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THE ROLE OF SURFACE FLUORINATION IN POLYMER ETCHING BY CF_4/O_2 PLASMAS

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ABSTRACT

A kinetic mechanism that explicitly considers the competition between surface fluorination and etching of polymers in CF_4/O_2 plasmas is proposed. The role of CF_x (x = 1, 2, 3) radicals is also considered.

1. INTRODUCTION

Currently there is considerable interest in the plasma etching of polymers like epoxy, polyimide, etc., and photoresists. The chemistry of the etching process needs to be better understood because of the central role played by these materials in first and second level packaging of electronic devices. Several studies on the plasma etching of polymers have been published. Battey [1] studied photoresist stripping and Goldstein and Kalk [2] studied the reactive ion etching, in pure O_2, of thick (>100 μm) epoxy, polyester, and photoresist. Turban and Rapeaux [3] measured the etch rates of epoxy and Kapton in O_2/CF_4 and O_2/SF_6 mixtures, while Moss, et al., Pederson, and Taylor and Wolf correlated the polymer structure with etching rates [4,5,6]. More recently, Egitto, et al.[1] reported results on polyimide etching along with XPS measurements of the surface layers after the completion of the etching process in CF_4/O_2 plasmas.

Competition between fluorination of the polymer surface and etching seems to play a key role in the etching kinetics. The importance of fluorination, from a kinetic point of view, follows from the observation of very rapid (approximately 12 seconds to 2 minutes) formation of CF_x groups (x = 1, 2, 3) on the polymer surface in the presence of oxygen deficient plasmas [8-11]. Dedinas, et al.[2] reported, based on ESCA analysis, that 72% of the C atoms on the surface of novolak are attached to one, two or three fluorine atoms after only a 12-second exposure to a 96% CF_4/4% O_2 plasma. After 30 seconds, this fraction of C atoms increases further to 87%. Correspondingly, the F/C atoms ratio reaches 1.37 after 12 seconds and then stabilizes around 1.66-1.68 after 30 seconds. Similarly, rapid

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[1] F. D. Egitto, et al., J. Vac. Sci. Tech. B, May/June (1985), in press.
[2] J. Dedinas, et al., Proceedings of the Second International Conf. Plasma Chem. and Tech., H. V. Boenig (ed.), to be published.

fluorination has also been observed by Anand, et al. [7], Yagi, et al. [8], and by Cantos, et al. [9], among others.

Fluorinated polymers, of course, can only be etched very slowly. However, the presence of oxygen in the plasma from the beginning will provide an alternate reaction channel for the polymer molecules on the surface. Under these conditions, with 30% or more CF_4 in the feed gas, surface fluorination occurs simultaneously and in competition with etching. Rembetski, et al.[1] have suggested that this competition may explain the reduction in the etch rate of epoxy polymers observed by them in a configuration in which the contribution of ion bombardment to the surface reaction should be minimal. This allowed them to determine the steady state value of the fraction of the polymer surface rendered inactive due to fluorination. A preliminary kinetic model was proposed in a companion paper[2]. Using a straightforward steady state analysis, they proposed a three parameter etch rate expression that provided a rather satisfactory representation of the etch rate dependence on the composition of the CF_4/O_2 feed gas in the range of 20% to 60% CF_4.

2. EXTENDED MODEL

Here we consider an extended kinetic model, continuing the earlier work by Lu, et al.[2] In that model, once the free radical production is initiated by hydrogen atom abstraction from the polymer chain, there is a competition between fluorination of the hydrocarbon radicals by only fluorine atoms and conversion of the hydrocarbon radicals to products by atomic and molecular oxygen. The degradation of the hydrocarbon radicals into volatile products by atomic and molecular oxygen is a well known process and occurs in several steps in which the alkoxy and alkylperoxy radicals are generated as intermediate species [10]. At the same time, there is an abundance of CF, CF_2 and CF_3 radicals in the plasma volume. Numerical simulation studies by Kushner [11] and by Srinivasan, et al.[3] indicate that the mole fraction of these radicals in the gas phase may reach relatively high values. Thus it is imperative to include the reactions in which these CF_x ($x = 1, 2, 3$) radicals participate. We suggest that the extremely rapid increase in the observed F/C atom ratio on the polymer surface in oxygen deficient plasmas is indeed a consequence of reactions between the hydrocarbon and F atoms and CF_x radicals. In oxygen-containing plasmas alkoxy radicals are also available for reaction with CF_x radicals.

