Depth Profile Analysis of Structures in ArF Resists by 172nm VUV Curing and Dry Etching Process Using μ-FTIR with Gradient Shaving Preparation

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The structural changes in the depth direction of ArF model resist with the VUV curing and/or the dry etching process were investigated by the combined use of a gradient shaving preparation and micro-FTIR line scanned measurements. The effect on the improvement in the resistance against the dry etching process by the VUV curing was also clarified. It was cleared that the estimated thickness of the layer, which was damaged by the dry etching, was approximately 50nm with out the VUV curing. Additionally, it was found that both of the dry etching process and the VUV curing decreased lactone group and formed carboxylic acid, but the degree of the structural change by the VUV curing was clearly greater than that by the dry etching process. It was confirmed that the VUV curing process had the effect on reducing the film shrinkage and the surface roughness by the dry etching process. In addition, the damaged layer by the dry etching process was not formed in the VUV cured samples. It was supposed that the improvement in the resistance against the dry etching process by the VUV curing was caused by the structural changes, which were the creation of carboxylic acid with the decrease of lactone group and the formation of the network structure.

Keyword: photoresist, ArF process, VUV curing, depth profiling, gradient shaving preparation, dry etching

1. Introduction

Lithography is a key technology for shrinking device design. Such shrinking has been mainly carried out by making the wavelength of the illuminating light source shorter. However, the resist materials for the ArF process are easily damaged by the dry etching process as compared with the materials for the KrF process due to the use of polymers without benzene structure. Additionally, the resistance against the dry etching process has become more important because it is necessary to make the resist thickness thinner to shrink the device design. There have been attempts to give resistance to the resists against dry etching, such as by changing a main chain structure and introducing dry etching resistive groups in the side chain of molecules. However, the lithography process was seriously influenced by these methods, so that the VUV curing has been examined as a method to improve the resistance and to reduce the surface roughness of the resists produced by the dry etching.[1-5] This process improves the dry etching resistance by the VUV irradiation after the formation of patterns. To clarify the structural change by the VUV curing and the distribution of it in depth direction were
very important to optimize the condition of the VUV curing. However, the conventional depth profiling method that uses an ion etching process has essential difficulties, namely, it destroys the structures and prevents the analysis of correct depth profiling of organic materials like the resists. Takeda et al. showed the difference of the degree of film shrinkage in some model polymers with different types of resistive group or main chain and so on [6]. However, the relationship between the film shrinkage and the structural change of the samples those include the additives, and the cause on the improvement in the resistance against the dry etching process by the VUV curing were not clarified. In this study, we attempted to clarify the structural change in the depth direction and the effect on the improvement in the resistance against the dry etching process by the VUV curing by means of a gradient shaving preparation and FTIR microscope technique [7-10].

2. Experimental
2.1. Materials
Methacrylate based model resist, which was generally employed in the ArF process, was used in this study. This model resist was offered by Sumitomo Chemical Co., Ltd. The structure of the model resist is shown in Figure 1. The model resist had an adamantane group and a lactone group in the side chain portion. The mol ratio between the two side chain units was 1:1. Furthermore, a triphenyl sulfonium salt type photo acid generator (PAG) and an octylamine type quencher were added in the resist.

![Figure 1. The structure of the model resist.](image)

2.2. Sample Preparation
The model resist was spin-coated on 300mm Si-wafer to obtain the target thickness of 400 nm. VUV curing was applied by using an in-line cure unit with 172nm radiating. The wafer was set into a lamp house whose atmosphere was replaced by nitrogen. The distance between the lamp and the wafer was 10 mm. The illumination power on the wafer was 80 mW/cm². The curing time was 15 and 60 seconds. The dry etching process was a similar process as a generally applied to STI opening etching process, which consisted of BARC step, SiN step and O/E step.

2.3. Measurement
The film thickness was measured by means of an ellipsometer (KLA-Tencor ASET-F5). The slope was formed on the sample by the Gradient Shaving Preparation (GSP). Figure 2 shows a schematic diagram of GSP. The linearity of the slope was verified by means of the Opti-probe™ (Thera-Wave) measurement system.

