

Reactive-ion etching

Plasma-based dry etching processes offer higher accuracy in replicating device patterns than wet etching patterns, but further advances may depend on a better understanding of gas-phase phenomena and plasma-surface interactions.

Gottlieb S. Oehrlein

Our ability to develop and build ever smaller microelectronic devices depends strongly on the capability to generate a desired device pattern in an image layer (photoresist) by lithography and then to transfer this pattern into the layers of materials of which the device consists. In the past the pattern transfer was almost exclusively accomplished by wet etching. Chemical dissolution of a film region that had to be removed took place in a suitable solvent. Although the wet etching processes stop precisely at a chemically different underlying layer, they typically have isotropic etch characteristics, which cost the researcher control over critical lateral dimensions. Such a tradeoff is not acceptable in the manufacture of micron- and submicron-scale devices, and wet, solution-based etching techniques were replaced in the late 1970s by dry, directional etching processes using plasmas or ion beams. Figure 1 shows a plasma-based dry etching system at IBM. In dry etching processes, surface atoms are removed via momentum transfer from bombarding, directed ions (physical sputtering), thus achieving a directional etch.

Technology is leading science in dry etching processes, and our lack of a detailed understanding of the chemical and physical basis of these processes will likely hinder further advances necessary to meet the technological

requirements of the future.

Reactive-ion etching

The most prominent of the new etching techniques is reactive-ion etching.¹ Figure 2 shows a scanning electron micrograph of the kind of structure that can be created by reactive-ion etching. The trenches—about 4 microns deep and 1 micron wide—were dry etched into a silicon wafer; they will be refilled with oxide and subsequently used for device isolation.

A typical system is schematically illustrated in figure 3. A glow-discharge plasma is used to generate the gas-phase etching environment, which consists of positive and negative ions, electrons, radicals and neutrals, from a suitable feed gas— CF_4 in the case of silicon and silicon dioxide. The material to be etched is placed² on a high-frequency-driven (commonly 13.56 MHz) and dc-biased electrode. (After ignition of the plasma, a capacitively coupled electrode acquires a negative charge because the electron mobility is much greater than that of the ions. The material on the electrode is thus exposed to energetic bombardment by positive ions.) Chemical reactions between the radicals and neutrals (fluorine, CF_3 , CF_2 and so forth) and the material being etched (silicon) occur at the surface and produce either volatile species such as SiF_4 or their precursors such as SiF , SiF_2 or SiF_3 . At the same time positive ions such as CF_3^+ are accelerated across the plasma sheath and remove material by sputtering. The combination of the chemical activity of reactive species and sputtering

can result in much higher material erosion rates in the vertical than in the lateral direction, which makes reactive-ion etching an essential tool for replicating device patterns in the fabrication of very-large-scale integrated circuits.

Our present technological applications require a controlled uniform etch rate, directionality for both vertical and tapered profiles, high selectivity (etch rate of one material as compared with a different, simultaneously etched material) and minimization of detrimental surface modifications related to plasma exposure. Often one technological requirement can be achieved only at the expense of another, as in the case of directionality and selectivity. The "output" of rf plasma etching depends in a nonlinear way on a multitude of adjustable input parameters: power density, frequency, pressure, dc bias, gas composition, flow rate and so forth. In the absence of a valid theoretical model, optimizing any particular process therefore requires extensive experimentation. Despite these complexities, rf-based plasma etching has been successfully used in semiconductor processing.

The etching requirements of the future will be very demanding compared with those of today. Directional etch rates of approximately 1 micron/min—at least an order of magnitude higher than existing rates—will be required, and selectivities should be greater than 50:1 (compared with our present selectivities of about 10:1). It is likely that these technological needs can be met only if we improve our

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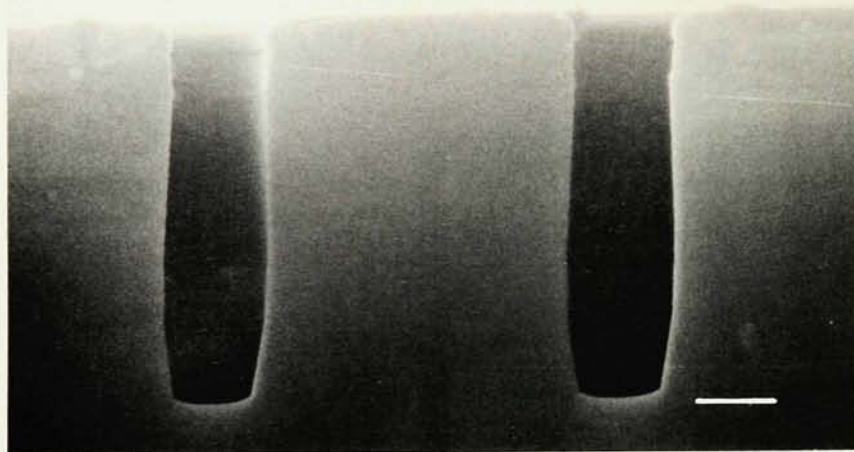


