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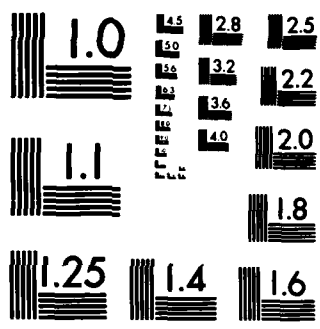
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on AFOSR Contract
F49620-83-C-0003

NON-LINEAR OPTICAL TECHNIQUES FOR VISIBLE AND UV LASERS AND THIN FILM DEPOSITION

for the Period
October 1, 1983 to September 30, 1984

Prepared for
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November 1984

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Experiments are described in which lasers are used to generate specific Column IIIA metal ions. The first studies involved ion pair production in the metal-halide molecules (such as thallium iodide) by illuminating the vapor with 193 nm radiation. More recent experiments have succeeded in producing Al³⁺ ions by the multiphoton ionization (MPI) of metal alkyls (such as trimethylaluminum) in the visible. Another aspect of the current work is focusing on the use of ultraviolet radiation to enhance the growth rate of semiconductor films grown near pyrolytic threshold. The use of gaseous sensitizers (such as ammonia) to		

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Improve film growth rates and quality is also being explored. Finally, a simple photochemical means for improving the efficiency of a commercial XeCl laser by more than 50% has also been discovered. Originator furnished

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MATTHEW J. KERPER
Chief, Technical Information Division

I. INTRODUCTION

Five years ago, AFOSR first funded work in this laboratory in the general area of laser physics. As a result of that work, several new visible and IR lasers were discovered. More recently, though, the work has expanded in two directions: non-linear spectroscopy of molecular electronic excited states and the application of this spectroscopy to the laser-stimulated growth of metal and semiconductor films.

We are pleased to report that this work continues to be successful and the highlights of this last year's work are described in the next section. Briefly, the accomplishments of this past year include:

1) The growth of Column IIIA metal films by the dissociative ionization of metal-halide vapors.

2) The application of the multiphoton ionization of metal alkyls to the growth of Column IIIA films.

3) The first (known) observation of the UV bands (250 - 300 nm) of GeH.

4) A simple photochemical scheme for enhancing the efficiency of an XeCl₂ excimer laser by \geq 50%.

5) The demonstration of the usefulness of gaseous sensitizers in the growth of Ge films by laser photochemistry.

6) The dramatic effect of low fluence excimer laser irradiation of a substrate on the film growth rate.

The work under #4 has been completed and a patent application will shortly be filed as a result of this work. The experiments under #2, #5, and #6 are still in progress and will probably extend through FY85. Finally, the work completed under #1 and #4 has been written up and will be published in the near future.

II. RESULTS OF EXPERIMENTAL WORK - FY'84

A. Column IIIA Metal Film Growth

The first experiments in this area exploited the production of ion pairs from certain diatomic molecules when irradiated near 200 nm. That is, if MX is a metal-halide diatomic molecule ($M = Tl, In, etc.$; $X = \text{halogen atom}$), then

