EPR Investigation of Plasma-Chemical Resist Etching in O₂ and O₂/CF₄ Discharges

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During the etching of AZ 1350 photoresist in O₂ and O₂/CF₄ discharges, ground-state concentrations of atoms (O, F, and H), and small radicals (OH, HO₂, RO₂) were measured in the discharge afterglow by EPR spectroscopy. In the case of CF₄/O₂ discharges, the dependence of O and F atom concentrations on the etch time reflects both surface oxidation and fluorination reactions in accordance with existing etch models. In the case of high-rate resist etching in pure O₂ discharges, high concentrations of product radicals (H, OH and HO₂) were detected and compared with resist-free O₂/HeO discharges. Kinetic modeling of the afterglow reactions reveals that the mean lifetime and, accordingly, the diffusion length of the etchant species O(3P) is drastically reduced in rapid reactions with OH and HO₂. The results are used to simulate both etch homogeneity and the loading effect in a simple etch model.

KEY WORDS: Resist etching; radical concentration; modeling.

1. INTRODUCTION

Resist stripping in O₂ discharges is one of the oldest plasma-chemical techniques used in the semiconductor industry.¹ In this process, the discharge is essentially a source of oxygen atoms which attack the organic polymer and convert it in an isotropic etch reaction into the final products H₂O, CO, and CO₂.²

As a result of the growing importance of both isotropic and anisotropic etching of new materials for multilevel resist techniques, the interest in processes taking place in O₂ and O₂/CF₄ discharges has considerably increased in the past five years.

The isotropic resist removal in the O₂ discharge afterglow (i.e., without bombardment) proceeds in a thermally activated reaction of O(3P) atoms
with an activation energy in the range 0.45–0.5 eV and requires, therefore, sample temperatures above 100°C. In order to remove organic resist layers at lower temperatures, active surface centers, which are able to react easily with O(3P) and O₂ molecules, can be created by fluorine atoms (e.g., from O₂/CF₄ discharges) and/or by ion bombardment.

The subject of this work is an investigation of the photoresist removal in O₂, O₂/Ar, and O₂/CF₄ discharges in parallel-plate reactors with distinct ion bombardment. Any useful modeling of the etch reactions requires knowledge of the concentrations of at least the most important species in the plasma. Radical concentrations can easily be determined by gas-phase EPR spectroscopy, which were first used by Cook and Benson in a study of resist removal in the O₂ afterglow. However, gas-phase EPR spectroscopy is unable to measure radical concentrations in the active zone of the plasma. Therefore, recombination losses and secondary reactions have to be taken into account in order to extrapolate afterglow concentrations to plasma-radical concentrations.

A simple and applicable complement of the EPR method is the in-situ determination of relative atomic concentrations from intensities of suitable plasma emission lines, where excitation conditions can be eliminated in part by the use of an actinometer emission (e.g., Ar with a molar fraction X_{Ar} ≤ 0.05). As has been demonstrated, however, uncritical application of this method can lead to totally wrong results, when the basic presuppositions of actinometry are not fulfilled, especially when the emission does not result from direct excitation of the ground-state radical. Before this method is utilized in a specific system, it is, therefore, desirable to directly compare concentrations predicted from optical emission intensities to the actual ground-state concentrations. Additionally, from such a comparison, for example, with gas-phase EPR, optical emission actinometry can be calibrated in order to predict absolute atomic concentrations.

Based on EPR measurements of concentrations and mean lifetimes of radicals like O(3P), OH(\text{2Π}_{3/2}), H(\text{2S}_{1/2}), and HO₂ in the afterglow of O₂ discharges during plasma etching of AZ 1350 photoresist, the simple model of the O(3P) distribution in the parallel-plate reactor presented in this work quantitatively describes the loading effect and the homogeneity of the etch reaction.

### 2. EXPERIMENT

The reactor types used are shown schematically in Fig. 1. Reactor (a) is a tube reactor (fused silica, inner diameter 15 mm). The discharge is excited via two external annular electrodes (spacing 5 cm, generator...