Etching of silicon wafers by an rf plasma (blue glow). In this photo the author is monitoring the process. The vacuum chamber in the foreground contains apparatus for mechanically transferring completed wafers into an ultra-high-vacuum system for further processing and analysis. Figure 1

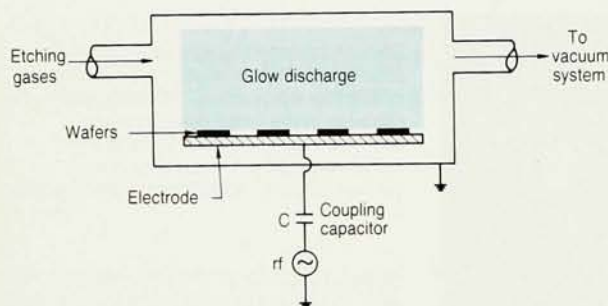
understanding of the complex physics and chemistry of rf etching plasmas and their surface interactions. A valid model of reactive-ion etching would identify the mechanistic factors that limit existing etching technology. But if we are to understand industrial rf plasmas we must first develop a host of probes for the characterization of the plasma and the etching process. These should preferably be nonintrusive (for example, optical) and provide information in real time. Diagnostic techniques that are simple to implement can subsequently be used in manufacturing for process control, as in detecting the etch end point.

In discussing reactive-ion etching we must consider both processes in the gas phase and interactions between the plasma and the surface. For gas-phase processes we wish to determine the densities of electrons, ions, radicals, parent molecules and product species, their energy-distribution functions and the temporal and spatial variation of these quantities. We further need to know the production rates (for example, by electron-impact reactions) and loss rates (by collision or deexcitation) of reactive species and the importance of heterogeneous processes (walls). The effective electric field and its spatial and temporal dependence must also be known.

Until now progress in the study of gas-phase processes in *real* production plasmas has come mainly from mass analysis, optical emission and laser-induced fluorescence spectroscopy of electronic transitions in the visible and ultraviolet regions.³⁻⁵



Trenches in a silicon wafer are typical of the kind of structure that can be created by reactive-ion etching. The white bar is 1 micron long. (Photo courtesy of David Danner, IBM Research.) Figure 2



Reactive-ion etching system for semiconductor processing. The system uses both chemical activity and physical sputtering to achieve much higher material erosion rates in the vertical than in the horizontal direction. Figure 3

Mass spectroscopy allows one to monitor the concentration of a wide variety of different species; it is limited, however, in that the results obtained are not necessarily true for the reactor itself, for the measurement is performed downstream.

Emission spectroscopy, especially what is called emission actinometry (in which an inert gas such as argon is used to account for changes in electron density), has been used⁵ to obtain *in situ* measurements of the relative intensity of etching species. For example, it is possible to determine the concentration of atomic fluorine in the ground state by monitoring emission from excited fluorine atoms and deducing the ground-state density via argon actinometry. Such studies verified that for plasma etching of silicon in CF_4 under conditions of minimal ion bombardment, the observed silicon etch rate depends linearly on the ground-state fluorine concentration.

Laser-induced fluorescence spectroscopy is used to measure ground-state ion and radical concentrations. Richard Gottscho and his colleagues at AT&T Bell Laboratories (Murray Hill, New Jersey) used⁴ this technique in 1984 to measure time-resolved ground-state ion concentrations in chlorine-

based rf discharges. By observing fluorescence of Stark-mixed parity levels they were able to determine the local electrical fields. This technique has the advantages of being non-intrusive, of providing space- and time-resolved information on some species and of allowing one to determine, from Doppler shifts and broadening of spectral lines, the kinetic-energy content of neutral and ionic species. Its main limitation is that many important species, such as fluorine in a CF_4 plasma, cannot be studied because of the frequency range of currently available dye lasers. Optogalvanic detection of Rydberg atoms and microwave, infrared and Raman spectroscopic studies of rotational and vibrational spectra of gas-phase ions, radicals and neutrals are other techniques that are expected to be very useful in the future.

