193 nm. Without the external UV radiation, the films are amorphous or heavily-defected polycrystal line. The low laser fluences necessary to produce epitaxial films suggest that the laser indirectly generates Ge_2H_6 which subsequently pyrolyzes at the surface. These results demonstrate the ability of a UV laser to produce non-equilibrium concentrations of a species which, in turn, permits (without the need for a sensitizer) the low temperature growth of epitaxial semiconductor films. Also, this represents a clear example of the ability to grow epitaxial films by LPVD under conditions in which growth is not attributable to substrate heating or adlayer photolysis but rather to species which are generated photochemically in the gas phase (and at least 10 mean free paths from surface).

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A Tem Study of the Structure of Polycrystalline Si Films on (111) Si Substrates Grown By Low Pressure Chemical Vapor Deposition

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A TEM STUDY OF THE STRUCTURE OF POLYCRYSTALLINE SI FILMS ON (111) SI SUBSTRATES GROWN BY LOW PRESSURE CHEMICAL VAPOR DEPOSITION

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ABSTRACT

A systematic series of films have been deposited on Si (111) wafers by the pyrolytic decomposition of disilane in a low pressure CVD reactor at temperatures below 765°C, at a variety of Si_2H_6 partial pressures. Usually, large columnar Si grains nucleate with the [110] fiber axis parallel to the [111] substrate normal, and exhibit a random arrangement of azimuthal orientations about this axis. Fine scale microtwinning and sub-grain boundaries which are often seen within individual columnar grains have been characterized by HREM. The facetted boundaries between individual columnar grains have also been characterized. The correlation between typical grain size, defect densities and Si_2H_6 partial pressure is presented and the effect of changing partial pressure during growth is shown to be detrimental to film quality. Finally it is noted that randomly oriented polycrystalline Si films can be formed under certain growth conditions.

INTRODUCTION

The deposition of thin polycrystalline silicon films at low temperatures on a variety of substrates at reduced pressures has become of widespread interest to the semiconductor industry. For instance, as a result of the higher carrier mobility of polycrystalline Si relative to amorphous Si, polycrystalline thin film transistors may be used as switching devices in active matrix liquid crystal displays (Sasaki et al. (1986)).

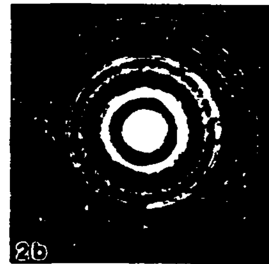
Since the structure of the as-deposited polysilicon film determines the electrical and mechanical properties of the film, the effect of various deposition parameters on the microstructure of the layers needs to be well understood. Several previous investigations have begun to correlate the effect of Si_2H_6 partial pressure, growth temperature and growth rates on film morphology (Meakin et al. (1987), Kamins (1980), Brokman et al. (1986), and Joubert et al. (1987)). These authors have shown that the crystalline texture, grain size and defect densities all depend on deposition parameters. The TEM results presented in this paper are a further contribution to the existing knowledge on this topic. We have concentrated on characterizing the important (110) columnar Si structure and in particular, its characteristic microtwinning and grain boundary facetting. Furthermore we have investigated the effect of the partial pressure of Si_2H_6 on grain size, microtwin densities and grain boundary sharpness. We also identify specific regimes where the Si layer grows in a random polycrystalline manner on the Si substrate.

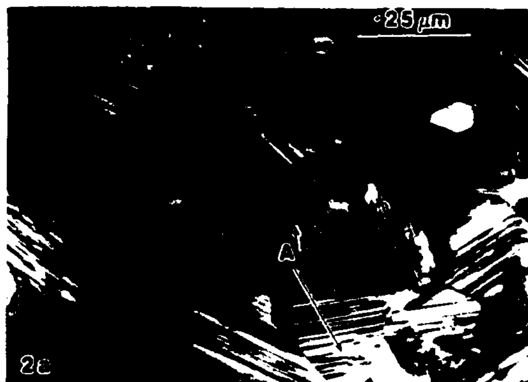
EXPERIMENTAL

Si films were deposited on (111) Si substrates by the pyrolytic decomposition of Si_2H_6 (in the temperature range 760 → 550°C), within a low pressure square quartz CVD reactor tube. The Si substrates were firstly prepared using the standard RCA cleaning procedure, and then subsequently subjected to a flash etch of HF/H_2O (1:50) to remove the native oxide layer. The substrates were resistively heated and the temperature monitored by both a thermocouple and optical pyrometry. The partial pressure of Si_2H_6 in a H_2 carrier gas was systematically varied between 250 and 12 mTorr, while the total pressure was kept constant at 10 torr. The entire deposition process was controlled by a DEC LSI 11/73 computer interfaced to (i) a temperature controller to maintain a pre-set substrate temperature, (ii) a capacitance manometer coupled to a downstream control valve to regulate process pressure, and (iii) a mass flow controller to regulate input source gas.

Plan view TEM samples were prepared by chemical backthinning using an HF/HNO_3/Acetic acid etch. Cross-sectional samples were prepared by the standard technique, and all specimens were examined in a Philips EM 430.

Fig. 1. Cross-section sample showing (110) textured columnar growth.





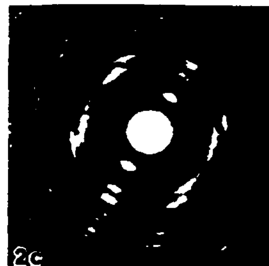


Fig. 2. (a) Plan view micrograph of columnar Si viewed exactly along the (110) fiber axis; (b) SADP along (110) fiber axis; (c) SADP tilted ~40° away from the fiber axis.

