

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comment regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 17 Sept. 1997	3. REPORT TYPE AND DATES COVERED Final Report 31 Aug. 94 - 30 Aug. 97		
4. TITLE AND SUBTITLE Mechanisms of semiconductor dry etching by translationally hot atoms and molecules		5. FUNDING NUMBERS DAAH04-94-G-0321		
6. AUTHOR(S) Stephen R. Leone				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) JILA, Campus Box 440 University of Colorado Boulder, CO 80309		8. PERFORMING ORGANIZATION REPORT NUMBER ARO-INT-03		
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211		10. SPONSORING / MONITORING AGENCY REPORT NUMBER <i>ARO 32694.4-PH</i>		
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.				
12a. DISTRIBUTION / AVAILABILITY STATEMENT  Approved for public release; distribution unlimited.		12 b. DISTRIBUTION CODE		
13. ABSTRACT (Maximum 200 words)  A three year program of study was performed to investigate the effect of kinetic energy on etching. Both electron cyclotron resonance plasmas and inductively coupled radio frequency plasmas were investigated to determine the kinetic energies and source gas cracking of species in the plasmas. Studies were performed to measure the kinetic energy dependence of chlorine sticking to Si(100). Thermal etching studies of Si(100) by chlorine were completed using a novel single photon ionization method to detect SiCl and SiCl <sub>2</sub> radical species directly.				
14. SUBJECT TERMS  etching, hyperthermal, neutral beam, silicon		15. NUMBER OF PAGES 7		
		16. PRICE CODE		
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

19971204 153

DTIC QUALITY INSPECTED 4

## **Final Technical Report**

Army Research Office Grant DAAH04-94-0321

### **"Mechanisms of Semiconductor Dry Etching by Translationally Hot Atoms and Molecules"**

31 August 1994 - 30 August 1997

**Principal Investigator:** Stephen R. Leone  
JILA  
University of Colorado  
Boulder, CO 80309-0440  
(303) 492-5128  
email: srl@jila.colorado.edu

**Program Manager:** David Skatrud  
Physics Division  
U.S. Army Research Office  
P. O. Box 12211  
Research Triangle Park, NC 17709-2211

## Problem Studied

The feature sizes of silicon semiconductors continue to decrease dramatically, with expected line dimensions reaching 100 nm within the coming decade. At these dimensions, various material thicknesses, such as the gate oxide dielectric, are projected to be on the nanometer scale. Refined methods for materials removal, or etching, are largely responsible for the relentless improvement in nanotechnology needed for this industry. High rates of semiconductor etching are presently achieved with gaseous plasmas, which supply radical and neutral chemically reactive species to the substrate and highly directional ions for bombardment. As semiconductor devices shrink in size, a critical concern is the possibility of damage caused by electrical charging of the very thin (5 nm) gate oxide by the ions generated in the plasma. Recently there is considerable interest to explore etching with kinetic-energy-enhanced neutral species, either as a replacement for or complement to ion-assisted plasma etching. In addition, the use of kinetic energy enhanced species can ultimately lower processing temperatures and may permit nanoscale feature sizes to be prepared without degradation from the subsequent thermal processing steps required to remove defects induced by ion etching.

This project involves investigations of the mechanisms of dry etching by kinetic-energy-enhanced neutral atoms and molecules. The results are central to atomic and molecular aspects of nanotechnology. A new apparatus was developed to study the interaction of translationally fast species with semiconductor surfaces. The goal of this work has been to attain a detailed understanding of the microscopic mechanisms of semiconductor etching. The approach chosen here is to accelerate the etching by supplying modest kinetic energies directly to the reactive neutral species of interest, for example, by using 1-20 eV Cl or Cl<sub>2</sub> for silicon etching. Typical bond energies for surface species are 1-5 eV, and thus incident kinetic energies of, for example, 1-20 eV can be successful to break Si-Si bonds, overcome activation barriers to reaction, and release product molecules, such as the SiCl<sub>x</sub> (x=1-4) species. In addition, the enhanced kinetic energy can increase both chemical adsorption probabilities and subsurface bond formation.

Requirements for a successful etching process include a wide range of criteria, such as overall etch rate, chemical selectivity, uniformity, lack of defects and

impurities, directionality, surface quality, and reproducibility. First of all, critical to the process of neutral kinetic-energy-enhanced etching is the anisotropy of the etch features. If the reactivity of the neutral species is not increased sufficiently over the normal thermal reaction probability, the anisotropy will be degraded due to reactions with isotropic background thermal species. Fundamental measurements of both reaction probabilities and anisotropies as a function of kinetic energy are essential. Secondly, the determinations of overall etch rates are important, since processing speed is a key element for the industry. Finally, the control of the depths of material removal on the nanometer scale is essential. The tremendous success of plasma processing, despite the potential problems of ion-induced damage, sets exceedingly high standards for processing speed, anisotropy, and feature size, with which any proposed new process must be compared. Nevertheless, for some critical steps, such as preserving a delicate gate oxide material, ion-free neutral processing may represent an important technique in the future.

