RELATIONSHIP BETWEEN PATTERNING AND DISSOLUTION CHARACTERISTICS
OF CHEMICAL AMPLIFICATION RESISTS USING PARTLY PROTECTED POLY(p-
VINYLPHENOL)

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With decreasing the minimum feature size of VLSI, the wavelength used for the lithography process becomes shorter. Excimer laser lithography is one of the most feasible candidates for the sub-half-micron pattern transfer. For sub- or half-micron pattern transfer, novolac-diazonaphthoquinone resist systems have been widely used because they give high resolution patterns due to very large dissolution rate ratio between exposed and unexposed area. However, they have poor transmittance in excimer laser wavelength region, so that steep patterns have not been obtained. In order to solve this problem, polyvinylphenol derivatives with higher transmittance than that of novolac resin in deep UV region have been investigated. It has been reported that the combination of poly(p-vinylphenol) (PVP) and any dissolution inhibitors have not exhibited high *masking effect* [1] because of the higher solubility of PVP for the alkaline developer than that of novolac resins [2]. Pawlowski and coworkers have attempted to control the solubility of PVP by substituting the benzene ring with hydrophobic alkyl groups.[3]

In this study, we have succeeded in controlling the solubility of PVP itself for the alkaline developer by protecting part of the hydroxyl group of the polymer with an acid degradable group. The modified PVP was applied to the chemical amplification resist system together with dissolution inhibitor and photoacid generator. The large dissolution rate ratio has been achieved to give high resolution down to 0.35 μm .

Materials

Modified PVP, which was protected with acid degradable group (tBOC-PVP), was synthesized by the reaction of the polymer with Di-tert-butyl-di-carbonate under the basic condition. The dissolution inhibitors were prepared by the normal esterification method between aromatic carbonyl chloride and the corresponding alcohol in the existence of pyridine. The photo-acid generators were used as received. These materials were solved in cyclohexanone and filtered before use.

Dissolution Rate

The dissolution rate was measured with 2.38% of TMAH (Tetramethylammonium hydroxide) aqueous solution. Fig.1 shows the dissolution rates of tBOC-PVPs itself. Increasing the protected ratio with the tBOC group, the dissolution rate for the alkaline developer was continuously decreased. This result indicates that the dissolution rates of PVP can be controlled by protecting part of the hydroxyl group. The dissolution rate of tBOC-PVP having ca. 30% protected hydroxyl group depressed a thousand times comparing with PVP itself. The dissolution rates for the system consisting of tBOC-PVP, dissolution inhibitor and photoacid generator are shown in Fig.2. The dissolution rate of every system decreased with the content of the dissolution inhibitor as well as the protected ratio. This results clearly indicate that the *masking effect* is closely related with the solubility of the base polymer itself.

The dissolution characteristics of the resist systems after exposing them with deep UV followed by baking are shown in Fig.3. In the case of the lower protected ratio polymer, the effect of the addition of the inhibitor on the dissolution characteristics was small (Fig.3(a)). On the contrary to the above case, the dissolution rate was accelerated with increasing the contents of the inhibitor in the higher protected tBOC-PVP (Fig.3 (b),(c)).

It has been made clear from these observations that the dissolution inhibitor used in this study effectively worked not only as an *inhibitor* in the unexposed area but also acted as an *accelerator* in the exposed area. Therefore we can obtain the large dissolution rate ratio between exposed and unexposed area.

Resolution

The resolution of our resist with an excimer laser stepper (NA=0.37) has been evaluated to be 0.35 μ m (Fig.4). We believe that our resist system is very promising for sub-half-micron

lithography.

References

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Fig.1 Dissolution rate dependence on substitution ratio of hydroxyl group

Fig.2 Dissolution rate dependence on dissolution inhibitor contents

(a) Substitution ratio 0.12

(b) Substitution ratio 0.21

(c) Substitution ratio 0.28

Fig.3 Dissolution curves of three components resists containing various amount of dissolution inhibitor after exposure. Exposure dose: $50\text{mJ}/\text{cm}^2$, PEB: 80°C 90sec.

Fig.4 SEM photographs of three components resist