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Impact of photoinitiators on the photopolymerization and the optical properties of inorganic–organic hybrid polymers

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Sol-gel synthesis allows one to produce inorganic–organic hybrid polymer materials which can be functionalized in order to tailor their physical and chemical properties. Besides, the resulting material properties are significantly influenced by further technological processing of the materials in thin film technology, i.e., the photochemical and thermal curing of the materials. In order to investigate the relationship between technological processing and material properties, a model system containing methacrylic groups as organically polymerizable units is chosen. The degree of conversion of the C=C double bond of the methacrylic group in dependence of the ultraviolet (UV) initiator concentration upon processing is characterized using Fourier-transform infrared spectroscopy. The data are correlated to measurements of the refractive indices at selected wavelengths. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1647706]

Over the last decade, silicate-based inorganic–organic hybrid polymers (ORMOCER®) have attracted great interest due to their physical and chemical properties resulting synergistically from their hybrid nature.[1,2] They are synthesized by sol-gel processing, which offers a large flexibility in polymer synthesis by variation of the catalysts, alkoxysilane educt, and temperature. This flexibility enables one to tailor their properties as recommended by the application.[3–6]

Upon sol-gel processing of alkoxysilane precursors, inorganic-oxidic nanoscale structural units $(0.7–1 \text{ nm})$[7] are formed which are organically modified. As organic polymerizable unit, typically acryl or styryl functionalities are used which account for the negative resist behavior of the hybrid resins. This allows one to pattern them by UV irradiation and thus makes them attractive for all kinds of wafer-scale applications.

Although the materials have been established already for a variety of applications,[1–6] there has been little effort so far to correlate their processing, i.e., their photochemical or thermal treatment, to their physical properties such as, e.g., optical properties. In this letter, the influence of the UV initiator concentration on the degree of conversion of the methacrylic side chain (henceforth referred to as degree of polymerization) within a hybrid polymer model system is followed by Fourier-transform infrared spectroscopy (FTIR) spectroscopy. In addition, the impact of the UV initiator concentration on the refractive index is characterized and discussed with respect to the network formed upon processing.

In order to shed light on the polymerization process and its dependence on the thin-film processing, particular focus will be on a two-component hybrid polymer model system (henceforth referred to as system I) typically used for waveguide applications. Its synthesis is reported elsewhere.[8] In this system, methacrylic groups are attached to inorganic-oxidic units in order to account for the photochemical cross-linking. The total size of these organically functionalized inorganic-oxidic units ranges between 2 and 5 nm.[7]

As photo-initiator, 2-benzyl-2-dimethylamino-4'-morpholinobutyrophenone (IRGACURE 369, Ciba-Geigy) was used which forms radicals (Norrish type I mechanism) upon UV irradiation.[9] For the experiments, the UV initiator concentration was varied between 0.25 and 8 wt %. In order to generate layers of several μm thickness, the resin (viscosity $\eta = 6–8$ Pa s at room temperature) has to be diluted with a solvent (propyl acetate). The mixture was then filtered through a 0.2 μm filter in order to guarantee highest optical quality materials.

The preparation of the hybrid polymer layers was carried out using Si and glass substrates. For the FTIR measurements, transparent p-doped Si(100) wafers were used as substrates. The lacquer was applied onto the substrates by spin coating, followed by a thermal treatment at 80 °C on a hotplate for 1 min (prebake). The layers were then exposed to UV light ($\lambda = 350$ nm) in a conventional mask aligner (Suss, MA45, power density approximately 17 mW/cm², 30 s). After the UV processing, the samples again were thermally treated on a hotplate at 80 °C for 1 min (postexposure bake), followed by a short cool-down period. Subsequently, the layers were developed for approximately 30 s using a mixture of methylisobutylketone (MIBK) and 2-propanol (1:1). Finally, the samples were thermally cured at 150 °C for 3 h, which was found to leave the sample with no residual thermo-mechanical stress upon processing.[10] The thicknesses of the final cured layers varied between 6 and 8 μm. For the characterization of the refractive index n, glass substrates have been used which were prepared analogously to the samples for the FTIR measurements.

