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Laser-assisted photothermal chemical reactions have been observed with silicon in a chloropentafluoroethane ambient using a KrF laser at 248 nm. Etching occurs only if the incident fluence exceeds the melt threshold (~0.75 J/cm²), and is monitored by the change in silicon reflectance at 633 nm. Above the ablation threshold (~2.2 J/cm²) increased surface roughness is observed. Etch rates ≤3 Å/pulse have been measured using both stylus profilometer and SEM cross-sectional techniques. The etch rate dependence on incident fluence, ambient pressure, doping concentration, crystal orientation and substrate temperature will be presented. This process allows single step patterning of silicon devices in a non-corrosive environment.

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NSN 7540-01-280-5500 **90 01 12 059** Standard form 298 much more rapidly than the signal delay in packaged circuits. As a consequence of this the packaging delay times have had to be reduced drastically, which means that a greater packaging density has had to be implemented.

A novel planar packaging technique, used in the new SIEMENS main frame computer 7500 H/90 has led to considerable progress in solving this problem. An essential part of this system is a multi-chip-module which can hold up to 144 bare chips. The carrier of these IC's is a 16-layer high density multilayer printed circuit board, which is fabricated in a sequential process.

Interlayer contacts are formed by 80 µm wide blind via-holes, which are generated by excimer-laser ablation of the dielectric. The process described in this paper shows that it is possible to produce blind via-holes with an aspect ratio of about one in an extremely reliable and reproducible way.

This process is already being successfully run on a production line. It is to our best knowledge the first time excimer lasers have been used on a large-scale in an industrial environment.

B6.2

UV LASER-INDUCED ETCHING OF FIRST-ROW TRANSITION METALS

George W. Tyndall IBM Almaden Research Center, 650 Harry Road, San Jose, CA 95120.

A quartz crystal microbalance (QCM) has been used to study the KrF* (248 nm) laser-induced etching of Ti, Cr, Fe, Ni and Cu by bromine. The experiment consists of focusing the pulsed output of an excimer laser at normal incidence onto the surface of a quartz crystal coated with the transition metal. Absolute etch rates are determined from the change in the resonant frequency of the QCM over time. Each of the metals studied can be etched by bromine at laser fluences significantly below those required for ablation of the pure metal. The dependence of the etch rate on bromine pressure and laser fluence was measured to ellucidate the etching mechanisms. The details of these etching mechanisms will be discussed.

B6.3

PHOTOCHEMICAL AREA-SELECTIVE ETCHING OF Si AND SiO_2 USING SYNCHROTRON RADIATION.

Jun-ichi Takahashi, Yuichi Utsumi, and Tsuneo Urisu, NTT LSI Laboratories, Kanagawa, Japan.

Material selectivity and the surface reaction scheme in the etching reaction are important factors for controllable area-selective processing. We have already reported [1,2] that photochemical etching using synchrotron radiation (SR) presents unique material selectivity, and that the surface reaction can be expressed as "photo-stimulated reactive desorption." This report discusses in some detail the mechanism involved in SR-stimulated area-selective etching of Si and SiO_2 using SF_6 gas.

Photon energy dependence of SiO_2 (thermal oxide) etching was studied to examine what kind of surface photo-excitation was dominant. Excitation wavelength range was selected by changing SR beam incident angles to Pt plane mirrors in the beam line. Experimental results indicate that the most important factor is core electron excitation of surface SiO_2 molecules. The influence of dopant in Si etching was also studied using B-doped, P-doped, and undoped poly-Si films. The etching rate decreased with increasing dopant concentration, independent of conduction type. This characteristic is quite different from the case for excimer laser or plasma etching. According to our reaction model this result can be explained as active species quenching by majority carriers.

(1) T. Urisu et al. J. Vac. Sci. & Technol. B5 (1987) 1436. (2) J. Takahashi et al. Extended Abstracts 1988 Int. Conf. Solid State Devices & Mat. p. 73.

B6.4

EXCIMER LASER-ASSISTED ETCHING OF SILICON USING CHLOROPENTAFLUOROETHANE.

