Nanoimprint Materials Systems

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In UV cure nanoimprint lithography the interfaces as well as the resist composition play an important role in determining the characteristics of the resulting patterned material, which can be used for subsequent pattern transfer, or be functional. It is important for applications that there be only rare defects, and that template release always be a clean process. In this paper fundamental physical and chemical aspects of the resist template interface are discussed, with a particular focus on how they influence the process of template removal.

Keywords: UV nanoimprint lithography, template release, nanoimprint resists, fluoroalkyl silanes, metal oxides, metal nitrides

1. Introduction

Nanoimprint lithography using low viscosity, drop-dispensed UV-curable resists [1,2] presents a number of advantages for potential applications involving very high resolution patterning such as semiconductor devices, dielectric layers and nanopatterned media for magnetic storage [3]. In particular, the use of a low viscosity resist in contact with a transparent template facilitates level-to-level alignment and enables a very high level of control over the residual layer left near the bottom interface of the cured resist once the template has been removed.

Several important criteria must be satisfied simultaneously by any successful nanoimprint materials system. The substrate onto which the resist is dispensed must have a controlled wetting property so that the resist droplets remain localized but can also flow properly when the template is lowered onto them, leaving no bubbles. After curing, the newly crosslinked material must adhere strongly to it. Both of these requirements can be met by applying a suitable underlayer which can be of any appropriate thickness, has a surface energy in the correct range and surface functionalities that the resist can react with. The template surface, on the other hand, must have the opposite characteristics: the resist should wet it well on contact so that the entire template surface relief structure can be completely filled with fluid, but be only weakly adherent to the cured resist so that on separation fracture occurs only at the resist-

template interface, not within the cured polymer. This is accomplished by applying a thin transparent release layer to the template surface. Finally the resist itself must have low viscosity, the correct wetting properties for use with the selected bottom and release-layers, a fast polymerization rate, and, when cured, excellent pattern fidelity and properties such as high cohesive strength, low shrinkage, high modulus, and low stress. If the cured material is to be used directly for pattern transfer it must also have suitable high contrast etch characteristics.

At present, defects in imprinted structures present a major challenge [4,5]. There are three major sources of defects: particles, failure to fill the template, and contamination of the template surface by newly cured resist during template removal [4]. Particles are a tooling and environment issue unrelated to the nanoimprint materials themselves [5]. Assuming wettability criteria are satisfied, failure to fill the template has been ascribed to bubble formation by trapped air for one commercial nanoimprint materials system, and tool engineering has been improved to reduce this source of defects [6]. Little attention has been paid to the problem of chemical contamination of the template, however, despite reports of requirements for frequent cleaning that would certainly be undesirable in a manufacturing situation [4,7].

Although the choice of curable components will affect the final film properties, relatively few

studies have been done to identify the most desirable chemical characteristics of a low viscosity formulation intended for UV cure nanoimprint patterning [8-12]. Less still is known about how these characteristics may be related to contamination defects that arise during template removal. In this paper we focus on the impact of materials selection on the template release process: the chemical stability of the template surface, the resist characteristics, and the interface between the cured resist and the template, and some aspects of the connections between resist composition and fracture mechanics such as location of the crack path, and crack arrest behaviors. By understanding the essential chemistry and physics of template removal we hope to be able to minimize or eliminate contamination defects.

2. Method

2.1 Materials

Free radical cure resists (acrylate, methacrylate) and cationic cure resists (vinyl ether) have been investigated. Results from a selected set are reported here. Their components are briefly described, with full compositions given in the references cited.

