REACTIVE ION ETCHING IN NF_3 AT LOW TEMPERATURE : A STUDY ON Si AND SiO_2

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ABSTRACT

Reactive ion etching of Si and SiO_2 in nitrogen trifluoride (NF_3) is studied at temperatures between +20 and −140 °C. Low sample temperatures promote the smoothness of the etched Si surfaces and the anisotropy of the etching process. We discuss the influence of temperature and r.f. power on the etch rate and sample morphology.

1. INTRODUCTION

High etching rate combined with high selectivity and high anisotropy are required for reactive ion etching (RIE)/1,2/. Two mechanisms have been proposed to explain the anisotropy of the etching process/1/. One of these mechanisms proceeds by ion bombardment perpendicular to the surface, enhancing recombinant desorption and material gasification on horizontal surfaces. Consequently, material removal occurs most rapidly in the vertical direction. In the other mechanism, diverse radicals in the plasma are assumed to recombine, deposit on the sidewalls, and inhibit the etching there. In real RIE systems, the etching processes involve both mechanisms combined. The disadvantages of these mechanisms are on the one hand the high ion energy needed to break Si-Si bonds. The highly energetic ions produce unwanted damage of the crystal lattice. On the other hand any recombination products which contain organic substances contaminate the etched surfaces/3,4/.

Most recently considerable improvement was achieved by low-temperature RIE of Si using SF_6 plasma/5/. The reactions that take place on the bottom surface of an exposed area are both ion-bombardment assisted and thermochemical reactions. The reactions which occur on the side walls and cause undercutting are pure chemical reactions of neutral radicals with Si. The undercutting can therefore be suppressed by sample cooling.

We have studied RIE of Si and SiO_2 in NF_3. The advantages of using NF_3 are cleanliness of the etched surface, especially elimination of carbon based deposits, and higher etch rates compared to those obtained in a CF_4 plasma. Most recently we reported RIE of Si in NF_3 at low temperature /6/. Cross sectional transmission electron microscopy gave evidence that no crystallographic damage was created in the bulk of the Si crystal. Low sample temperatures clearly promoted smoothness of the etched surfaces and anisotropy of the etching process.

In this paper we describe RIE of Si and SiO_2 in an NF_3 plasma at low temperatures. The etch rates are determined as a function of r.f. power and temperature, and the etching mechanisms are discussed.

2. EXPERIMENTAL

The apparatus used for RIE was described earlier/6/. The cathode on which samples were placed was cooled by water or liquid nitrogen. The cathode temperature was controlled by the liquid nitrogen supply. The accuracy of the sample temperature was ± 5 °C.

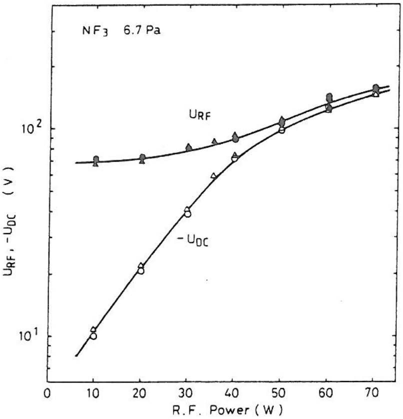
Three types of Si samples were used: (111), n-type P-doped, 1300 Ω cm; (111), n-type P-doped, 0.005 Ω cm; and (100), n-type P-doped, 5 Ω cm. We also used wet thermally grown SiO_2. The specimens were prepared as described earlier/6/. Prior to RIE, the reaction chamber was evacuated to a pressure of 10^{-5} Pa by a turbo-molecular pump. Then electronic grade NF_3 was introduced into the reaction chamber. As the chamber pressure arrived at 13.3 Pa, the supply of liquid nitrogen to cool the electrode was started. After the electrode temperature had reached the desired value, the chamber was evacuated again, and NF_3 was immediately introduced at a flow rate of 15 standard cubic centimeters per minute. This procedure provided for good thermal contact between the sample and the electrode. The chamber pressure, measured with a capacitance manometer, was fixed at 6.7 Pa during RIE. The r.f. power with a frequency of 13.56 MHz was supplied from a vacuum tube controlled generator.

The etched depths in partially covered samples were measured with a mechanical stylus profilometer.

