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Contract N00014-85-K-0474

Technical Report No. 10

REACTIVE ION ETCHING OF POLYMER FILMS

by

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Accepted for publication in
"International Polymer Processing"

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MAY 12, 1989

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The need for nanometer-sized features in integrated circuits calls for the use of dry etching techniques using glow discharge plasmas. The reactive ion etching, RIE, mode in which there is a large difference in potential between the gas phase and the solid surface yields particularly desirable, straight-walled etched structures. The design of processes and materials for RIE requires a knowledge of the effects of operating...
variables on various parameters. In the present work, the parameter emphasized is the etch rate. A novel aspect of the apparatus used incorporates a laser interferometer for in situ measurements of etch rate.

Some observations on operating variables are:
1. Chamber pressure is more critical when a fluoride-oxygen plasma is used than when oxygen alone is used. This is due to polymer deposition that occurs with the former along with etching.
2. The etch rate in the oxygen/RIE mode is almost the arithmetic sum of the oxygen/plasma mode together with the nitrogen/RIE mode except at low incident power levels where etch rate with oxygen/RIE is much greater than the sum of the other two.
3. Aromatic polymers etch more slowly than aliphatic polymers.
4. The oxygen/RIE rate of poly(vinyl chloride), PVC, decreases on addition of a compatible organotin compound. A 1:1 mixture of PVC with a tin compound etches at 1/10 the rate of PVC alone.
REACTIVE ION ETCHING OF POLYMER FILMS

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Introduction

The need for smaller features in integrated circuits is making increasing demands on the materials and processes involved. The minimum dimension of lines and spaces for the 1 Mb DRAM chips now in production is less than one μm. Indeed, some gate widths of 0.25 μm have been commercialized by combining optical lithography with special etching techniques [1]. The usual features on a chip surface include transistors and other devices as well as the connecting wires. Further miniaturization is needed not only to pack more devices on a chip surface, but also to make the connecting wires between devices short so as to keep up the speed of operation. All of these features are put in place by a succession of as many as a hundred processing steps. The pattern transfer to the surface of a silicon wafer is accomplished by creating a stencil or mask of polymer through which a dopant, a metal, or some other material can be selectively passed. As part of the surface preparation, or even in the creation of the stencil in the first place, the polymer may be subjected to a reactive plasma.

The polymer layer is typically about one μm thick and is applied from solution. The pattern is created by controlled radiation through a mask (in the case of UV or x-rays) or by direct-write techniques (in the case of the electron beam). A change in solubility on radiation allows the stencil to be formed by removing a portion with a solvent wash. The polymers used in this process of "microlithography" have been reviewed recently in several papers [2-4].
Once the polymer stencil is in place, it may be necessary to remove some silicon (Si) or silicon oxide (SiO₂). A fluorocarbon-based plasma can be used to etch the surface of the wafer, removing volatile SiF₄ from those areas unprotected by polymer. Thus, the etch rate of organic polymer films compared to the etch rate of SiO₂ in a plasma with CF₄ + 8% O₂ is one standard measure for comparison. The oxygen is added to control redeposition of fluorinated polymers on the surface by scavenging prepolymer moieties (CF₂, C₂F₄, etc.) in the gas phase.

In another technique, etching by an oxygen plasma can be used to cut through an underlying “planarizing” layer of an organic polymer. This may be necessary in later pattern-transfer steps when previously-introduced devices have made the surface uneven. For some processes, a radiation-sensitive polymer is used as a thin top-layer above the inert planarizing layer. The pattern can be established by ordinary means in the top layer even with a limited depth of focus. The pattern then is carried through the planarizing layer using the top layer or an additional intermediate layer as a stencil to screen out the plasma selectively. Small features in thick layers with anisotropic etching can give rise to structures with aspect ratios greater than 10:1 [5]. In this case the top layer should act as a barrier to etching, while the lower layer should etch as rapidly as possible to access the silicon (or SiO₂) surface. Thus, a second standard of comparison is etch rate of an organic polymer film in an oxygen plasma compared to that for a reference material, often poly(methyl methacrylate), PMMA.