RESULTS AND DISCUSSION

Si films grown on Si (111) in the temperature range 760 → 650°C and with Si_2H_6 partial pressure in the range 170 to 13 m Torr, all exhibited (110) textured columnar growth. For the typical example shown in Fig. 1, (growth temp = 760°C, Si_2H_6 p.p. = 160 m Torr), the columns are about ¼ μm in diameter and have a preferred (110) growth direction perpendicular to the substrate. The crystallites have a slight V appearance starting from a thin SiO_2 interface layer and terminating at the film surface.

The micrograph in Fig. 2(a) shows the same sample in plan view and Figs. 2(b) and (c) are selected area diffraction patterns taken along the [111] substrate normal and tilted by ~40° from this direction respectively. The Si grains are viewed along [110] and are heavily microtwinned. The laminar structure of the Si columns is obvious, each grain being composed of a stack of very thin plates of microtwinned material. The reciprocal lattice points for a crystal in the form of a thin plate are elongated along the direction normal to the plate to give spikes, hence giving rise to the distinctive symmetrical spiking observed in Fig. 2(b). When the sample is tilted away from the substrate normal, the polycrystalline ring pattern is broken into a series of arcs, (Fig. 2(c)). Along the diameter perpendicular to the tilt axis, the original rings disappear and new ones appear as the tilting causes the Ewald sphere to intersect further planes of reciprocal lattice circles. This behavior corresponds to a fibrous texture in which a particular crystal axis, ([110] in this case), is

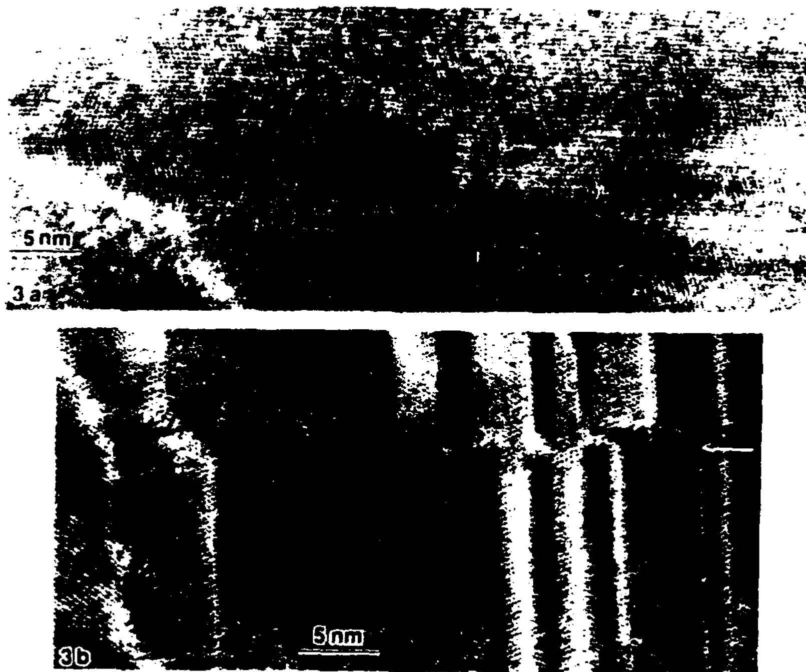


Fig. 3. (a) HREM micrograph showing microtwinning within a columnar Si grain; (b) HREM micrograph showing a line of 'microtwin mismatch.'

aligned along the fiber axis, with a random arrangement of azimuthal orientations about this axis.

Fig. 3(a) is a HREM image taken along the [110] fiber axis in which the (002), $(\bar{1}11)$ and $(1\bar{1}1)$ lattice planes are resolved. Microtwins lying on $(1\bar{1}1)$ planes, (in this case), and with lamellae thicknesses down to 16 Å are observed. Microtwinning can occur on either the $(1\bar{1}1)$ or the $(\bar{1}11)$ planes, (which are energetically equivalent), but both twin axes are not usually observed in any one grain, indicating that formation of one type of twin tends to mutually exclude the existence of the other. Sometimes 'sub-grain boundary' like features can be seen within individual grains, (e.g., A in Fig. 2(a)). HREM images, (Fig. 3(b)) show that these faults are distinct lines of "microtwin mismatch." This effect seems to imply that crystal growth, (with its inherent microtwin formation), sometimes occurs from opposite sides of the columnar grains, and when the growth fronts eventually meet, the microtwins are frequently found to be "out of step."

A further point worth noting from Fig. 2(a) is that the boundaries between individual grains are often facetted along certain characteristic crystallographic planes. Measurement of the angle between an adjoining {111} twin plane and grain boundary facet when viewed along the [110] fiber axis has allowed us to deduce that the majority of the boundary facet planes are {110} type, whereas many others are {112} type. However, there are many facets which do not fall into either of these categories.

At any particular growth temperature, the columnar grain diameter increased slightly with decreasing Si_2H_6 partial pressure. Since grain growth is initiated by clusters of atoms forming which can then grow laterally and vertically until impinging on another grain, decreasing the pressure reduces the probability of cluster formation and hence allows grains to grow larger before impinging. Decreasing the Si_2H_6 partial pressure led to improved crystal quality in that the microtwin density was lowered, but at the same time the grain boundary facetting became less distinct and sharp.