### **Important Findings**

In the past three years, experiments have been performed to develop a new method to selectively detect SiCl and SiCl<sub>2</sub> radical etch products by laser single photon ionization. We elucidated the neutral kinetic energies produced in both an electron cyclotron resonance source and an inductively coupled plasma radio frequency source. The methodology has been developed for probing the anisotropy of etching with masked samples using a scanning electron microscope. We explored the reactive sticking probabilities of chlorine molecules and atoms as a function of kinetic energy. The results of these studies are discussed after a brief introduction to the new apparatus that has been constructed for these etching studies.

### **Electron Cyclotron Resonance Source Characterization**

Low pressure plasmas that produce high densities of reactive radicals and ions mark a recent advance in the etching industry. These sources are based on electron cyclotron resonance (ECR) plasmas, radio frequency inductively coupled plasmas (RF-ICP), or radio frequency helicon resonance plasmas. While most of the kinetic energies emanating from these sources are modest,  $\leq 1$  eV, there is some evidence that higher kinetic energies can be achieved.

We developed a versatile modulated molecular beam approach to interrogate the velocities and fraction of dissociated species emanating from compact ECR and RF-ICP sources. The source is positioned in front of a high speed chopper which has narrow slits to permit the flux to be transmitted over a 41 cm flight path to the quadrupole mass spectrometer. A direct comparison was made between the two types of sources, and the distribution of kinetic energies were measured for Ar,  $N_2/N$ , and  $Cl_2/Cl$ .

Mean kinetic energies were derived from the resulting time-of-flight traces over a wide range of pressure conditions after deconvolution for the chopper opening function. The results indicate that the neutral kinetic energies increase smoothly with decreasing pressure in the source, and in the case of Ar, the neutral kinetic energy is definitely correlated with the ion yield; the greater the ion yield the greater the kinetic energy of the neutrals emanating from the source. This is most likely due to charge exchange of higher velocity ions with neutral argon atoms. For N and  $N_2$  the  $N/N_2$  dissociation ratio varies from 0.2 at high pressures to 1.4 at the lowest pressures. Mass spectral cracking, ionization cross sections, and mass discrimination are taken into account in this determination, permitting an accurate measure of the dissociation fraction. The extent of nitrogen dissociation is substantial in the compact ECR source. The amount of dissociation is a very important quantity since these sources are used to produce N atoms for growth of III-V materials such as GaN.

Qualitatively similar results are observed for chlorine plasmas in the compact ECR source, but the extent of dissociation is even more substantial, giving  $Cl/Cl_2$  ratios from 10 to 16. Since the extent of dissociation is large and the residual  $Cl_2$  observed in the time-of-flight has nearly a thermal energy, this possibly indicates that a small fraction of the molecules of  $Cl_2$  effuse from the source region without significant collisional impacts with higher energy species in the source.

The results observed under typical ECR plasma conditions have only modest mean kinetic energies of  $\leq 0.5$  eV. Thus the typical neutral energies emanating from these sources appear to be quite low. When the plasma conditions are arranged such that low,  $< 0.5 \times 10^{-5}$  Pa, pressures are achieved, the ion densities increase dramatically and there is some evidence for higher kinetic energy neutral species,

perhaps of the order of 10-20 eV. However, the fraction of these species is very small, which would not be practical for etching studies.

Finally, we compared the results of the ECR source to those of the RF-ICP source. The mean kinetic energies of the neutral species emanating from the two sources are remarkably similar at low input powers. However, the kinetic energies from the RF-ICP source are considerably larger than those from the ECR source above 200 watts of input power. For both sources, very similar results are found for Ar. The power supply for the RF-ICP source can deliver almost 600 watts, and the mean kinetic energies continue to increase with power significantly, but start to level off. Interestingly, although the mean kinetic energies from the ECR source are less than the RF-ICP source under similar conditions, the extent of dissociation in the RF-ICP source is considerably less. For example, at 250 watts and  $7 \times 10^{-2}$  Pa pressure, the N/N<sub>2</sub> ratio in the ECR source is 0.18, while it is only 0.02 for the RF-ICP source. Thus, the different mechanisms for injecting energy into the plasma produce more dissociation in the ECR source and lower kinetic energy, while there is less dissociation and more kinetic energy in the RF-ICP source. While RF-ICP sources have been used successfully to grow GaN films, it is generally thought good quality GaN cannot be grown with an ECR source of N atoms. The results show that the reason may not be due to an effect of kinetic energy or extent of dissociation, suggesting further checks on the amount of excited metastable neutrals or ions in both sources.

