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| 6. AUTHOR(S) Stephen R. Leone |
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| 13. ABSTRACT (Maximum 200 words) The goal in the work has been to investigate the microscopic basis for materials removal using neutral atoms and radicals at high kinetic energies (1-10 eV). With support from this ARO grant, it was possible to develop and characterize a new beam source of translationally fast atoms, radicals, and molecules. This beam source is based on a laser vaporization technique. The mechanisms of laser vaporization have been pioneered by many groups in the past several years; the method can be used to produce a variety of reactive neutral atoms, radicals, metal vapors, and other compounds with high kinetic energies. In this work, the laser vaporization process is used to produce a beam source of energetic, reactive neutral species which can be used to study collisions with semiconductor surfaces for fundamental investigations of etching and deposition. |
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FINAL REPORT

1 May 1988 - 30 April 1991

Title: "Semiconductor Deposition and Etching Interactions of Laser-Generated Translationally Hot Atoms and Radicals"

Principal Investigator: Stephen R. Leone

Institution: University of Colorado, Boulder
Joint Institute for Laboratory Astrophysics
Department of Chemistry and Biochemistry

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Dr David D. Skatrud

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Statement of the Problem

There is widespread interest in the elucidation of the mechanisms of dry etching processes and gas-surface materials deposition for the manufacture of submicron features in semiconductor devices.¹⁻⁸ State-of-the-art techniques utilize the chemical specificity of certain radical species to effect selective materials removal with the anisotropic characteristics of high energy ion bombardment to produce sharp sidewall profiles. A typical example might involve the etching of silicon by XeF_2 in the presence of Ar^+ bombardment.⁹ In this case the chemical nature of the radical F species gives elemental discrimination, providing rapid etching of silicon. The Ar ion bombardment shows little selectivity for particular elements, but it does provide for directed removal of etching products or for the supply of some energy in overcoming activation barriers in the reactions involved in materials removal.

The use of ion bombardment, however, can produce material damages, which can be undesirable.^{5,10} These damages are particularly troublesome in the limit of ultrasmall devices in which electrons are confined to dots or wires that are smaller than the wavelengths of the electron.¹¹ The necessity for using ion bombardment to enhance the etching rate suggests that in many cases there are barriers to desorption or in the reactions to form products. Etching by low energy species, such as F, Cl, and Br alone, which are some of the primary etchant radicals in plasma etching, produces little selectivity in direction;^{12,13} however, it has been suggested that translationally fast neutral species may also be formed by directed ions in plasma reactors and can play a role in plasma etching.^{7,8} Thus, low energy

reactive neutral particles may be important for maximizing etching rates and anisotropies, and minimizing defects.

The goal in the work here is to investigate the microscopic basis for materials removal using neutral atoms and radicals at high kinetic energies (1-10 eV). With support from this ARO grant, we recently developed and characterized a new beam source of translationally fast atoms, radicals, and molecules.¹⁴⁻¹⁸ This beam source is based on a laser vaporization technique. The mechanisms of laser vaporization have been pioneered by many groups in the past several years;¹⁹⁻³⁶ the method can be used to produce a variety of reactive neutral atoms, radicals, metal vapors, and other compounds with high kinetic energies. In our work, we use the laser vaporization process to produce a beam source of energetic, reactive neutral species which can be used to study collisions with semiconductor surfaces for fundamental investigations of etching and deposition.

In the laser vaporization beam source, high kinetic energy species are formed with energies of \approx 1-10 eV in the laboratory frame by laser vaporization of cryogenically condensed films of the desired molecules.¹⁴⁻¹⁸ The source is operated in a repetitively pulsed mode by continuous deposition and vaporization of molecules which are condensed onto a cold window. We have characterized the kinetic energies, fragmentation patterns, and some internal states of the ejected species for films of Cl_2 , NO , and XeF_2 . The energy of the pulsed beams can be selected by a single high speed chopper wheel. The fast atom beams can also provide directionality in the etching process. The first collision of a fast atom with the

substrate material has a high velocity and subsequent collisions are slowed dramatically by trapping-desorption mechanisms. The translationally fast atoms and radicals have substantial additional energy to surmount activation barriers and to overcome energetic constraints for desorption. Thus product molecules may evolve into the gas phase without the necessity for simultaneous ion bombardment. First studies are described below which demonstrate sustained etching of Si(100) with fast beams of Cl₂.