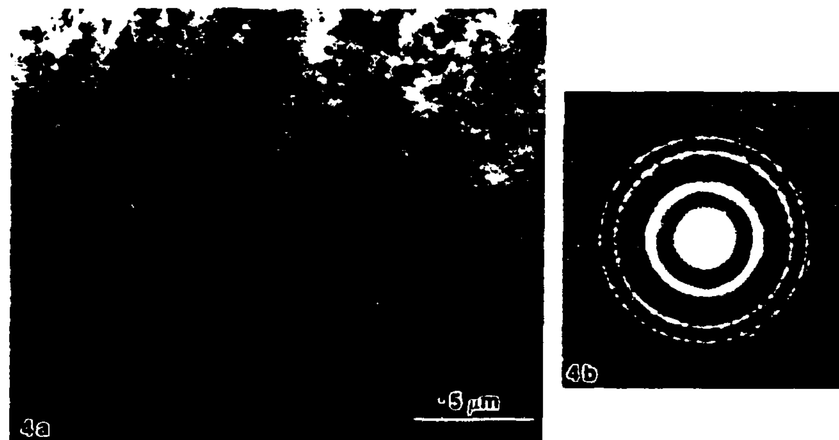


Fig. 4. (a) Cross-sectional sample showing non-textured polycrystalline Si growth; (b) SADP illustrating the random orientations of the Si polycrystals.

It was experimentally found that at growth temperatures of around 620°C and high partial pressures (250 mTorr), the overlayer was randomly oriented polycrystalline with a 1000 Å average grain size. The SADP from this layer (Fig. 4(b)) shows no evidence of texturing. The microtwinning density was low and no intervening interfacial SiO_2 layer was seen. This particular microstructure is not expected on the basis of the LPCVD Si morphology predictions of Joubert et al. (1987). Finally, all films grown below a temperature of 590°C were amorphous as expected.

Experiments were also performed at a growth temperature of 760°C where the Si_2H_6 partial pressure was abruptly changed from 0.013 → 0.08 mTorr during the growth run. In reality, this meant that there was a transient period of about 20 seconds where the Si_2H_6 partial pressure (and substrate temperature), fluctuated rapidly. Fig. 5 shows that this procedure was obviously detrimental to the film quality, since the film initially begins normal columnar growth, then turns totally amorphous for about 1500 Å before resuming (110) textured columnar growth once the growth parameters had stabilized at their new values. Similar effects were observed when the total pressure in the reactor was altered during a growth run.

Finally some films were grown on pre-cleaned Si(100) substrates to investigate if the exact nature of the substrate was critical in influencing subsequent overlayer growth. This was indeed found to be the case at temperatures around 760°C and Si_2H_6 p.p's of ~0.013 mTorr, since they initially formed randomly oriented fine grain (~150 Å diameter) polycrystalline layers for thicknesses of several hundred Å, followed by the usual (110) textured columnar growth.

A more detailed account of the characterization of the microstructure of these LPCVD films will be given elsewhere.

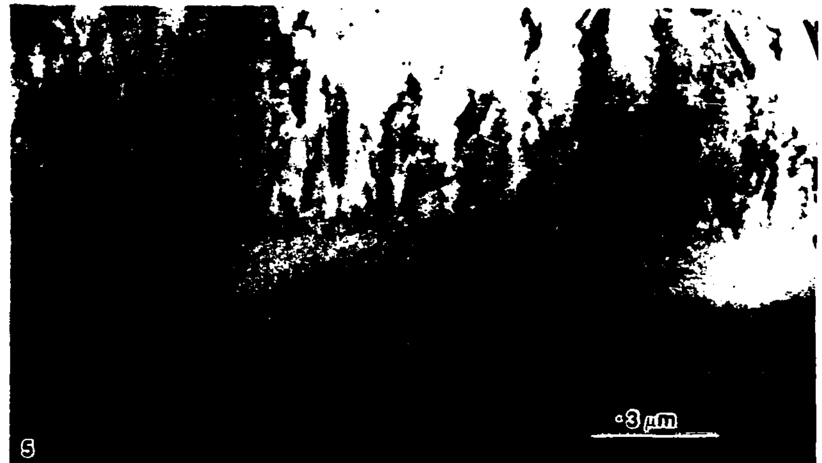


Fig. 5. Cross-section sample illustrating the effect of changing the Si_2H_6 partial pressure during a growth run.

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Epitaxial growth of Ge films on GaAs (285–415 °C) by laser photochemical vapor deposition

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Epitaxial growth of Ge films on GaAs (285–415 °C) by laser photochemical vapor deposition

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Epitaxial Ge films have been grown on [001]GaAs by laser photochemical vapor deposition (LPVD) for substrate temperatures (T_s) in the $285 \leqslant T_s \leqslant 415$ °C interval. Films 400–700 Å thick were grown at rates up to ~ 1 Å s^{-1} (0.6–5 nm/min) by photodissociating GeH_4 with an ArF (193 nm) laser in parallel geometry (i.e., laser beam passes above and parallel to substrate). The quality of the Ge/GaAs heterointerfaces has been examined by plan-view and cross-sectional transmission electron microscopy. Convergent beam electron diffraction, selected area diffraction patterns, and lattice images show the LPVD films to be epitaxial, whereas films grown in the absence of ultraviolet laser radiation (i.e., by conventional chemical vapor deposition) are amorphous ($T_s = 305$ °C) or heavily defected polycrystalline ($T_s = 415$ °C). Epitaxy apparently hinges on the laser production of a species which migrates more than 10–60 mean free paths to reach the substrate (or is collisionally transformed *en route* into a more stable species) and dramatically alters the surface chemistry. The large number of collisions involved points to the transformation of photochemically generated GeH_2 or GeH_3 into Ge_2H_6 as the key gas phase reaction.