![Figure 2. Schematic diagram of the gradient shaving preparation and μ-FTIR measurements.](image)

The surface roughness of the dry etched samples was measured by means of Atomic Force Microscope (AFM). The AFM measurements were carried out by using Nanoscope IIIa AFM system (Digital Instruments, INC.).

The chemical changes in depth direction were measured by micro Fourier Transform Infrared Spectroscopy (FTIR) line scanned measurements. Micro-FTIR line scanned measurements were carried out by using Spotlight-300™ (Perkin Elmer). The spectra were scanned from 4000 to 7000cm⁻¹ with a resolution of 4cm⁻¹. The measurement spot size was 20μm squares and the measurement step of the line scan was 30μm.
3. Results and Discussion

Figure 3 shows the film shrinkage of the model resist by the dry etching process with the VUV curing, which is normalized by that without the VUV curing. Figure 4 shows the root mean square surface roughness (RMS) of the dry etched samples with and without the VUV curing by means of AFM measurements. It was confirmed that the VUV curing reduced the shrinkage and the surface roughness of the film by the dry etching process, namely, the VUV curing improved the resistance against the dry etching process. And, it was cleared that the VUV curing process for only 15 seconds could improve the dry etching resistance. Moreover, the VUV curing for 60 seconds was more effective to improve the dry etching resistance than 15 seconds.

Figure 3. The film shrinkage of the model resist by dry etching normalized with the VUV curing by that without the VUV curing.

Figure 4. The surface roughness (RMS) of the dry etched (DE) samples.

The structural change of the model resists by the VUV curing and the dry etching process was analyzed to clarify the mechanism of improving the resistance against the dry etching process by the VUV curing. Figure 5 shows the FTIR spectrum of the untreated model resist. The assignments of characteristic bands were showed in the figure, the bands around 2800-3100 cm⁻¹ were assigned to CH stretching and, the bands around 1600-1900 cm⁻¹ were assigned to C=O stretching, the bands around 1300-1400 cm⁻¹ were assigned to CH bending and the bands around 1100 cm⁻¹ were assigned to C-O stretching. These bands were assigned to the characteristic functional groups of the model resist.

Figure 5. The FTIR spectrum of the untreated model resist.

Figure 6 shows the micro-FTIR line scanned spectra of VUV cured sample for 15 seconds in the depth direction, which were obtained by measuring the slope made by the gradient shaving preparation. The lower and upper sides of the spectra in the figure correspond to the surface and the inside of the sample, respectively. From comparing with
the spectrum of the untreated sample, the characteristic change of the spectrum was appeared at carbonyl region around 1600-1900cm⁻¹. And, the carbonyl group related to the resistive group was very important for the lithography process, so that this region was mainly analyzed in this study.

Figure 7 shows the spectra expanded around 1600-1900cm⁻¹ which was the carbonyl region, and two major peaks were detected in this region. It was confirmed that the bands at 1790cm⁻¹ and 1720cm⁻¹ were respectively assigned to carbonyl group of lactone ring and acryl ester from analyzing the spectra of standard samples that contained only adamantane or lactone group in the side chain. It became clear that the carbonyl group of lactone ring decreased in intensity by VUV curing and there was obvious distribution of the structural change in the depth direction. The peak intensity of the lactone group near the surface was weaker than that of the inside. Additionally, as compared with the spectrum of untreated sample, it was confirmed that the structural change reached the interface between Si-wafer and resist. These structural changes were similar to the results of model polymers without any additives[5]. Therefore, these structural changes were directly caused by VUV irradiation and the obvious influence of the additives was not observed.

![Figure 7](image)

Figure 7. The line scanned spectra of model resist with VUV curing for 15 seconds expanded around 1600-1900cm⁻¹ which was the carbonyl region.

Figure 8 shows the line profiles of the peak intensity ratio of 1790cm⁻¹ band to 1720cm⁻¹ band of model resist with the VUV curing and/or dry etching process in the depth direction. The peak intensity ratio of the VUV cured samples linearly decreased from the interface at Si-wafer to the surface. In other words, it was confirmed that the structural change caused by the VUV curing distributed linearly in the depth direction in the case of both curing time. It was presumed that this distribution was caused by the absorption of the irradiated light by the model resist.

![Figure 8](image)

Figure 8. The line profiles of the peak intensity ratio of 1790cm⁻¹ band to 1720cm⁻¹ of model resist with VUV curing and/or dry etching process in the depth direction.

