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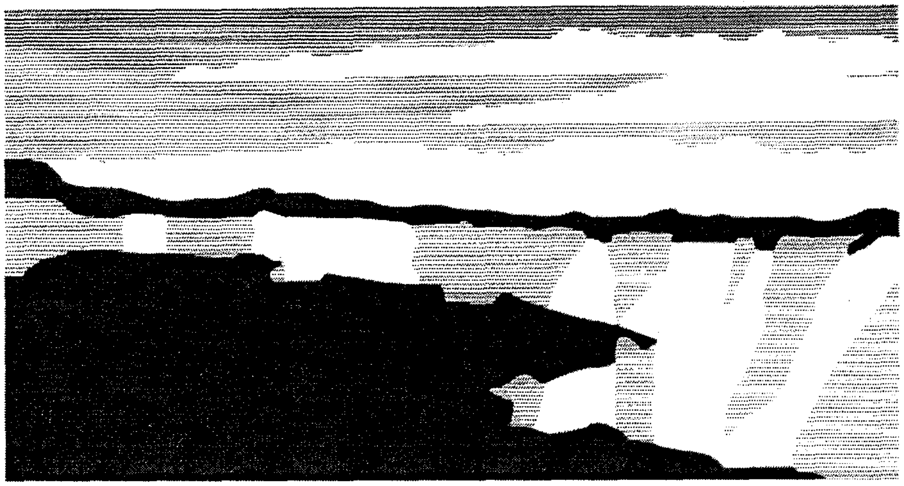

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Neutral Beam Processing of Semiconductor Materials

Jon Cross* and Mark Hoffbauer

Abstract

This is the final report of a one-year, Laboratory-Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). The most important challenge facing the U.S. and global microelectronics industry is to identify and develop the next generation of processing technology to produce device structures with dimensions substantially less than 0.25 microns. This project sought to develop controlled, contamination-free etching techniques that are more selective and less damaging than current methods, which are based on inducing surface chemical reactions by rather crude ion-damage mechanisms. The use of non-charged particle etching and cleaning processes in the production of memory and microprocessor chips has been identified by The National Technology Roadmap for Semiconductors as a new manufacturing technique that may aid in the quest for feature sizes of 0.1 micron and lower. The Hyperthermal Neutral Beam Facility at Los Alamos has demonstrated significant improvement over ion-assisted etching in experiments using energetic oxygen and chlorine atoms.

1. Background and Research Objectives

Over the last two decades, a revolution in processing microelectronics materials has succeeded in making much smaller and faster computers. This has been possible through advances in electronic-materials processing based on selective etching for patterning of devices, carefully controlled oxidation for forming dielectric layers, and precise implantation of impurity atoms for doping active layers. The most important challenge facing the United States microelectronics industry in the next ten years is to identify and develop the next generation of processing technology needed to produce device features with dimensions approaching 0.1 microns or less. The industry (The National Technology Roadmap for Semiconductors-

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http://www.sematech.org/public/home.html) realizes that it is essential to develop controlled, contamination-free etching and processing techniques that are more selective and less damaging than current methods, which are largely based on inducing surface chemical reactions by rather crude ion-damage mechanisms and high-temperature growth and annealing procedures.

The use of high-energy, non-charged particles for etching and processing of electronic materials at moderately low temperatures has recently been identified by SEMATECH and the microelectronics industry as a new technology that will play a critical role in manufacturing electronic devices well into the next century. SEMATECH is a consortium of the Federal Government and domestic semiconductor manufacturers whose mission is to solve the technical challenges required to keep the U.S. number one in the global semiconductor industry. Los Alamos is in a unique position to address this challenge because it has a world-class capability to produce an intense, continuous flux of high-energy neutral atoms. The LANL Hyperthermal Neutral Beam Facility has recently demonstrated the use of energetic oxygen and chlorine atoms to improve significantly the anisotropic etching of photoresist polymers and polysilicon yielding more selectivity and greater fidelity than ion-assisted techniques.