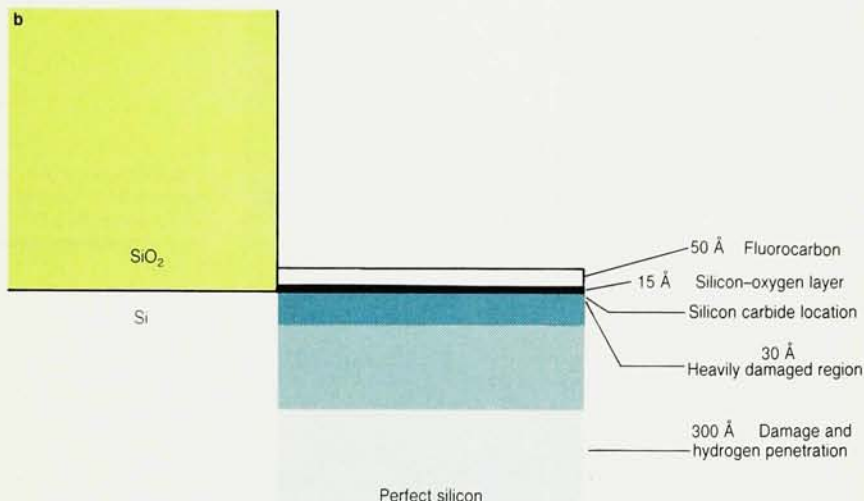
Plasma-surface interactions

Plasma-surface interactions encompass the chemistry and physics of gas-surface reactions relevant to etching in the presence of bombardment by energetic ions, electrons or photons. Here one is interested in surface impingement rates of the various plasma species, their energy content and sticking coefficients, identification of species

residing on surfaces during etching, and the types and rates of surface chemical reactions. We also need information on how ion, electron and photon bombardment affect these quantities and how they affect the formation, type and extent of a chemically altered near-surface region. We need to investigate the role played by the bombardment in the formation and ejection or desorption of volatile etch products, how it affects the energy and angular distribution of the ejecta, how these reactions are altered near interfaces and so forth. The impact of dry etching processes on the surface, the near-surface properties of the etched or exposed material and the need for surface preparations prior to further processing is a large topic of its own and I will discuss one prototypical example in detail later.

Some aspects of gas-surface interactions relevant to reactive-ion etching have been clarified by simulation experiments of production plasmas involving reactant ion beams on solid surfaces in ultra-high vacuum. In such experiments John Coburn and Harold Winters of the IBM San Jose laboratory modeled⁶ plasmas by exposing a silicon surface to a well-defined dosage of a chemical etchant, XeF_2 , and simultaneous energetic Ar^+ ion bombardment. Experimental configurations have been built^{6,7} where the etch products leaving the surface can be detected and analyzed by a mass quadrupole filter and by time-of-flight techniques. A key result of these investigations has been the observation of a large synergistic effect for the Si-XeF_2 positive argon ion-beam etching system: The silicon erosion rate for a silicon surface simultaneously exposed to the XeF_2 chemical etchant and to the Ar^+ ion beam is much greater than the sum of the etch rates for exposure to the ion beam and chemical etchant separately. This synergism can explain the etch directionality of reactive-ion etching in some cases: The directionality may be due⁶

Silicon dioxide to silicon reactive-ion etching process using $\text{CF}_4\text{-H}_2$: an enlargement (b) of the silicon surface shows changes incurred in the near-surface region of the substrate. Figure 4



to accelerated formation of the final etch product, SiF_4 , in the presence of ion bombardment, which causes enhanced atomic mobility and penetration of the substrate lattice. An alternative viewpoint contends⁷ that the role of the ions is to amorphize the silicon top layer, then to mix chemically reactive species into and sputter products from this modified layer much faster than from unmodified silicon.

At this time reactive-ion etching is the dry etching technique of choice because it offers the best combination of etch directionality, material selectivity and process control. However, undesirable side effects are associated with etch directionality and material selectivity. Etch anisotropy is caused by energetic ion bombardment. Although the ion energies are typically below 500 eV, the fluence is high—about 10^{15} ions per square centimeter per second—and bombardment damage can occur. Displacement damage alters the near-surface region of the material that is being etched or exposed to the plasma and changes its electrical properties. Etch selectivity appears to be primarily due to the deposition of etch inhibitors, which will remain on the exposed material after completion of the dry etching step and interfere with device processing following reactive-ion etching.