S. D. Russell, and D. A. Sexton, Solid State Electronics Division, Naval Ocean Systems Center, San Diego, CA.

Laser-assisted photothermal chemical reactions have been observed with silicon in a chloropentafluoroethane ambient using a KrF* laser at 248 nm. Etching occurs only if the incident fluence exceeds the melt threshold (~0.75 J/cm²), and is monitored by the change in silicon reflectance at 633 nm. Above the ablation threshold (~2.2 J/cm²) increased surface roughness is observed. Etch rates ~7 Å/pulse have been measured using both stylus profilometer and SEM cross-sectional techniques. The etch rate dependence on incident fluence, ambient pressure, doping concentration, crystal orientation and substrate temperature will be presented. This process allows single step patterning of silicon devices in a non-corrosive environment.

B6.5

LOCALIZED LASER-ASSISTED ETCHING OF COPPER FILMS BY CHLORINE USING RAMAN SPECTROSCOPY FOR *in situ* FILM ANALYSIS.

Hua Tang and Irving P. Herman, Department of Applied Physics and the Microelectronics Sciences Laboratories, Columbia University, New York, NY.

Etching of copper films on glass was studied by localized laser substrate heating (4880 Å) in the presence of chlorine gas. The spontaneous reaction of Cu with chlorine at room temperature forms a film [1], which was identified to be CuCl by Raman spectroscopy at 77 K. If the chlorine is then evacuated, laser heating can remove this CuCl film locally, down to the remaining copper film. If instead chlorine is present during laser heating, a bump is formed. In producing this feature, the CuCl layer and some of the underlying Cu film are converted to $CuCl_2$, as identified by *in situ* Raman analysis at room temperature. After removal of the chlorine, etched CuCl/Cu regions are formed with micron-dimension patterns after subsequent *in situ* laser heating of these features or *ex situ* rinsing in solvents.

This work was supported by the Office of Naval Research and IBM.

[1] W. Sesselmann and T. J. Chuang, Surf. Sci. 176, 32 (1986).

B6.6

SELECTIVE TUNGSTEN CVD ON A-SI:H BY PULSED UV LASER MODIFICATION OF THE NATIVE OXIDE.

Arthur T. Howe, K. V. Reddy, Darrell L. Wuensch and Jeff T. Niccum, Technology Division, Amoco Technology Company, PO Box 400, Naperville IL 60566; and Gerry W. Zajac, Analytical Division, Amoco Corporation, PO Box 400, Naperville IL 60566.

Laser patterning processes which use comparatively low laser intensities are of interest for applications requiring masks, or involving thermally sensitive devices. We have studied such a process involving the indirect control of tungsten chemical vapor deposition on a-Si:H by laser modification of the native oxide. The process has potential for use in the fabrication of active matrix flat panel displays.

Excimer laser pulses, of wavelengths 193, 248 and 308 nm, and fluences of approximately 100 mJ/cm², were shown to cause slight growth of the native oxide on a-Si:H, and XPS studies of the effect will be described. The oxide growth was sufficient

ATTACHMENT

EXCIMER LASER-ASSISTED ETCHING OF SILICON USING CHLOROPENTAFLUOROETHANE

Stephen D. Russell and Douglas A. Sexton

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OUTLINE

I. OVERVIEW of EXPERIMENTS

II. DATA

* Pressure, Temperature, Orientation, Fluence, Repetition Rate, Doping Type and Concentration

