

LASER PHOTOCHEMICAL VAPOR DEPOSITION OF Ge FILMS ($300 \leq T \leq 873$ K) FROM GeH_4 : ROLES OF Ge_2H_6 AND Ge

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ABSTRACT

The photochemical growth of polycrystalline and amorphous Ge films on SiO_2 , GaAs and NaCl by photodissociating GeH_4 with excimer laser radiation in parallel geometry is reported. For substrate temperatures (T_S) below the pyrolytic threshold for GeH_4 (553 K), two distinct regions of film growth are observed. In the $425 < T_S < 553$ K range, the ultraviolet (UV) laser "seeds" the reactor with Ge_2H_6 which readily pyrolyzes at the surface, forming several monolayers of Ge which subsequently catalyze the pyrolysis of GeH_4 . The activation energy (E_a) in this region is the same as that for the normal CVD growth of Ge from GeH_4 ($E_a \approx 0.9$ eV). If, however, the laser is pulsed throughout the film growth run, E_a falls by a factor of at least 2 and growth is observed for T_S as low as 300 K. In this laser sustained region, film growth ceases in the absence of UV laser radiation. These results clearly demonstrate the ability of a UV laser to alter the reactor chemistry and dictate the species responsible for film growth.

Vapor phase photochemical reactions are capable of producing non-equilibrium number densities of atomic and molecular species in a CVD reactor. In particular, one can selectively create (in situ) transient species that are not normally present in a conventional reactor. Consequently, the growth conditions in the reactors can be altered artificially. The implications of such capabilities are significant for the low temperature growth of metal and semiconductor films. Devices based on the temperature sensitive III-V compounds (such as the Ge/GaAs heteroepitaxial system), in particular, would benefit from reduced temperature operation owing to reductions in the out-diffusion of Column V atoms and minimal impurity redistribution.

Andreatta and coworkers [1, 2] have reported the photochemical growth (LPVD: laser photochemical vapor deposition) of Ge films on SiO_2 , 1102 sapphire and NaCl by photodissociating GeH_4 at 193 (ArF laser) or 248 nm (KrF). In these experiments, the excimer laser beam irradiated the substrate at normal incidence and polycrystalline films were grown at substrate temperatures as low as 300 K. In subsequent spectroscopic studies, Osmundsen et al. [3] demonstrated that, for $\lambda = 248$ nm, the Ge film growth process is initiated by the two photon dissociation of GeH_4 to yield the germylene radical, GeH_2 . Although the experiments showed that GeH_2 and hydrogen atoms are produced immediately, kinetic analysis [3] of the ensuing collision sequence identified digermane (Ge_2H_6) and atomic Ge itself as

the dominant (long-term) "stable" by-products of the photolysis of GeH_4 . In this context, it is interesting that the potential importance of disilane (Si_2H_6) to the growth of a-Si:H films was inferred from experiments recently reported by Taguchi et al [4].

This paper describes experiments in which polycrystalline and amorphous Ge films were grown photochemically by photodissociating GeH_4 at 193 or 248 nm in a parallel configuration (i.e., the laser beam does not irradiate the substrate). For temperatures below pyrolytic threshold ($T = 553$ K) [5], two distinct modes of film growth are observed and attributed to separate gas phase species. The results clearly show that the ultraviolet (UV) laser is capable of controlling the reactor chemistry and so determine the atomic or molecular species that is responsible for film growth.

A partial schematic diagram of the experimental apparatus is shown in Fig. 1. The beam from an excimer laser passed through a rectangular ($0.5 \times$

