EXPERIMENTAL EVIDENCE FOR THE ABSENCE OF
LOCAL THERMODYNAMIC EQUILIBRIUM
IN CHEMICAL SPATTERING

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ABSTRACT

A crucial test of the applicability of the model of local thermodynamic equilibrium (LTE) in chemical sputtering is provided by studying kinetic energy distributions of products of the sputtering of silicon by Ar$^+$ ions under simultaneous exposure to Cl$_2$ or SF$_6$ fluxes. It appears that the LTE model does not hold. On the contrary, the measurements indicate that a physical sputtering model with a collision-cascade like behaviour explains the observations well.

1. INTRODUCTION

Synergistic effects, in which adsorption of chemically active species and simultaneous low-energy bombardment cooperate, are crucial in obtaining anisotropic etch profiles in plasma etching of very large scale integrated circuits. Essentially two mechanisms have been proposed to explain this synergism (1). The first is ion bombardment-enhanced chemical etching and the second chemically enhanced physical sputtering. The first mechanism will lead to a kinetic energy distribution of the products of the Maxwell-Boltzmann type with one common "temperature" for the various etch species. The second one will result, in principle, in various collision cascade-like distributions, one for each of the product species. It has recently been shown that Ar$^+$ ion bombardment of silicon surfaces simultaneously exposed to chemisorbing Cl$_2$ or physisorbing SF$_6$ yields a manifold of, partially molecular, etch products (2,3). Thus, these systems are ideally suited for testing the applicability of the above two mechanisms.

2. EXPERIMENTAL

The experimental setup used in this study, has been described in detail in previous papers (4,5). A schematic picture of the heart of the experiment is shown in Figure 1. A silicon target, the temperature of which can be varied between 20 and 1000 K can be bombarded with Ar$^+$ ions with a flux of about $5\times 10^{14}$ Ar$^+$ cm$^{-2}$ s$^{-1}$ in the energy range between 0.25 and 6 keV and at the same time sprayed with a beam of Cl$_2$ or SF$_6$ with fluxes in the range $10^{15}$-$10^{17}$ molecules cm$^{-2}$s$^{-1}$ in an UHV chamber with a background pressure of between 10$^{-7}$ and 10$^{-5}$ Torr during ex-
periments. The kinetic energy distributions of the product species are derived from time-of-flight studies using electronic modulation of the Ar ion beam by a hardware generated pseudorandom binary sequence. Using the correlation technique only these signals are accepted which stem directly from neutrals ejected during Ar ion bombardment.

3. RESULTS AND DISCUSSION

When silicon is exposed to a flux of Cl molecules at temperatures of about 300 K it is chemisorbed on the silicon surface where Si-Cl bonds are formed (6). No etching occurs at these temperatures (2). When silicon is bombarded with low-energy Ar ions physical sputtering is observed in which the main products are atomic Si and Ar. When silicon is exposed to a flux of Cl molecules and simultaneously to low-energy Ar ion bombardment the etch rate is enhanced a few times as compared with physical sputtering (7). In the latter case the main products are molecular SiCl2 and SiCl and atomic Si, Cl and Ar. The contribution of molecular and atomic products are of comparable order of magnitude. If ion bombardment-enhanced chemical etching is the main mechanism for material removal, the kinetic energy distributions of these five products should be Maxwell-Boltzmann-like and should correspond to the same temperature. Figure 2 shows these distributions in the form of normalized product flux versus t/m = c/E, where t = time, m = mass, c = constant and E = kinetic energy. The figure unequivocally indicates that the kinetic energy distributions of all five products are different and vary over a large energy range. In addition it has been shown that the form of these distributions is collision-cascade-like and not Maxwell-Boltzmann. The conclusion to be drawn from these results is that for this system chemically enhanced sputtering dominates.

When silicon is exposed to SF6 gas fluxes at temperatures above 100 K, SF6 does not condense on or react with the silicon. Below 100 K, SF6 condenses to a molecular solid, and forms a film on top of the silicon (3,8). Heating removes this film completely. Simultaneous exposure of silicon to an SF6 flux and to Ar ion bombardment yields purely physical sputtering at target temperatures above 100 K. Below 100 K a wealth of products, both molecular and atomic is observed. These products can be summarized in the following six classes.

a. the SiFx-group, with x = 1-4
b. the SFx-group, with x = 1-6
c. the SiSx-group, with x = 1,2
d. the SiF2x-group, with x = 1,2
e. the molecules F2 and S2
f. the atomic products F, Si, S, Ar

The relative proportion of the above products depends on target temperature and SF6 flux. Figure 3 shows kinetic energy distributions for three of the numerous products. Again the distributions are different for different products and they are collision-cascade like, which shows that also in this system chemically enhanced physical sputtering seems to dominate.

In conclusion the model of local thermodynamic equilibrium does not hold for the above two systems, but a physical collision-cascade sputtering model is applicable.
REFERENCES


Figure 1. Schematic, not to scale, view of the experimental equipment. 1. Ar+ ion source; 2. Wien filter; 3. electronic beam modulator; 4. decelerator; 5. oven or cooling machine annex target holder; 6. Silicon target; Cl2 or SF6 gas inlet; 8. diaphragm; 9. ionizer; 10. quadrupole mass spectrometer; 11. magnetic electron multiplier.
Figure 2. TOF spectra for Si, Cl, Ar, SiCl and SiCl₂ obtained by bombarding Si, at 300 K with 3 keV Ar⁺ ions (flux $5\times10^{14}$/cm² sec) under simultaneous exposure to a Cl₂ gas flux of about $5\times10^{16}$/cm² sec.

Figure 3. TOF spectra for SiF₂, SF₅ and S obtained by bombarding Si, at 50 K with 3 keV Ar⁺ ions (flux $10^{15}$/cm² sec) under simultaneous exposure to an SF₆ gas flux of about $7\times10^{16}$/cm² sec.