III. SUMMARY

* Etch Rate

* Rate Limiting Mechanism

* Processing Advantages

ETCHANT GAS

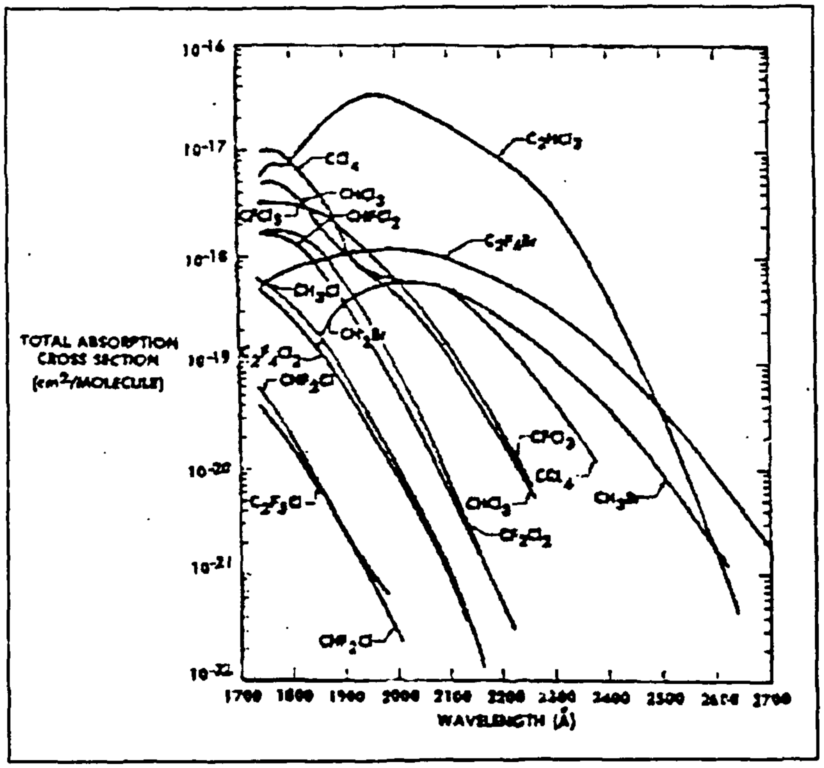
Chloropentafluoroethane

Chemical Formula: C_2ClF_5

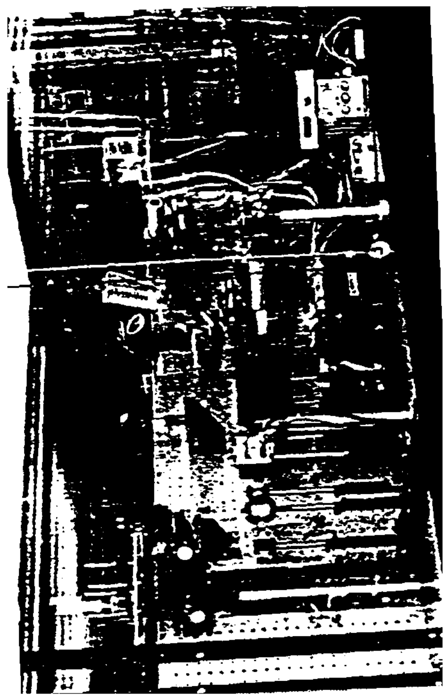
Synonyms: Freon-115, Halocarbon-115, Genetron-115, etc.

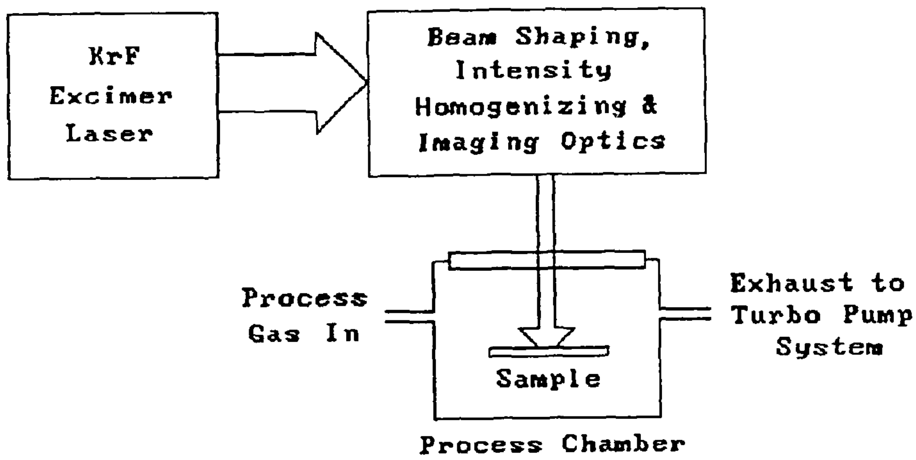
Typical Uses: Refrigerant, Propellant, and Chemical Intermediate