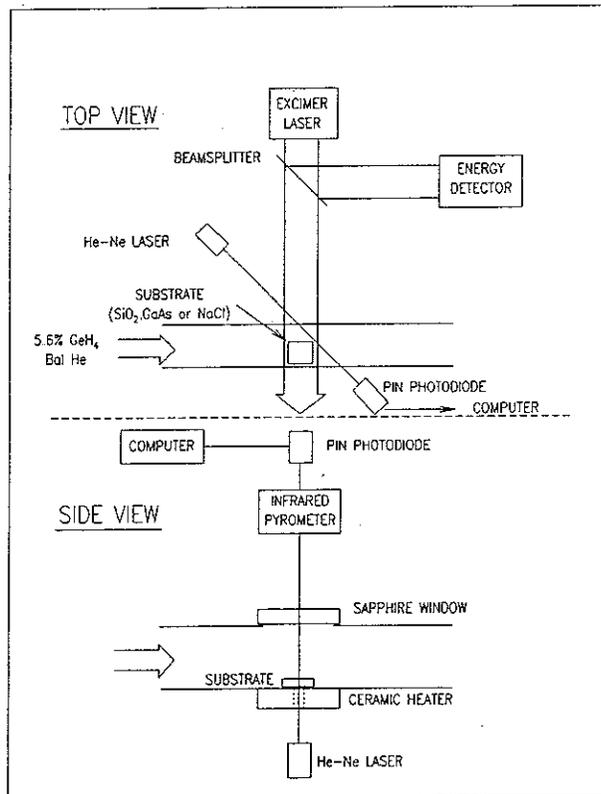


Fig. 1 Partial schematic diagram of the experimental apparatus

2.0 cm^2) slit and entered a quartz reactor having a square cross-section ($2.5 \times 2.5 \text{ cm}^2$, $\sim 30 \text{ cm}$ in length). Although the UV laser beam was not focussed, the beam intensity in the reactor was easily varied from 0.1 to $\sim 1.3 \text{ MW-cm}^{-2}$ by adjusting the thyatron charging voltage or inserting quartz flats in the beam path. Pulse energies and the average laser power were measured by pyroelectric (Gen-Tec) or absorbing calorimeter (Scientech) detectors, and the laser energy actually entering the cell was measured by determining the transmission of the cell walls with the reactor evacuated. The substrate (quartz, GaAs or NaCl—typically $\sim 0.4 \text{ cm}^2$ area) lay on the bottom of the reactor and was resistively heated. Substrate temperatures as high as $\sim 870 \text{ K}$ could be obtained and the NaCl substrates were prepared by cleaving large crystals in argon. The excimer laser beam passed over and parallel to the substrate. Although the distance from the center of the beam to the substrate surface could be adjusted from 0 to 25 mm , all of the data reported here were acquired at a height of 2.2 mm . Care was taken to ensure that the excimer laser beam did not irradiate the substrate.

A 1 mm diameter hole drilled in the inconel heater allowed for the passage of a He-Ne laser beam through quartz substrates and so the thickness of growing Ge films was measured *in situ*. The growth of thin Ge films on the window through which the excimer radiation entered the cell attenuated the UV laser beam, making it necessary to measure the film growth rate at that point with a second He-Ne laser. An infrared pyrometer monitored the substrate temperature by viewing the substrate through a sapphire window at the top of the reactor. In order to ensure that the pyrometer monitored the same region of the region of the substrate that was viewed by the He-Ne probe, the IR pyrometer was aligned by that red laser beam. He-Ne laser transmission data and the substrate temperature were stored by a DEC LSI 11/73 computer. Gas pressure and flow in the reactor were simultaneously controlled electronically.

Figure 2 displays Ge film growth curves (laser transmission through growing film versus time) that are representative of those obtained in

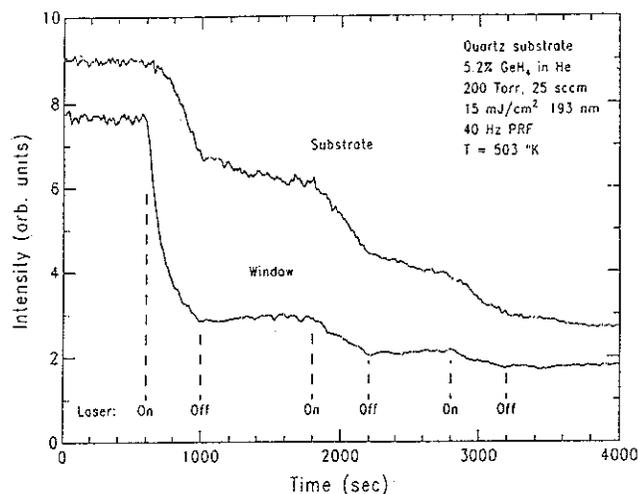


Fig. 2 He-Ne laser transmission curves illustrating the growth of Ge films on an SiO_2 substrate and on the wall where the excimer laser enters the reactor. Note that film growth at the entrance "window" does not occur in the absence of UV laser radiation, but growth on the substrate is clearly noticeable.

range. For substrate temperatures well below that given in Fig. 2 (i.e., $T_S \lesssim 425$ K), film growth at the substrate also stops when the UV radiation is blocked.

