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主論文の要旨

論文題目　**Measurement and analysis of plasma induced damages on fabrication processes of ultra large scale integrated circuits**
（大規模集積回路製造プロセスにおけるプラズマ誘起ダメージの計測と解析）

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論文内容の要旨

With the shrinking of the critical dimensions (CD) of the semiconductor devices, high precise plasma etching technologies are required to realize high accuracy pattern transfer. In plasma etching, deformation of the pattern profiles are induced by degradation of polymer materials as etching masks due to their directly exposure to plasma.

Reactive species such as ions, radicals, vacuum ultraviolet (VUV) in plasma and process temperature usually lead to complicated reactions by their synergistic effects. Therefore, the reactions between plasma and polymer materials have been a critical issue on understanding and controlling to realize the precisely pattern transfer with a nanometer scale. The reactive species significantly affect the properties of the polymer materials physically, e.g., film thickness, surface morphology, and chemically, e.g., chemical structures. Surface modifications induced by plasma and polymer reactions also affect the electrical properties such as wettability of polymer materials.

Reactions between plasma and several kinds of polymer materials have been investigated with a focus on individual effects of the reactive species in plasma. Individual and synergistic effects of VUV, radicals and ions on polymer modification have been clarified.

The dissertation is organized as following: the background of this research was introduced in chapter 1. To realize the miniaturization and high performing speed of semiconductor devices, improvement of pattern transfer technologies like plasma etching with an accuracy in nanometer scale is highly required. As polymer materials play an important role during pattern transfer, damages on these materials induced by plasma and polymers greatly affect the precision of pattern transfer To understand and control the generation of the damages, it is important to understand the individual effects of reactive species such as ions, radicals and VUV photons in plasma and process temperature on the physical, chemical and electrical properties of polymer materials.

In chapter 2, evaluation techniques and principals of measurements were described. VUVOES was applied to measure the absolute photon flux in VUV region, Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) was applied to characterize the changes in chemical structures of plasma irradiate polymer films, spectroscopic ellipsometry and scanning electron microscopy (SEM) was applied to measure the etched depth, atomic force microscope (AFM) was applied to measure the surface morphologies, Raman spectroscopy was applied to investigate the formation of amorphous carbon structures on the polymer film irradiated by plasma and water contact angle (WCA) was applied to predict the alteration of surface wettability.

In chapter 3, effects of VUV photons in HBr plasma on a photoresist were quantitatively investigated and discussed with the information of absolute photon flux measured by VUV optical emission spectroscopy (VUVOES). The methacrylic acid (MAA) in the photoresist significantly decreased with the dosages below 16×10^{16} photons/cm^2. The removed MAA groups generated volatile products and released from the photoresist which decreased the film thickness. The nonuniform release of volatile products and crosslinking reactions by the dangling bonds generated by the removal of MAA groups increased surface roughness.

In chapter 4, effects of ions from Ar plasma and VUV/radicals from HBr and H_2 plasmas on the photoresist were investigated and discussed by changing the irradiation sequences of ions or VUV/ radicals. VUV/radical treatment before ion irradiation (pre-treatment) suppressed the roughness development by ion irradiation. Oppositely, the treatment after ion irradiation (post-treatment) significantly increased the surface roughness. Measurements by FTIR and ellipsometry indicated that the removed thickness and change in chemical structures were almost the same by pre- or post-treatments. The roughness decrease by ion irradiation after pretreatment was due to the formation of a crosslinked layer which increased the etch resistance. The enhancement of roughness by post-treatment was correlated with the removal of MAA groups by VUV photons which induced nonuniformity of crosslinking reactions on the roughened photoresist by ion irradiation.

In chapter 5, effects of process temperature on the reactions between reactive species in plasma and polymer materials were investigated and discussed. A thermal resistant novolac-based polymer film were investigated by irradiation with Cl_2 plasma, VUV or radicals were investigated during high temperature plasma etching processes. Film thickness showed no decrease after VUV or radical irradiation until 400 °C and only full exposure to ions, VUV and radicals removed the film thickness. This indicated the ions dominantly remove the film thickness. The etch rate of this film decreased with the increase in temperature, indicating the increase in etch resistance. FTIR measurement showed that benzene ring structures significantly decreased during high temperature irradiations by Cl_2 plasma as well as the VUV or Cl radicals. Raman measurement showed that a large amount of sp^2 C=C structures appeared after 400 °C irradiations, indicating the benzene ring structures were cleaved by VUV photons and Cl radicals and formed an amorphous carbon layer with abundant C=C structures. The formation of the amorphous carbon layer significantly increased the etch resistance of the thermal resistant film during high temperature irradiations.

In chapter 6, effects of VUV photons and radicals in H_2 and O_2 plasmas on the alterations of wettability of PET were investigated based on the modifications of surface morphologies and chemical structure changes. The WCA drastically decreased only for the case of irradiation with oxygen radicals, indicating the improvement of wettability of PET. Irradiation without oxygen radicals by VUV or H_2 plasma contrarily increased the WCA. Effects of VUV irradiations were investigated based on the photon dosages. XPS measurement showed that the C-O and O-C=O groups in PET were rapidly decreased at an early irradiation period with a low photon dosage. The removed C-O and O-C=O groups generated volatile products and release from PET indicating the decrease of film thickness. The dangling bonds formed by the removal of C-O and O-C=O were terminated by oxygen or hydrogen radicals or experience crosslinking reactions. For the cases with the absent of oxygen radicals, the large WCA was due to the lack of polar groups formed by oxygen containing groups. FTIR measurement showed no obvious change in bulk structures indicating the reactions were limited at several nanometers near the surface. On the other hands, irradiations by VUV or H_2 plasma slightly increased roughness by removal of C-O and O-C=O groups but oxygen radicals reacted with carbon atoms in PET and the nonuniformity release of volatile products significantly increase the roughness.

In chapter 7, conclusions of this research are remarked. (1) VUV photons preferably cleave the oxygen containing groups at early period of irradiation with low photon dosages. The removed oxygen containing groups leave dangling bonds which will be terminated by radicals or experience crosslinking reactions. (2) Radicals react with polymers at surface and modify the surface chemical structure. Radicals do not affect the roughness unless the radicals strongly etch off the polymers by releasing large amount of volatile products and increase roughness. (3) Ions mainly generate rough features and remove film thickness by physically bombardment of energetic ions. Further investigation with photons in EUV region and actual fluxes of ions and radicals is required to improve understand and control of reactions between plasma and polymer materials on molecule levels.