The ability of visible or ultraviolet (UV) lasers to selectively produce (*in situ*) transient atomic or molecular species that are not normally present in a conventional chemical vapor deposition (CVD) or molecular beam epitaxy (MBE) reactor (thus allowing the growth conditions to be altered) has significant implications for the growth of semiconductor interfaces whose metallurgical and electrical characteristics are critically dependent upon the processing temperature (T_s). Considering the Ge/GaAs heteroepitaxial system, for example, epitaxial Ge films have been grown on GaAs by a variety of techniques (laser recrystallization, evaporation, etc.),[1-3] but since T_s is typically >400 °C, autodoping of the Ge layer frequently occurs.[3]

This letter describes experiments in which epitaxial Ge films have been grown on [001]GaAs for T_s as low as 285 °C by photodissociating GeH_4 (in He) at 193 nm (ArF laser). All experiments were conducted in parallel geometry (to avoid transient heating of the film and adlayer photolysis), and in the absence of laser radiation, the films were (depending on T_s) amorphous or polycrystalline. The results reported here demonstrate the ability to grow epitaxial films by laser photochemical vapor deposition (LPVD) under conditions in which growth is clearly not attributable to substrate heating, but rather to species generated photochemically and in the gas phase. The species in question migrate *at least* 10–60 mean free paths to the substrate and dramatically alter the surface chemistry.

The experimental apparatus is similar to that described previously.[4] Constructed from commercial quartz tubing having a square (2.5×2.5 cm^2) cross section, the reactor was ~ 30 cm in length and each end was gradually tapered down to 8 mm cylindrical quartz tubing. Gas flow was electronically controlled and monitored upstream and downstream of the reactor by mass flow controllers and transducers, respectively. The unfocused beam from an excimer laser (193 nm) was spatially filtered by a rectangular (0.5×2.0 cm^2) slit, entered the reactor (transverse to gas flow) through one quartz wall (transmittance $\sim 60\%$ at 193 nm), and passed ~ 2.2 mm above (measured from the bottom of the beam), and parallel to, the substrate. After exiting the reactor through the opposite wall, the beam was deflected by a prism onto a pyroelectric detector or absorbing calorimeter for measurements of the beam pulse energy or average power. The energy fluence typically available above the substrate at the beginning of a growth run was ~ 15 mJ cm^{-2} (in a ~ 20 ns full width at half-maximum pulse). For the gas pressures utilized in these experiments, the distance from any point in the gaseous region above the substrate (and illuminated by the beam) to the substrate was $\geqslant 10$–60 mean free paths (MFP's) for a collision with GeH_4.

For a given growth run, two substrates—one $\sim 0.5 \times 0.5$ cm^2 SiO_2 (quartz) and the other $0.5 \times \sim 2.0$ cm^2 Cr or Si-doped [001] GaAs—were placed in the reactor and could be resistively heated to temperatures as high as 870 K. A 1-mm-diam hole drilled in the heater allowed for a He-Ne laser beam to pass through the quartz substrate, thereby permitting *in situ* measurements of film growth to be carried out in transmission. An infrared pyrometer monitored the substrate temperature by viewing either the quartz or GaAs surfaces through a sapphire window sealed to the top of the reactor. The thickness of the Ge film on the GaAs substrate was also measured *in situ* and in real time by monitoring the interference fringes produced by infrared blackbody radiation emanating from the GaAs substrate and propagating through the growing Ge film.

GaAs substrates were chemically cleaned by the procedure described by Anderson *et al.*[2] The quartz substrates were rinsed in spectrophotometric grade acetone and methanol, and blown dry with N_2 prior to being introduced into the reactor. The experimental procedure consisted of pre-

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baking the substrates at ~510 °C under vacuum for ~30 min followed by dry etching at the growth temperature (285–415 °C) by flowing a 5% HCl/He mixture (total pressure = 3.5 Torr, ~50 sccm flow rate) for 5 min. The latter procedure renders unnecessary the prebaking of the substrate at much higher temperatures ($T_s > 600$ °C). After etching the substrates, a 5% GeH_4 in He mixture at a total pressure of 5.6–30.4 Torr and 100 sccm mass flow rate purged the reactor for ~270 s. The gas pressure limits correspond to flow velocities of 40 and ~6 cm s^{-1}, respectively. Subsequently, the UV laser was turned on and pulsed at 40 Hz (peak intensity ~0.75 MW cm^{-2}) throughout the growth period, which typically lasted 40–50 min. Film growth rates varied from ~6 to 50 Å/min, depending upon T_s and gas pressure.

Plan-view and cross-sectional samples of the LPVD-grown Ge/GaAs interfaces were prepared by the methods previously described by Rackham,[5] and Bravman and Sinclair,[6] respectively. Transmission electron microscopy (TEM) of the specimens was carried out in a Philips EM 430 microscope operating between 150 and 300 kV. Since the plan-view samples were backthinned to perforation (with a chlorine/methanol jet), TEM examination of only the LPVD-grown Ge film or the Ge/GaAs bicrystal was possible. Figure 1 shows the selected area diffraction pattern (SADP) observed along the substrate normal direction for a Ge film grown at 305 °C and $P_{GeH_4/He} = 30.2$ Torr. The diffraction pattern is characteristic of that for Ge[001] single crystal. Note that g = {200} reflections, which are kinematically forbidden for Ge, are absent. However, the presence of diffuse rings reveals the existence of an amorphous layer. Energy dispersive x-ray analysis of this region exhibited only characteristic Ge peaks, indicating that the Ge overlayer consists of an amorphous layer atop a single-crystal film. A similar SADP for the Ge/GaAs bicrystal is displayed in Fig. 2 which reveals a superposition of a GaAs[001] pattern (with g = {200} reflections now evident), the Ge[001] diffraction pattern (observed in Fig. 1), and a weak diffuse ring from the thin amorphous Ge layer.