Both "modes" of film growth, laser initiated and laser sustained, are depicted in the Arrhenius plot of Fig. 3. Above 553 K, conventional CVD growth of Ge films (from 5.2% GeH_4 in He) on SiO_2 (quartz) occurs. The activation energy in this region ($E_a \approx 0.90$ eV) is in accord with previous measurements [5]. As mentioned earlier, for $425 \lesssim T_S \lesssim 553$ K, Ge film growth can be initiated by irradiating the gaseous region above the substrate with a train of UV laser pulses. In practice, a fixed number of 15 ns FWHM, $15 \text{ mJ}\cdot\text{cm}^{-2}$ pulses were admitted to the reactor after which the

these experiments. For a substrate temperature of 500 K, no film growth occurs at the substrate or the entrance window (reactor side wall where beam enters) before the laser is turned on. In the presence of 193 nm radiation (laser PRF = 40 Hz, initial fluence = $15 \text{ mJ}\cdot\text{cm}^{-2}$), growth at the substrate and entrance window commences, although the substrate growth rate is considerably slower than that at the window. Note also that once the laser is later turned off, film growth at the window stops completely while substrate growth continues, but much slower than before. That is, in a restricted temperature region below the pyrolytic temperature for GeH_4 ($T_p \approx 553$ K)[5] --where CVD film growth does not normally occur--UV laser radiation is capable of initiating ("triggering") the growth of Ge films from GeH_4 . The laser is, in other words, not necessary to sustain film growth in this temperature

laser was turned off. Subsequently, film growth continued indefinitely. Because the minimum number of pulses required to initiate film growth was found to rise rapidly with decreasing I_S , the film growth rates given in Fig. 3 for this region were not measured until the laser was extinguished.

