Synchrotron Radiation Patterning of Plasma Polymerized Organo Silicons in Oxygen Atmosphere

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1. Introduction

Recently some reports have been published on the development of new approaches for all dry photo lithographic processing based on silicon containing plasma polymerized resists [1,2]. Silylation technology is well known and widely used in micro lithography [3,4]. Silicon containing crosslinked thin films, on the other hand, were plasma polymerized for different purposes of surface coating such as optical, mechanical, and electrical [5,6]. It was also shown, that Si-Si network can be plasma polymerized from, for example, aromatic silanes undergoing particularly scission of Si-CH$_3$ and Si-H bonds [7]. Silylated resists have been patterned by UV irradiation in an oxygen atmosphere as well. However, only the combination of plasma polymerization of silicon containing networks with their UV irradiation in the presence of oxygen gives a breakthrough for all dry photo lithographic processing [1,2].

UV lithography being the only candidate for a recent mass production will be probably replaced in the future with X-ray processing having much lower critical dimension. All the merits of X-ray lithography can be revealed with ultra thin perfect resist layers, which can be deposited and processed exclusively in dry technology cycles. The present paper describes our preliminary results on plasma polymerization and synchrotron X-ray patterning of silicon containing organic films in an oxygen ambient.

2. Experimental

Plasma Polymerization. Silicon organic films were deposited in RF capacitively coupled plug flow box-type reactor [8]. The reactor represents a rectangular prism with a well shaped uniform gas flow and a plasma volume, strictly limited with the rectangular copper thermal stabilized
electrodes, teflon walls, and a copper mesh. The reactor was mounted inside the cylindrical stainless chamber.

Two sets of discharge condition have been used: continuous discharge of 20% hexamethyldisilazane/Ar mixture and low frequency pulse time modulated discharge of pure hexamethyldisilazane. The last was applied to suppress particulate formation and cross linking of polymer structure. Film thickness was monitored in situ with a quartz crystal microbalance. The distributions of film thickness on silicon substrates along the gas flow were measured after deposition with an automatic ellipsometer.

Patterned samples have been scanned with a mechanical profilometer to reveal their self-development features.

Synchrotron X-ray patterning. Deposited films have been irradiated with an X-ray beam through 15 microns beryllium foil. The facility of UVSDR at the Institute of Molecular Science in Okazaki, Japan, was used. The wavelength of maximum X-ray intensity corresponds for about 0.8 nm. A stainless sample chamber was connected to the synchrotron ring through the diaphragm supplied with a differential pumping system providing a possibility to irradiate samples under relatively high oxygen pressure of about 0.3-0.5 Torr.

Plasma polymerized resists deposited on silicon samples were covered with a microscope copper mesh (100 lines/inch, 50% transparent) as a mask, irradiated for a prescribed period of time in the presence of oxygen, and then removed to the ambient atmosphere.

3. Results and Discussion

All irradiated samples being negative type resists demonstrate however well distinguished self-development features (Fig. 1). Irradiated areas become harder and thinner. The minimum X-ray dose in our experiments was about 0.2 J/cm², which is essentially low. The irradiated area can be easily distinguished from non-irradiated by colors for all irradiated samples. Initial steep low dose part of the curve corresponds for initial high rate oxidation reactions. Under the higher doses the rate of thickness decrease is probably dealt with increasing of the degree of oxidation and less probably with a partial polymer ablation.

The data known from literature suggest, that the level of sensitivity of best silicon organic polymer resists to oxidation under UV 193 nm irradiation and adjacent wet development is about 35-60 mJ/cm² [9] and can be even improved with chemical sensitizers. Total dose of about 1.2 J/cm² transferred silicon containing plasma deposited polymers to the level characteristic of stoichiometric SiO₂ [1].

The efficiency of X-ray synchrotron oxidation, and especially Be filtered radiation, must be essentially lower in compare with UV processing, taking into consideration lower absorption and mechanisms of energy transfer from high energy penetrating X-ray photons to low energy chemical bonds accompanied with several energy dissipating processes.
Color microphotographs exhibit also some change of interferometric colors of the intact films. Bright yellowish self-developed areas corresponding for a minimum of 0.2 J/cm² are changing to dark blue as the irradiation dose is increasing, while the color of unexposed areas is changing from dark reddish to bright gray. It manifests definitely oxidation reactions modifying the polymer film under the copper mesh as well.

It is rather difficult to explain such phenomenon with some part of X-ray beam redistributed below the mesh mask. The most probable origin of oxidation of masked areas can be a direct interaction with activated oxygen. X-rays are partly absorbed by the gas phase oxygen molecules. Secondary processes of energy dissipation produce ionized species, excited metastable molecules, atomic oxygen, and radiative electronically excited states. Every of these component can promote appropriately distributed surface oxidation of the films thus decreasing the contrast of the X-ray exposure.

Fig. 2 shows a signal from the mechanical profilometer typical for high dose irradiated sample. The surface of masked areas is very rough in compare with the irradiated squares thus exhibiting some surface etching reactions. Similar noisy profile of unexposed areas can be found on low dose samples under increased load on the profilometer’s stylus. In that case the effect is caused by the difference of hardness of irradiated and non-irradiated areas and indentation of the stylus inside the polymer film.
Further experiments on X-ray oxidative patterning and wet and plasma development are now in progress.

Conclusion

Silicon containing plasma polymerized resist films have been patterned by synchrotron X-ray exposure in an oxygen ambient. Typical X-ray patterning by self-development of irradiated areas of polymer films have been observed under any doses from about 0.2 J/cm². Clear optical images have been developed in all samples including those with the lowest dose.

Unexposed areas of the resists have been modified under the high X-ray doses as well. This phenomena can be assigned to the secondary processes of energy dissipation through the gas phase activated oxygen.

Plasma deposited organo silicon films can be considered as promising candidates for oxidative X-ray photo lithography in all dry microelectronics technology cycles.

References