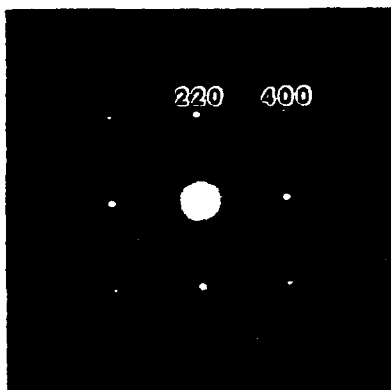

FIG. 1. Selected area electron diffraction pattern of a LPVD-grown Ge film indicating the presence of a Ge[001] single-crystal film in addition to an amorphous layer. This film was grown at 305 °C and a GeH_4 partial pressure of 1.5 Torr. Nearly identical results were obtained for other laser grown films in the 285 ≤ T_s ≤ 330 °C range.

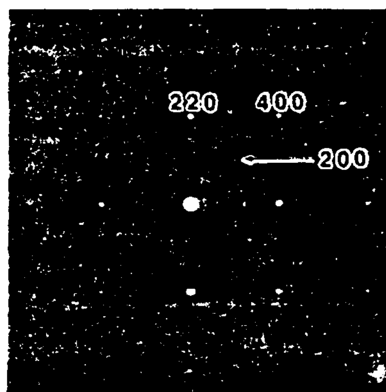

FIG. 2. SADP of the Ge/GaAs bicrystal for the sample of Fig. 1 (note that g = {200} reflections characteristic of GaAs[001] are now present).

Cross-sectional images of the sample examined in Figs. 1 and 2 confirm the supposition that the Ge film initially grows epitaxially, but later switches to amorphous material. As shown in Fig. 3, the crystalline Ge layer exhibits rough morphology and varies in thickness from 250 to 350 Å, while the amorphous Ge film is ~600 Å thick. The surface roughness (~30 Å) is an artifact of the *in situ* HCl etch process.

Convergent beam electron diffraction studies of both plan-view and cross-sectional samples demonstrate that the crystalline Ge film has the following epitaxial relationship with the substrate:

Ge[001]//GaAs[001]; Ge[010]//GaAs[010].

As illustrated in Fig. 4, lattice images of the GaAs/crystalline Ge interface, taken along [110]GaAs at 300 kV, show two sets of {111} lattice fringes running continuously from the GaAs substrate into the Ge crystalline layer, thus illustrating the epitaxy between the two crystals.

The TEM results of Figs. 1–4 are representative of the observations made of four other LPVD-grown films. To date, the lowest substrate temperature at which epitaxial Ge films have been grown is 285 °C. Typically, the epi Ge layer grows at a rate of 4–6 nm/min (up to ~1 Å s^{-1}) until reaching an average thickness of 400–700 Å. (The film shown in cross-sectional view in Fig. 4 is thinner because, for this particular run, the HCl etchant was also flowed *during* growth.) No obvious difference in film growth parameters or quality, other than an increase in the film growth rate, was observed when raising the GeH_4/He pressure from ~5 to ~30 Torr. Also, no apparent improvement in the film morphology or structure was detected if the film was etched dur-

FIG. 3. Cross-sectional image of the Ge/GaAs interface (examined in Figs. 1 and 2) showing a 250–350 Å thick crystalline film and a ~600-Å-thick amorphous layer. Thicker epi films were obtained if (contrary to this case) HCl was not flowed through the reactor during film growth.

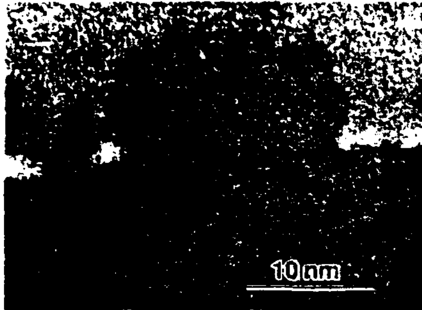

FIG. 4. Lattice image of the Ge/GaAs interface taken along [110] GaAs at 300 kV. The growth temperature is again 305 °C. The continuity of {111} lattice fringes across the interface demonstrates the epitaxy between the two crystals.

ing growth. However, failure to etch the substrate prior to film growth resulted only in amorphous Ge films. In the absence of UV radiation (i.e., conventional CVD), films grown at 300–310 °C are completely amorphous, while those grown at higher temperatures (415 °C) are heavily defected (microtwinning, dislocations, and stacking faults) polycrystalline. Details of the structural characterization of the LPVD- and CVD-grown films will be discussed elsewhere.[7]

From the TEM cross-sectional studies, it appears that the Ge initially nucleates on the substrate as epitaxial islands which subsequently grow in size and eventually coalesce to form a film. The switch from epitaxial to amorphous material appears to occur immediately after coalescence ($t \sim 400$–700 Å).

One of the most interesting aspects of these results is that film growth (albeit amorphous or polycrystalline) *does* occur in the absence of external UV laser radiation. One concludes, therefore, that the laser produces a species which migrates > 10–60 MFP's to reach the surface or is collisionally transformed *en route* into a more stable species. Upon reaching the substrate, this species alters the surface kinetics in such a way as to make the growth of epitaxial films possible. Those considerations suggest the collisional production of Ge_2H_6 from GeH_2 or GeH_3 radicals formed by the 193 nm photodissociation of GeH_4. One possible explanation for the epi film thickness limitation observed to date is to assume that GaAs[001] is more catalytically active (in dissociating Ge_2H_6) than is the LPVD Ge surface. Other possibilities revolve around the relative mobilities of Ge adatoms on different surfaces. Experiments designed to differentiate among these alternatives are in progress, and the results will be discussed elsewhere.