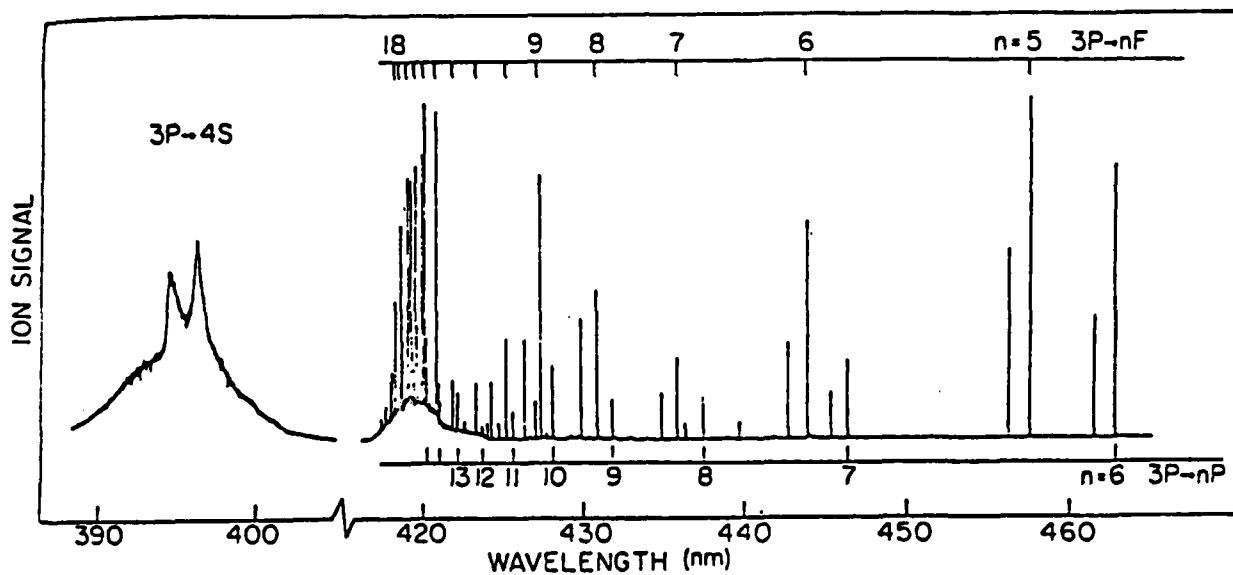


The advantages of producing metal ions in this way are that only one positive ion is produced (that of the metal) and this process is within the operating range of excimer lasers. (Producing M^+ and a free electron requires optical sources with wavelengths less than 150 nm, but ion pair production allows λ to be as large as ~ 220 nm).

These experiments have worked quite well and the attached reprint describes the growth of Tl, In and Al films in this way.

A second technique for producing Column IIIA atomic ions was also recently demonstrated here and involves the multiphoton ionization of metal alkyls at room temperature. Figure 1 (top) shows a low resolution MPI spectrum of $Al_2(CH_3)_6$ which was observed by Mitchell and Hackett in 1983. The bottom trace is a higher resolution scan obtained in our laboratory for $440 \leq \lambda \leq 450$ nm. We note that the sharp resonances in these spectra are characteristic of only the metal atom and appear to be completely independent of the organic ligand. We are currently examining the MPI spectra of triethylaluminum ($Al_2(Et)_6$) and triisobutylaluminum to confirm this conclusion. Of course, another advantage of this approach is that one can use a visible laser.

We use a cell design in which the gas flows between parallel plate electrodes mounted in a square quartz tube. The substrate is mounted on the



1.0 TORR $\text{Al}_2(\text{CH}_3)_6$

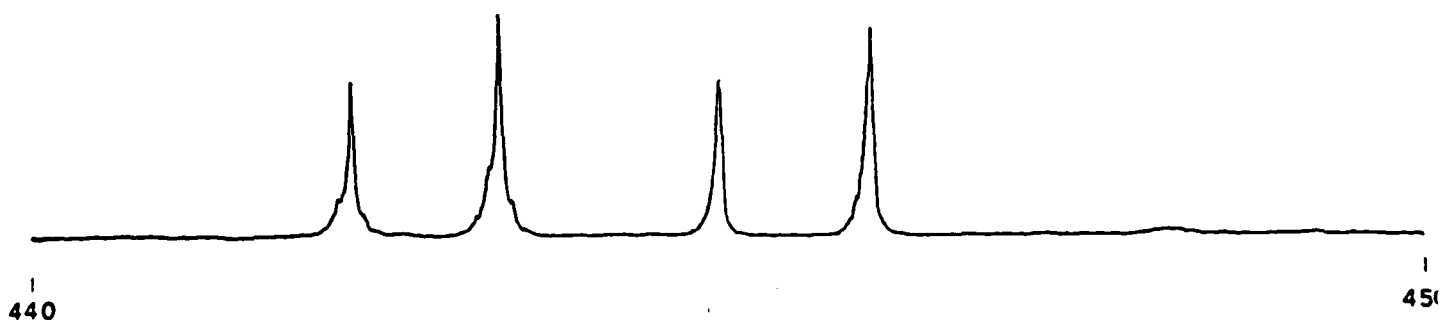


Fig. 1. MPI spectra of $\text{Al}_2(\text{CH}_3)_6$ in the violet.

negative electrode and the laser is allowed to run long enough to collect significant amounts of charge. This process has been used with Si, GaAs, and Pt substrates so far.