Major Findings

The apparatus was designed to produce translationally fast particles by laser vaporization of materials from solid surfaces or cryogenically condensed films. A goal of this work was to develop a beam source which was repetitive, reliable, and able to deliver high fluxes of reactive species with kinetic energies of ≈ 1 -10 eV to the surface of a semiconductor substrate, which is held in ultrahigh vacuum. These initial goals have been achieved during the previous grant period.

Our beam source¹⁴⁻¹⁸ is designed to improve upon the capabilities demonstrated in earlier work.²⁰⁻²⁴ In particular, the quartz window is refrigerated to allow continuous condensation of volatile molecules on the window between laser pulses. We presently have demonstrated the capability to create fast beams of atoms, molecules, and radicals such as Cl₂, F, F₂, and NO, and the ability to measure their velocity distributions by time-of-flight and to determine the composition of the beam by mass spectrometry.

The beam source works as follows. A quartz window or other transparent material is mounted in a differentially pumped chamber. Molecules or atoms are condensed continuously on the window by either cryogenic deposition from a gas jet or vaporization from an oven source. High energy pulses from an ArF rare gas halide laser (193 nm) or a frequency tripled or quadrupled Nd:YAG laser (355 or 266 nm, respectively) are directed through the window from the other side of the growing film to vaporize the film and eject translationally "hot" radicals and fragments by rapid heating, photodissociation, and hydrodynamic expansion. This part of the apparatus is intended primarily as a reliable source of translationally fast particles for the surface scattering, etching, and deposition experiments which are carried out in the main interaction chamber. However, we also analyze the species in the vaporized beam and determine their internal energies (vibration and rotation).

The translational energy of the ejected particles are first analyzed by time-of-flight mass spectrometry using a quadrupole mass spectrometer located on the other side of the interaction chamber. The total flight distance is typically 100 cm. The fast beams are then directed onto a substrate material in the main interaction chamber, which is maintained under ultrahigh vacuum (UHV). The substrate's cleanliness and oxidation state are determined by X-ray photoelectron spectroscopy, and initial cleaning is accomplished with mild Ar ion sputtering. A second mass spectrometer system is positioned at right angles to the primary beam to analyze the scattered species for products of the etching, to obtain sticking coefficients as a function of

kinetic energy, and to study the direct dissociation of molecules upon collision with the substrate.

Beam Source Characterization

The Cl₂ molecule is a prototypical source for laser vaporization of Cl₂ films condensed on the refrigerated window. Typical Cl₂ dosing gas flows are 10¹⁷-10¹⁹ molecules s⁻¹ and laser fluences are 1-30 mJ cm⁻². We estimate that film thicknesses are approximately 100-1000 layers. Nearly all of the film is cleared from the window with each laser pulse at higher laser fluences. Given the geometry of the dosing gas line and assuming a sticking coefficient of unity, the total ejected fluxes may be conservatively estimated at 10¹⁶-10¹⁸ cm⁻² per laser pulse. Our measurements show that the Cl atom component of the ejected flux is <7% of the beam, possibly due to caging and subsequent recombination.

There is a dramatic effect on the arrival time with the energy of the vaporization laser; the higher energy laser pulses produce considerably shorter arrival times and consequently higher kinetic energies (1-5 eV). The variation of kinetic energy with laser fluence and film thickness is used to tailor the broad range of kinetic energies that is desired for a given experiment. The repetitive nature of the source, which has been perfected in our experiments, allows both signal averaging and time-sequence experiments to be accomplished.