SiA [13]:

(3acryloxypropyl)tris(trimethylsiloxy)silane, t-butyl acrylate, 1,3 butanediol diacrylate

IOA [14]:

n-hexyl acrylate, isobornyl acrylate, 1,3 butanediol diacrylate

mPSS-IBMA [11]:

methacrylate functionalized polyhedral silsesquioxanes (8- to 12-sided) (mPSS), isobornyl methacrylate (IBMA)

mPSS-EHMA [11]:

mPSS, ethyl hexyl methacrylate (EHMA)

mPSS-CHMA [11]: mPSS, cyclohexyl methacrylate (CHMA)

SiVE [10]:

dimethyl bis(vinylloxymethyl)-silane, diethylene glycol divinyl ether

BnVE [15]: benzyl divinyl ether

DVE [10]: diethylene glycol divinyl ether

Resists were usually prepared with approximately 2-4 weight % of photoinitiator (Irgacure 819 + Irgacure 184 or Darocur 1173) or photoacid generator (PAG) (CGI 1906 or CGI 1907). A series of formulations containing lower photoinitiator concentrations was prepared for in-depth photorheology studies of the mPSS-containing resists, because the achievable plate gap

in the instrument (300 μ m) was too large to allow uniform irradiation through the film thickness at normal photoinitiator concentrations.

Unpatterned quartz was used as a template material for all the studies reported here. Release layers were deposited on the quartz surfaces as well as onto oxide-covered silicon for additional characterization.

Fluoroalkylsilane release layers were deposited as described elsewhere [16]. Diamond-like carbon (DLC) was deposited using a plasma method [17]. Metal nitride and metal oxide release layers were deposited by reactive sputtering, sputtering of compound targets, and in a limited study by atomic layer deposition [18]. The amine release layer was deposited from the vapor phase using γ -aminopropyl triethoxysilane (APTES). The release layers were 1-10 nm thick, with UV transparencies measured to be 40-100% depending on the material composition.

Two primary self-assembled monolayer surface treatments using an approximately 1 mM solution of organosilane in toluene have been used to provide good adhesion to the silicon substrates: o-(vinylxybutyl)-n-(triethoxysilylpropyl) urethane and methacryloxypropyl trimethoxysilane. Both are applied as described previously [16]. It has been found that the urethane silane reacts well with most resists, but better adhesion is obtained for mPSS-CHMA with methacryloxypropyl trimethoxysilane.

2.2 UV curing

Full details on sample preparation are given elsewhere [11,16], except that an improved sample assembly method is now used. All samples are prepared under nitrogen in a glove box to avoid incorporation of water vapor and oxygen, which are known to inhibit curing of vinyl ethers [19] and acrylates/methacrylates [20], respectively. 1-3 μ L of a curable resist are placed onto a prepared silicon substrate and immediately covered with a release-coated quartz plate. The samples were irradiated with filtered 365 nm light to the desired dose, typically 100-200 mJ/cm².

2.3 Characterization

A variety of techniques are used to measure properties of interfaces, uncured resist and cured resist [10,11,13,16,21] and are summarized here. Real-time weight loss measurements using a modified thermogravimetric analyzer allow determination of the volatility of the resist

components which affects the stability of the resist composition after dispense and before template placement. Resist viscosity measurements are made with a rheometer. The cure kinetics and extent of crosslinking are evaluated by photo-rheometry, photo-differential scanning calorimetry (photoDSC), gel fraction and infrared spectroscopy measurements. Release coatings on template material surfaces are characterized by x-ray photoemission spectroscopy (XPS), ellipsometry (to determine thickness) and contact angle measurements. Adhesion is measured by double cantilever beam delamination tests, with subsequent examination by XPS to determine the location of the crack path.

Almost all adhesion tests were done on virgin specimens in order to ensure consistent initial conditions. In some cases quartz bars were reused to assess surface chemical changes following multiple debonds. Durability tests of release coatings have not yet been performed since the current focus of our work is on understanding trends in chemical and mechanical behaviors across a wide variety of materials.

Although patterning is not the main objective of our studies we have performed limited testing to assess imprintability of our formulations. This was primarily done with a home-made patterned template on a modified Suss contact aligner. Some imprints were also made using a Molecular Imprints Imprio 55 at the University of Texas at Austin.