3. EXPERIMENTAL RESULTS

The etch depth appeared to be directly proportional to the etching time with no induction period. This result suggests that the sample temperature remains constant during etching and that surface contamination does not occur. A sample temperature rise in RIE is caused primarily by ion bombardment/7/. It is estimated that a possible temperature rise which may occur should be within the temperature accuracy in our experiments in which the self bias potentials range between 10 and 160 V. The self bias potentials are shown in Fig.1 as a function of r.f. power, together with the r.f. peak voltage. The etch rate is therefore simply given by the etch depth divided by the etching time.

The etch rates for Si (111), n-type P-doped, 1300 Ω cm and thermally grown SiO_2 are shown in Fig.2 as a function of r.f. power for two different temperatures. The etch rates increase with increasing r.f. power for both Si and SiO_2. The main contribution to the increase in etch rates may be attributed to the increase of ion flux to the sample surface with increasing



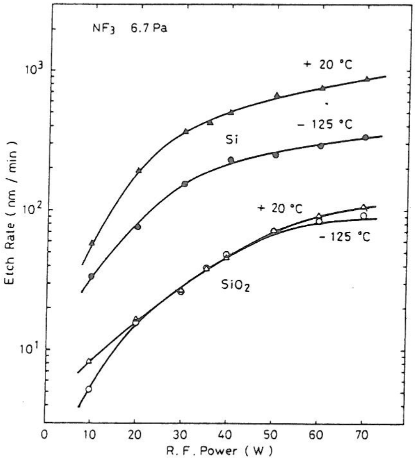


Fig.1 Self bias potential, $-U_{DC}$, and r.f. peak voltage, U_{RF}, as a function of r.f. power.

Fig.2 Etch rate for Si (111) and thermally grown SiO_2 as a function of r.f. power.

self bias. The basic etching mechanism is not expected to change with r.f. power in the ranges given in Figs.1 and 2. Some particular reaction steps, which affect the overall etch rate for Si may, however, take place between +20 and -140 °C. The corresponding mechanisms will be discussed later.

The etch rates as a function of reciprocal temperature for Si (111), n-type P-doped, 1300 Ω cm are shown in Fig.3. Between +20 and -40 °C, the etch rates decrease rapidly with decreasing temperature. Below -70 °C the etch rates follow an Arrhenius expression of the form:

$$\text{Etch rate} = A \exp (-E_a / kT).$$

The activation energy E_a is evaluated from a least-square fit. It has a constant value of 8 meV (0.2 kcal/mol). The activation energy is found to be independent of the r.f. power i.e. the self bias potential, the orientation (111) or (100), and the conductivity of the Si.

The etch rates for SiO_2 do not depend on temperature as the results in Fig.4 show.

4. DISCUSSION

At first we consider the etching mechanism of Si. Temperature dependencies of the reaction rates between Si and NF_3 have not yet been reported. It is supposed however, that the active species which mainly contribute to the etching of Si in NF_3 plasma are the neutral F atom and the F_2 molecule/8,9/. The activation energies of the etching reaction of Si (100) with F

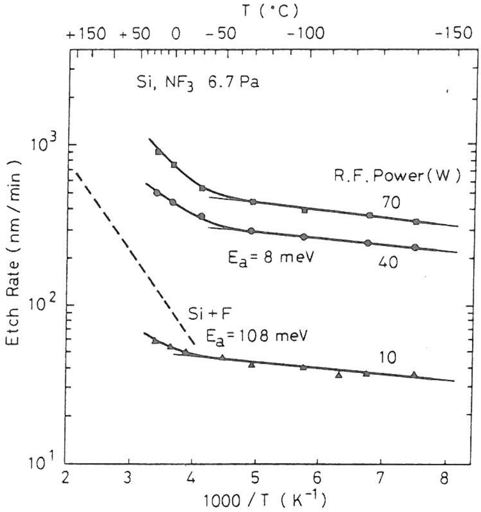


Fig.3 Etch rates for Si (111) as a function of reciprocal temperature. The dotted line shows the etch rate due to purely chemical reactions with F atoms/10/.