In order to investigate the internal states produced by a laser vaporization process, we select a study of NO molecular films, because the NO molecule is well-

suiting to laser probing of its internal states. The apparatus for measuring the vibrational, rotational, and spin-orbit state distributions of the NO molecules consists of the laser vaporization source and the time-of-flight measurement of the translational energy, coupled with a tunable laser, 1+1 multiphoton ionization probe of the internal states of the NO molecule. By varying the energy of the vaporization laser and the film deposition rate, various time-of-flight traces of NO are obtained with kinetic energies ranging from approximately thermal to 1 eV. By timing the pulse of the second probe laser, various velocities are interrogated to probe the internal state distributions systematically at different kinetic energies. The rotational excitation is extremely low, about 100 K. The vibrational and rotational state data suggest that there is either (1) rotational cooling following the vaporization process, perhaps due to collisions like in a supersonic expansion, or (2) some dynamical constraint that prevents vibration and rotation from becoming excited, while at the same time partitioning most of the excess energy into translation. At the present time, we favor a mechanism that invokes a supersonic cooling in the subsequent collisions of the vaporization process. This is also based on the corroborating calculations of Noorbach, *et al.*³⁷ and the results of Natzle, *et al.*,³⁸ which reveal high rotational excitation for NO molecules initially near the surface.

Use of XeF₂ as a film deposition material produced the first example where substantial molecular fragmentation occurs in the laser vaporization process, resulting in an excellent source of reactive F atoms, with kinetic energies in the

range of 0.1-4 eV. The observations strongly suggest that the fragments are produced in the laser vaporization process rather than from simple mass spectral cracking of XeF_2 . The lightest species, F atom, has by far the highest velocity. While the Xe species arrive later in time, the kinetic energies of the Xe species are enormous (e.g. 13 eV). We speculate that the Xe species are propelled forward by the lighter species in the hydrodynamic expansion.

Laser vaporization has been observed for a variety of other systems, which are briefly mentioned here. These include films of cryogenically condensed Ar, NF_3 , CCl_4 , CH_3I , ICl , and $(\text{CH}_3)_2\text{CO}$. Argon is perhaps one of the most intriguing in this group, since there is not an obvious electronic absorption which can be accessed by the ultraviolet lasers. Approximately every fourth laser pulse produces Ar vaporization with kinetic energies of 0.4 eV. We speculate that the first laser pulses might induce some trapped exciplex species, which then absorb more strongly and initiate the vaporization, or that impurity absorptions are important in this process. In ICl , we see a substantial fraction of fast Cl atoms, in contrast to Cl_2 .

The vaporization of NF_3 produces fast NF_3 molecules. While signals are observed also at the masses for NF_2 and NF , these signals arrive identically in time with the NF_3 and are thought to arise only from mass spectral cracking. The vaporization process of NF_3 terminates after a short period of laser irradiation, perhaps because of the buildup of some polymeric material on the window. A distinct coloration appears on the window and no further vaporization is observed.

The laser vaporization processes of various carbon-containing materials, such as CCl_4 , CH_3I , CFCIH_2 , CF_2Cl_2 , and $(\text{CH}_3)_2\text{CO}$, are also hampered by the buildup of photoproducts. The results are erratic and it is difficult to make reproducible beams. We did, however, observe ejection of parent molecules in several of these cases, as well as some fragmentation, for example CCl_2 from CCl_4 , which can be attributed directly to the vaporization process. We have also detected more volatile products that are apparently formed in the solid upon laser radiation, molecules which evaporate at much lower temperatures than the parent molecule upon warm-up of the window. Thus we suspect that Cl_2 is formed in the irradiation of CCl_4 and is trapped in the solid. Further work on these systems is necessary to understand the effects of polymer buildup and how to circumvent this problem in order to make reliable sources of fast beams.

We have also succeeded recently in forming vaporization products from mixtures, e.g. Xe and Cl_2 . The Xe is swept along with the lighter species and achieves high kinetic energies.

Sticking, Scattering and Etching of Si(100) by translationally fast Cl_2

Our first study to interact one of the fast beam sources with a semiconductor surface is applied to the collisions of fast Cl_2 with silicon. While the pure chemical interaction between Cl_2 or Cl atoms and undoped silicon is insufficient to produce a rapid etching of the silicon,⁷ both doping of the silicon and the interplay between the ions, radicals, and fast neutral species in plasma etching devices do produce efficient

etching of silicon by chlorine. In addition, there are numerous studies of the etching of silicon by the simultaneous application of laser beams and chlorine above the silicon substrate.³⁹⁻⁴² Recently products of chlorine etching of Si(111) have also been observed on the surface with scanning tunneling microscopy.⁴³ Theoretical work provides estimates of the SiCl radical binding energy and the lowering of this energy by subsurface halogens.⁴⁴

While the fraction of Cl in our Cl₂ beam is small, these preliminary results may be subject to re-interpretation because of the presence of the radical species. Further experiments are being performed to determine the individual roles of Cl and Cl₂ and to detect whether dissociation of Cl₂ occurs upon collision with the surface. Nevertheless, if we overlook for the moment the effect of a slight Cl contamination of the Cl₂ beam, an interesting series of experiments can be performed to determine the initial features of the interaction of the high energy Cl₂ beam with silicon.