A prototypical process

Currently, openings for electrical contacts through silicon dioxide to the underlying silicon substrate are fabricated by reactive-ion etching using a $\text{CF}_4\text{-H}_2$ plasma. The addition of H_2 to the CF_4 gas is necessary to minimize the etching of silicon. We have found⁸ that typically it is possible to etch SiO_2 at a rate of about 500 Å/min, while the silicon etch rate is about 20 Å/min. I describe here an etching situation that illustrates the possible problems of reactive-ion etching in VLSI processing: To open a contact region, one material (SiO_2) has to be etched selec-

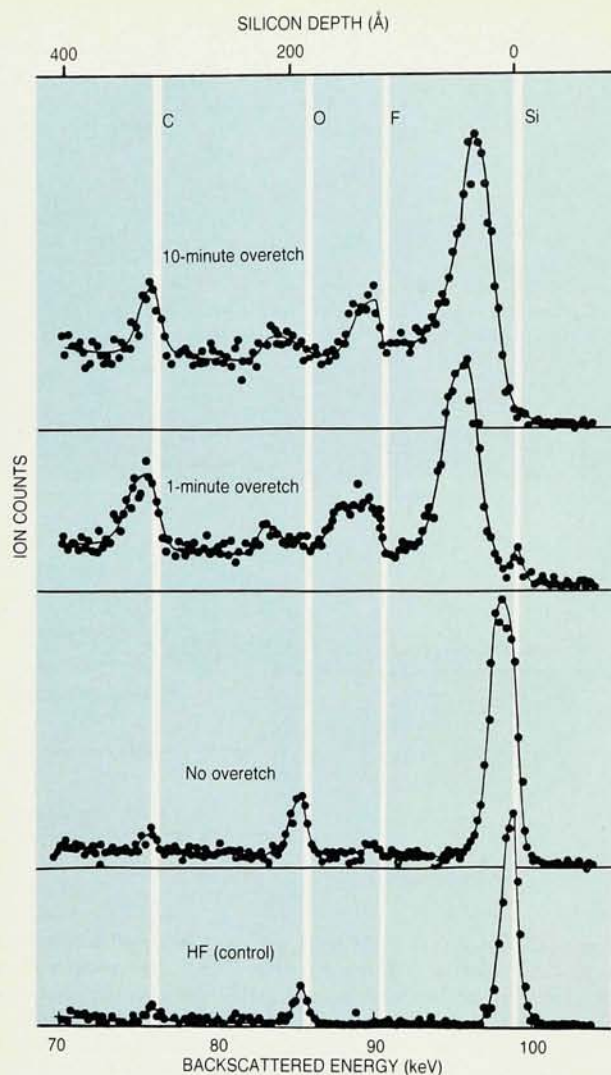
tively over another material (silicon), and, as a result, a critical, active surface region of a silicon device is exposed to the plasma.

The effects of plasma exposure on the state of electronic materials can be extremely complex and the tools of both bulk-defect science and surface science are required to analyze them. Often one can understand the effects only by combining consistent information provided by more than one technique. Some of these complementary experimental techniques are helium-ion channeling, x-ray photoelectron spectroscopy, $\text{H}^1 + \text{N}^{15}$ nuclear reactions, Raman scattering, ellipsometry, photoluminescence, transmission electron microscopy and electrical device characterization.

Figure 4 shows a composite view of the region near the silicon surface as altered by reactive-ion etching. The severely altered region is about 300 Å deep. The observed modifications include fluorocarbon film deposition, a high degree of disorder in the near-surface region and very high concentrations of implanted impurities: For example, hydrogen atoms at concentration levels of a few percent are introduced as far as several hundred angstroms from the surface, and carbon implanted within tens of angstroms of the surface gives rise to centers involving SiC bonds.

At IBM, we have studied⁸ subsurface damage introduced by reactive-ion etching using the He^+ channeling technique. For a helium-ion beam aligned with a major crystallographic silicon direction, only a few near-surface silicon atoms interact by nuclear elastic scattering with the ion beam, giving rise to backscattered helium particles with an energy $k_{\text{Si}} E_0$ (the silicon surface peak). Here k_{Si} is a kinematic factor that depends on the scattering angle and the mass ratio of the projectile (helium) and the scattering center (silicon). The subsurface silicon atoms are shadowed. The presence of an overlayer gives rise to additional backscattering peaks at different energies, provided the overlayer atoms and substrate atoms have different masses. For example, if the silicon near-surface region is disordered, due to displacement damage or to the presence of a thin disordered phase such as silicon dioxide or silicon carbide, the intensity of the silicon surface peak will be increased. Measurements of the silicon-surface-peak intensity can thus be used to detect the presence of silicon disorder in the crystal near-surface region with high sensitivity, even in the presence of an overlayer (as long as the overlayer is not silicon).

Figure 5 shows the intensity versus the energy of backscattering for some representative experiments. The bot-



Helium-ion-channeling spectra of Si specimens exposed to a $\text{CF}_4\text{-H}_2$ reactive-ion plasma for various times in the course of selective etching of SiO_2 over Si. The spectrum of a buffered hydrogen fluoride-etched Si specimen is shown for comparison.