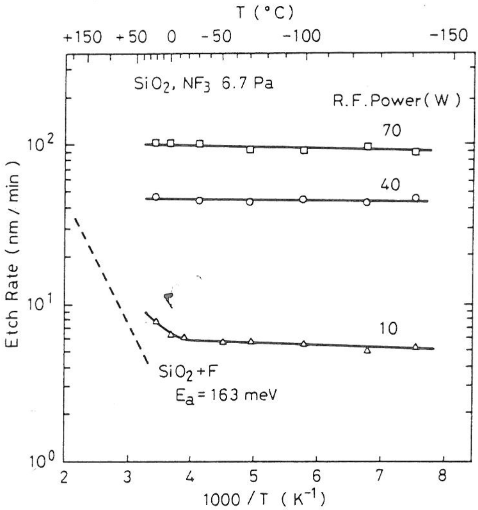


Fig.4 Etch rates for SiO_2 as a function of reciprocal temperature. The dotted line shows the chemical etch rate by F atoms/10/.

atoms and with F_2 molecules without plasma are reported to be 108 meV in the temperature range 223-403 K and 392-400 meV in the temperature range 337-473 K, respectively /10-13/. The results for the reaction between Si and F atoms are corrected for the pressure used in the present study and are shown in Fig.2 as a dotted line. The etch rates of Si by F_2 molecules are more than a factor of three smaller than those by F atoms at

25 °C. Presently we can not discuss absolute etch rates due to the undetermined gaseous composition of the NF_3 plasma. The slope of the curves on the high temperature side is similar to the slope of the dotted line. This suggests that the main reaction contributing to etching is of chemical nature and occurs between solid Si and the F atoms produced in the NF_3 plasma. The rate of this chemical reaction decreases rapidly as the temperature decreases due to the relatively high activation energy.

On the other hand, the very low activation energy which was observed in the temperature range below -70 °C may be attributed to an ion-bombardment induced reaction. The contribution from ion bombardment is therefore assumed to predominate at low temperature.

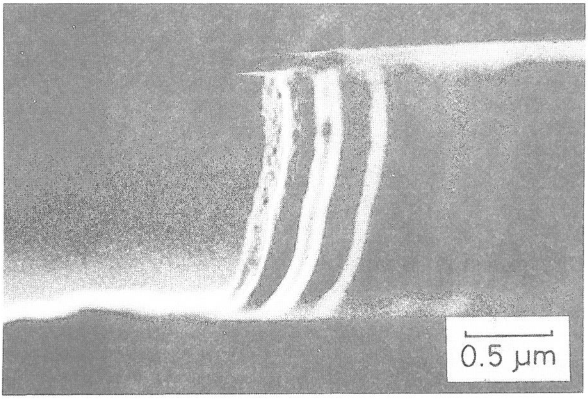


Fig.5 Cross section of a step etched in Si close to the edge of the SiO_2 mask. SEM-Photograph. Etching parameters : r.f. power 60 W, etching time 4 min, and temperature -125 °C.

The ratio by which chemical reactions and ion bombardment induced reactions contribute to the total etch rate can be deduced from the etched step profiles. The side etch caused by ions back scattered from the surface is extremely small because of the relatively small self bias. We assume, therefore that in a first approximation sidewall etching is caused by pure chemical reactions and that vertical etching is caused by combined chemical and ion bombardment induced reactions. Figure 5 shows the profile of a step in Si(100) etched at -125 °C. The sample was masked with SiO_2 on the right hand side of the figure. The anisotropy, defined as the ratio (side etch width) /(etch depth) is 0.08 in this case. We conclude from this observation that about 8 % of the total vertical etching is achieved by a chemical reaction. The removal of the remaining portion that is about 92 % of the etched material, is facilitated by ion bombardment induced reactions. A precise determination of the anisotropy in the etching processes is required for further quantitative discussion.

The improvement in smoothness of the etched surfaces by cooling the samples is also explained by the influence of ion bombardment. In the chemical etching process at higher temperature the desorption of SiF_x (x = 2 or 4) may limit the total reaction rate. A slightly nonuniform desorption may give rough etched surfaces. Ion bombardment is known to enhance the surface migration of adsorbed species, for example F atoms, and hence effects a uniform desorption of SiF_x. Ion bombardment yields smoother surfaces at lower temperature.

In contrast, the temperature independence of the SiO_2 etch rate suggests that SiO_2 is etched only when it is exposed to ion bombardment.

5. CONCLUSION

Reactive ion etching of Si in NF_3 below -70 °C obeys an Arrhenius temperature dependence. The activation energy found is only 8 meV and suggests that the main contribution to the overall etch rate comes from an ion bombardment induced reaction. Ion bombardment promotes the anisotropy of the etching process and the smoothness of etched surfaces. Etch rates of SiO_2 are temperature independent.

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