Evaluation of Curing Characteristics in UV-NIL Resist

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Mechanical characteristics of UV curable resist for UV nanoimprint lithography are investigated using UV rheology meter. Modulations of visco-elastic properties and thickness shrinkages in typical resists are evaluated in variation of exposure UV intensity. The mechanical modulation speed of the resist depends on the UV intensity, which affects to throughput of UV nanoimprint lithography process. To handle the characteristics universally, effective conversion time is newly introduced, which fairly expresses the resist modifications.

Keywords: UV nanoimprint, UV curable resist, modulus, shrinkage, conversion time

1. Introduction

Nanoimprint lithography is expected to fabricate fine patterns in cost efficiently. Recently, UV nanoimprint [1] is especially applied for various industrial applications such as sub wave length optical element or pattered media because resist is easy to be filled into pattern in the mold and cured rapidly by UV exposure. The total turnaround time of the UV nanoimprint process is expected to be short and it is applicable for mass production of nano scale devices.

In UV nanoimprint process, mechanical characteristics such as modulus are essential because it is basically mechanical lithography. However, the mechanical characteristics in UV curing resist have not been reported in details for any UV nanoimprint resists.

In this paper, PAK-01 and C-TGC-02 (TOYO GOSEI) resist are investigated; where PAK-01 is widely used in UV nanoimprint process [2-4] and C-TGC-02 is examinational resist for researches usages and its chemical components are released. To evaluate the visco-elastic properties, commercial available UV rheology meter is used. Time dependent characteristics for loss elastic modulus and storage elastic modulus are investigated in variation with UV exposure intensity.

2. UV curing resists and measurements of mechanical properties

UV curable resists for UV nanoimprint lithography are distributed by several companies in elsewhere. There exist mainly two kinds of resist. One is a radical polymerization type and the other is an ion polymerization type. Both of PAK-01 and C-TGC-02 are radical polymerization type. Radical polymerization type has advantage in stability of photo-polymerization initiators but
instable for Oxygen inhibition in polymerization.

The C-TGC-02 resist has acrylic acid adduct of polypyrreneglycol diglycidyl ether (EPOXYESTER 70PA) as polymerization resin with 2-methyl-1-((4-methylthiophenyl)-2-morpholinopropane-1-one (IRGACURE907) as UV-polymerization initiator.

In UV nanoimprint process, the most important interest is not chemical reactions of the resist, but mechanical modulation by UV exposure, which is closely related to resist curing and design optimum exposure conditions such as exposure time and light intensity in UV nanoimprint process. To investigate the mechanical modulation of the resist characteristics by UV exposure, UV rheology meter is used.

Figure 1 shows schematic diagram of typical UV rheology meter MCR301 (Anton Paar). The UV resist is dropped on quartz stage and rotating rod is put on the resist. The rod is vibrated and UV light is irradiated through quartz stage. The differences of the applied torque and the response including phase lag are measured under rotational frequency.

In this paper, the storage modulus, phase lag and thickness shrinkage are measured under various UV exposure intensities and discuss about the mechanical modulation in UV resists.

![Schematic diagram of UV rheology meter](image)

Figure 1 Schematic diagram of UV rheology meter.

3. Experimental results

3.1 Storage modulus

In UV nanoimprint process, the UV curable resist turns to be rigid material from liquid body and maintain mechanical structure after releasing template. Storage modulus expresses elastic deformation strength, which is one of the most important characteristics in nanoimprint lithography.

Figure 2 shows modulation of storage modulus for PAK-01 and C-TGC-02 resists under various exposure UV intensity.

![Modulation of storage modulus](image)

Figure 2. Modulation of storage modulus in various exposure UV intensities. The initial resist thickness is set to be 100 μm.

The storage modulus increases as the exposure time proceeds. In both resists, the modulation processes strongly depend on the exposure UV intensity.

3.2 Loss tangent

Figure 3 shows modulation of loss tangent by UV exposure. Both C-TGC-02 and PAK-01 show viscous liquid properties (tan(δ)=∞) at the initial stage and the loss tangents decrease. They are converged to be stable states as the UV exposure time proceeds.

The C-TGC-02 converges to be visco-elastic body (tan(δ)=1.0), however the PAK-01 turns to be elastic body. On the other hand, the modulus is lower than that of the C-TGC-02 as shown in Fig. 2.

3.3 Thickness shrinkage

A UV curable resist generally shrinks by polymerization, which could induce residual stress...
and makes it difficult to release template. Also, it causes critical dimension error. During the rheology measurement, the machine keeps adhesive force between resist and rotating rod adjusting the gap between the rod and quartz stage. We evaluate the resist thickness change by monitoring the gap.

Figure 4 shows resist thickness modulation during UV exposure for various UV intensities. The resist shrinkages occur at the early stages of the UV exposure either at C-TGC-02 or PAK-01.

4. Discussions
The mechanical properties strongly depend on exposure UV intensity $I$. To clear the relations, dependences on exposure dosages (energy) are investigated as conventional photo resists. Figure 5 shows the relations between exposure dosages and storage modulus in various UV intensities.

The storage modulus is not well expressed by exposure dosage. This is because that the initiation reaction depends on exposure UV intensity.

Based on simple radical polymerization theory [5], the relative concentration of monomer $m$ is described as follows:

$$-\frac{\partial m}{\partial t} = K\sqrt{C} m$$

where $C$ is the concentration of initiator and $K$ is reaction constant. If the concentration of initiator $C$ is proportional to UV intensity $I$, it turns to be

$$-\frac{\partial m}{\partial t} = K'I m$$

where $K'$ is constant. As a result, the monomer concentration $m$ is expressed as:

$$m = e^{-K'\sqrt{I} t}$$

So, the conversion ratio by the polymerization becomes $(1-m)$, which relates to $\sqrt{I} t$, where $I$ is UV intensity and $t$ is exposure time.

Figure 6 shows relations between the storage elastic modulus $G'$ and $\sqrt{I} t$. The relations
between $G'$ and $\sqrt{t_I}$ are almost the same for various UV exposure intensity $I$ in both resists. We call the $\sqrt{t_I}$ effective conversion time for universal handling.

This conversion model is very useful process model in numerical simulations for UV resist and process designing could be achieved without measurements for various UV exposure intensities.

### 4. Conclusions

Mechanical characteristics of UV curable resist are evaluated using UV rheology meter.

Modulation of modulus, status of resist and shrinkage in time domain are evaluated in various UV exposure intensities for PAK-01 and C-TGC-02 resists.

The characteristics of the resists depend on UV exposure intensity but they are independent of exposure dosages (energy). Higher exposure intensity leads to rapid curing.

**Figure 5.** Modulation of storage elastic modulus for exposure dosages.

**Figure 6.** Relations between $\sqrt{t_I}$ (effective conversion time) and the storage elastic modulus. (I in mW, t in second)

To handle the characteristics universally, effective conversion time $\sqrt{t_I}$ is newly introduced, which fairly expresses the characteristics.

### References