In summary, epitaxial Ge films have been grown on [001]GaAs by photodissociating GeH_4 ~2–3 mm above the substrate for T_s as low as 285 °C. These results demonstrate the ability of an UV laser to produce highly nonequilibrium concentrations of atomic or molecular species, thereby altering the reactor chemistry so as to permit the low-temperature growth of epitaxial semiconductor films. We are aware of no other clear example in which photons have altered the gas phase chemistry of a reactor so as to make possible the growth of epi films at a surface which is itself not illuminated.

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Spectroscopy of absorbers in rare gas-halide laser plasmas

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ABSTRACT

The spectroscopy and chemical kinetics of small molecules known (or believed) to absorb in rare gas-halide laser plasmas are being studied by laser excitation and probing techniques. Two examples from recent experiments -- inter-Rydberg absorption spectroscopy of Ar_2 and photoassociation (bound ← free absorption) of Kr-F collision pairs -- are described.

1. INTRODUCTION

The rare gas-halide excimer lasers were discovered in the spring of 1975 and, as attested to by the other papers in this conference, the intervening years have witnessed dramatic improvements in the technology and performance of these devices. Much of this progress has been realized by an empirical approach and yet the future development of the rare gas-halide excimer lasers will hinge on better understanding the physical mechanisms occurring in the active medium itself. Not only will an improved understanding of the basic chemistry and spectroscopy of the laser plasma suggest ways in which the laser's extraction efficiency can be improved, but measurements of fundamental optical and collisional constants will enhance the predictive capability of computer models on which the design of the next generation of lasers depends. The latter issue becomes an increasingly important consideration as the cost of ever more powerful excimer lasers rises.

This paper briefly describes two recent experiments that were conducted at the University of Illinois. The emphasis in both was to examine optical processes and small molecules which are believed to restrict the efficiencies of rare gas-halide lasers but about which little is known. The premise behind our work is that laser spectroscopy can be used to isolate a particular atomic or molecular species of interest for study. Extremely detailed information can now be obtained regarding, for example, the identity of molecular absorbers, absolute absorption cross-sections and considerable detail concerning the electronic structure of the molecule. The advantage of laser spectroscopic experiments over kinetics studies conducted in electron beam (e-beam) devices is that the latter produces a wide array of electronically excited and ionic species which makes it difficult to selectively study any one of them.

2. INTRA-CAVITY MEASUREMENTS OF RARE GAS DIMER ABSORPTION

Although single pass measurements of rare gas dimer (Rg_2) absorption in e-beam-produced plasmas have been reported,[1-3] only the strongest features are discernible in such experiments. Consequently, identifying vibrational sequences and Rydberg series would be greatly facilitated by improving the sensitivity of the classical technique. Intra-cavity laser techniques have been adapted for absorption spectroscopy in e-beam plasmas and have yielded more than an order-of-magnitude increase in the overall experimental sensitivity.

The experimental apparatus is similar to that described in ref. 2 except for the installation of an optical cavity around the coaxial e-beam diode. Composed of two aluminized mirrors (one flat and the other having a 3 m radius of curvature), this cavity also contained a quartz dye cuvette that was irradiated by a ~10 ns (FWHM) frequency-doubled Nd:YAG (532 nm) or ~ 20 ns XeCl (308 nm) laser pulse. A quartz beamsplitter placed in the cavity enabled the resulting intra-cavity dye laser pulse to be monitored by a photodiode or by a spectrograph (1.0 or 0.25 m) - optical multichannel analyzer combination.

The improvement in sensitivity that is readily obtained with this arrangement is illustrated in Fig. 1 which shows the inter-Rydberg absorption spectrum of Ar_2 between 490 and 535 nm. The upper portion of the figure is the single pass absorption spectrum obtained with the broad band dye laser pulse only (Nd:YAG pumped). With the addition of