Auger analysis of films grown in this manner will be carried out later this month. Finally, we have also begun intensity dependence studies of the ion production at two-photon resonances. This data will aid in better understanding the basic physical mechanisms involved in ion production.

B. Detection of Gaseous Impurities by Laser-Induced Breakdown

As the sophistication of electronic devices rises and their size decreases, increasing demands are being placed on material purity. Whether introduced by the source gases or the reactor itself, impurities are becoming increasingly important.

We have recently started a series of experiments to determine the impurities present in various semiconductor source gases. For this work, we are using laser-induced breakdown and an experimental apparatus similar to that shown in Fig. 2. Initial work is focussing on the impurities present in GeH_4 . According to the manufacturer, argon should be present in a 5% GeH_4/He mixture at a level < 1 ppm. Figure 3, however, shows strong Ar emission lines in the LIB spectrum of ~ 1 bar of the mixture. We are presently in the process of calibrating this spectrum. One of our near-term goals is to detect the presence of Ge in AsH_3 . Growers of high purity GaAs continue to be plagued by three impurities: S, Si and Ge and it is suspected that the latter is introduced via the arsine used in growing GaAs by MOCVD or VPE. Once the apparatus is calibrated, it will be a simple matter to detect Ge in AsH_3 at the sub-ppm level (if it is indeed present).