Anisotropic etching is used for fabricating sub-micron features and is carried out by surface chemical reactions that are made to occur in a controlled spatial direction. On the other hand, isotropic etching proceeds at equal rates in all spatial directions. The anisotropic etching of electronic materials used to manufacture memory chips and microprocessors presently relies upon charged-particle bombardment to produce damage sites that react with suitable adsorbed chemical species. The reaction products have a high vapor pressure and leave the surface resulting in surface recession in selected regions. Masks of various types are placed over areas that need to remain intact. Ideally, these masks do not react with the impinging ions or any of the surface-adsorbed chemical reactants. This technique of reactive-ion etching has gained widespread acceptance for the mass production of large-scale integrated circuits and is routinely used at the present time in the manufacture of memory and microprocessor chips having feature sizes down to 0.25 μm.

By the year 2000, the U.S. semiconductor industry has targeted device-feature sizes less than 0.1 μm to be manufactured with high reliability and yield, thereby increasing chip functionality by many orders of magnitude. This drive for smaller feature size necessitates that process induced damage mechanisms be minimized in order to maximize device-production yield.

Three key technological problems currently limit development of faster generation devices required for gigaflop processing are: (1) ion and electrical issues, including surface damage and aspect-ratio-dependent etching caused by ion flux and ion/electrical influences; (2)

integration and defect issues, including device defects that limit yield, interconnection contact quality, and thus place a practical limit on device and integration size; and (3) chemical etching and cleaning selectivity issues. Efforts have traditionally focused on replacing low-density, high-energy ion-impact processes presently in use, with high-density, low-ion-energy plasma processes, such as inductively-driven plasmas. Low-energy ions, however, are also influenced by electrical field disturbances present in the plasma and on the surface of devices resulting in unacceptable device profile distortion (see Figure 4), especially for feature sizes smaller than 0.1 mm. Use of inductively driven radio-frequency plasmas will suffice for 1990's generation devices having oxide gate thickness greater than 100 Å and line widths of 0.25 µm. However, for future, fast-generation devices, gate-oxide thickness of approximately 30 Å and line widths of 0.1µm will be necessary. These extremely thin oxide films and line widths are highly vulnerable to ion damage, even for low-energy ion impact. The gate oxides are also subject to dielectric breakthrough caused by electrical field gradients or surface impurities. The current use of plasmas for etching and deposition processes presents a technological barrier for these future devices because of the highly charged environment of the plasma and the workpieces placed therein. Fast neutral reactants provide a better choice for an etchant because the etching mechanism is not damaged based, as is that for ions, i.e., fast neutral reactions rely upon direct chemical interaction with the surface rather than creating damage sites that then react with absorbed species. Use of hyperthermal neutral streams as a substitute for plasma etching processes minimizes surface damage due to the absence of ions and also avoids feature-profile problems (see Figure 3) as well as dust formation.

2. Importance to LANL's Science and Technology Base and National R&D Needs

These techniques are directly applicable to weapons cleaning and manufacturing issues and are thus of great importance to LANL's science and technology base. The development of plasma cleaning techniques is underway for use in weapons manufacturing and cleaning of weapon components. This non-invasive technique holds the promise of reducing or eliminating liquid waste streams as well as reducing personnel radiation exposure. Plasma cleaning technology was borrowed from the technology developed for the microelectronics industry where it has been employed to induce anisotropic etching of silicon and for the cleaning of surfaces. This technique relies upon surface damage induced by charged-particle bombardment to enhance the reaction rate of the thermally neutral reactants such as free radicals and atomic species that reside on the surface. As cleanliness becomes of greater concern, non-charged-particle methods of cleaning are being developed by the microelectronics industry to reduce or eliminate dust production, substrate and chamber sputtering, and charged-particle device damage. The primary enabling technique relies upon neutral reactants with high translational energy that directly induce unique chemical reactions on room temperature surfaces. We have shown that the reaction efficiency (cm^3/atom) of atomic oxygen for a variety of hydrocarbon-based polymers is very similar and occurs via a direct hydrogen-abstraction reaction. Therefore, it is reasonable to expect that high-kinetic-energy neutral reactants will likewise increase the etching (cleaning) rate of hydrocarbon contaminants, such as machining oils, by nearly four orders of magnitude over plasma cleaning techniques especially where charged-particle bombardment is not possible due to electrostatic shielding. Further, the reactivity is independent of the degree of polymerization or the polymer structure. The use of high-translational-energy neutral reactants will provide efficient cleaning of insulating materials, and areas where plasmas can not penetrate including confined spaces such as screw holes, cracks, crevasses, and complex shapes where electric fields can not penetrate. Further, low-energy neutral reactants will eliminate actinide sputtering that can both transport material to undesired locations and create dust particles that increase high-level radioactive waste-stream volume.