Figure 5

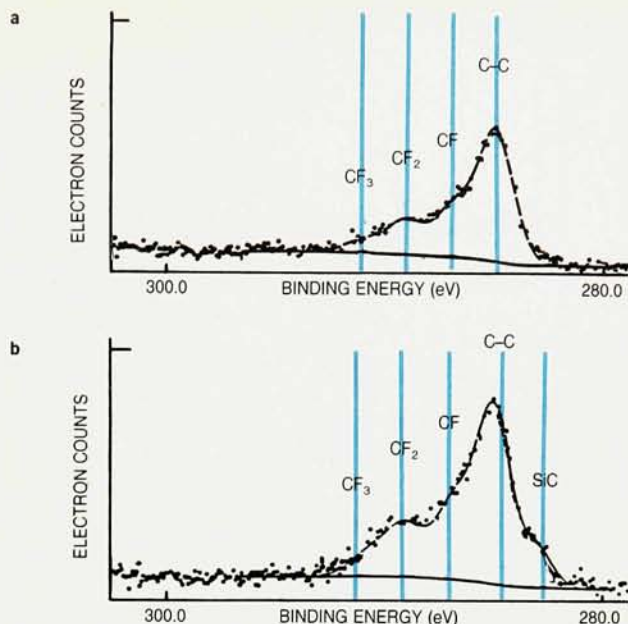
tom curve (for the wet-etched control sample) shows a pronounced peak due to scattering from silicon at the surface and additional peaks due to oxygen and carbon atoms in the native oxide layer. The other curves show results for dry-etched specimens for various overetching times—that is, for various times that the silicon substrate was exposed to the plasma. The Si surface peak is larger for the reactive-ion-etched silicon specimens than for the control sample and the background level at lower energies is higher. The increased area of the silicon surface peak for plasma-exposed Si specimens observed in the ion-channeling measurements is due to disordered silicon, presumably Si atoms dislodged from regular lattice sites by the energetic ion bombardment accompanying reactive-ion etching. The extent of the disordered layer for these specimens was determined from the increase in width of the silicon surface peak and was found to be about 34 Å, but further analysis shows that the disordered region is not completely

amorphized. The greatly increased background at energies below the silicon surface peak for the reactive-ion-etched specimens, especially for the samples with greater overetching times, can be explained by defects at greater depth, resulting from hydrogen implantation, that cause dechanneling of the analyzing helium beam. An additional fluorine peak and an increased carbon signal are also observed for the dry-etched specimens, while the oxygen peak is weaker. For greater overetching time the silicon surface peak and the oxygen signal are also shifted to lower energy; this shift is related to the presence of carbon and fluorine and implies a carbon-fluorine overlayer.

Although helium-ion channeling gives the degree and extent of silicon disorder with high accuracy, it is chemically "blind," and cannot distinguish a thin disordered, silicon-containing phase (such as amorphous SiO_2) from near-surface silicon lattice disorder. A powerful probe that can provide this

complementary information is Raman scattering. Jim Tsang (IBM Thomas J. Watson Research Laboratory) and his colleagues have used a multichannel Raman scattering system to observe⁹ normally forbidden Si-Si Raman scattering due to the destruction of long-range order by reactive-ion etching within the first 50 Å of the silicon crystal. They directed s-polarized argon-ion laser light such that the incident electric field vector was parallel to a silicon $\langle 100 \rangle$ crystal axis and the scattered electric field vector was perpendicular to this orientation. First- and second-order Raman scattering, which would otherwise dwarf the signal from the thin disordered overlayer, is then forbidden by the symmetry. No translational symmetry exists for the disordered near-surface region, and all of the material's vibrational modes may contribute to the scattering process. Tsang and his group observed a broad signal reflecting the density of vibrational states for reactive-ion-etched silicon, which is very similar to spectra previously obtained with amorphous silicon. These data establish that some of the disordered silicon atoms observed in the helium-ion-channeling measurements originated from silicon lattice disorder.

The way disordered Si produced by reactive-ion etching recrystallizes during annealing at elevated temperatures is different from the well-studied case of amorphous silicon layers produced by silicon self-implantation. Unlike fully amorphized silicon, which starts to regrow epitaxially at annealing temperatures of approximately 500 °C, an annealing temperature of 350 °C is sufficient for silicon damaged by reac-



Photoelectron spectra for the carbon 1s state measured in glancing and normal electron emission geometries. The electron emission angles were 63° (a) and 0° (b). The absence of the silicon carbide component in the glancing-angle spectrum demonstrates its subsurface location. Figure 6

tive-ion etching to reduce the number of disordered silicon atoms by 50%. On the other hand, annealing at higher temperatures is rather ineffective in reducing the density of disordered silicon atoms further. For example, additional heating at 800 °C for 30 minutes recovers only another 30% of the disordered atoms. The difference in efficiencies is due to high concentrations of implanted hydrogen, fluorine and carbon, which are responsible for some of the observed silicon disorder. The reduction in silicon disorder after low-temperature annealing can be accounted for by the release of hydrogen and fluorine species. But part of the disorder is due to the bonding of silicon atoms to implanted carbon; silicon carbide is very stable at high temperatures and a simple thermal treatment will not reduce this type of silicon disorder.