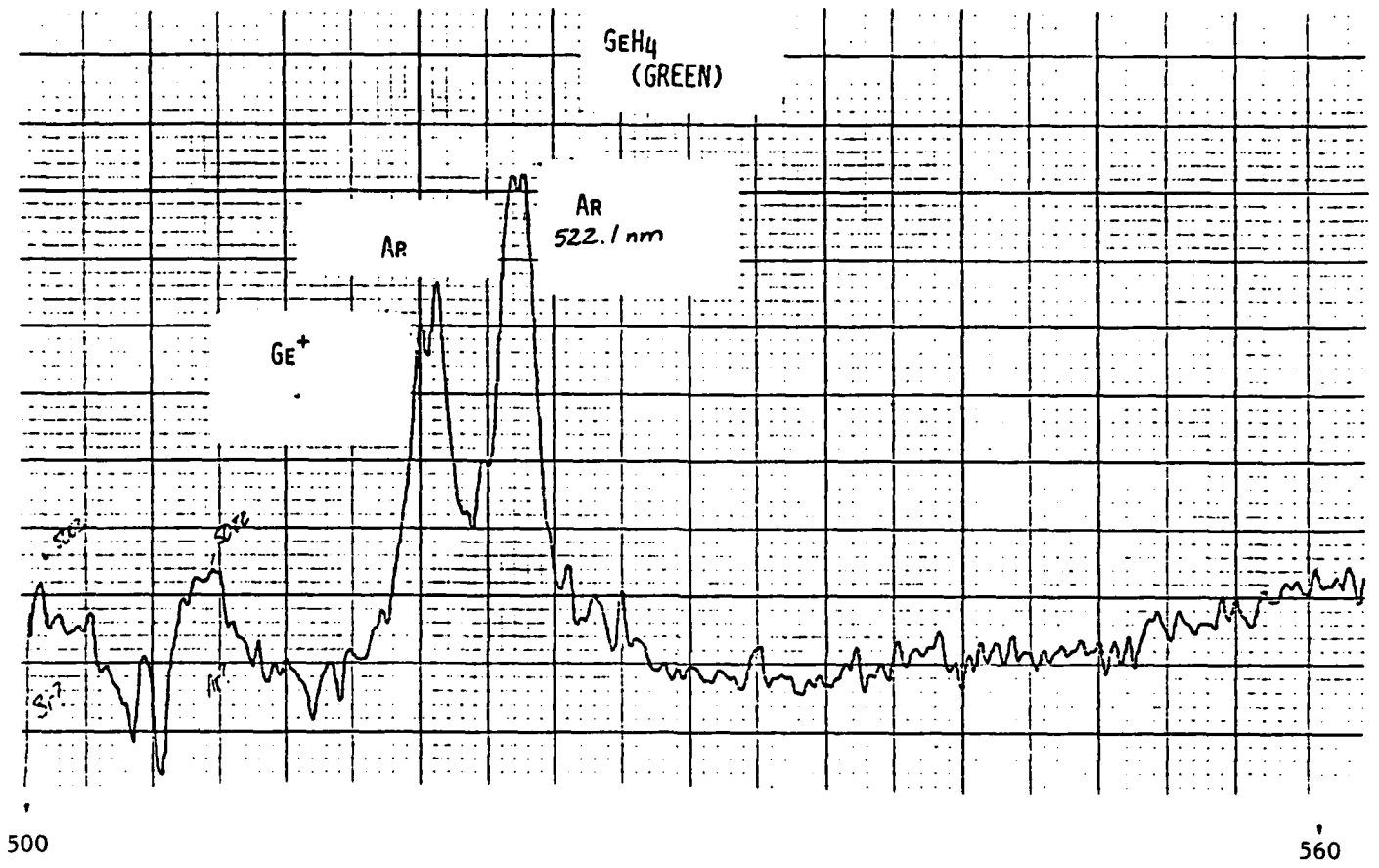


Fig. 3. LIB spectrum of 5% GeH₄/95% He in the green showing the presence of Ar.

C. Growth of Semiconductor Films by Laser Photochemistry: Effect of UV Irradiation of Substrate on Growth

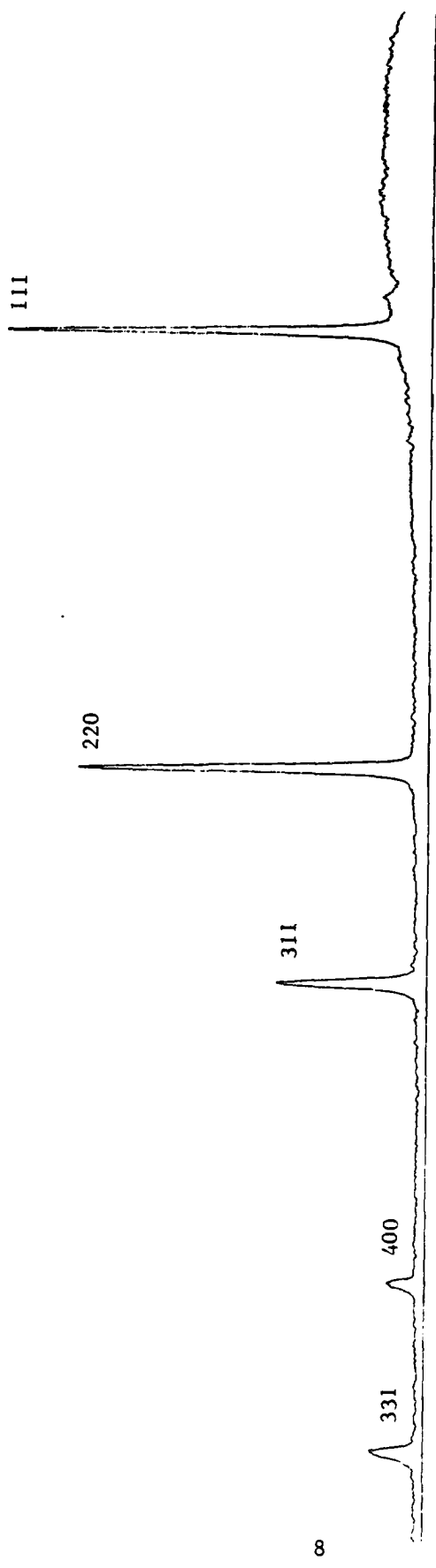
We are currently in the process of quantifying the effect that the UV radiation from an excimer laser has on the growth rate and film quality of LCVD grown Ge films near pyrolytic threshold. Earlier work carried out in our lab showed a rather striking effect in that the excimer radiation permitted film growth at temperatures below pyrolytic threshold and enhanced the growth rate above pyrolytic threshold. The dependence of the growth rate, grain size, and other important parameters of the films on the intensity and wavelength of the excimer radiation is presently being studied.