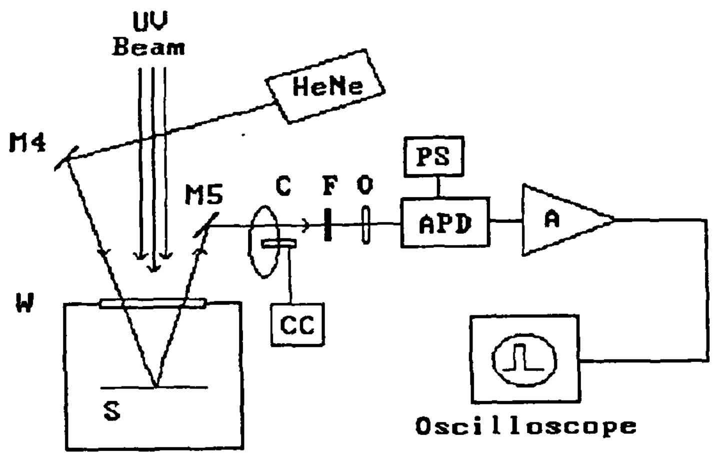
Description: Chemically Stable, Irert, Nonflammable, Relatively Nontoxic
Vapor Pressure @ 294 K = P_0 = 804.6 kPa



SOURCE: D.E. Robbins, NASA-CR-154106 (1986)




KrF
Excimer
Laser
Beam Shaping,
Intensity
Homogenizing &
Imaging Optics
Process
Gas In
Exhaust to
Turbo Pump
System
Sample
Process Chamber


