A-3-5 (Invited) Dry Development of Resist Patterns in Submicron Lithography

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1. A Principle for the Formulation of Plasma Developable Resist

A quantum chemical research revealed that the radiation effects on polymers are clearly interpreted as the chemical reactions in the lower excited states of the polymers.[1] From this result we can understand that a main chain degradable polymer by radiations is a candidate for the positive resist usable for the electron beam and X-ray lithography and at the same time a candidate for the positive Deep UV resist.[2] Moreover, we can predict the spectral sensitization in the main chain degradation of polymers to the Deep UV light. The prediction is applied in the new formulatins of highly sensitized Deep UV resist materials. The same consideration is applicable to the formulation of plasma developable resist materials: namely, in this case the desensitization should be designed in either the exposed or the unexposed part of resist coatings. When a desensitizer, which removes the energy of the electronic excitations of degradable polymers, is formed in either the exposed or the unexposed part of resist coatings, one part which contains no desensitizer will be rapidly decomposed by the plasma exposure compared with the other part. In this paper, we shall discuss on the case that the desensitizer is produced in the polymer coating by radiations. Therefore, the formed resist image after dry development is a negative image. A preliminary work revealed that aromatic azides produce desensitizers when they are decomposed in the excited states in the polymer coatings. The photochemical reaction machanism and the reaction products in polymer coatings are already known in the case of poly(vinyl p-azidobenzoate), where the main products are azobenzene and azoxybenzene derivatives and primary and secondary amines.[3]

From these results we can estimate the product which crosslinks the polymer chain in the resist coatings of the mixture of poly(methyl isopropernyl ketone), PMIPK, and an aromatic bisazide that is formulated as a dry developable resist in our research. Powerful deactivation effects of the hydrogen bond forming compounds are widely known.[4,5] Some of them are practically used as UV absorbers for the stabilization of polymer films against UV radiations. The deactivation effect may arise from the formation of the double-well potential surface that is favorable, especially in the electronically excited state, for the movement of hydrogen atom forming the hydrogen bond,[6] which is considered to be the origin of the quenching effect.[7]

2. Negative Resists for the Dry Development Process

There are many combinations of the degradable polymers and the desensitizer forming compounds. As an example, we choose PMIPK as a degradable polymer and 4,4'-diazide diphenyl thioether as a desensitizer forming compound by radiation. The selection of the species of aromatic azides provides the plasma developable negative resists for the photolithography, the Deep UV lithography and the electron beams and X-rays lithography, respectively, where the line narrower than 0.3μm wide by the elecron beam lithography and the line of 0.5μm wide by the Deep UV lithography were easily obtained. In the following considerations, we shall focus on the Deep UV lithography.

2.1 Experimental procedure: Resist was coated on the 3-inches wafer by the spin coating machine (20sec) and dried in the heat chamber with warm blow for 30min at 60°C. The resist thickness is 1μm. The Deep UV pattern transfer was carried out by PLA-520F aligner (Exposure:10sec) and the electron beam patterning by the HHS-2R, respectively. Post baking was made at 140°C for 30 min. Dry development was carried out in the plasma etching machine, OAPM-301B, by the oxygen gas plasma, where the chamber was pumped down to 0.1Torr in 5sec, the gas was charged in 5sec, the RF power(100W) was on for 1 or 2min with or without parallel electrodes, respectively, at 100°C (Table Temperature) at 1.0Torr of the gas pressure and the pumpdown and the backfill were carried out in 5sec. The time for the RF power on was varied, depending upon the RF power, the table temperature, the gas pressure, etc. The fine pattern resist images were obtaind uniformly over the 3-inches Si or SiO_2 on Si wafer surface. The endpoint of the development was detected by the 283 nm emission of carbon monooxide. The OAPM 301B plasma apparatus is used as either a parallel electrode type equipment or a barrel type one with or without the parallel electrodes which can be removed, respectively.

The importance of the dry developable resist in the submicron fabrication technology,the characteristics of the new resist compositions in the dry development process and the dry development mechanism will be discussed. The total dry microfabrication including the development of resist,the etching of Si and SiO_2 the resist removal,was performed in the process using the new resist compositions.

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