Not only does high-kinetic-energy atomic oxygen exhibit exceptional cleaning properties, it has been shown to be the only oxidation reactant that can form the highest oxidation state of compound semiconductors and alloys. This feature can be exploited to form a fully oxidized, corrosion resistant, passivation film that is free of pin holes. We have also assembled a halogen source (F, Cl) for etching of silicon having an energy of approximately 2 eV. Since the halogen reactivity with actinides should exhibit a similar translational energy dependence to that observed with semiconductor materials, such a source can be employed for actinide cleanup of weapons components.

3. Scientific Approach and Results to Date

Atomic Oxygen Etching of Polymers

The necessary conditions for high-resolution etching processes are best illustrated by hyperthermal atomic oxygen anisotropic etching of polymers. Figure 1 shows the absolute reactivity of atomic oxygen with the polyimide Kapton as a function of translational energy of the incident atomic oxygen. The rate of etching is highly dependent upon translational energy of the atomic oxygen and increases more than four orders-of-magnitude going from thermal energy to approximately 5 eV. In addition, atomic oxygen that does not react upon the first collision is efficiently thermalized and scatters from the surface with an energy largely characteristic of the surface temperature. The reactivity of the thermalized oxygen is then 10^{-4}

times that of the direct oxygen beam and is essentially removed from the reaction scheme. Figure 2 shows a typical kinetic energy distribution for the laser-sustained beam source that is employed to produce the high kinetic energy atomic oxygen. The same type of source is employed to produce atomic chlorine.

The scanning-electron-microscope photograph shown in Figure 3 illustrates the quality of etching performed using fast neutral atomic oxygen on a tri-layer photoresist polymer. Note that aspect-ratio-dependent etching is NOT observed as with plasma-based processing shown in Figure 4 and that microloading also does not occur. In addition, local charging phenomena and mask damage are not observed at this resolution.

The oxidation of polymers by high-kinetic-energy atomic oxygen is thought to involve a mechanism based on hydrogen abstraction. After hydrogen is abstracted, the polymer backbone (carbon-carbon bond) is broken by surface-adsorbed free radicals. The reaction rate of hyperthermal atomic oxygen with polymers is not sensitive to the polymer structure as long as the polymer is not a fluorocarbon polymer. This fact is illustrated in Table 1 which lists the reaction rate of hyperthermal atomic oxygen with various polymers. In fact, the reaction rate scales with the extent of hydrogen saturation.

Material	Reaction Cross Section-cm3/atom
Kapton (polyimide)	3.0×10^{-24}
Mylar	3.4×10^{-24}
Tedlar	3.2×10^{-24}
Polyethylene	3.7×10^{-24}
Polysulfone	2.4×10^{-24}
Polystyrene	1.7×10^{-24}
Polyester with antioxidant	heavily attacked
Carbon (various forms)	$\approx 1 \times 10^{-24}$
Teflon-FEP	0.05×10^{-24} (no VUV radiation)
Teflon-FEP	$\approx 1 \times 10^{-24}$(intense VUV radiation)
Silver	heavily attacked

Table 1 shows polymer reactivity in units of cm^3/atom which allows convenient calculation of surface recession through multiplication of reaction cross section by atomic oxygen fluence (#/cm^2). Note that for non-fluorocarbon polymers, the reactivity is nearly constant (within a factor of two) and independent of polymer structure, but dependent on hydrogen saturation. (VUV is vacuum ultraviolet).