Low-temperature photoluminescence is another optical technique that has recently been applied to reactive-ion-etched silicon. Spectra obtained by Gregory Northrop (IBM) indicate¹⁰ a variety of types of damage, including point-defect complexes in the silicon substrate lattice that are commonly observed in silicon damaged by high-energy particles; among these are vacancy oxygen centers, silicon self-interstitial atoms paired with two substitutional carbon atoms and penta-vacancy complexes. Of particular interest has been the sensitivity of the optical emission to the concentration of H₂ in the CF₄-H₂ plasma. The well-known radiation damage centers dominate at low H₂ concentrations (rapid silicon etching), while only broader, hydrogen-related bands are observed at higher H₂

concentrations (slower silicon etching).

Surface residue layer

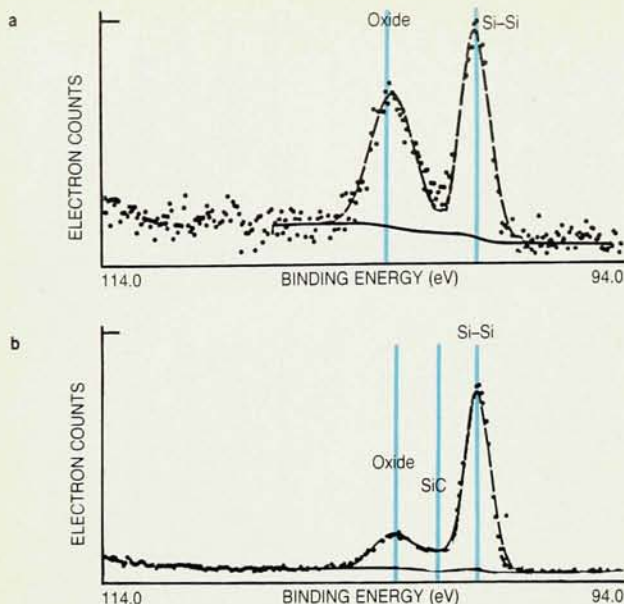
We have also examined dry-etched silicon surfaces using x-ray photoemission spectroscopy. In this process a beam of monochromatic x rays irradiates the specimen, causing the photoemission of strongly bound inner-shell electrons from its atoms (see the article by Franz Himpsel and Neville Smith, December, page 60).

The x-ray photoemission spectrum of a silicon sample where the SiO₂ had been removed by dry etching showed additional core-level photoelectrons due to fluorine at the surface, decreased oxygen core-level intensity and increased carbon intensity when compared with specimens from which the SiO₂ had been removed by wet etching. The silicon 2p and 2s photoelectron peaks, which arise from photoelectrons originating largely in the silicon substrate, are much less intense than for a control. These results agree with the ion-scattering results in suggesting that a layer consisting primarily of fluorine and carbon uniformly covers the silicon substrate. This interpretation is substantiated by high-resolution spectra of the carbon 1s and silicon 2p peaks. Figures 6 and 7 show carbon 1s and silicon 2p x-ray photoemission spectra obtained¹¹ at different electron emission angles by George Coyle (IBM, East Fishkill, New York) and his collaborators. Figure 6a shows a high-resolution carbon 1s spectrum for a 1-minute-overetched silicon sample. The principal peak at 285.3 eV is typical of carbon-carbon or hydrocarbon species. Further, various carbon-fluorine species, such as CF, CF₂ and CF₃, are

clearly resolved by their different chemical shifts to higher binding energy from the main carbon line at 285.3 eV. Because of the large electronegativity of fluorine, each fluorine atom pulls off a certain amount of charge from the carbon, which makes the carbon atom more positive and increases the binding energy of an electron in the carbon 1s core level. We extracted the intensities of the characteristic components shown in the figure by line-shape analysis of the spectral envelope.

Energetic ions that bombard the silicon lattice during the etching process can enter into the silicon lattice, causing lattice damage. Hydrogen, carbon and fluorine species can all penetrate the silicon lattice during CF₄-H₂ etching and may bond to silicon atoms. While the stopping range of hydrogen for typical ion energies is approximately 100–200 Å, the range⁸ of carbon and fluorine is about 30 Å, a depth accessible to x-ray photoemission spectroscopic analysis.