Based on all these considerations, we propose the following extended kinetic model for polymer etching in CF_4/O_2 plasmas.

$$RH + F \longrightarrow R^* + HF \qquad (i)$$

$$RH + O, {}^*OH \longrightarrow R^* + {}^*OH, H_2O \qquad (ii)$$

$$R^* + F \longrightarrow RF \qquad (iii)$$

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[1] J. F. Rembetski, S. V. Babu, N. H. Lu and J. G. Hoffarth, Proceedings of the Fifth Plasma Symposium Electrochemical Society (1985), in press, Rembetski and S. V. Babu, submitted to J. Electrochem. Soc.

[2] N. H. Lu, C. Nilsen, J. A. Welsh, S. V. Babu and J. F. Rembetski, ibid.

[3] Submitted to the 7th International Symposium on Plasma Chemistry for these proceedings.

$$R^* + O, O_2 \longrightarrow RO^* \qquad \text{(iv)}$$

$$RO^* \longrightarrow \text{Products} \qquad \text{(v)}$$

$$RO^* + {}^*CF_x \rightleftharpoons ROCF_x \qquad \text{(vi)}$$

$$R^* + {}^*CF_x \longrightarrow RCF_x \qquad \text{(vii)}$$

$$RF,\ ROCF_x,\ RCF_x + O, O_2 \longrightarrow \text{Products} \qquad \text{(viii)}$$

In addition, the effect of ions on the kinetics must also be considered. Ions can enhance the etch rate by accelerating product desorption, degradation of the fluorinated surface, and by facilitating product formation. Further, several reactions that contribute to the hydrocarbon radical generation by dissociative ionization or hydrogen ion abstraction are also possible.

Detailed and quantitative verification of this model is dependent on the availability of simultaneously measured O, F, and CF_x concentrations and etch rates. The reversibility of reaction (vi) is central to the mechanism and is necessary to explain some of our experimental observations. We will return to this point shortly. Some qualitative observations can be made more easily and will be discussed first. The competition between surface fluorination and etching is evident. Reactions (i) and (iii) or (vii) lead to fluorination of a single site on the polymer molecule. However, repeated fluorination at other sites either on the same monomer unit or on other monomer units in the polymer can, and indeed will, take place through these processes occurring over and over again. These reactions will dominate the kinetics in oxygen-deficient plasmas and can clearly lead to a rapid buildup of the F/C atomic ratio. (Addition of one CF_3 radical will produce a local F/C ratio of 3.) The rate of this buildup will be determined by the individual rate constants, which are related to the structure of the polymer, and may vary from polymer to polymer. The relative importance of the remaining reactions depends on the oxygen concentration in the plasma, which will also determine whether fluorination or etching will dominate.

It is relatively straightforward to derive an etch rate expression from the set of reactions presented above, assuming the steady state hypothesis holds for the reactive radicals and that the etch rate is proportional to the rate of product formation. We obtain

$$\text{Etch Rate} = \frac{k4\ [R^*]\ [O + O_2] + km6\ [ROCF_x]}{1 + (k6/k5)\ [{}^*CF_x]} + k8\ [RF{+}RCF_x{+}ROCF_x]\ [O{+}O_2]$$

Here k4 and k8 are effective rate constants associated with reactions (iv) and (viii) above. If we can consider that the concentration of F atoms and CF_x radicals are related, then it is possible to argue that this relation is somewhat analogous to the expression derived by Lu, et al.[1] The second term in this equation is not expected to contribute significantly to the

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[1] Lu, et al., Proceedings of the Fifth Plasma Symposium Electrochemical Society (1985), in press.

overall etch rate. Evaluation of the various rate constants in the above equation requires knowledge of the concentrations of O, O_2, $ROCF_x$, $*CF_x$, and R*, and some of these are not currently available. The hydrogen atom abstraction reactions are facile in comparison to the subsequent degradation of R* to volatile products. Hence it may be argued that during the etching process, the surface of the polymer essentially consists of a variety of radicals and fluorinated polymeric species. However, the relative concentrations remain uncertain.

In spite of the complexity of the dependence of the etch rate on different radical and atomic concentrations, an intriguing possibility can be visualized. This occurs due to the competition implied by reactions (v) and (vi) for the alkoxy radical. A sudden reduction of the availability of CF_x radicals forces the reversible reaction (vi) backwards and eliminates the competition for the degradation of RO* through reaction (v). The consequent enhancement in the etch rate can be significant if the ratio k6/k5 is large. However, the etch rate will eventually return to its value in the pure oxygen plasma, which is significantly lower. The time scale associated with the increase of the etch rate may then be used to extract information about k5 and k6.

Indeed a substantial enhancement in the etch rate, lasting for a short time, has been observed using FR4 epoxy polymer coated silicon wafers in a parallel plate plasma reactor.[1] Some of the results are to be presented elsewhere in this volume.[2]

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