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Study of 193nm resist degradation under various etch chemistries

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ABSTRACT

The effectivity of 193nm photoresists as dry etch masks is becoming more and more critical as the size of integrated devices shrinks. 193nm resists are known to be much less resistant to dry etching than 248nm resists based on a poly(hydroxystyrene) polymer backbone¹. The decrease in the resist film budget implies a better etch resistance to use single layer 193nm photoresists for the 65nm node and beyond. In spite of significant improvements made in the past decade regarding the etch resistance of photoresists²⁻⁵, much of the fundamental chemistry and physics that could explain the behaviour of these materials has to be better understood. Such knowledge is necessary in order to propose materials and etch processes for the next technology nodes (45nm and below).

In this paper, we report our studies on the etch behaviour of different 193nm resist materials as a function of etch chemistry. In a first step, we focus our attention on the interactions between photoresists and the reactive species of a plasma during a dry etch step. Etch experiments were carried out in a DPS (Decoupled Plasma Source) high density chamber. The gas chemistry in particular was changed to check the role of the plasma reactive species on the resist. O_2 , Cl_2 , CF_4 , HBr and Ar gas were used.

Etch rates and chemical modifications of different materials were quantified by ellipsometry, Fourier Transformed Infrared Spectroscopy (FTIR), and X-Ray Photoelectrons Spectroscopy (XPS). We evaluated different materials including 248nm model polymer backbones (pure PHS or functionalized PHS), and 193nm model polymers (PMMA and acrylate polymers) or resist formulations. Besides the influence of resist chemistry, the impact of plasma parameters was addressed.

Keywords: Photoresists, etch resistance, etch chemistry, etch rate, FTIR, XPS, DMA

1. INTRODUCTION

As critical dimensions shrink, the stability of photoresist materials during the integration steps is becoming more of an issue. The dry etch step is particularly aggressive for these organic materials. As a matter of fact, 193nm positive tone photoresists, based on acrylate and metacrylate chemical platforms, are known to be much less resistant to dry etching than the previous generation. According to the Ohnishi parameter⁶, this lack of resistance is due to the lower carbon density of 193nm chemical platforms. Therefore, with the resist film budget continuously decreasing, it is critical to have a better understanding of the physical and chemical modifications of a 193nm photoresist during a dry etch step. Dry etch plasma processes involve several different gases, which may not have the same impact on the resist components. Whether the interactions between the plasma reactive species and the photoresist are more physical or more chemical, the resist degradation could be completely different.

In order to understand the resist degradation during an etch step, we have mainly focused our work on the resist chemical modifications after a plasma exposure. Two resists, a commercial 248nm resist and a 193nm one based on a Metacrylate model polymer, were etched under various gas conditions. The etch processes were carried out with only one gas at a time, in order to evaluate the influence of each gas independently from one another. In the case of the 193nm model polymer, two formulations were compared (one with a photoacid generator (PAG) and one without the

PAG) in order to observe a potential influence of the PAG on the resist etch resistance during the etch process, considering that an increase of the temperature during the etch could induce the chemical amplification reaction⁷. We also showed the changes in the resist chemistry after the etch step, both over the entire film volume with FTIR analysis and with a finer study of the resist surface with XPS analysis. Finally, based on our observations, we focused on the HBr chemistry, which showed to be particularly reactive with the 193nm model polymer compared to our 248nm resist. Thus we started evaluating the influence of a plasma curing step on our material. The model polymer was exposed to a HBr plasma cure and then analyzed by FTIR and Mechanical Dynamic Analysis (DMA). The first results of this study are presented in this paper.

2. EXPERIMENTAL

The materials used in this study was a 248nm resist from Rohm&Haas Electronic Material (RHEM) and a model polymer based on a methacrylate polymer backbone as shown in Figure 1. Two sets of formulations were used for this polymer: one with a PAG and one with the polymer only. The resists were coated on HMDS primed 200mm wafers with a thickness of 580nm for the 248nm resist and 260nm for the 193nm resists. The SoftBake conditions were 130°C/60s for the the 248nm resist and 115°C/60s for the 193nm resists. All experiments were carried out on non-patterned wafers.

The wafers were etched in a high density chamber (Decoupled Plasma Source, DPS). The reactor is part of the 5200 etch platform from Applied Materials. The following etch parameters were used: 300W source power, 50W bias power, 10mTorr pressure and 100 sccm gas flow rates. For the HBr treatment step, the following conditions were applied: 1200W source power, 0 W bias power, 5mT pressure and 100sccm gas flow rate.

The etch rates were measured with a KLA Tencor UV-1050 ellipsometer. Chemical modifications of the resist were analyzed with a FTIR tool from Biorad (FTIR spectra are corrected as a function of the film thickness) and with an XPS chamber from Meca 2000. The XPS source used in this study was a non monochromatic Al source. The wafers are transferred from the etch reactor into the XPS chamber under an ultra-high vacuum. Thus the material is not exposed to an oxidative atmosphere before the chemical analysis. Some of the samples were further analyzed with Mechanical Dynamic Analysis (DMA) tool from TA Instruments (DMA 2980).