The existence of implanted and bonded carbon in the silicon substrate has been demonstrated with x-ray photoemission spectra obtained using electrons emitted at different angles relative to the surface. Because the intensities of the characteristic photoelectrons emitted from atoms beneath the top monolayer are attenuated by the material through which they pass, only electrons originating within a certain distance from the vacuum-sample interface (the electron escape depth) contribute to the observed signal. Therefore, the effective photoelectron sampling depth is a maximum for photoelectrons emitted along the



High-resolution x-ray photoemission spectra for the silicon 2p core level. The electron emission angles were 63° (a) and 0° (b). The absence of the silicon carbide component in the glancing-angle spectrum shows that it is located below the oxide layer.

Figure 7

surface normal and a minimum for glancing electron emission. By tilting a sample with respect to the electron analyzer, one can establish differences in material composition as a function of depth. For normal electron emission a peak at 283.5 eV is apparent in the carbon 1s data of figure 6b that is absent (or very small) for glancing-angle emission data. The energy of this peak agrees with the binding energy of silicon carbide; this silicon carbide must also give rise to a silicon 2p component at 101.3 eV.

High-resolution silicon 2p spectra are shown in figure 7. The principal line at 99.6 eV is due to elemental silicon from the bulk of the sample. A silicon dioxide component located on top of the silicon substrate is centered at 102.8 eV. Most importantly, an extra 101.3-eV component is observed under normal electron emission that is absent for glancing electron emission. We obtained other carbon 1s and silicon 2p spectra similar to those shown in figures 6 and 7 at other electron emission angles. Those measurements established that the intensities of the 283.5-eV and 101.3-eV components decayed identically with increasing electron emission angle. The data not only supported the silicon carbide assignment but also allowed us to determine the location of the silicon carbide from a comparison of the angular variation of its intensity with that of other chemical species present in the same spectra—elemental bulk silicon, silicon dioxide and carbon-fluorine species. The silicon carbide is located below the silicon dioxide in the elemental silicon matrix, that is, within the region that ion-channeling data had indicated was

heavily disordered.

We detected the presence of hydrogen in the silicon lattice using William Lanford's nuclear-reaction-profiling facility¹² at the State University of New York at Albany. The technique makes use of resonant nuclear reaction between a proton and a nitrogen-15 atom at a center-of-mass energy of 402 keV. The reaction yields an alpha particle, carbon-12 and a characteristic 4.43-MeV gamma ray. By bombarding a sample with a 6.39-MeV N^{15} beam (402-keV center-of-mass energy), one obtains 4.42-MeV gamma rays whose yield is proportional to the concentration of hydrogen on the sample surface. If the N^{15} energy is greater, the nuclear reaction can occur only at a certain depth inside the sample—that is, only after the N^{15} has slowed down to the resonance energy. By varying the energy of the N^{15} ion beam, one can obtain a profile of hydrogen concentration versus depth in a nondestructive way. Such data are shown in figure 8 for wet-etched control and reactive-ion-etched silicon specimens. The data show clearly that reactive-ion etching can introduce hydrogen at the atomic percent level to a depth of several hundred angstroms from the silicon sample surface.

While the nuclear-reaction-profiling studies establish the presence and depth distribution of hydrogen in the silicon substrates, they do not distinguish among hydrogen bonded to silicon, to itself (H_2) and possibly to a silicon atom next to a shallow acceptor. The vibrational frequencies of the infrared modes of the different hydrogen bonding configurations are well established and distinct. Therefore we ex-

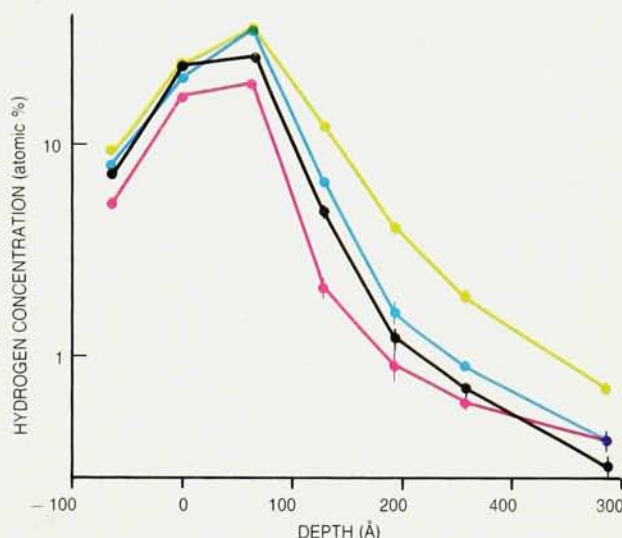
amined the reactive-ion-etched silicon samples by Raman spectroscopy to establish the bonding environment of the hydrogen. We were able to observe the well-known broad infrared band just above 2000 cm^{-1} due to silicon-hydrogen modes for reactive-ion-etched silicon, the band being absent for samples without plasma processing. The hydrogen is therefore primarily bonded to silicon neighbors.