UV
Beam
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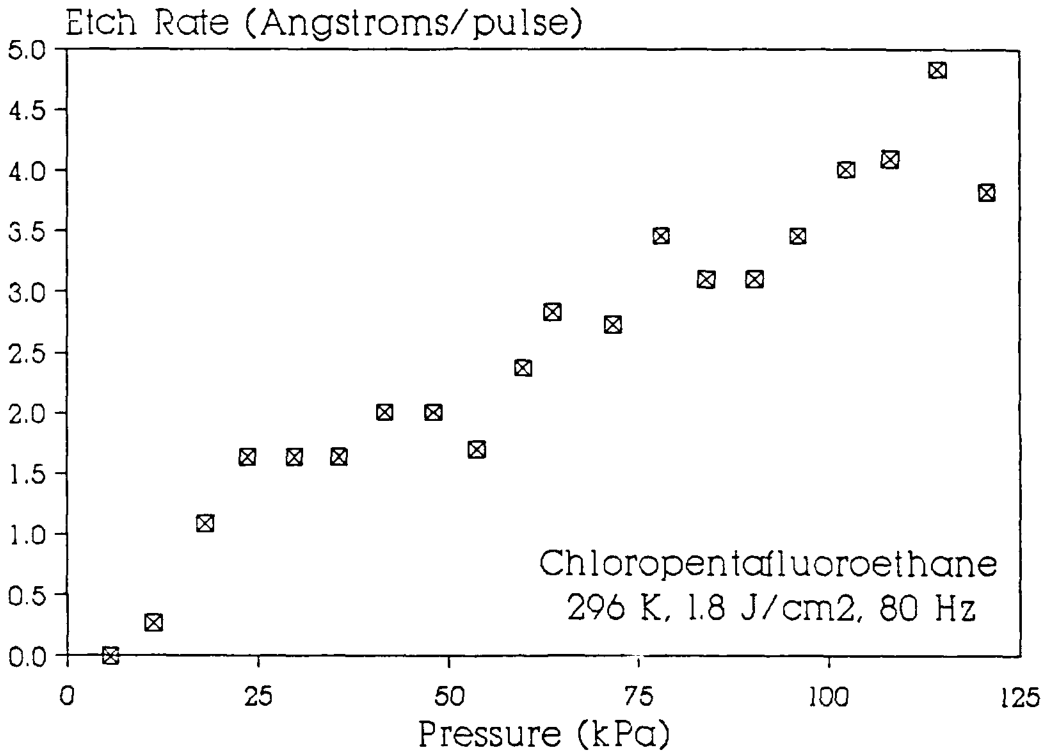
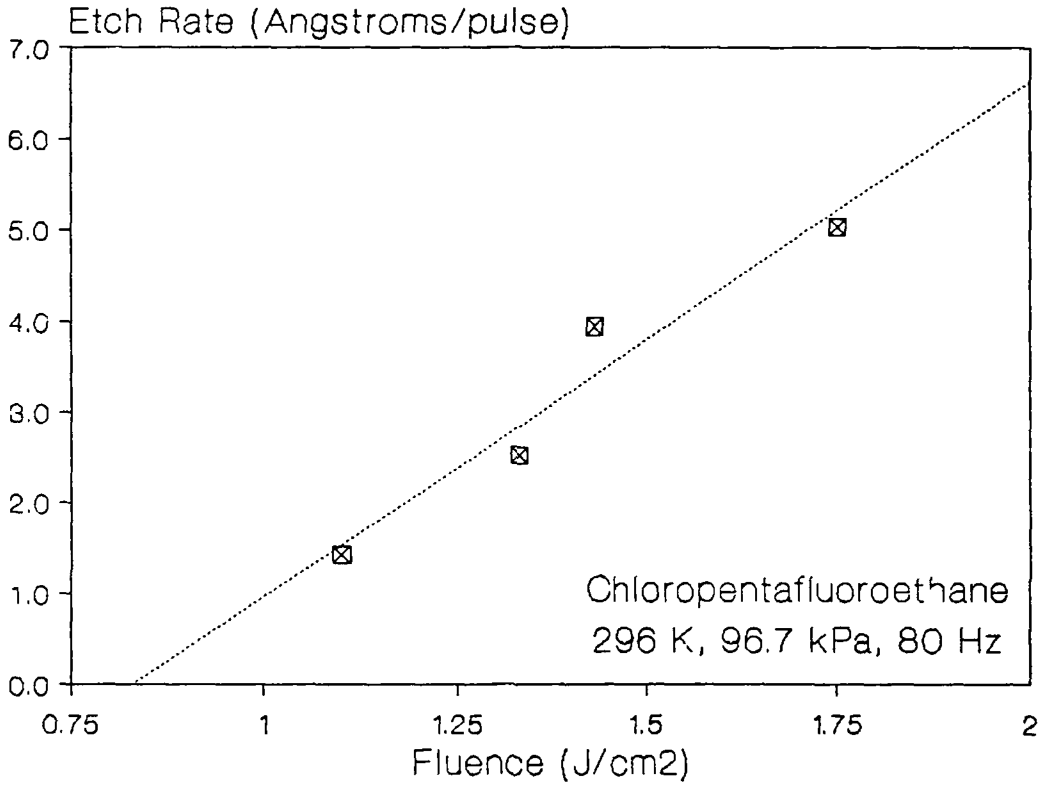
Oscilloscope