Nanoindentation measurements to determine viscoelastic properties of selected fully cured films are made but not included here. Determination of cure-induced shrinkage and the resulting stress in cured resists, and stresses in the inorganic release coatings, which will affect the shape of the cured pattern, are planned.

3. Results and Discussion

The data reported here summarize our progress in characterizing two aspects of nanoimprint materials systems: resist chemistry, especially formulation integrity and degree of cure, which impact resist structure, and debonding chemistry and physics of diverse resist-release layer combinations.

3.1 Characteristics of resist formulations

3.1.1 Viscosity and volatility

In order to rapidly and completely fill the surface relief of the template, the resist must be able to flow. This can be achieved by working with

Figure 1. Viscosities of a series of formulations containing mPSS and IBMA, CHMA or EHMA reactive diluents.

Table 1. Relative evaporation rates of selected resists

Resist	Weight loss. %/s
<i>SiA</i>	0.04
<i>mPSS-IBMA</i>	0.002
<i>mPSS-EHMA</i>	0.003
<i>mPSS-CHMA</i>	0.008
<i>DVE</i>	0.003
<i>BnVE</i>	~0

very low viscosity fluids or by applying sufficient pressure to the template for more viscous resists [22]. Wetting characteristics of the contacted surfaces also play a key role [23].

Drop dispense resists require viscosities in the range of 30 cps or less to achieve low residual layers [2]. Such low viscosities can be achieved by selecting only low viscosity components, as in the case of the acrylate and vinyl ether formulations, or by combining suitable low viscosity reactive diluents with high viscosity components to reduce viscosities to a suitable level as for mPSS-based methacrylate formulations, as shown in Figure 1.

The volatility of the resist components is a critical consideration [9], particularly if the components do not all evaporate at the same rate and droplets are dispensed serially rather than in parallel. Incongruent evaporation will lead to large variations in resist composition from location to location on the substrate, affecting curing and

properties of the cured polymer. Two volatility measurement techniques have been reported: size measurements of a sessile drop [9], and weight measurements of relative volatility at constant surface area using a microbalance [10]. Results of weight measurements of selected resists are shown in Table 1. They show that relative volatilities can vary substantially, with the vinyl ethers having the best combination of low volatility and low viscosity [10].

3.1.2 Reaction rates

The UV-induced polymerization rates of free radical and cationically cured formulations have been studied intensively [20]. In general, the curing reaction has two distinct stages: an initial rapid stiffening to form a solid followed by a slower reaction as shown in Figure 2 for *SiA* resist. It is frequently the case that 100% cure is not achieved, which means that the cured resist should be considered as a highly crosslinked solids plasticized with small molecules [11]. This polymer structure affects its viscoelastic properties, which are important for clean template release.

PhotoDSC data of this type can be converted to reaction rate curves as shown in Figure 3, which compares the *SiA* reaction rate to those of a series of mPSS-based resists. In addition to providing a good example of the well-known reaction rate differences between acrylates and methacrylates, the data show the pronounced effect of diluent selection on the rate and degree of cure. The diluent series, IBMA, CHMA and EHMA, spans a wide range in T_g [11]. The initial rates of reaction follow the order CHMA > IBMA > EHMA. Gel fraction measurements show the same trend, with

Figure 2. Extent of conversion of double bonds (degree of cure) of *SiA* as a function of dose by photoDSC.

Figure 3. Cure rate of *SiA* and the mPSS resists as a function of extent of conversion of double bonds. The mPSS:diluent weight ratio is 1:2.