Consequences

Electrical measurements undertaken with devices fabricated using reactive-ion etching indicated degraded electrical behavior consistent with figure 4. Working with C. M. Ransom, we observed a large decrease in current across the metal-silicon contact for a fixed electric field. These data could be modeled under the assumption that an insulating layer existed between the semiconductor and the metal. Other measurements implied defects in the silicon substrate that introduced electrical levels into the semiconductor bandgap. The electrical measurements demonstrated that to obtain satisfactory electrical device performance one must subject a reactive-ion-etched silicon surface to an intermediate cleaning or annealing treatment before proceeding with subsequent device processing.

The increased understanding of reactive-ion-etched silicon surfaces provides the necessary prerequisite for designing effective silicon surface treatments to be undertaken between reactive-ion etching and any further device processing steps. The objectives of the treatment are to remove the carbon-fluorine residue film, the heavily damaged and impurity-penetrated

Hydrogen concentration versus depth obtained by the nuclear reaction technique in reactive-ion etching for overetching times of 0 (black), 1 (blue) and 10 minutes (yellow) and in buffered hydrogen fluoride etching (red); vertical lines indicate the uncertainty in plotting. The H surface concentration is the same in the Si specimens overetched for 1 and 10 minutes due to similar carbon and fluorine residue thicknesses, while the H concentration deeper in the silicon bulk is greater in the specimen overetched for 10 minutes.



near-surface region and any impurities and defects residing at greater depths. While it is probably impossible to develop one processing step that would achieve all three objectives simultaneously and efficiently, several successful methods that can provide device-quality silicon surfaces have been designed. The efficacy of these methods has been tested by electrical-device measurements and by the same experimental tools that were used to establish the nature of modifications caused by reactive-ion etching in the region near the silicon surface.

One of the post-etching treatments consists of following the reactive-ion etching process with an oxygen discharge. The reactive oxygen in the discharge removes the carbon-fluorine residue layer through the formation of volatile CO , CO_2 , CF_4 and so forth. Reactions between oxygen and disordered silicon atoms located within the first approximately 30 Å of the crystal create SiO_2 . This thin SiO_2 layer is removed by a wet-cleaning step prior to metallization.

A second method consists of annealing reactive-ion-etched silicon specimens at 400 °C for 30 minutes in dry oxygen. Again, oxidation of the carbon-fluorine film creates volatile products, and the reaction of oxygen with the heavily damaged silicon layer results in the formation of SiO_2 . In this case the moderate annealing temperature, which is high enough to cause hydrogen evolution from the substrates, is thought to be beneficial.

Reactive-ion etching as currently practiced suffers from a low ionization efficiency of roughly 10^{-4} , which is due

to loss of secondary electrons to the vacuum-chamber walls. The low ionization efficiency and a working pressure near 0.01 torr limit the obtainable etch rates of electronic materials to about 0.1 micron/min. The etch-rate requirements of future semiconductor processing are at least 1 micron/min without loss of directionality. Increasing the rate of reactive-ion etching requires an increase in the concentration of reactive intermediates—for example, by increasing the electron impact reaction rates. To accomplish this one can use either a magnetron or a hollow-cathode discharge. In magnetron etching crossed electric and magnetic fields trap secondary electrons in cycloidal trajectories close to the wafer and produce an intense plasma. In hollow-cathode etching a cavity inside the negatively charged cathode traps electrons, which then oscillate between the inner electrode surfaces until a gas-phase collision occurs. The plasma ionization efficiency can be up to 50 times greater than in reactive-ion etching, and a nearly identical enhancement in etch rates has been measured. These etching techniques also show promise of reducing radiation damage because the accelerating voltages are lower.

As in the case of "simple" reactive-ion etching, the development of these new technologies is slow and consists primarily of a trial-and-error approach. A fundamental understanding of glow-discharge gas-phase phenomena and of plasma-surface interactions will improve the control of reactive-ion etching and aid in the rapid development of the processes used to transfer patterns for microelectronics.

I would like to acknowledge the important contributions of my colleagues, especially G. J. Coyle, Y. H. Lee, G. A. Northrop, R. M. Tromp and J. C. Tsang.

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