* P ≤ 6 kPa ... No Evidence of Etching

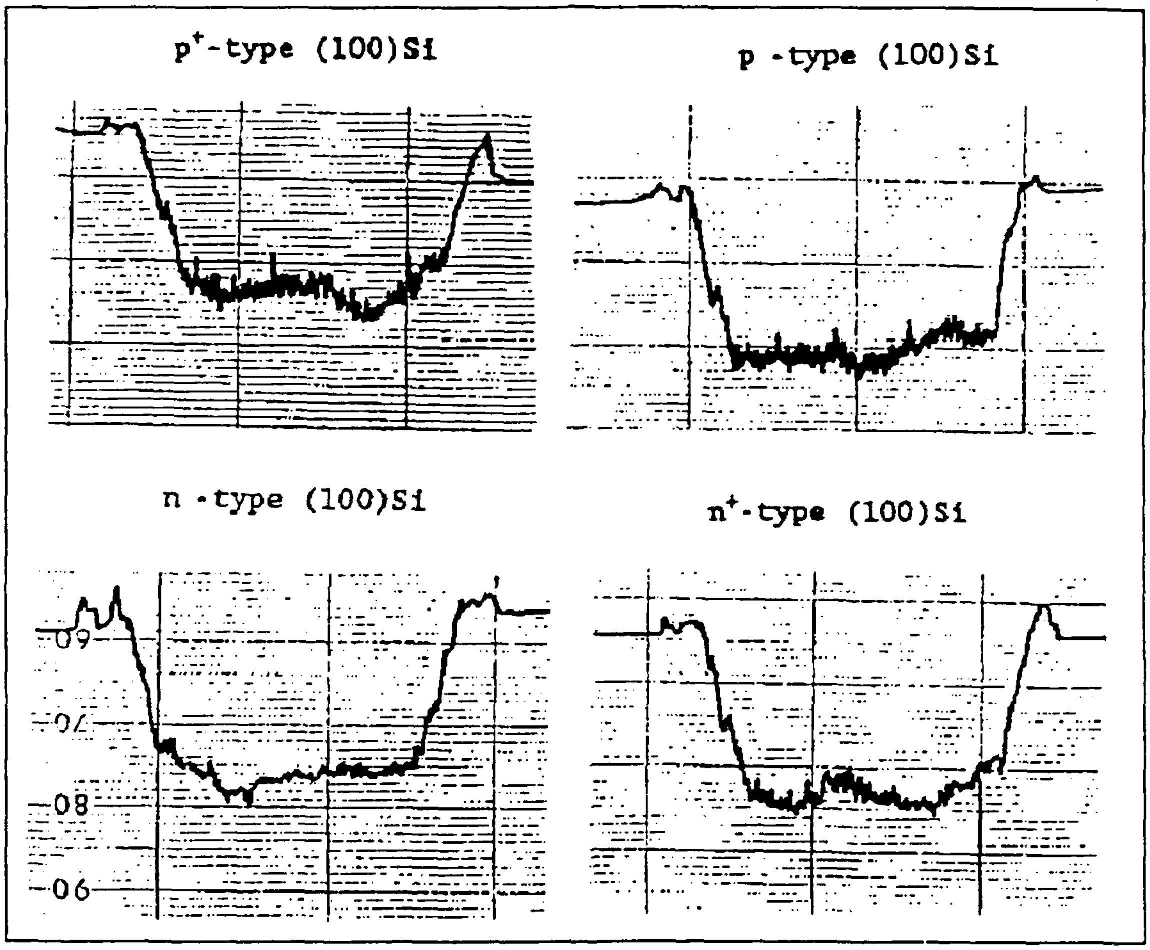
* P ≥ 6 kPa ... Etch Rate increases with Pressure



* No Etching Below Melt Fluence

* Etch Rate has Linear Dependence with Fluence within the Melt Regime ... Consistent with 1D Thermal Model

* Ablation Threshold ~2.2 J/cm^2



$\langle W(p^+)\rangle = 6.8 \pm 0.3$ Angstroms/pulse

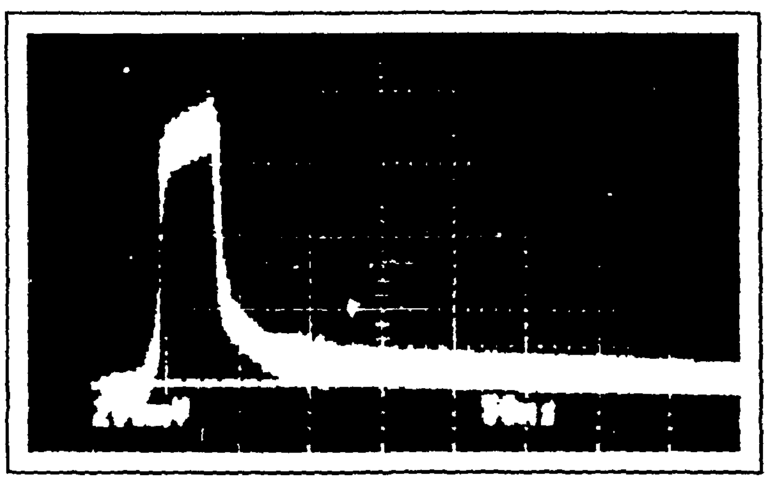
$\langle W(p,n,n^-)\rangle = 7.3 \pm 0.3$ Angstroms/pulse

