Fluoroalkyl-Containing Surfactants to Reduce Release Energy of UV-Cured Acrylate Resin

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Considering the electron beam drawing period and cost of a silica master mold for ultraviolet nanoimprint lithography (UV-NIL) applied to nanofabrication of advanced semiconductors and magnetic patterned media, it is desirable that resist patterns as many as possible can be fabricated. If a ten of thousands of replica molds can be copied from one master mold and a ten of thousands of resist patterns can be fabricated from the single replica mold, a hundred of millions of resist patterns can be obtained from the master silica mold. In the case, at least, tens of thousands of step-and-repeat nanoimprint cycles should be assured. It is considered that the ways to elongate the life of a master and replica mold is to prevent resin components from adhering to the mold surface and to reduce mechanical stress to a mold generating during demolding step. Therefore, a sophisticated UV-curable resin is considered in general to show low surface free energy after curing and release energy as small and constant as possible.

In this study, we used a radical-type UV-curable resin containing 1,1'-[1-methyl-1,2-ethanediyl]bis[oxy(2-hydroxy-3,1-propanediyl)] diacrylate as a base acrylate monomer and Irgacure 907 as a photoinitiator. Seven long-chain fluoroalkyl alcohols and four related compounds, listed in Table 1, were selected as additive surfactants, because a surface governed by long-chain fluoroalkyl moieties makes a low-energy surface. The release energies of the base resin adding 2.0 wt% each surfactant were measured and compared using a lab-made mechanical measurement system [1] equipped with a load cell (Fig. 1). A silica lens was used instead of a silica mold to detect mainly release energy vertical to a silica plane. The silica lens surface was modified with a release layer of a self-assembled monolayer formed from tridecafluoro-1,1,2,2-tetrahydrooctyl-trimethoxysilane (FAS13) by chemical vapor surface modification [2]. The mechanical measurements were carried out under air atmosphere and condensable gas pentafluoropropane (HFC-245fa) atmosphere.

Figure 2 shows release energies per area of the UV-curable resins without and with additive surfactants. C8F13 reduced significantly the release energy in air. The release energy was very consistent with that of the UV-curable resin without additives in HFC-245fa. The results suggested that a surface of the base resin adsorbs molecules of HFC-245fa and its physisorbed layer plays a role of reducing the release energy. It was revealed that C10F17 was the most effective in reducing the release energy in HFC-245fa.

[1] Japanese Patent 2011-60843-A. [2] K. Kobayashi *et al.*, Jpn. J. Appl. Phys. **50**, 06GK02 (2011).

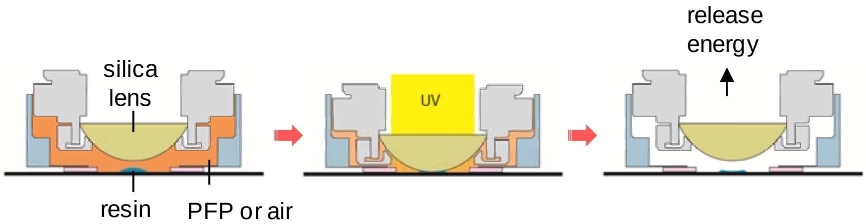

Fig. 1. Illustration of a method for detecting release energy of a UV-cured resin using a lab-made mechanical measurement system. The measurement atmosphere is changeable to air and HFC-245fa by blowing gas before contact of a modified silica lens surface with a droplet of a UV-curable resin.

Table 1. Chemical structures and abbreviations of long-chain fluoroalkyl alcohols and related compounds used as additive surfactants.

additive surfactant	abbreviation
no additive	Ref
$CF_3(CF_2)_3CH_2CH_2OH$	C6F9
$CF_3(CF_2)_5CH_2CH_2OH$	C8F13
$CF_3(CF_2)_6CH_2OH$	C8F15
$CF_3(CF_2)_7CH_2CH_2OH$	C10F17
$CF_3(CF_2)_9CH_2CH_2OH$	C12F21
$CH_3(CH_2)_7OH$	C8
$(CH_3)_3CCOCH_2COCF_3$	C8F3K
$OHCH_2(CF_2)_4CH_2OH$	C6F8D
$CF_3(CF_2CF_2O)_2CF_2CH_2OH$	C7F13E

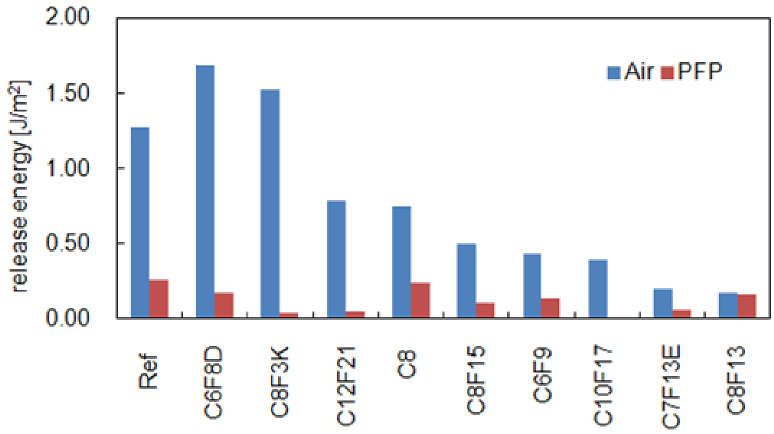

Fig. 2. Release energies of UV-cured resins with and without fluoroalkyl-containing surfactants. The UV-curable resins were composed of a diacrylate monomer and a photoinitiator, and 2.0 wt% respective additive surfactants were added.