Halogen Etching of Silicon

Several atomic chlorine sources are now operational with mass-spectrometric (MS), time-of-flight (TOF), and absolute-flux diagnostics. Preliminary analysis indicates good dissociation into Cl atoms with a translational energy distribution peak at 2 eV (Figure 5), a width of approximately 2 eV, and a flux of approximately 10^{16} Cl atoms/sec-cm^2.

Figure 6 shows chlorine etching of poly-silicon. The straight wall profile of the poly-silicon etch beneath the SiO_2 mask indicates that there is little if any reaction of scattered or diffused Cl species. These results indicate that there is a strong translational-energy dependence of the halogen reaction with silicon and that there is efficient thermalization of the non-reacted chlorine. In addition, there is no apparent damage of either the mask oxide or the gate oxide. However, the gate oxide damage needs to be investigated further by measuring the electrical properties of the oxide to determine the defect density of the oxide film. These results are very similar to the hyperthermal atomic-oxygen etching of photoresist polymers as discussed in the first part of this report. The absolute reaction rate is about a factor of ten less than for atomic oxygen etching of polymers, i.e., only about 1% of the chlorine reacts to produce surface recession whereas roughly 10% of the atomic oxygen reacts with polymers. There are several possible explanations for this. First, is that the nascent reaction rate is truly lower in the halogen/silicon case than the atomic oxygen/polymer case. Second, it may be that since the silicon/halogen reaction products have much lower vapor pressures than the H_2O, CO, CO_2 oxygen-reaction products, they may partially protect the virgin silicon surface from the direct attack of the hyperthermal halogen species, resulting in an apparent low reaction rate. There are several independent studies suggesting this mechanism. Indeed, the apparent thermal activation energy for the halogen/silicon reaction system is roughly an order of magnitude higher than for oxygen/polymer reactions indicating that a thermal process is important in the reaction mechanism, i.e., the removal of the reaction products is thermally activated. Raising the translational energy of the halogen or incorporating a heavy species such as Xe (i.e., high kinetic energy) in the beam will most likely sputter the weakly bound reaction products, resulting in an apparent higher reaction rate and lower thermal activation energy.

Conclusions

The results presented here demonstrate that the elimination of charged particles and the use of high translational energy neutral reactants produces high fidelity, low damage etching of photo-resist polymers and silicon. It is concluded that the use of high kinetic energy oxygen and halogen neutral species lead to:

- highly anisotropic etching profiles on photoresist polymers with low residual damage to gate and mask oxides.
- highly anisotropic etching profiles on silicon.
- 1-2 eV chlorine and fluorine (XeF_2) show very high selectivity for Si etching over SiO_2-gate and mask-oxide etching.

- XeF_2 removes native oxides whereas atomic chlorine does not.
- 1-2 eV chlorine and fluorine show low reactivity; 1% of flux reacts with an apparent thermal activation energy of approximately 5 kcal/mole.
- Both high-translational-energy oxygen and chlorine can be employed in anisotropic etching of silicon and resist polymers to avoid residual-damage problems in chip manufacturing and thus increase chip density.

The technologies discussed here are not only important in silicon device manufacturing but are also directly relevant and applicable to nuclear weapons fabrication and refurbishment.

