Analysis of etched low-k organic material surface Keisuke Nakamura, Sumio Sekiyama, and Hiroshi Yanazawa

Environmental Process Technology Laboratory, Semiconductor Technology Research Department, Association of Super-Advanced Electronics Technologies (ASET)

292, Yoshida-cho, Totsuka-ku, Yokohama Kanagawa 244-0817, Japan

nakamura@epl-aset-unet.ocn.ne.jp

Recently, ULSIs employ low-k material as interlayer dielectrics in order to reduce RC delay. And ASET is trying to develop a non-PFC high efficient dry etching processes for low-k materials, in order to abolish exhaustion of gas that have high global warming products and save energy. Plasma processes with mixtures of nitrogen gas and hydrogen gas are commonly used for etching of low-k organic materials. But these etching mechanisms are not well understood. In this study, we characterized the surface of low-k organic materials after exposure to various etching plasmas in order to understand how etching took place.

Figure 1 shows a schematic diagram of experimental apparatus used in this study. Etching experiments were carried out in Neutral-Loop-Discharge (NLD) plasma reactor. We used SiLKTM as etching sample. Pure nitrogen gas, a mixture of nitrogen gas and hydrogen gas (N₂/H₂), and pure NH₃ gas were used in etching processes, and their etch rates of SiLKTM were measured in 150 nm/min, 220 nm/min, and 280 nm/min, respectively. X-ray photoelectron spectroscopy (XPS) and time of flight secondary ion mass spectroscopy (TOF-SIMS) were used to analyze etched SiLKTM surface.

Figure 2 shows a XPS spectra of etched SiLKTM surface. A strong C1s peak and an O1s peak are shown in reference spectrum. By etching a N1s peak appears, and an O1s peak becomes stronger. Table A shows atom concentration ratios calculated from XPS results. In the lower etch rate process, the more nitrogen atoms consist in surface region.

Table B shows TOF-SIMS data focused on the fragments that consist of NH_2 -base. These fragments that don't consist in the reference sample are shown in etched samples. In the higher etch rate process, the more fragments consist of NH_2 -base are observed.

From results of XPS and TOF-SIMS, we suppose following reaction models. In pure nitrogen process that have lower etch rate, nitrogen ions/molecules play a important role in etching reaction. But nitrogen ions/molecules produce byproducts that have low volatility. So these byproducts don't desorb from the surface easily, and therefore nitrogen atom concentration ratio is higher in the surface region. Otherwise, In N₂/H₂ process and NH₃ process, more NH_x ions/molecules consist in those process plasmas. And these ions/molecules produce volatile byproducts, and these byproducts desorb from the surface, therefore nitrogen concentration is lower in the surface.

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Figure 1 Schematic diagram of experimental apparatus



Figure 2 XPS Spectra of etched SiLKTM surface

Table A Atom concentration ratios calculated from XPS results

	С	Ν	0
REF (not etched)	98	-	2.0
N ₂	77	15.1	7.1
N ₂ /H ₂	82	11.4	5.8
NH ₃	84	8.5	6.4

Table B TOF-SIMS data focused on the fragments that consist of $\mathrm{NH}_2\text{-}\mathrm{base}$

mass number	18	30	60	69
fragment	NH ₄	-CH ₂ -NH ₂	-C(NH ₂) ₃	C ₅ H ₉
REF (not etched)	-	-	-	74
N ₂	11	20	4	121
N ₂ /H ₂	12	33	11	105
NH ₃	19	78	12	125