3. RESULTS AND DISCUSSION

1. Effect of the etch chemistry on the resist chemical modifications

The reference resist (248nm resist) was etched under various gas conditions (O_2 , Cl_2 , Ar, CF_4 and HBr). The other etch parameters were kept constant. The samples were analyzed before and after etch by FTIR to observe the chemical stability of the resist polymer during the etch. Two specific regions of the spectrum are interesting: the C-OH bond corresponding to the 3200cm⁻¹ frequency and the C=C bond corresponding to the 1600cm⁻¹ frequency. We observe the excellent stability of the 248nm resist as shown in Figure 2. The only modification appears for the O_2 plasma.

In the case of the 193nm polymer, strong modifications of the Infrared spectrum are obtained as shown in figures 3a and 3b. We focus our attention on three regions: the 1795 cm^{-1} frequency corresponding to the lactone carbonyl group (C=O), the 1700 cm^{-1} frequency corresponding to the ester carbonyl group and the 1200 cm^{-1} corresponding to the ether bond. All etch chemistries induce a strong chemical degradation of the polymer, indicating a very unstable behaviour of this chemical platform during an etch step.

The lactone group (1794 cm^{-1}) is particularly affected by the plasma. This group is detached from the polymer backbone, or degraded, for every etch gas we used. However, the intensity of this effect differs from one gas to another. As for the reference resist, the O₂ plasma is the more aggressive. The Ar plasma also implies a chemical degradation although this plasma is 100% physical, but this degradation is the less intense. CF₄ and Cl₂ gases seem to have a very similar impact on the chemical structure of the resist while HBr is more aggressive. According to previous studies⁸, the new peak that appears around 1765cm⁻¹ indicates that the lactone unit is detached from the polymer backbone and stays in the resist film (there is no modification of the lactone cycle). Presently, we are not able to tell if the total amount of

the detached lactone stays in the film or if a part of it is out gassed from the resist film. Further studies are under way to clarify this point.

In order to have a closer view of the chemical modifications induced by the plasma at the resist surface, we performed XPS analysis on our etched samples. XPS gives access to the chemical composition of the resist over a thickness of about 10nm depending on the material and the analysis conditions. The chemical compositions of the two materials surface layers are shown in the figure 4. We observed very similar surface modifications after etch for the two types of resists and for all etch gases but one. In the case of an HBr etch, the incorporation of Bromine atoms into the 193nm polymer is significantly higher than for the 248nm reference resist (36% vs 21%). The C/O ratio is also particularly higher for the 193nm model polymer after an HBr etch than before (15 vs 4). These results indicate that this resist platform is strongly reactive with the HBr plasma compared to the other gases that we evaluated. This increase of carbon content could improve the etch resistance of the material, according to the Ohnishi parameter. The strong interaction of the 193nm resist with the HBr plasma can be also confirmed by the measurement of the resist etch rate under the different etch conditions. As shown in Table 1, the etch rates for the 193nm model polymer increase strongly compared to our reference resist. Moreover the HBr plasma induces a very strong increase (+173%) of the etch rate compared to the other etch chemistries. We can also observe that the difference is more significant when the plasma has a stronger physical action (HBr and Ar). On the other hand, when we tend towards more chemical plasmas (Cl_2 , CF_4 and O₂), the difference in etch rate decreases between the two materials. These results seem to indicate a particular behaviour of the model polymer with the HBr plasma. As a result, we decide to focus on the effect of an HBr curing step on 193nm resist properties (see paragraph 3).

Before considering the impact of an HBr plasma on our 193nm model resist we have to check that mainly the polymer backbone is involved in the etch process. As a result, the influence of other resist components and especially the PAG which is the catalyst of the polymer deblocking has to be clarified. Such possible influence of the PAG on the resist etch resistance was thus evaluated with etch rates measurements and FTIR analysis.

2. Effect of the Photoacid Generator (PAG) on the resist etch resistance

Two formulations containing our 193nm model polymer were used: one containing only the methacrylate terpolymer as shown in Figure 1, and the other containing the polymer and a PAG. The two formulations were etched under the exact same conditions, with the same gases previously evocated in this work. The resist behaviour during the etch was evaluated with etch rate measurement and FTIR analysis.

The etch rates of the two formulations (with and without PAG) are presented in the Table 2. We observed that the different etch rates do not show significant differences from one formulation to another. This is a first indication to say that the PAG does not seem to have an influence on the resist etch resistance.

In the figure 5 we show the results of the FTIR analysis on the two formulations after the different etch. We observed that the chemical modifications induced in the formulation containing the PAG are very similar to what we observe with the methacrylate polymer only. There is no significant influence of the PAG on the chemical degradation of the 193nm resist. This is in good correlation with previous studies on this topic⁹.

The etch resistance of the 193nm model polymer was not affected by the presence of a PAG in the formulation. This means that the resist degradation during the etch is only due to the physical and chemical interactions of the plasma reactive species with the polymer of the resist. There is no sensibilization of the PAG by the plasma.