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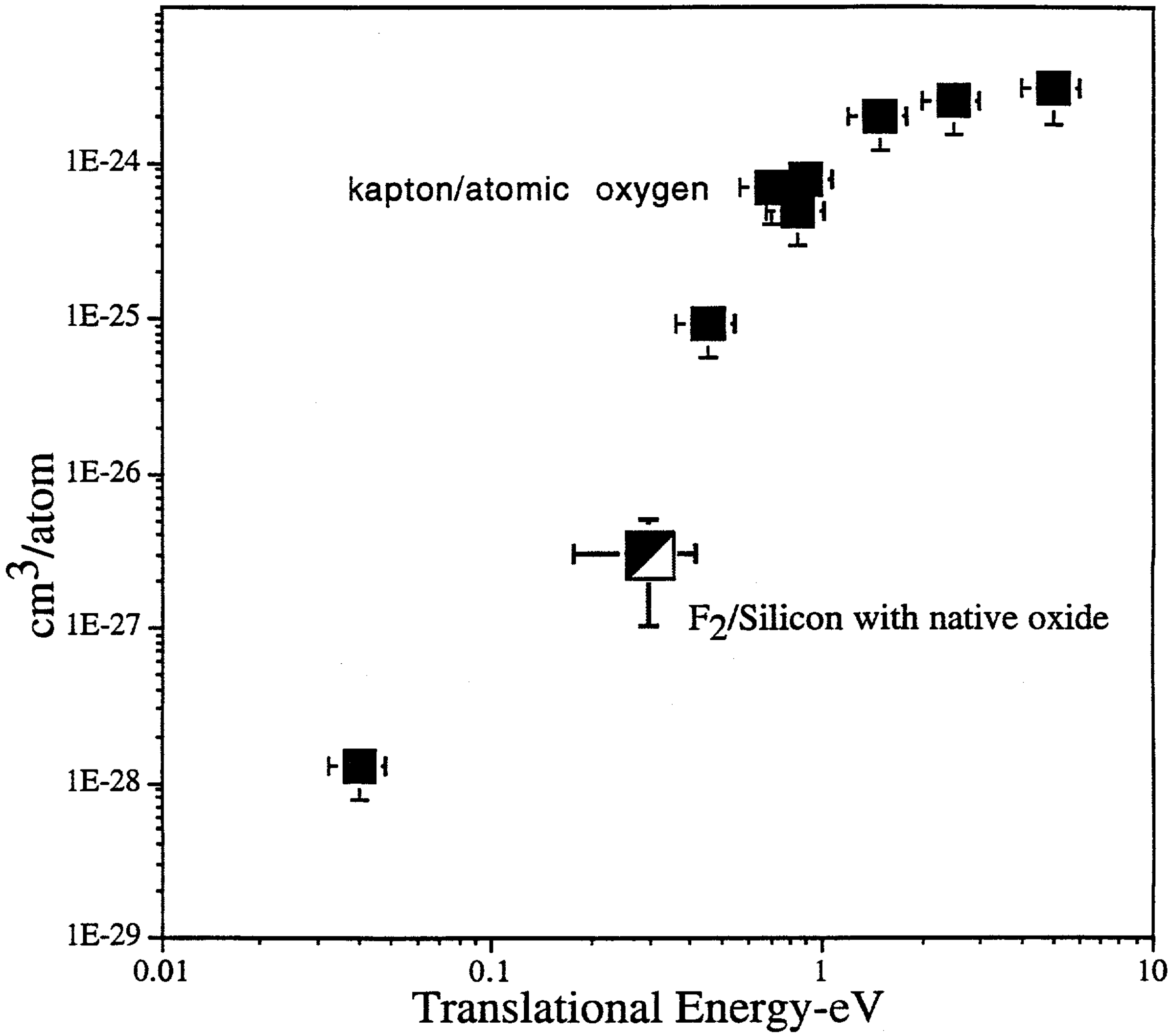

Figure 1. Translational energy dependence of atomic oxygen reaction rate with Kapton. Note the four order-of-magnitude increase in reaction rate in going from thermal energies to 3 eV.