The FTIR measurements were performed in a Nicolet MAGNA-IR spectrometer 760, which has a resolution of 4

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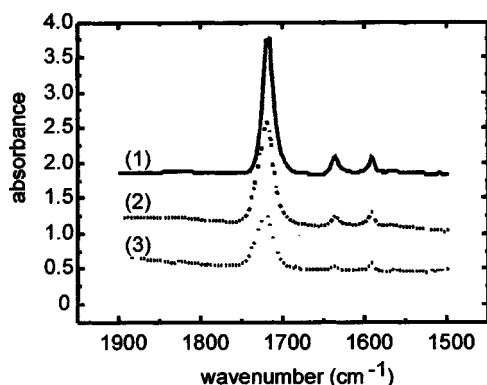
1105

FIG. 1. FTIR spectra of system I in dependence of the processing condition. (1) Wet layer, (2) layer after UV exposure and development, and (3) finally cured layer. For a better presentation, the peaks are shifted vertically.
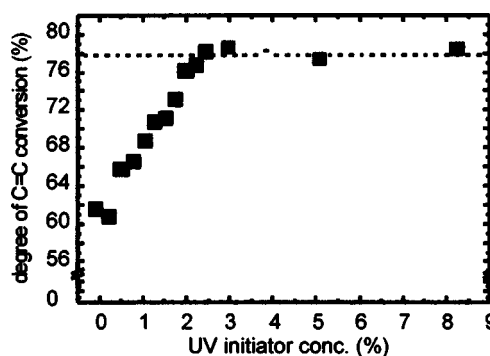

FIG. 2. Evaluated degrees of polymerization of system I from FTIR spectra in dependence on the UV initiator concentration. The spectra were recorded on finally processed layers.

cm^{-1}. Each processing step was characterized separately for each initiator concentration, thus enabling one to completely follow the impact of processing on the coated layer.

Figure 1 shows a zoom into FTIR spectra of a hybrid polymer layer for different processing steps, particularly for the as-coated layer [wet layer, (1)], after UV exposure (2), and after the final thermal curing (3). Three individual peaks can be distinguished for each processing step.

At 1640 cm^{-1}, the C=C stretching vibrational mode resulting from the methacrylic groups appears. Besides, a peak at 1720 cm^{-1} is observed which results from a methacrylic C=O stretching vibrational mode.[11] The position of the C=O peak remains nearly unchanged (shift 2.5 cm^{-1}). The stretching vibrational mode of the C=C peak at 1640 cm^{-1} resulting from the methacrylic side chains changes its intensity upon photochemical processing, which is followed by FTIR spectroscopy. Although a tiny shift of the C=O peak is observed and thus a change in absorption cross section has to be considered, this peak can be used as an internal reference peak for a semiquantitative determination of the degree of polymerization of system I.

The third peak which appears at 1590 cm^{-1} results from the aromatic C=C double bond stretching vibrational mode of the phenyl groups within the coated layer. Although these species are photochemically nonreactive, a decrease in peak intensity is observed for the thermally cured layer. As determined from gel permeation chromatography, hexaphenyltricyclosiloxanes as well as split products are also present in the inorganic–organic resin. The final thermal curing step might result in an evaporation of these species, thus accounting for the decrease in peak intensity. This is supported by thermo-gravimetry which will be published elsewhere.

In order to account for film thickness changes for the different samples, the degree of polymerization N of the C=C double bond is calculated using relative peak intensities,

$$N = 100 \times \left\{ 1 - \left(\frac{A_{C=C}}{A_{C=O}} \bigg/ \frac{A'_{C=C}}{A'_{C=O}} \right) \right\}, \qquad (1)$$

where $A_{C=C}$ and $A_{C=O}$ are the integrated peak intensities of the C=C and the C=O double bonds of the respective processed sample, respectively, while $A'_{C=C}$ and $A'_{C=O}$ are the integrated peak intensities of the wet layers. Additionally, it

was assumed that each initial wet layer only contains 100% of nonreacted methacrylic C=C double bonds.

As is obvious from Fig. 1, the C=C peak intensity from the methacrylic groups decreases significantly upon processing from 100% (wet layer) down to approximately 35% (UV exposed and developed layer) and finally down to about 25% (thermally cured layer), i.e., 75% of the C=C double bonds from the methacrylic groups are polymerized.

Since the optical properties are determined from completely processed layers, particular focus will now be on FTIR spectroscopic measurements of the finally processed layers. Figure 2 presents the evaluated degrees of polymerization of the C=C double bond from the FTIR spectra using Eq. (1) in dependence of the UV initiator concentration, determined after the final thermal curing step. Each data point corresponds to an average value measured on three different spots of the samples. In principle, two different slopes are observed in the viewgraph. In the range between 0.25 and 3 wt % UV initiator concentration, a continuous increase of the degree of polymerization from approximately 62% up to 78% occurs, whereas for initiator concentrations above 3 up to 8 wt % the degree of polymerization saturates at about 78%. From the point of view of the final polymerization of the layers, an UV initiator concentration of 3 wt % is sufficient to polymerize the layers as completely as possible for the chosen processing parameter set.