The peak intensity ratio of the dry etched sample without the VUV curing decreased near the surface as circled in Figure 8. Therefore, it was confirmed that the lactone group was decreased near the surface by the dry etching process, while the line profile of this sample was almost constant around the inside of the sample. Therefore, the influence of the dry etching process was thought to be limited near the surface. And the estimated thickness of the layer, which was damaged by the dry etching, was approximately 50nm according to the profile.

The line profile of the samples with the VUV curing and dry etching process almost agreed with that of the samples with only VUV curing, although the thickness of the film decreased by the dry etching process. And, the damaged layer was not detected near the surface. Consequently, it was confirmed that the VUV curing process had the effect on preventing the formation of the damaged layer near the surface by the dry etching process. It was also cleared that this effect could be expected in a short time VUV curing like 15 seconds as well as 60 seconds.

Figure 9 shows the spectra of each sample expanded around the carbonyl region. And,
each figure corresponds to the surface layer, middle layer and interface at Si-wafer. From comparing with the spectrum of untreated sample, the decrease of the lactone group in intensity was observed near the surface in the sample with only dry etching process. Additionally, it was found that a shoulder component appeared around 1700 cm\(^{-1}\). A carboxylic acid was thought to be generated near the surface by the dry etching process. This evidence shows that the dry etching process induces the formation of carboxylic acid with following by the decomposition of the lactone group.

![Spectra of each sample](image)

Figure 9. The spectra of each sample correspond to the surface layer, middle layer and interface at Si-wafer.

In the case of the sample with only the VUV curing, the main structural changes were also the decrease of the lactone group and the formation of carboxylic acid. Thus, it was cleared that the structural change by the VUV curing was similar to that by the dry etching process. From these results, the lactone group was thought to be the weakest component in chemical bonding in the resist. But, the degree of the structural change by the VUV curing was clearly greater than that by the dry etching process. A little broadening to a lower wave number side of the lactone peaks was detected in the spectra of the VUV cured sample. Although there were some interpretations for a broadening of a peak, a representative one was the formation of the network structure. In this case, the carboxylic acid generated by the VUV curing was supposed to be the connecting point of the network structure. And, the formation of the network structure was also suggested from the broadening of the spectral region below 1600 cm\(^{-1}\) which was assigned to the methacrylate main chain.

From above results, it was supposed that the improvement in the resistance against the dry etching process by the VUV curing was due to the structural changes which were the creation of carboxylic acid with the decompositions of the lactone group and the formation of the network structure. It seemed that the reason of appearing no effect to improve the resistance was due to losing the film surface by the dry etching before the structural change came up to enough degree to improve the resistance, in spite of occurring similar structural changes with only the dry etching process.

4. Conclusion

The structural changes in the depth direction of ArF model resist with the VUV curing and/or the dry etching process and the effects on the improvement in the resistance against the dry etching process by the VUV curing were clarified by the combined use of a gradient shaving preparation and micro-FTIR line scanned measurements.

The damaged layer was generated near the surface by the dry etching process and the thickness of it was about 50 nm without the VUV curing. Additionally, it was confirmed that the lactone group decreased and carboxylic acid was formed by the dry
etching process in the damaged layer. On the other hand, the structural changes by the VUV curing were the decrease of lactone group and the formation of carboxylic acid. Although these structural changes were similar to those by the dry etching process, the degree of them was clearly greater than that by the dry etching process. It was found that these structural changes reached the interface between Si-wafer and resist in both case of the VUV curing for 15 seconds and 60 seconds. The degree of the structural change decreased linearly from the surface to the interface.

The VUV curing process had the effect on reducing the film shrinkage and the surface roughness by the dry etching process. And, the damaged layer was not created in the VUV cured samples although the film thickness was decreased. It was supposed that the improvement in the resistance against the dry etching process by the VUV curing was due to the structural changes which were the creation of carboxylic acid with the decomposition of the lactone group and the formation of the network structure. It seemed that the reason of appearing no noticeable effect on the improvement in the resistance against the dry etching process was due to losing the film surface by the dry etching process before the structural change came up to enough degree for improving resistance, in spite of occurring similar structural changes with the only the dry etching process.

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