All of the etching described here can be done by a wet process using various acid or oxidizing aqueous solutions. The advantages of dry
processing over wet processing include a less severe waste disposal problem, a system more amenable to automation, and, most importantly, anisotropic etching. The wet process undercuts the stencil (Fig. 1a). Although many variations on the plasma exposure have been described and used [6], we will confine ourselves to parallel plate geometry. Plasma etching with the wafer on the grounded electrode gives some directional control (Fig. 1b). Control is enhanced when the wafer is on the powered electrode in a plasma chamber where the grounded area is much larger than the area of the powered electrode (RIE, Fig. 1c). This increases the potential difference between the wafer and the bulk of the plasma. Ions are directed more forcefully towards the horizontal wafer surface in RIE conditions with consequently improved vertical wall profiles than in the configuration of Fig. 1b. Careful process control is essential since the degree of anisotropy in the RIE configuration is quite sensitive to the processing parameters.

**Experimental Procedures**

a) The Reactive Ion Etching Apparatus

A schematic diagram of the parallel-plate, reactive-ion etcher is shown in Fig. 2. The chamber (31.5-cm inside diameter), lid, and powered electrode (22.5-cm diameter) are made of aluminum. The gap spacing between the powered electrode (cathode) and the inside surface of the lid is 5.0-cm. Chamber walls and lid are electrically grounded. The ratio of grounded area contacted by the plasma to the cathode area is approximately 11.

The cathode is powered by a radio frequency (rf) generator (PlasmaTherm Inc., model HFS 2000D) operating at 13.56 MHz. The signal is first passed through an impedance matching network (PlasmaTherm Inc.,
model AMN-2000) that "matches" the line impedance to the plasma impedance in order to maintain maximum power transfer to the plasma. The negative DC-bias voltage established on the cathode is measured by a digital voltmeter after passing the signal through a rf choke circuit.

Gases used for etching are controlled by one of two mass flow controllers (MKS Instr., Inc., model 1259B) with a maximum range of 100 std. cm$^3$/min of nitrogen. They enter the reactor through a radial flow nozzle centered in the lid and are pumped out of the apparatus through a 1.5-cm annulus between the chamber wall and the cathode. Two mechanical vacuum pumps and a 4-inch diffusion pump (Varian model M-4) are used.

Chamber pressure is controlled for a given flow by a throttling orifice plate (various sizes interchangeable) located between the chamber outlet and the high vacuum side of the pumping system. An ion gauge is used to measure the system's base pressure with no gas flow, typically 10 μTorr. During etching, a capacitance manometer (MKS model 227A) with a maximum range of 1 Torr is used. Foreline pressure is monitored with a thermocouple vacuum gauge.

A 2 mW laser mounted on the chamber lid is aimed at the wafer surface through a quartz window in the lid. The reflected light intensity, monitored with a photocell, gives an in situ measure of etch rate. The operation of this simple kind of laser interferometer has been described for dissolution experiments [7]. Nominal etch rates can be estimated also by using a stylus profilometer for initial film thickness and dividing that thickness by the total etching time required for film removal.

b) Materials used.

For evaluation of operating parameters, a commercial resist, poly(methyl methacrylate), PMMA, was used as received (KTI Chemicals,
M_w = 950k). Films were spun on 3-inch diameter silicon wafers at 1,500 rpm for 60 seconds. After baking 1 h at 160°C, PMIIA film thicknesses on the wafers were 1.0 to 1.1 μm.

Casting solutions containing organometallic compounds were prepared by dissolving an organotin mercaptide and poly(vinyl chloride), PVC, in chlorobenzene to make an 8% solids solution. The PVC was actually a terpolymer of vinyl chloride, 86%, vinyl acetate, 13%, and maleic anhydride, 1% (Union Carbide Corp., VMCH). After spinning at 1,500 rpm for 60 seconds, the films were baked for 1 h at 100°C.

Reactive gases included pre-purified oxygen and a commercial CF_4/8% O_2 mixture (Matheson Corp., LFE-100).

**Operating Parameters (Effect on RIE Rate of PMMA)**

a) Chamber Pressure

Etch rate in oxygen appears to be independent of chamber pressure above 10 mTorr (Fig. 3). When pressure is varied with a flow of CF_4 + 8% O_2, the rate goes through a maximum at about 30 mTorr total pressure (Fig. 4). As with oxygen, the data at two flow rates coincide, indicating that the reaction is not reactant limited. The decrease in rate at higher pressures is brought on by significant deposition of fluorine-containing polymers, which starts to control the rate by a surface inhibition mechanism [8]. The initial deposition rate is estimated to be about 500 nm/min when total pressure is 100 mTorr.

b) Power Density

Etch rate in various plasmas is linearly dependent on power density (Fig. 5). The nitrogen and argon lines reflect the rate at which PMMA is removed by purely physical sputtering when the sample is placed on the powered electrode (RIE mode). In this case, the plasma-to-powered
electrode bias voltage, $V_B$, ranges from 250 to 600 volts. The sputtering rate increases with incident power for two reasons. First, the ion flux ($N_2^+$ or $Ar^+$) is enhanced. Second, $V_B$ increases which results in higher average ion energies at the surface.