#### **Laser Single Photon Ionization Detection of SiCl, SiCl<sub>2</sub>**

A new method to probe radical etch products has been developed, based on laser single photon ionization time-of-flight mass spectroscopy (SPI-TOFMS). This method permits radical species, such as SiCl and SiCl<sub>2</sub>, to be detected without mass spectral cracking, since the radicals are photoionized with a photon energy that is just sufficient to ionize but not enough to ionize and dissociate the species. The method utilizes the 9th harmonic of a pulsed Nd:YAG laser at 118 nm to ionize the radical species. The ions are extracted with potentials from in front of the wafer and accelerated into a TOF mass spectrometer for analysis. A thermal etching study of Si(100) by chlorine was performed to characterize the SiCl and SiCl<sub>2</sub> products.

The results show the liberation of SiCl<sub>2</sub> at the lowest temperatures, then both

SiCl<sub>2</sub> and SiCl at intermediate temperatures, and finally the desorption of Si at the highest temperatures. A series of tests were performed to verify that both SiCl<sub>2</sub> and SiCl are detected without mass spectral cracking. In addition, activation energies were derived for the desorption of SiCl and Si. The value for Si (5.4±0.4 eV) agrees with the usual heat of sublimation of Si, however the value for SiCl (0.26±0.02 eV) is low compared to expected desorption energies for this species, suggesting that a complex kinetic mechanism plays a role in the formation of this species. The formation of SiCl<sub>2</sub> goes through a maximum with temperature, also indicating a competition between the formation and loss mechanisms. These are the first studies to confirm the production of SiCl in thermal etching directly, since there are no obscuring signals from mass spectral cracking of heavier mass SiCl<sub>x</sub> species to form the ion observed products with the laser ionization method.

### **Scanning Electron Microscopy of Etch Anisotropy**

We have developed the internal capability to produce and measure conventional etch processes for a silicon wafer using a chlorine-argon plasma in the ECR source and an electron microscope for post-analysis. Having this capability in-house and successfully operated by the student and postdoctoral on the project are invaluable for experiments to etch silicon with neutral kinetic-energy-enhanced species.

### **Sticking and Scattering of Hyperthermal Cl<sub>2</sub> and Cl by Si(100)**

A systematic study was completed to measure the sticking probability of Cl<sub>2</sub> and Cl on Si(100) as a function of kinetic energy up to 2.6 eV. In these experiments a pulsed laser vaporization source of cryogenic films of Cl<sub>2</sub> was used to form the kinetic-energy-enhanced species, and the velocities were selected by a high speed chopper. The scattered Cl<sub>2</sub> and Cl were monitored with a quadrupole mass spectrometer. The incident beam was at 45° and the mass spectrometer detection at the specular angle. The chlorine species were scattered from both a quartz substrate and from Si(100). Since there is little or no sticking on the quartz substrate, the comparison of the integrated scattered flux permits a measure of the sticking probability on Si(100). Angular studies were performed with both substrates to ensure that the entire scattered flux was included in the measurements.

Measurements were also obtained for the scattering probability as a function of

chlorine coverage on Si(100).

The sticking probability increases significantly with kinetic energy, suggesting that there is an activation energy for chemisorption which is overcome by the kinetic-energy enhancement. These results show that kinetic-energy-enhancement plays a strong role in the initial chemisorption probabilities.

### **Publications**

S. R. Leone, F. X. Campos, and G. C. Weaver, "Silicon etching by kinetic-energy-enhanced chlorine," 1994 Proceedings of Symposium on Dry Process, Tokyo, Japan, p. 85 (1994).

S. R. Leone, "Kinetic-energy-enhanced neutral etching," *Jpn. J. Appl. Phys.* **34**, 2073 (1995).

G. C. Weaver and S. R. Leone, "Scattering of Cl<sub>2</sub> beams from Si(100) for kinetic energies up to 2.6 eV: Implications for sticking coefficients and reaction product formation," *Surf. Sci.* **328**, 197 (1995).

G. C. Weaver and S. R. Leone, "Fragmentation and recombination of molecules during laser vaporization of cryogenic films," *J. Phys. Chem.* **100**, 4188 (1996).

N. Materer, R. S. Goodman, and S. R. Leone, "Laser Single Photon Ionization Mass Spectrometry Measurements of SiCl and SiCl<sub>2</sub> During Thermal Etching of Si(100)," *J. Vac. Sci. Technol. A* (in press).

R. S. Goodman, N. Materer, and S. R. Leone, "Neutral Kinetic Energies and Source Gas Cracking of Ar, N<sub>2</sub>, and Cl<sub>2</sub> Electron Cyclotron Resonance Plasmas measured by Time-of-Flight Mass Spectrometry," *J. Vac. Sci. Technol. A* (in press).

N. Materer, R. Goodman, and S. R. Leone, "Time-of-Flight Analysis of Neutral Kinetic Energies and Source Gas Cracking: Comparison of Electron Cyclotron Resonance and Radio-Frequency Inductively Coupled Plasmas of Ar and N<sub>2</sub>," *J. Appl Phys.* (submitted).

### **Personnel**

Gabriela Weaver - Ph. D. 1994

Rory Goodman - Graduate Student - Ph. D. anticipated 1998

Nicholas Materer - Postdoctoral Associate