Figure 4. Change in storage modulus G' as a function of time during exposure to UV light by photorheology. The mPSS formulations are mPSS:diluent 2:1 and have reduced photosensitizer concentrations to accommodate the instrumentation requirements. The trends in modulus increase follow the trends in reaction rates for the standard formulations in Figure 3.

values of 78% (*mPSS-CHMA*), 70% (*mPSS-IBMA*) and 63% (*mPSS-EHMA*). This is consistent with known reactivities of these methacrylates [24], however the extent of reaction for *mPSS-CHMA* measured by photoDSC (Figure 3) was somewhat lower than that found by gel fraction which suggests the polymerization reaction is not completely exothermic in this system. According to the literature on curing of high viscosity methacrylates it was expected that the order should follow that of diluent viscosity and T_g , EHMA >

CHMA > IBMA, the underlying physics being that the reaction rate is controlled by diluent mobility [25]. That this is not observed indicates that diluent reactivity is more important than mobility in affecting extent of cure in these low-viscosity fluids.

The reactivity trend is found in other mPSS-diluent weight ratios. Photorheology studies of stiffening during the initial phases of cure show that the storage modulus increases with a relative rate also governed by diluent reactivity as shown in Figure 4. Nanoindentation measurements on fully cured films show the same trends [28]. Storage and loss modulus curves for several diluent ratios can be used to characterize the polymer that is formed. Gel points are observed for formulations containing CHMA, while IBMA-containing formulations vitrify before becoming fully crosslinked [11].

3.2 The release layer

Because of its extremely low surface energy, a fluoroalkyl silane release layer was identified early on as a useful means of reducing resist-template adhesion [25]. Its durability was found to be low, however, limiting the numbers of imprint-cure-release cycles that could be performed before requiring surface regeneration. Through systematic surface composition studies before and after an imprint cycle it was found that significant chemical degradation of the release layer occurs [13,16]. We have examined changes in fluoroalkyl silane layers after curing numerous resist formulations, and for both free radical and cationic cure systems very similar results are found. Typical XPS data are shown in Figure 5 for *SiA*. A virgin 1-2 nm thick fluoroalkyl silane layer will have about 45% F in the surface region. After curing and separation, about half the fluorine remains. This fluorine loss is not due to transfer of weakly bound silanes to the resist surface: the data show that little F remains on the resist, indicating that the silanes are vulnerable to chemical attack by free radicals or ions and that the release layer has been partly converted to volatiles. If free radicals are present, abstraction and displacement reactions can occur, forming smaller fluoroalkyl fragments [27]. Proton attack at siloxane bonds occurs readily [28].

Having a low surface energy alone does not ensure that a release layer will be useful. To identify better criteria we have explored two alternatives. The first is identification of release materials that are unreactive toward the curing resist, such as DLC [17] and metal oxide and

Figure 5. *SiA* carbon XPS data showing changes in the fluoroalkylsilane release layer after a single cure cycle, and the surface composition of the cured resist after release.

nitride films [18,21], which are used successfully with selected resist-release combinations. The second is identification of release materials that can undergo very specific interactions with a resist as it cures in order to inhibit chemical attack. This has been demonstrated for cationic cure resists by applying an amine to a template surface to trap protons [29].

Results of studies of specific resist-release combinations are presented in the following section.

3.3 Resist characteristics and template release

A broad range of phenomena are associated with release of a template from a newly cured resist depending on the chemical properties of the interface and the resist structure. Because these

investigations are still in an early phase common principles linking all the physical systems have not yet been identified. We present a selection of results here to illustrate some trends that have been observed.

3.3.1 Releasing from fluoroalkyl silanes

Although the fluoroalkyl silanes degrade with use, it is instructive to use it to compare debonding characteristics of a variety of resists from a single type of release layer, with a particular focus on the fracture process itself. Selected fracture energies measured by double cantilever beam are presented in Table 2. It is evident that the characteristics of the release layer alone do not control the debonding process. The chemical composition of the resist is a far more important variable.