In the oxygen plasma mode, the wafer is on the grounded surface (chamber lid). The ion bombardment effects are reduced significantly since the plasma-to-ground potential is typically on the order of 10 to 20 volts [9]. Thus, the removal of polymer is largely due to chemical attack by reactive species (radicals). The etch rate in this configuration increases with power due to an increase in the oxygen free-radical concentration.

The combined effects of chemical and physical etching are illustrated by oxygen in the RIE mode. The measured rate is two to three times that of either the chemical or physical rate alone. The algebraic sum of the two rates (oxygen/plasma mode and argon/RIE mode) tracks closely with the measured oxygen/RIE rate (Fig. 5). The implication is that the chemical and physical processes occur in parallel. However, a synergism is seen at the lower power densities (< 0.3 W/cm$^2$) where the oxygen/RIE rate is greater than the sum of the other two. Enhanced desorption of reaction products and/or increased energy from ion bombardment might cause the synergism. In fact, typical RIE processing is carried out at power densities less than 0.3 W/cm$^2$ to minimize ion and radiation damage.

c) Sample Surface Area

At a fixed flow rate and chamber pressure, the etching rate decreases as reactant is depleted when the surface area to be etched is increased (Fig. 6). This effect is not as great on a percentage basis for pure oxygen which is run at a much higher partial pressure. The "loading" effect, as this is known, has to be taken into account even when the same
apparatus is used to compare materials. It is obviously hazardous to compare results from one laboratory to another without reference to standard materials and geometries.

**Structure Dependence of Etch Rates**

a) Aromatic Content

Ideally, a single radiation-sensitive organic polymer can serve as both the stencil-former and the etch resistor. Unfortunately, the generalization has been made that changes in composition which enhance chain scission (to change solubility) usually reduce etch resistance. For example, poly(butene-2-sulfone), PBS, requires only $1/10$ the electron-beam radiation dose to form a usable stencil compared to PMMA, but the etching rate of PBS usually is about 30 to 100 times that of PMMA [4]. Aromatic groups incorporated into the polymer increase etch resistance but decrease radiation sensitivity. For example, Anderson [10] found that the etch rate is almost a linear function of phenyl content for a series of chain-scissioning polymers (Fig. 7). It seems not to matter whether the phenyl group is directly attached to the chain as in the alphamethylstyrene polymer, or removed by several atoms as in the case of the benzyl ester of an itaconic acid copolymer with methyl methacrylate. Other studies of plasma-resistance of various organic polymer structures have reached similar conclusions [11-15].

b) Organometallic Compositions

Inorganic materials often form resistant oxides in oxygen plasmas which make them candidates for incorporation into radiation sensitive top layers in multilayer resist schemes. Shaw and Hatzakis [16] showed early on that a top layer of ordinary silicone rubber can be crosslinked by an electron beam through the vinyl unsaturation and developed into a stencil by dissolving the unreacted rubber. On exposure to an oxygen plasma the
crosslinked silicone is converted to SiO₂. The oxide stencil allows the oxygen plasma to cut selectively through a bottom planarizing layer of PMMA.

Although many metals could conceivably be incorporated into resists via organic derivatives, there are limits due to electrical properties, compatibility, and availability [17-19]. Several groups have explored the use of tin compounds in contributing oxygen etch resistance [20-22]. The tin can be incorporated by copolymerization of an alkyltin monomer with another monomer [23].

We have found that the etching rate of poly(vinyl chloride), PVC, can be changed by simple addition of a commercial organotin mercaptide (MAF-OTBu, from Argus Div., Witco Corp.). The tin compound in this case has been designed specifically to be compatible with this polymer since its major use is as a stabilizer against the thermal decomposition of PVC. The initial etch rate in an oxygen plasma decreases linearly with increasing tin content (Fig. 8). Although the PVC-organotin system is only somewhat sensitive to electron-beam crosslinking, the sensitivity can be increased by other additives which do not change the etch rate substantially.

c) Plasticization

The effect of changing the physical state of a polymer from a glass to a rubber on etching rate was explored. Since the powered electrode and the wafer on it are water-cooled, the unplasticized PVC is well below its Tg during etching. The interferometer trace of the etching of PVC (Fig. 9) indicates that the etching proceeds at a uniform rate. Each sinusoidal oscillation corresponds to a change in thickness of about 0.2 µm for this polymer and geometry. Also, no noticeable changes in amplitude occur,
meaning that film composition and surface smoothness are not changing significantly during etching. No acceleration due to autocatalyzed dehydrochlorination or deceleration due to oxidation-resistant char products is observed.