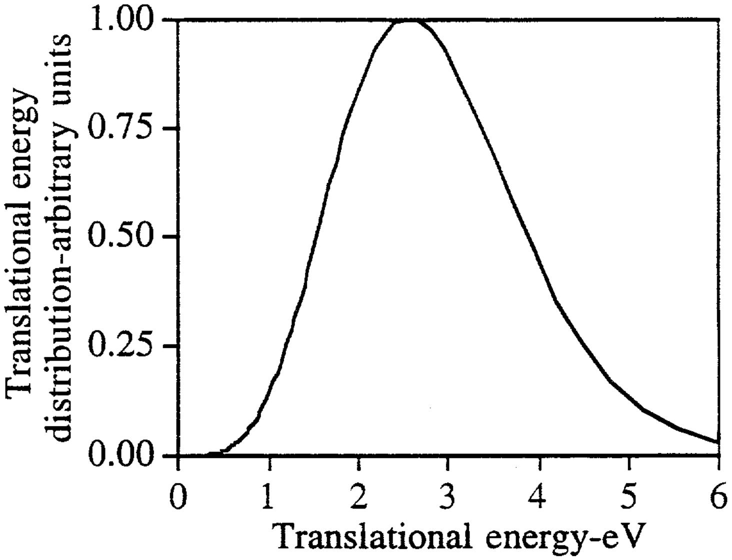

Figure 2. Translational-kinetic-energy distribution of atomic oxygen from the laser-sustained beam source.

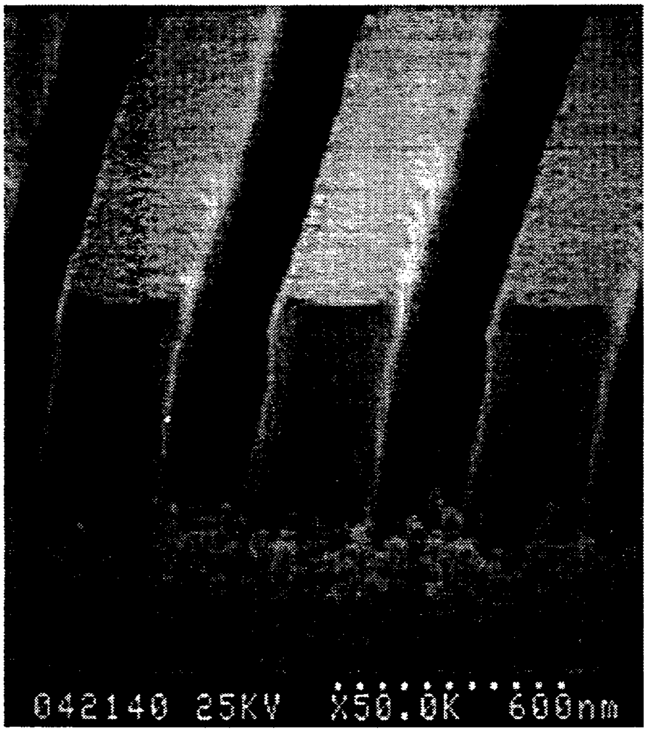

Figure 3. Scanning-electron-microscope photograph of atomic oxygen etching of photoresist polymer. Feature size is 0.3 microns.

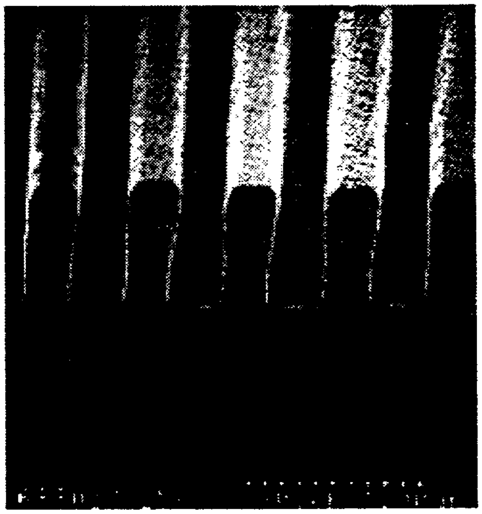

Figure 4. Scanning-electron-microscope photograph of plasma etching of same photoresist polymer as used in Figure 3.