From fracture mechanics it is known that the fracture energy of an adhesive polymer film is inversely proportional to the modulus of the material(s) at the crack path [30]. Therefore it might be supposed that degree of cure and crosslinker concentration could be key parameters, with more highly crosslinked materials having lower adhesion because the materials are relatively stiffer and act to confine strain energy close to the crack tip. However, the data in Table 2 [13,16,29] show that fracture energy is unrelated to crosslinker concentration or degree of cure (Figure 3).

More subtle factors play a role. For example, a study of the surface compositions of three mPSS-containing formulations showed that there is significant segregation of resist components to the surface of the resist prior to cure that results in interfacial inhomogeneities in the cured material [21]. While the composition (as measured by

Table 2. Crosslinker content (functionality mole%) and fracture energies G_c (J/m²) for resists cured in contact with a fluoroalkylsilane release layer.

Resist	Crosslinker %	G_c
<i>SiA</i>	20	0.65
<i>IOA</i>	29	1.1
<i>mPSS-CHMA</i>	37	0.55
<i>mPSS-EHMA</i>	41	0.8
<i>mPSS-IBMA</i>	44	0.25
<i>DVE</i>	100	4.5
<i>SiVE</i>	100	5.6
<i>BnVE</i>	100	>10

Table 3. Vinyl ether resist surface atomic concentration ratios by XPS

Resist	F/C	O/C
<i>BnVE</i> , cured	0.08	0.22
<i>BnVE</i> , uncured	0.03	0.17
<i>DVE</i> , cured	0.16	0.43
<i>DVE</i> , uncured	0.03	0.37

silicon content) of the interfacial region of *mPSS-IBMA* is the same as in the film bulk, the near-surface silicon content of the *mPSS-CHMA* film is reduced by about 25%, and that of the *mPSS-EHMA* film by 50%. This indicates that the region of the film nearest the template surface is enriched in reactive diluent for these two formulations, necessarily reducing the local degree of crosslinking and possibly affecting other important aspects of the structure of the polymer. This segregation is the only materials characteristic that is clearly associated with variations in fracture energy.

The vinyl ether systems contain a fluorinated PAG which becomes enriched in the near-surface region when a fluoroalkyl silane release layer is used [29]. Data are presented in Table 3. Variable angle XPS of a cured and debonded *DVE* surface was used to determine whether the increase in F concentration was simply due to surface reactions with the fluoroalkyl silane layer. The data showed that the top surface had a F/C ratio of 0.42 while the average ratio over a 2-3nm escape depth was 0.16 as given in Table 3. Although the scattering physics involved is too complex to be interpreted quantitatively at this stage [31], simple estimates indicate that the average F/C ratio is too large to be attributable to an F-rich surface on 2-3nm of polymer with the F/C ratio of the uncured resist. This enrichment in PAG leads to relatively large acid concentrations at the release layer, which will increase the local rate of acid-related chemistry. This enrichment will also tend to reduce the concentrations of polymerizable resist components near the interface, which will reduce the degree of crosslinking. Either of these effects, in addition to resist-release chemical bond formation, may be implicated in the much higher adhesions observed experimentally (Table 2).

The acrylate resists investigated to date have been found to have generally higher adhesion to fluoroalkyl silane release layers than the mPSS-based resist systems (Table 2), for reasons that

Table 4. Acrylate resist surface atomic concentration ratios by XPS

Resist	F/C	O/C	Si/C
SiA, cured	0.06	0.35	0.11
SiA, uncured	0	0.37	0.13
IOA, cured	0.01	0.20	--
IOA, uncured	0	0.24	--

are not yet understood. Interfacial composition data are presented in Table 4. As will be discussed below the SiA resist tends to undergo cohesive failure when debonded from non-fluorinated release layers. Since the fluoroalkylsilane surface chemical composition prohibits a similar assessment, the interfacial characteristics of the SiA-fluoroalkyl silane system are as yet unknown. Resist surface carbon concentrations are elevated compared to the uncured resist, pointing to composition differences at the interface where fracture occurs.