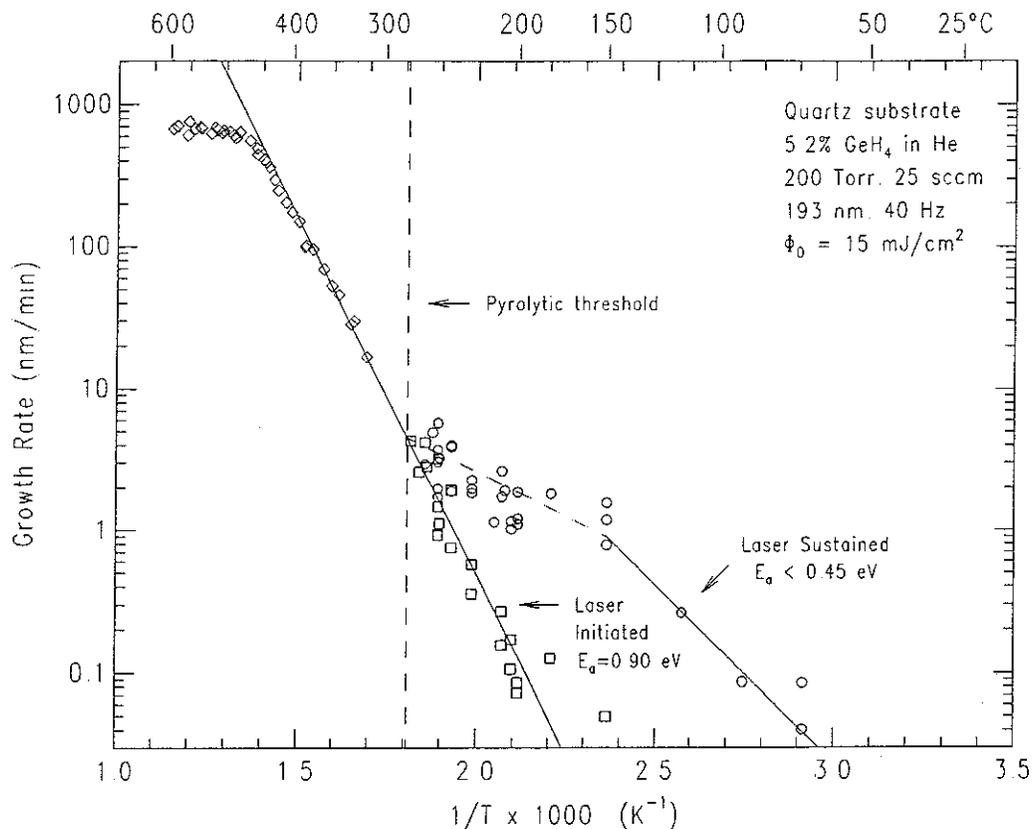


Fig. 3 Arrhenius plot for the growth of Ge films on SiO_2 (quartz) for substrate temperatures in the range $300 \leq T_S \leq 873$ K. Note that, below the pyrolytic temperature ($T \approx 553$ K), two modes of film growth (laser initiated and laser sustained) are available. In acquiring all of the data above in which the UV laser was involved, the height of the beam center above the substrate was 2.2 mm.

Not surprisingly, the activation energy that best describes these data is the same as that observed above pyrolytic threshold.

The logical interpretation of these results is that the laser locally "seeds" the reactor with Ge_2H_6 which is a known by-product of the photodissociation of GeH_4 (Ref. 3). In contrast to the work described in Ref. 3 at 248 nm, the photodissociation of GeH_4 at 193 nm appears to require only the absorption of a single photon, yielding GeH_3 . The formation of Ge_2H_6 subsequently proceeds by the reaction:



where M is any third body (such as a He background atom). Similar conclusions were reached in experiments in which matrix-isolated GeH_4 was photolyzed in the VUV (Ref. 6). The hydrogen atom produced in the initial

photolysis of GeH_4 is also effective in producing germyl radicals [3, 6-8]. Further support for associating digermene with the laser-initiated film growth region lies in the minimum temperature (T_p) required to pyrolyze the molecule.

Preliminary experiments conducted with pure Ge_2H_6 indicate that T_p for this molecule is ~ 460 K (Ref. 9). This result is consistent with the initial measurements of the lower temperature limit ($T_s \leq 460$ K) of the laser-initiated growth regime at a system pressure of 200 Torr. Improvements in the minimum detectable growth rate along with variations of the system pressure and flow rate allowed for laser-initiated growth to be subsequently demonstrated for T_s as low as $\sim 425^\circ$ K.

As noted by Tsao and Ehrlich [10], "The initiation of chemical vapor deposition (CVD) is known to be sensitive, in many cases, to the starting surface. This sensitivity, which often takes the form of a nucleation barrier...." In the work of Ref. 10 (and, later, the experiments reported by Higashi and Fleming [11]), it was demonstrated that several photo-deposited monolayers of Al catalyzed the pyrolysis of triisobutylaluminum to grow aluminum stripes. It appears that a similar process is occurring here. The major difference is that the ArF laser produces Ge_2H_6 in the vapor phase (not at the surface) which subsequently pyrolyzes (not photo-dissociates) at the substrate. It is clear that the few monolayers of Ge resulting from the pyrolysis of Ge_2H_6 are more catalytically active than the original surface and are able to promote or catalyze the pyrolysis of GeH_4 . Thus, the lower temperature limit of the laser-initiated region in Fig. 3 appears to be the pyrolytic temperature for Ge_2H_6 on SiO_2 and not the limit for pyrolysis of GeH_4 on Ge.

Taguchi and coworkers [4] have recently suggested the importance of Si_2H_6 in the growth of a-Si:H films grown on glass at 623 K. The role of disilane was inferred from the thickness of films grown for a fixed "run" time with the laser on throughout the growth period. The beneficial effect of Si_2H_6 was attributed to excitation transfer from Si_2H_6 to SiH_4 . The experiments reported here suggest that an alternative explanation is the pyrolysis of Si_2H_6 at the substrate followed by catalytic decomposition of monosilane. In summary, the laser initiated region in Fig. 3 appears to arise from the pyrolysis of laser-produced Ge_2H_6 at the SiO_2 substrate and the subsequent Ge film-catalyzed pyrolysis of GeH_4 .