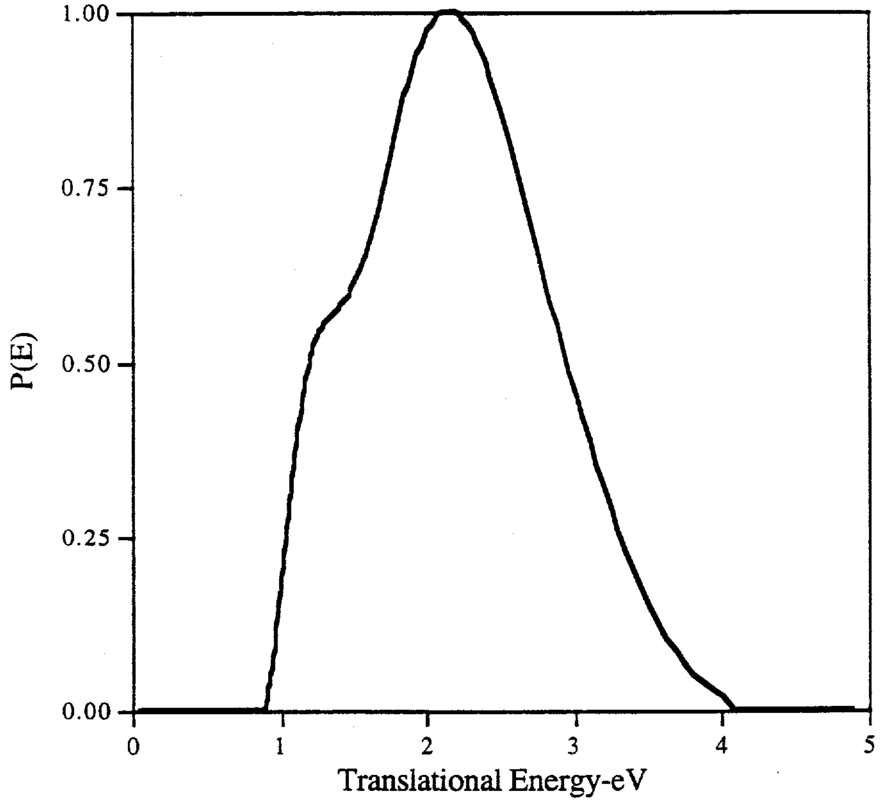

Figure 5. Cl-translational-energy distribution obtained from laser-sustained plasma source

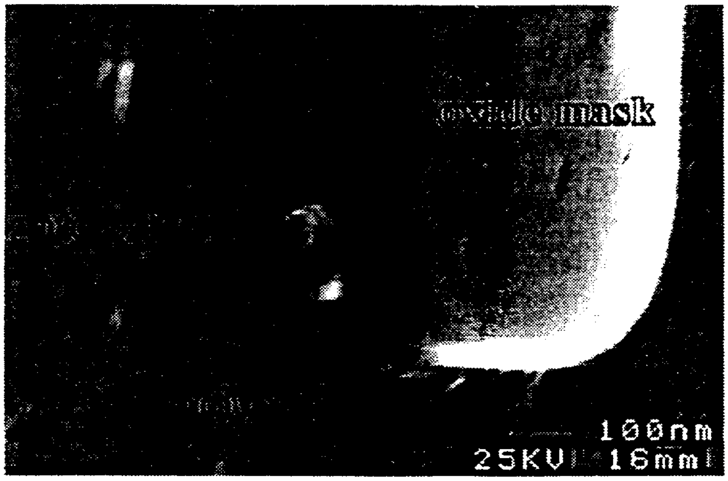

Figure 6. Chlorine etching of poly-silicon after pretreament with XeF_2 to remove native oxide.