3. Effect of an HBr curing step on the physical and chemical properties of a 193nm resist

We observed that the HBr plasma induces an important modification of the resist chemistry. Therefore we focused on the influence of an HBr curing step on the resist polymer. The formulation containing the polymer and the PAG was used for this study. The chemical and physical modifications of the resist were analyzed by FTIR and DMA.

The Figures 6 and 7 show the results of the FTIR analysis for the polymer after the curing step. We observe an increase in the hydrocarbon content of the resist after the cure. This higher carbon content after the HBr cure could help stabilizing the resist during the following etch step. We also observe a strong decrease of the absorbance corresponding to the lactone unit. The decrease is much higher than in the case of an HBr etch step. Again we observe that the lactone unit stays, at least partially, within the resist film. This detached lactone group inside the film could have some effects on the physical state of the film. This could have some consequences on the resist behaviour during the following step of the process like the dry etch step. Compared to what we observed with an HBr etch, the decrease of the lactone peak is very important with the HBr treatment. The difference between the two processes is that there is no bias power in the case of the cure process and the source power is much higher. As a result, the higher source power and thus the higher ion density is probably responsible for the important chemical modifications observed in the case of the HBr treatment.

In order to evaluate the impact of the free lactone group in the resist film, we performed DMA analysis on the material before and after an HBr curing step. On the Figure 7 we present the results of the DMA analysis. The Tan (Delta) is plotted as a function of temperature. The glass transition temperature of the film was measured directly on the silicon substrate and clearly appears on this graphic. After an HBr curing step, the glass transition temperature strongly decreases from 176°C to 102°C. This result confirms the hypothesis that the detached lactone stays within the film and acts as a plasticizer for the resist⁷. This hypothesis had not been confirmed yet by a measurement of the glass transition temperature of the resist thin film. This observation can have important consequences on the behavior of resist patterns during an etch step following an HBr treatment. Indeed, instead of "hardening" the resist from a physical point of view, we have plasticized the resist film. This can also help for pattern roughness control¹⁰. However, this effect may not be uniform and the study of the surface properties will now be pursued.

4. CONCLUSIONS

We have studied the influence of different etch gases on the chemical modifications of a 193nm model polymer. The material was etched and then characterized to evaluate the chemical degradations induced by the plasma. We observed that the 193nm metacrylate resist is much more sensitive to the plasma than the 248nm counterpart, and this is true with all etch chemistries we used. We also showed that, compared to a 248nm reference resist, the difference of behaviour is much more important with physical plasmas (HBr and Ar) while chemical plasmas induces minor differences. We showed that during the etch step, the lactone unit of the resist is detached from the polymer backbone but stays within the resist film. We also observed that there is no interactions between the PAG and the plasma during the etch. FTIR analysis showed that the presence of the PAG in the formulation does not induce any additional chemical modification compared to what we observed when we etch the resist polymer without the PAG. Therefore we can conclude that the resist degradations during an etch step are not the consequence of an interaction between the PAG and the plasma, but only of the interaction of the resist polymer and the plasma reactive species.

We also evaluated the impact of an HBr curing step on the chemical modifications of a 193nm resist. Compared to the HBr etch process, we observed a much stronger detachment of the lactone unit. This indicates strong chemical interactions with the resist. We also observed that the lactone unit actually acts as a plasticizer for the resist film. As a result, the HBr cure step is more a softening process for the material. Further studies will be needed to evaluate the impact of this process on the etch resistance and on the resist roughness as the softening of the polymer could have a big impact on the polymer reorganization.

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A : Protecting group **B** : Lactone group **C** : Polar group

Figure 1: Chemical structure of 193nm model terpolymer



Figure 2: FTIR spectra of 248nm resist before (reference) and after O2, Cl2, CF4, HBr and Ar etch



Figure 3a: FTIR spectra of 193 resist before and after after O2, Cl2, CF4, HBr and Ar etch



Figure 3b: 1650-1900cm⁻¹ wavenumber region of the FTIR spectra



Figure 4: Chemical composition of resist surface for 248nm (left) and 193nm (right) resists after different etch chemistries

Etch gas	248nm resist etch rate (nm/min)	193nm resist etch rate (nm/min)	Etch rate increase (193nm vs 248nm)
O_2	390	465	19%
Cl ₂	66	102	55%
CF_4	108	135	25%
Ar	36	68	89%
HBr	24	66	173%

Table 1: Etch rates of 248nm and 193nm resists



Figure 5: Influence of the PAG on the chemical modifications of the 193nm resist after Ar and HBr etch

Etch gas	Etch rate (nm/min) (polymer only)	Etch rate (nm/min) (polymer + PAG)
O ₂	465	492
Cl ₂	102	105
CF ₄	135	139
Ar	68	45
HBr	66	67

Table 2: Influence of the PAG on the 193nm resist etch rate



Figure 7: hydrocarbon (a) and carbonyl (lactone) (b) regions of the FTIR spectra for the 193nm resist before and after an HBr cure



Figure 8: DMA thermogramm of 193nm resist before and after an HBr cure