Addition of a non-functionalized fluorinated surfactant has been described as being beneficial [14,32-34], particularly when there is a pre-existing fluoroalkyl silane layer on the template [34]. Indeed, we have measured a reduction in fracture energy G_c from about 1 J/m² to 0.5 J/m² when the surfactant Zonyl FSO-100 is added to IOA [14] and the formulation is cured in contact with a fluoroalkyl silane release layer. There is an apparent suppression of fluorine loss from the template surface during debond however it is not possible to assess the total F concentration changes in the system. The durability of a fluoroalkyl silane-coated template's release properties when used with a surfactant-containing resist through many debonds remains to be investigated [34].

3.3.2 Releasing from non-fluorinated release layers

3.3.2.1 Vinyl ethers

Fracture energies for vinyl ether resists can be reduced significantly if non-fluorinated release layers are used. Data are presented in Table 5 for several selected release systems along with the F concentrations at the resist surfaces which are a marker for resist PAG segregation. These data are to be compared to those in Table 3. Some interesting trends are found. Use of metal nitride or oxide release layers results in significantly lower PAG segregation, accompanied by a reduction in fracture energy. The metal-containing release surface compositions are unchanged except

Table 5. Selected vinyl ether resist surface compositions by XPS and fracture energies G_c (J/m²)

Resist	release	G_c	F/C	O/C
<i>BnVE</i>	TiNx	2.14	0.02	0.23
	TaOx	0.9	0.04	0.28
	AlNx	0.57	0.06	0.23
<i>DVE</i>	TiNx	3.0	0.05	0.43
	TaOx	1.1	0.04	0.43
	CuOx	0.27	0.05	0.43

Table 6. Resist and release surface atomic ratios by XPS

Surface	F/C	O/C	N/C	Si/C
APTES, unused	0	1.63	0.05	0.68
APTES, 1 st use	0.25	1.62	0.06	0.69
<i>SiVE</i> , cured	0.02	0.39	0.001	0.04
<i>SiVE</i> , uncured	0.02	0.39	0.001	0.04

for the presence of small amounts of F. It is not yet clear whether the lower G_c values are a result of formation of a less plastic material near the resist surface, or whether the fluoroalkyl silane layer was acting as an adhesion promoter rather than an anti-sticking layer and its absence weakens the interface.

The use of the amine APTES as an active release layer reduces the interfacial fracture energy for *SiVE* resist from 5.6 to 2.1 J/m². Surface analyses are presented in Table 6. The stability of a reactive molecular layer that is most commonly used as an adhesion promoter [35], not an adhesion inhibitor, is of concern in this reactive environment. The XPS data show that the APTES layer itself is not degraded because the nitrogen concentration remains constant. Although there is no significant amount of resist on the layer, it does contain a small amount of fluorine after a first debond, indicating that some surface reactions do occur. The data suggest that by providing strongly basic sites for reaction with protons formed by the PAG, local degradation of the release layer by siloxane bond attack [28] is inhibited. The data also show that the resist composition is closer to that of the formulation, therefore PAG segregation

is reduced. All of these factors may be important for the much lower fracture energy observed.

3.3.2.2 Acrylates

SiA and *IOA* provide interesting examples of other phenomena encountered during template release. Fracture energies are presented in Table 7 for selected metal nitride and metal oxide release layers. It can be seen that unlike the vinyl ethers, fracture energies are not necessarily reduced when metal-containing release systems are used with these resists, and they can be found to be higher. Specific resist characteristics are likely to be responsible. As shown in Figure 6, *IOA* resist has a high fracture energy and in general very strong crack arrest behavior during debond, consistent with significant resist plasticity. *SiA*, on the other hand, can have significantly weaker interfaces with the metal-containing release layers. XPS studies of the crack paths reveal that interfacial fracture is not clean, however (Table 7): debonding occurs near the resist-release layer interface, not along it. There is significant silicon on the release layer surface, indicating that surface reactions with (3acryloxypropyl)tris(trimethylsiloxy)silane cause a weakened layer to be formed inside the resist. This indicates that this monomer is not suitable for nanoimprint applications with metal-containing release systems.