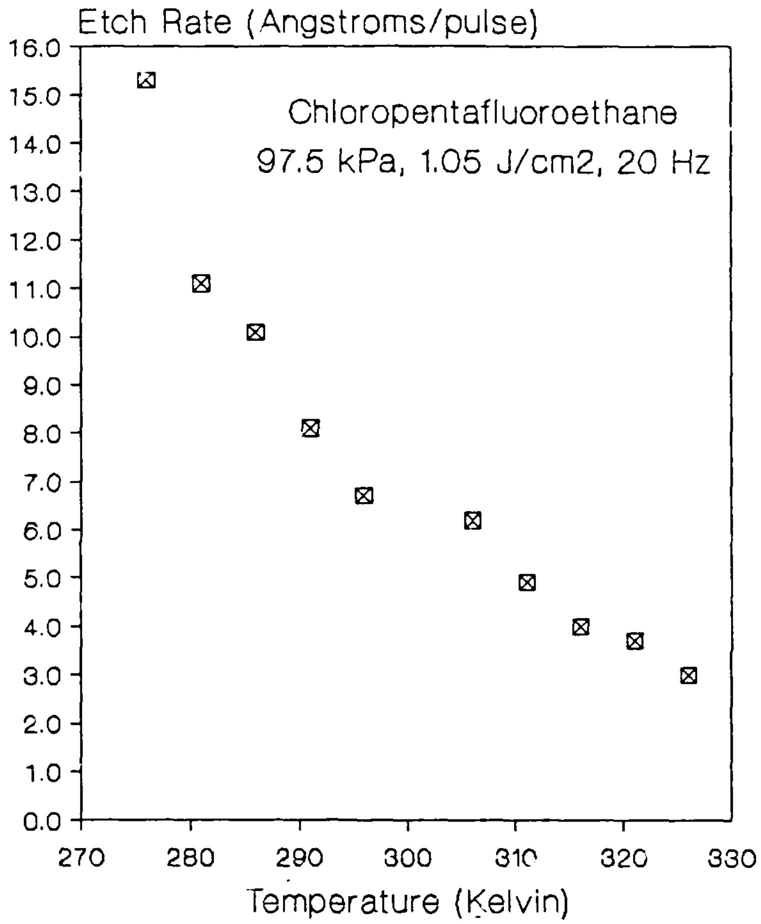
* Differences in Etch Rate not Experimentally Significant

* Implies Thermally Activated Reaction, Not Field Enhanced

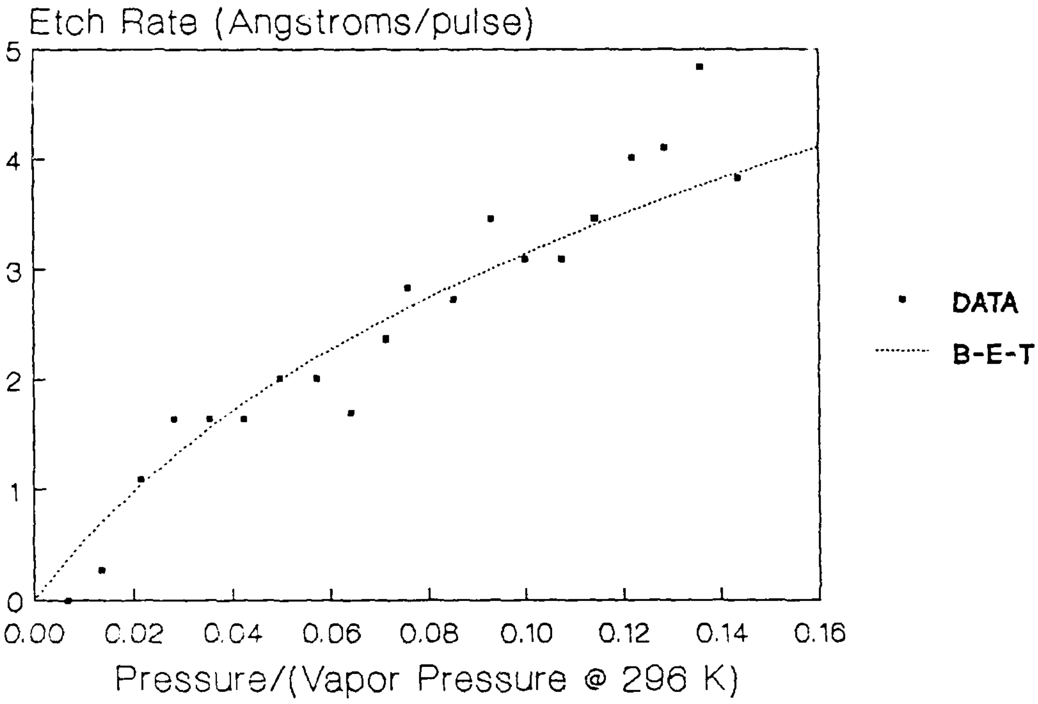
* No Etch Rate Dependence Between Identically Processed (100) Si and (111) Si