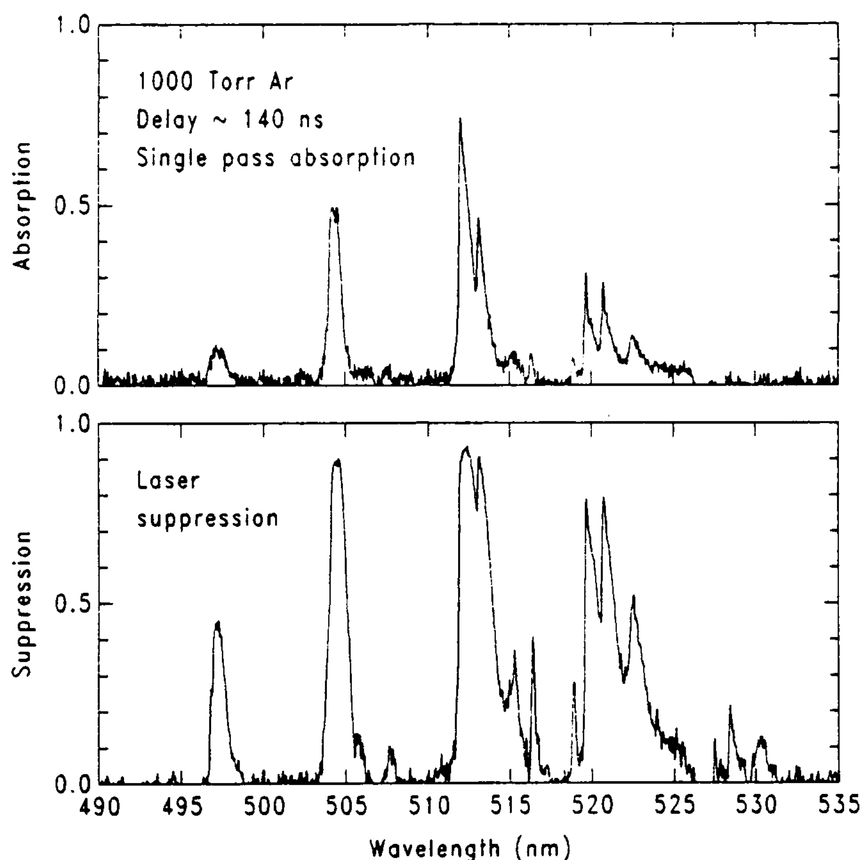

Figure 1. Absorption spectra of Ar_2 $4s^3\Sigma_u^+$ (1_u, 0_u^-) in the green-single pass spectrum (top) and enhancement of sensitivity obtained by adapting intra-cavity techniques (bottom). Both spectra were obtained by acquiring data ~ 140 ns following the e-beam pulse and the intra-cavity spectrum was obtained by exciting the dye with an Nd:YAG (frequency-doubled) beam.

the optical cavity, the strongest peaks (504, ~ 512 nm) are noticeably saturated and several features that were not previously discernible are now quite obvious. This is especially true of the group of three vibronic bandheads lying between ~ 527 and 532 nm. Further increases in sensitivity have been observed if the dye cell is photopumped by the longer (~ 20 ns FWHM) pulse available from an excimer laser.

As far as an interpretation of the spectrum itself is concerned, the prominent features in Fig. 1 (bottom) can be divided into two categories. All of the molecular bands having wavelengths > 510 nm are strongly red-degraded and are attributed to transitions from the lowest excited state of Ar_2 ($4s^3\Sigma_u^+$ - 1_u, 0_u^-) to three states associated with the $A\pi_u 5p$ manifold of Rydberg levels. That is, all of the states involved in these transitions have $A^2\Sigma^+_{1/2u}$ ($1[\frac{1}{2}]_u$) molecular ion cores and a 5p Rydberg electron. (The notation for the group of Rydberg levels was proposed by Mulliken.[4]) Note the periodicity of the transitions in this long wavelength portion of the spectrum - namely the grouping of the transitions into sets of three, with each group split from the adjacent one by 280 ± 10 cm^{-1}. The assignments of these transitions will be described in more detail elsewhere.[5]

Before leaving the long wavelength features of the Ar_2 green spectrum, we note that the strong transition at ~ 522.5 nm is indeed molecular. Figure 2 illustrates the temporal dependence observed at several wavelengths in the vicinity of this transition. Atomic transitions, such as that at 525.6 nm (cf. top trace of Fig. 2) decay rapidly as expected whereas undisputed molecular bands (bottom of Fig. 2) decline with a much longer time

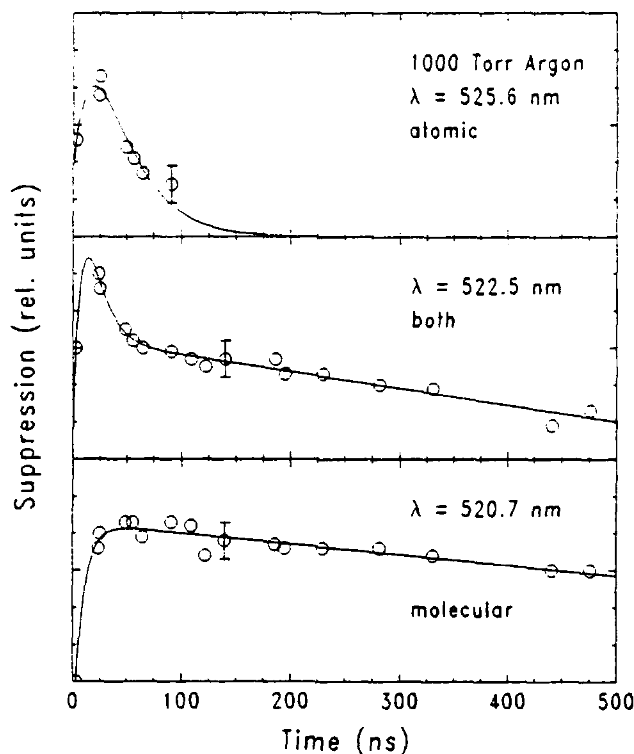

Figure 2. Temporally-resolved data for absorption at 525.6, 522.5 and 520.7 nm.

constant (~ 1 μs). Absorption at 522.5 nm, on the other hand, displays characteristics of both. As shown by the middle trace in Fig. 2, the absorption consists of two superimposed components with molecular absorption clearly dominating beyond ~ 100 ns following the e-beam excitation pulse.

The two strong transitions at the short wavelength end of Fig. 1 exhibit characteristics completely different from the other bands discussed above. Neither displays evidence of red-degrading and the peaks of both reveal considerable structure. We attribute, therefore, the 498 and 504 nm bands to $\Delta v = 0$ and $\Delta v = -1$ transitions, respectively, of Ar_2 4s (1_u, 0_u^-) to one of the two 1g states in the 4 state $A\pi_u5p$ manifold. Although little theoretical guidance is available regarding this manifold, it is expected to have characteristics similar to the analogous $A\pi_u4p$ manifold discussed by Chang and Setser[6] from the guidelines presented by Mulliken[4] for Xe_2.

In summary, it appears that all four members of the $A\pi_u5p$ manifold have been observed. Spectra similar to Fig. 1 have also been acquired in the violet and near-UV and display characteristics nearly identical to those in the green except that transitions to the highest-lying 1g level are no longer observed.