Considerable improvements in the design of our reactor have been made in the last year. This reactor allows for heating the substrate from the front or the rear by a CO₂ laser. Also, the substrate is nearly flush with one of the reactor walls (reactor has a rectangular cross-section) which leads to laminar flow over the sample. This arrangement has led to the best quality films grown to date. For example, Figure 4 is an x-ray diffraction pattern of a Ge film grown on quartz above pyrolytic threshold. The Bragg peaks are exceptionally narrow, reflecting the fact that the grain sizes in the film exceed 2000 Å, which is larger than the machine resolution.

Therefore, in the next year we will be carefully characterizing the effect of UV radiation of different wavelengths on the growth rate and quality of films grown near pyrolytic threshold. We will also continue to study gaseous sensitizers (such as NH₃) which greatly improve the film growth rate.

D. XeCl₂ Laser Efficiency Enhancement

One of the spinoffs from our spectroscopic work that has arisen in the past year is a simple means for improving the efficiency of an XeCl₂ laser (and presumably the other excimer lasers as well) by more than 50%. Since a patent



X-ray Powder Diffractometer Spectra

Fig. 4. Bragg diffraction spectrum for a Ge film (> 1 μm thick) grown on quartz above pyrolytic threshold.

disclosure on this discover is currently being prepared by the University, it is not possible to describe this in detail here. However, a preprint of the paper describing the experiments in detail will be sent to Dr. Schlossberg as soon as it is finished.

E. K₂ and KXe

Finally, this past year saw the completion of some inexpensive but tedious experiments on KXe that were begun 3 years ago. These experiments were carried out by Dan Johnson who will receive his Ph.D. degree in Physics this year. Although drawn out, these experiments were very successful, in that new states of K₂ and the green (515 nm) band of KXe were observed for the first time.

F. Summary

This has been a productive year and the work now encompasses several aspects of the laser growth of semiconductor films. We expect that the experiments involving UV irradiation of the substrate will yield physical insight into the mechanisms responsible for the accelerated growth of films. The discovery of a means to enhance the efficiency of excimer lasers by > 50% is expected to be of immediate use to DOD as well as the research community.

III. PAPERS PUBLISHED IN FY'84

1. D. B. Geohegan and J. G. Eden, "Column IIIA Metal Film Deposition by Dissociative Photoionization of Metal Halide Vapors," Appl. Phys. Lett. (Nov., 1984).
2. D. B. Geohegan, A. W. McCown and J. G. Eden, "Photoionization of Vapor Phase Thallium and Indium Monohalides in the Ultraviolet: Absolute Cross-sections and Photofragment Spectroscopy by Photodetachment of I⁻," J. Chem Phys. (Nov., 1984).

3. J. F. Osmundsen, C. C. Abele and J. G. Eden, "Multiphoton Dissociation of GeH_4 : Ultraviolet Emission Spectrum of GeH " (submitted to J. Chem. Phys.).
4. J. F. Osmundsen, C. C. Abele, and J. G. Eden, "Activation Energy and Spectroscopy of the Growth of Germanium Films by Ultraviolet Laser-Assisted Chemical Vapor Deposition," (to be published in J. Appl. Phys.).

IV. DEGREES GRANTED

J. F. Osmundsen, Ph.D. (E.E.), Thesis Title: "Low Temperature Growth of Thin Semiconductor films by Laser Induced Chemical Vapor Deposition," October 1984.

V. PERSONNEL

J. G. Eden

J. F. Osmundsen (graduated)

C. C. Abele

D. Kane

V. Davidian

K. Johnson

A. W. McCown (post doc, leaving for a position at
Los Alamos in December 1984)

D. B. Geohegan

END

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