If the UV laser is pulsed throughout the film growth run, dramatic changes in the growth process are observed. Detailed measurements of the Ge film growth rate (for various pressures and flow rates) in the region of $T_s < T_p$ consistently show the two growth modes shown in Fig. 3. However, E_a of the laser-sustained process does vary with pressure and flow. Therefore, while it is not presently possible to be dogmatic as to the identity of the species responsible for film growth in the laser-sustained region, it can be concluded that this species is neither Ge_2H_6 nor GeH_4 . In summary, we note that:

- 1) Specular Ge films can be grown down to room temperature in the parallel configuration (i.e., no laser heating of substrate).
- 2) Two modes of film growth are obtained, depending on whether the ArF laser is pulsed throughout the run or not. The laser-initiated mode is attributed to photochemical production of Ge_2H_6 which pyrolyzes at T_s as low as $\sim 463^\circ$ K. The presence of several Ge monolayers on the SiO_2 substrate catalyzes the pyrolysis of GeH_4 . If the laser is "on" throughout the run, the activation energy decreases by at least a factor of two and is believed to arise from a photofragment of GeH_4 .

Other experimental evidence also points to the photochemical origin of both the laser initiated and laser sustained growth of Ge. Not only does the UV laser beam not strike the substrate, but a strong wavelength dependence to the film growth rate is observed. While film growth does weakly occur for $\lambda = 248$ nm, nothing is observed when $\lambda = 277$ nm (first Stokes of

248 nm Raman scattered in H_2). Thus one concludes that the photon energy necessary to initiate the photochemical chain (two photon dissociation of GeH_4) lies between 4.5 and 5.0 eV.

Transmission electron micrographs of films grown (on NaCl) in the 473-553 K region show the films to be amorphous at the low end of this interval and polycrystalline at the higher temperatures. Details of the properties of films grown in the two different modes, as well as the dependence of growth rate on laser intensity and beam height, will be reported elsewhere.

In summary, the growth of Ge films on various substrates by photodissociating GeH_4 at 193 nm clearly demonstrates the ability of external UV radiation to produce highly nonequilibrium concentration of radicals in the reactor and thus affect the chemical kinetics and growth rates of thin semiconductor films.

The authors are grateful to R. Masel and M. Ediger for several interesting discussions and suggestions. Also, the excellent technical assistance of C. Abele and K. Kuehl are appreciated. This work was supported by the Air Force Office of Scientific Research (H. Schlossberg) under contract F49620-85-C-0141 and the National Science Foundation under grant DMR83-16981.

REFERENCES

1. R. W. Andreatta, C. C. Abele, J. F. Osmundsen, J. G. Eden, D. Lubben and J. E. Greene, *Appl. Phys. Lett.* **40**, 183 (1982).
2. J. G. Eden, J. E. Greene, J. F. Osmundsen, D. Lubben, C. C. Abele, S. Gorbakkin and H. D. Desai, *Laser Diagnostics and Photochemical Processing for Semiconductor Devices*, *Mat. Res. Soc. Symp. Proc.*, Vol. 17, R. M. Osgood, S. R. J. Brueck and H. R. Schlossberg, eds. (North-Holland, New York, 1983), pp. 185-192.
3. J. F. Osmundsen, C. C. Abele and J. G. Eden, *J. Appl. Phys.* **57**, 2921 (1985).
4. T. Taguchi, M. Morikawa, Y. Hiratsuka and K. Toyoda, *Appl. Phys. Lett.* **49**, 971 (1986).
5. L. N. Hall, *J. Electrochem. Soc.* **119**, 1593 (1972) and references cited therein.
6. G. R. Smith and W. A. Guillory, *J. Chem. Phys.* **56**, 1423 (1972).
7. For a discussion of similar processes in SiH_4 , see K. Nakamura, N. Masaki, S. Sato and K. Shimokoshi, *J. Chem. Phys.* **83**, 4504 (1985).
8. E. R. Austin and F. W. Lampe, *J. Phys. Chem.* **81**, 1134 (1977).
9. R. Masel (private communication) and unpublished experimental results.
10. J. Y. Tsao and D. J. Ehrlich, *Appl. Phys. Lett.* **45**, 617 (1984).
11. G. S. Higashi and C. G. Fleming, *Appl. Phys. Lett.* **48**, 1051 (1986).