* Consistent with Thermal Reaction ... Etching Occurs During the Duration of the Melt (typically 30 to 80 nsec)





* Etch Rate Decreases with Increasing Temperature

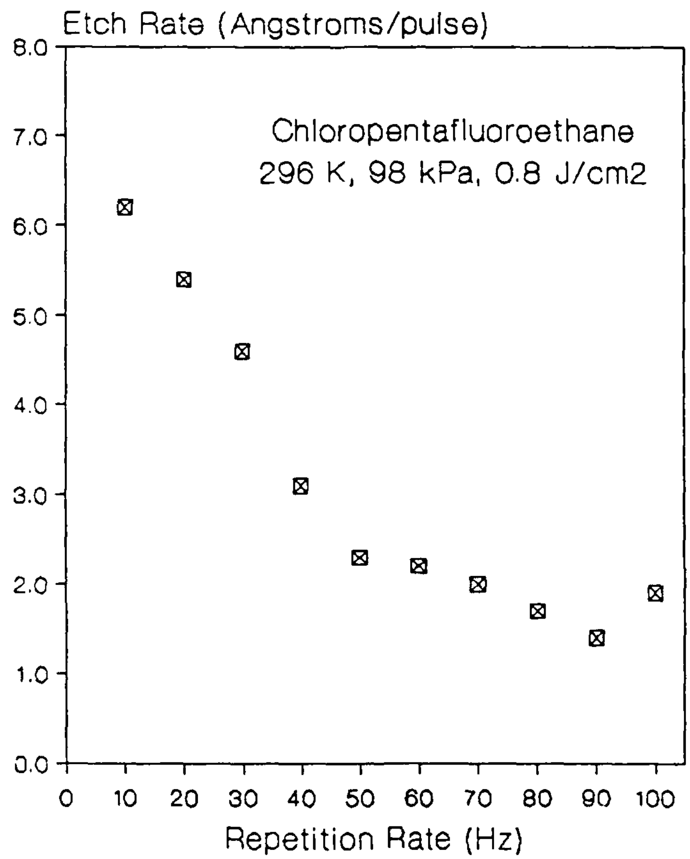


* W = W(P) Consistent with B-E-T Isotherm

* Rate Limiting Mechanisms:

  Adsorption

  Laser Induced Desorption



* W Decreases as Rep Rate Increases

* Increased Steady-State Heating due to Increased Laser Duty Cycle

* W Dependence Consistent with W = W(T)

SUMMARY

* W not a Function of Orientation, Doping Type or Doping Concentration

* W is Linearly Proportional to Fluence ($\sim 0.75\ J/cm^2 \leq \phi \leq \sim 2.2\ J/cm^2$)

* W Increases with Pressure Consistent with B-E-T Adsorption

* W = W(T,Rep Rate)

* Mechanisms: Thermally Activated Etching, Rate Limited by Adsorption and Possibly Laser Induced Desorption

PROCESSING ADVANTAGES

* Etch Rates of about 5 Angstroms/pulse (at 296 K, $\phi > \phi_{MELT}$) (15 Å/pulse with sufficient cooling)

* Non-Corrosive C_2ClF_5 Compatible with VLSI Materials and Processing