When a 1:1 mixture of PVC with a standard plasticizer (di-2-ethylhexyl phthalate, DOP) is etched (Fig. 10), the film is well above its T_g (about -50°C). And yet, the amplitude of the interferometer trace does not change with etching and the rate changes only slightly. The constant amplitude indicates that the film does not change in composition. The first three oscillations in the trace (once again about 0.2µm per cycle) yield a rate about 20% faster than the last four oscillations. However, the rate for the last four cycles is almost the same as that for unplasticized PVC. One concludes that the increase in etch rate with wafer temperature seen by some workers [24] cannot be attributed solely to the etch temperature approaching or exceeding T_g.

**Conclusions**

Etch resistance in radiation-sensitive films is difficult to achieve with purely organic polymers. Incorporation of phenyl rings offers only a limited increase in resistance while sacrificing a great deal of sensitivity. Polymer systems containing silicon, tin, and, perhaps, barium and some other metals, do exhibit oxygen etch resistance. The heavier atoms also have been shown to enhance sensitivity to x-rays and electrons.

A possible extension of the use of organometallic materials is the process of dry development. The elimination of solvents in pattern transfer would offer advantages in waste disposal, avoidance of contamination sources, and automation. Dry development demands a substantially different etch rate between exposed and unexposed resist.
Acknowledgments

This work was supported in part of the Office of Naval Research.
Work was performed in cooperation with the National Nanofabrication
Facility which is partially supported by the National Science Foundation.
The rf generator was a gift to Cornell University from the IBM Corporation.

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1. Etching a film through a resist mask, a) Wet process, b) Plasma etching, and c) Reactive ion etching (RIE). Wet process, a, often gives undercut profiles in the film being etched where dry processes, b and c, give more vertical walls.

(a) Wet Process

(b) Plasma Etching

(c) RIE
FIGURE 2: REACTIVE-ION ETCHING APPARATUS
3. Reactive ion etch rate for PMMA in oxygen with power density = 0.25 W/cm$^2$, and sample area = 1.5 cm$^2$. Solid symbols for 7.5 SCCM and hollow symbols for 20 SCCM (standard cm$^3$/minute).
4. Reactive ion etch rate for PMMA in CF$_4$/8% O$_2$ with power density = 0.25 W/cm$^2$, and sample area = 1.5 cm$^2$. Solid symbols for 7.5 SCCM and hollow symbols for 20 SCCM (standard cm$^3$/minute).
5. Reactive ion etch rate for PMMA versus incident power density under various conditions. a) Oxygen in RIE mode, b) Oxygen in plasma mode, c) Argon in RIE mode, d) Nitrogen in RIE mode. Chamber pressure 35 mTorr except circles at 12 mTorr. Flow rate was 20 SCCM in all cases.
6. The loading effect showing a decrease in rate with increasing surface area. a) Oxygen at 35 mTorr and b) CF$_4$/8% O$_2$ at 13 mTorr. Power = 0.25 W/cm$^2$ and Flow = 20 SCCM in both cases.
7. Decrease in RIE rate with increasing aromatic content of organic polymers and copolymers in CF$_4$/8% O$_2$. △, PMMA; ○, alphamethylstyrene, and derivatives of itaconic anhydride copolymers with 6, benzyl alcohol, O, aniline, and ●, p-chloroaniline.

![Graph showing relative RIE rate vs. mol% comonomer](image)
8. Decrease in initial oxygen/RIE rate with increasing tin content in a vinyl chloride terpolymer.
9. Laser interferometer trace for oxygen/RIE of unplasticized vinyl chloride terpolymer (original film thickness about 1 µm). The small step after the dissolution is complete occurs when the glow discharge is extinguished.
10. Laser interferometer trace for oxygen/RIE of vinyl chloride terpolymer plasticized with an equal weight of di(2-ethylhexyl)phthalate (original film thickness about 1.6 μm).
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