Table 7. Selected release surface atomic ratios by XPS and fracture energies G_c (J/m^2)

Resist	Release	G_c	C/M	Si/M	O/M
<i>SiA</i>	TaNx		0.71	0	1.88
	TaNx	0.5	2.08	0.32	2.75
	TaNx	2.27	1.03	0	1.93
<i>IOA</i>	TiNx		0.76	0.11	1.25
	TaNx	0.54	6.75	1.3	5.18
	TaNx	3.78	0.92	0.08	1.23
<i>SiA</i>	TiOx		0.83	0.08	2.58
	TiOx	1	4.99	0.9	5.3
	TiOx	5.96	0.93	0.07	2.41
<i>SiA</i>	AlOx		0.5	0.09	2.59
	AlOx	0.1	0.8	0.13	2.43
	AlOx	1.28	0.73	0.1	2.47

Figure 6. Force-displacement data measured for *IOA* and *SiA* during double cantilever beam tests of fracture from TaNx-release-coated quartz. Compressive displacement was used to measure compliance (examples are marked with boxes). The abrupt crack extension zones (force drops) seen for *IOA* but not *SiA* are characteristic of the marked crack arrest behavior found in *IOA* resist.

3.3.2.3 mPSS-IBMA

DLC is a complex material, however its surface chemistry is considerably simpler and potentially less reactive than a fluoroalkyl silane release layer because it presents primarily C-C bonds at the surface, with a minority of reactive sites such as C=C bonds and C-H bonds [36]. This release layer concept was tested with *mPSS-IBMA* resist [17]. It was found that the surface composition of the DLC release layer after debond was unchanged, indicating that fracture occurred cleanly at the DLC-resist interface. The fracture energy was reduced from 0.25 to 0.17 J/m^2 despite the higher energy (contact angle) of 68°, while that of our fluoroalkyl silane coatings is 113°. The reduction in fracture energy is not attributable to changes in resist surface composition or to use of a lower surface energy release layer, pointing to lower surface reactivity as an important factor.

3.3.2.4 mPSS-CHMA

The *mPSS-CHMA*-release layer systems provide more extensive evidence that surface energy is not generally correlated to fracture energy in UV cure nanoimprint materials. Fracture data for a range of metal oxide and metal nitride release layers as well as fluoroalkyl silane are presented in Figure 7. Although the fundamental

Figure 7. Fracture energy data for *mPSS-CHMA* resist as a function of release layer contact angle.

physical reason for this phenomenon is not yet well understood, it is possible that it is related to the nature of the fracture process which is controlled by strain energy dissipation through surface bond breaking and plastic deformation of the materials near the interface [30]. It may be that the resist structure rather than the interface plays an important role in controlling adhesion strength in this system. This finding may not be general for weak interfaces. Further research is required to identify the key relationships between resist components and interfacial interactions that govern template release. The contact angle of the template release coating does affect uncured resist flow, however, and release layer selection should be coupled to formulation design.

4. Conclusion

Consideration of nanoimprint materials as strongly coupled resist-release systems enables detailed insights to be gained to the factors that affect interfacial adhesion and clean debonding at the resist-template interface. Mechanical properties of cured resist materials, surface interactions that influence resist segregation, and chemical reactions between components in the curing resist and the release layer itself all play important roles. There is considerable variation in the chemical characteristics of release layer surfaces in contact with curing systems. Fluoroalkyl silane release layers are altered by a single debond, while alternative molecular and inorganic release systems may be more stable after repeated template removal. From data acquired so far it seems unlikely that a universal release layer that

works well with all types of resists will be easily identified. Although the resist systems discussed here are all low viscosity fluids, many of the concepts will also apply to spin-on UV-cure resists.

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