The first interest is to determine the sticking coefficient as a function of kinetic energy of the Cl₂ beam. Initially the XPS system was used to measure the concentration of Cl on the silicon surface as a function of beam exposure time and Cl₂ beam energy. Each spectrum requires about 5 minutes time, and measurements were carried out for a sequence of 5 or more beam exposure times. With the XPS we can observe the uptake and saturation coverage of Cl on the surface. Since the XPS probes about ten layers deep into the silicon substrate, it is also possible to map the depth profile by varying the angle of incidence of the silicon, and this work is in

progress. The preliminary results from XPS measurements using two different Cl_2 beam energies (0.9 and 1.9 eV average) suggested that the sticking probability increased by about 20% with the increased kinetic energy. However, the XPS measurements are rather time-intensive, and thus it was determined that direct scattering measurements with the quadrupole mass spectrometer would obtain results more efficiently.

Initial scattering experiments focused on determining the probability of forming a surface bound species by analysis of the scattered flux as a function of beam exposure time together with suitable models for the kinetic order of the sticking and uptake process. A first experiment was carried out at 1.4 eV average kinetic energy and the scattering was measured as a function of surface temperature for different exposure times. Both Cl and Cl_2 were detected in these first experiments. The signals are interpreted in the following way. Initially the surface is clean and the sticking probability is high. As the surface becomes covered with chlorinated species, eventually there are no further sites to uptake chlorine. Thus the scattered flux is initially small and increases until saturation of the surface is achieved. Additional measurements down to 350 K and up to 800 K demonstrate the same result. We conclude that the sticking probability is essentially independent of the surface temperature over this range.

Scattering measurements were then performed at varying average kinetic energies of the incident beam, and the results were normalized for different fluxes, determined in separate measurements. There is evidence for an enhanced sticking

probability with increased kinetic energy. The more rapidly rising signal in the higher kinetic energy data suggests that the saturation coverage is reached much sooner. Application of suitable kinetic models to incorporate the kinetic order of the process will allow a determination of the sticking probability, reaction rate constants, and an assessment of the mechanisms. While there is still considerable scatter in the data and the spread of kinetic energies is large, the effect has been reproduced now several times, and represents an exciting new finding.

Typically the sticking probability for simple species initially decreases with kinetic energy as the kinetic energy becomes large enough to overcome trapping and adsorption wells. At very high kinetic energy, the sticking probability again increases as there is a tendency to implant particles into the substrate. With a molecule such as Cl_2 , on a relatively noninteracting surface like silicon, it is possible that our measurements are probing the dissociative chemisorption probability. It indicates that the sticking probability is enhanced at these mildly elevated kinetic energies (2 eV).

Experiments have recently been performed to observe the formation of SiCl_n species during the reactive scattering or etching event. At present we have observed products of the etching at masses of 170 and 135, which correspond to the most abundant isotopes of SiCl_4 and SiCl_3 . Etching experiments were performed at a range of surface temperatures. They suggest that sustained etching does occur for 0.5-2.5 eV incident Cl_2/Cl mixtures. In addition, there is a dramatic enhancement of the etching rate with increased kinetic energy (factors of 10 and 20 from 0.5 to 1.5 and 2.5

eV average energy, respectively). Thermal energy beams are found to produce no etching at all by comparison.

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Co-workers

Robert J. Levis, postdoc, presently Assistant Professor of Chemistry, Wayne State University.

Lisa M. Cousins, graduate student, Ph.D. 1989, presently postdoctoral associate, University of Toronto.

Curtis J. Waltman, undergraduate, attending graduate school, University of Wisconsin, Department of Chemistry.

Francis X. Campos, Postdoctoral Associate

Gabriela Cornejo-Weaver, graduate student

Inventions - no patentable inventions have resulted from this work.