3. BOUND ← FREE ABSORPTION (PHOTOASSOCIATION) OF Kr – F

Some of our most recent work involves producing exciplex molecules by photoassociation - that is, bound ← free absorption by a colliding pair of atoms. For example, the KrF molecule can be formed in its lowest excited state ($B^2\Sigma_{1/2}$) by irradiating a pair of Kr-F atoms with $\hbar\omega$ ~ 5 eV photons. This is, if the colliding pair of atoms has an internuclear separation within a given interval, the free atoms can absorb a photon to yield a bound, electronically-excited molecule. After the excimer is formed, it can be detected by monitoring emission from KrF (i.e., B → X at 248 nm) or from one of its collisional products (KrF C → A or $Kr_2F(4^2\Gamma \rightarrow 1^2\Gamma)$ at 275 or 420 nm, respectively). Thus, this process not only provides a powerful means for accurately determining the molecule's potential curves but is also a potentially serious loss mechanism in excimer lasers. The reason for the latter is that photoassociation is particularly strong in the vicinity of the laser wavelength.

Figure 3 shows the photoassociation spectrum of Kr-F colliding pairs in which KrF(B) state molecules were produced by the absorption of a photon from a tunable (frequency-doubled) dye laser and subsequently detected by monitoring the blue Kr_2F fluorescence. The clear oscillatory (Franck-Condon) structure in the spectrum arises from transitions of the Kr-F pair to various $KrF^*(B)$ vibrational levels.

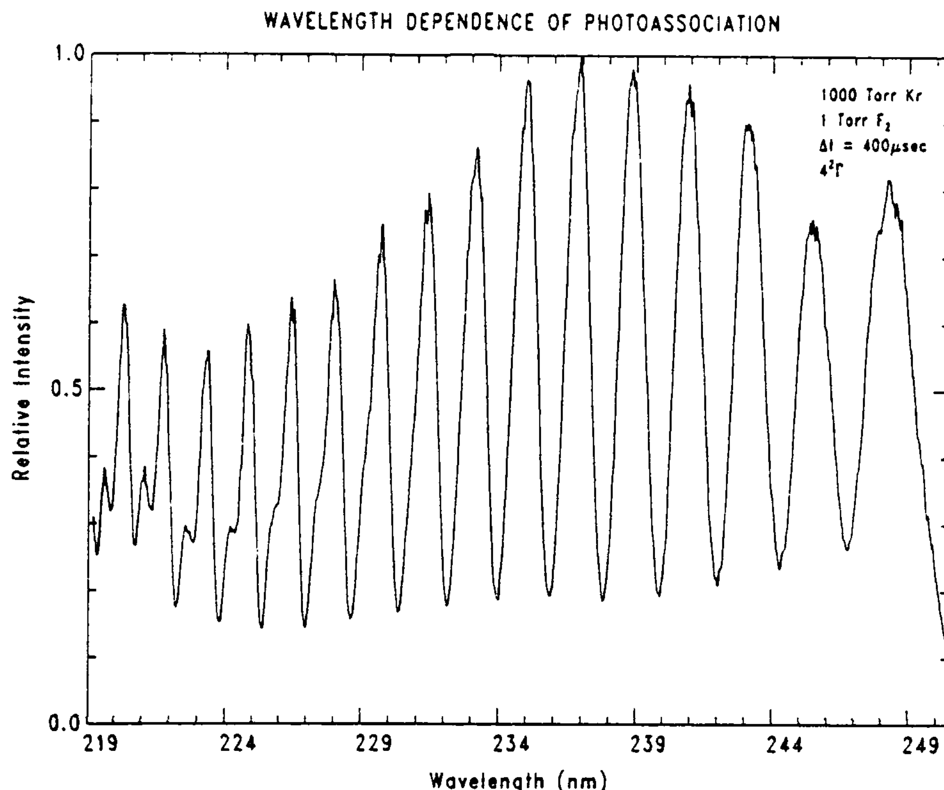

Figure 3. Excitation spectrum for the bound ← free (photoassociative) process: $Kr + F + \hbar\omega \rightarrow KrF(B^2\Sigma^+_{1/2})$. The spectrum was obtained by monitoring Kr_2F emission at $\lambda \sim 420$ nm as a tunable dye laser was scanned. The Kr/F_2 gas mixture in the optical cell is indicated.

Note how strong photoassociation is in the vicinity of 248.4 nm (the KrF laser wavelength). Thus, this process represents an unavoidable loss unless efforts are made to scavenge free halogen radicals <u>during</u> the laser pulse. It is possible then, that photoassociation is responsible for the droop in excimer laser output power that is frequently observed in long pulse operation (or, perhaps, even for short (~ 50 ns) pulses but at high excitation levels). Consequently, although fuel depletion (i.e., "burn up" of the halogen donor) has received much attention in recent years and is generally believed to be responsible for the annoying droop in laser output power that occurs as the pulse is increased, it is quite possible that the generation of halogen atoms, coupled with the slow recombination of these species, results in photoassociation having an equal impact on long pulse performance. One may speculate that, if this is indeed the case, it may be possible to observe a <u>slight</u> "red shift" of the KrF laser wavelength as the pulse progresses and the growing absorption at 248 nm forces the medium to move towards longer wavelengths where photoassociation declines rapidly.

In conclusion, photoassociation of free Kr-F colliding pairs is expected to become increasingly important as the laser pulse width (or excitation level) is increased and may be responsible for the "droop" in output energy (and efficiency) that has been widely observed.

4. SUMMARY

Two recent experiments have been described for which the goal has been to resolve issues that have intrigued (and plagued) the excimer laser community for several years. The

results underscore the ability of laser techniques to examine in detail absorbers and optical processes contributing to the limited excimer laser energy extraction efficiencies obtained to date.

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