From the FTIR data in dependence of the UV initiator concentration, an increase in the degree of polymerization of about 16% was evaluated beginning with a wet to a finally cured layer. As mentioned earlier, the hybrid polymer consists of organically functionalized inorganic-oxidic units. The detailed structure of the resin, however, is not known completely. From multi-nuclei magnetic resonance measurements, a structural model was derived by Buestrich *et al.*,[8] which shows that system I consists of a mixture of chains and rings, where neither the lengths of the individual units nor the amount of the respective structures within the resin are known.

In order to understand how the UV initiator influences the degree of polymerization of the hybrid polymers, the radical chain polymerization[12] process will be considered. The two slopes of the degree of polymerization of the resin in dependence of the UV initiator concentration [cf., Fig. (2)] can be explained as follows, where it is assumed that the initiator is homogeneously distributed within the resin. If the
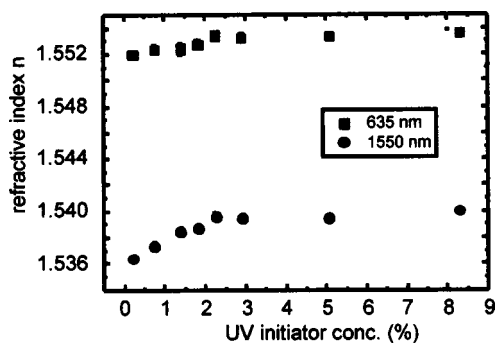
FIG. 3. Refractive index of system I in dependence of the UV initiator concentration, determined at 635 and 1550 nm, respectively.
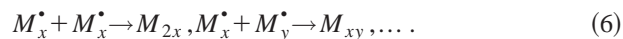
UV initiator is very diluted (low concentrations) in the resin, photochemically induced cross-linking is initiated at each point where a radical is formed.[9] The reactive part is species $I^{\bullet}$ [cf. Eq. (2), starting reaction]. Both parts of the UV initiator resulting from this reaction are photochemically active, initiating further polymerization [cf., Eqs. (3)–(5)] until the reaction is terminated [Eq. (6)]:

$$I \xrightarrow{h\nu} I^{\bullet} + I'^{\bullet}, \tag{2}$$

$$I^{\bullet} + M \rightarrow M^{\bullet}, \tag{3}$$

$$M^{\bullet} + M \rightarrow M_2^{\bullet}, \tag{4}$$

$$\cdots$$

$$M_{x-1}^{\bullet} + M \rightarrow M_x^{\bullet}, \tag{5}$$

e.g.,

$$M_x^{\bullet} + M_x^{\bullet} \rightarrow M_{2x}, M_x^{\bullet} + M_y^{\bullet} \rightarrow M_{xy}, \ldots. \tag{6}$$

In the beginning of the polymerization reaction, the rate of polymerization is increased due to the buildup of radical concentration in the system. Subsequently, polymerization takes place at a constant rate.[12] With further proceeding of the polymerization reaction, the polymerizable units will be depleted, thus resulting in a termination of the polymerization reaction [Eq. (6)].

Thus, it seems likely to state that a small amount of initiator leads to large structural units within the finally processed layer containing still an amount of nonreacted C=C, while a large amount will lead to smaller structural units with less nonreacted C=C double bonds.[13] Consequently, higher initiator concentrations would lead to a denser packing of the structural units, thus resulting in a denser material. Contrary to this, small photoinitiator quantities will lead to larger units where the degree of polymerization cannot be increased due to sterical hindrance of the large structural units.

This is supported by refractive index measurements from finally cured layers coated on glass substrates. Figure 3 pre-

sents refractive index measurements in dependence of the UV initiator concentration at 635 and 1550 nm, respectively. The refractive index increases from 1.536 up to 1.539 (at 1550 nm) for initiator concentrations up to around 3 wt %. For higher initiator concentrations, the refractive index has reached a constant value, which is in good agreement with the observation of a constant value for the degree of polymerization (cf., Fig. 2). It has to be mentioned, however, that investigations on the optical loss in dependence of the UV initiator concentration have still to be performed.

In conclusion, the degree of polymerization of a model inorganic–organic hybrid material system upon UV exposure was followed by FTIR spectroscopy in dependence of the UV initiator concentration. It was shown that the degree of polymerization increases with increasing UV initiator concentration. For concentrations above 3 wt %, no further increase in the degree of polymerization is observed. The results of the FTIR measurements directly correlate with refractive index data.

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