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Labile Hyperbranched Polymers Used as Nanopore-Forming Agents in Polymeric Dielectrica

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Summary: Hyperbranched polyesters containing labile triazene units in the main chain have been synthesized and characterized. These structure decompose photochemically upon UV irradiation and thermally above 160 °C. Homogeneous incorporation of these globular, functional polymers in thermostabile polymer matrices (polyimides and BCB polymers) was possible. Smooth films from blends of thermolabile matrix and up to 50% hyperbranched polymers could be prepared and have been studied as insulating material in microelectronic multilayer applications.

Introduction

Special hyperbranched, arborescent graft, or hyperbranched-co-star polymers which e.g. degrade thermally at a certain temperature can be used as pore forming templates in a temperature stable matrix.[1] This can lead to porous nanomaterials which is e.g. of interest in chromatography and for the formation of aerogels and xerogels. Hence, Boury et al.[2] described the use of dendrimers and arborols with carbosilane cores for the preparation of hybrid xerogels. In this regard, Muzafarov et al. [3] studied the degradation behavior of hyperbranched poly(bis(undecenyloxy)methylsilane)s. Of high interest is also the preparation of nanoporous polymers with low dielectric constants for use as novel interlayer dielectric material (ILD)[1,4,5]. The high demand for faster computers, higher storage capacities and at the same time smaller devices requires the development of new dielectric materials with dielectric constants below 2.5 or even 2 for chip production of very high structure density. Already realized porous systems have reached dielectric constants from $\varepsilon_r = 2.5$ [6] to approximately 1 as found for aerogels [7]. The decrease of ε_r is given by the inclusion of air filled cavities which have been formed by degradable star or dendritic polymers or by phase separated block

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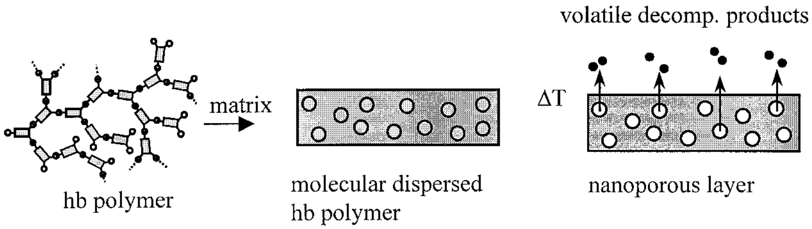
copolymers with labile segments[9,10]. A major problem of nanofoams is their processability or compatibility with the integrated circuits (mechanical stability, adhesion, stability towards CMP process or selective etching). By the use of labile polymers as pore forming material in a stable polymer matrix, one should be able to introduce porosity into ILD polymers already being used for microelectronics. Important requirements for the success of the concept is a high compatibility of the hyperbranched polymers - or any globular shaped polymer - with the matrix polymer to achieve a molecular dispersion of the globular molecules. Only in this case, pore sizes below 10 nm might be achieved after complete decomposition of the labile molecules into volatiles (Scheme 1). The matrix polymer has to be temperature stable with no softening while the degradation of the globular molecules takes place. Otherwise, the pores will collapse. For low k materials, the matrix itself should exhibit already dielectric constants below 3 and the content of the pore forming material should exceed 20 %. Furthermore, there exist many other requirements for polymeric materials as dielectric materials in multilayer microelectronic applications which correspond to the conditions of the processing of chips, e.g. high temperature stability, low leakage current, high breakdown voltage, low metal migration into the polymer[11], good adhesion to metal and barrier layers, etching selectivity, low water absorption, chemical mechanical polishing compatibility[12,13] a.o.

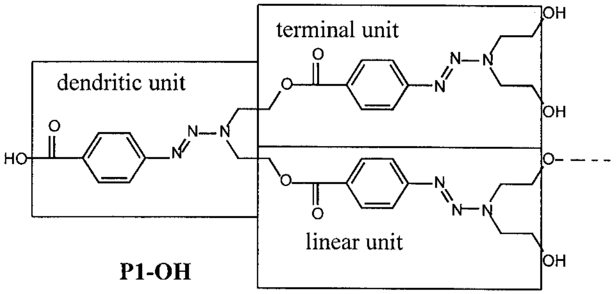


Scheme 1

Results and Discussion

We choose functional hyperbranched polymers containing thermally labile units for this concept. For this, a hyperbranched polymer (HBP) with labile triazene units in each repeating unit (**P1**) was synthesized. Linear polymers containing triazene units in the main chain have proven to be very suitable for polymer ablation processes. They decompose fast upon laser irradiation without leaving solid residues.[14]

For the preparation of the hyperbranched poly(triazene ester)s a low temperature polycondensation of triazene containing AB_2 monomers was performed to avoid undesired early degradation of the labile units. Polymers with molar masses M_n up to 8000 g/mol could be achieved.[15] Scheme 2 shows the structural repeating units.



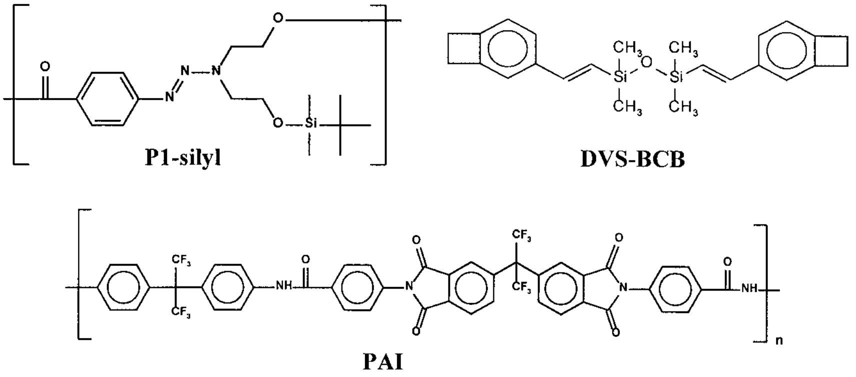
P1-OH

Scheme 2

The structure of the hyperbranched polymers was studied in detail. NMR analysis revealed a statistical degree of branching of 50%. The triazene unit exists in two isomeric forms with the double bond located next to the aromatic ring or next to the aliphatic chain as can be verified by Raman spectroscopy. The polymers can be degraded upon UV irradiation (UV absorption of the triazene functions is in the range of 330 nm) within several minutes or upon thermal treatment. The thermal degradation starts at 160 °C but follows several decomposition steps. About 50% weight loss is observed on isothermal heating at 250 °C after 15 min.

The hyperbranched polymer is very well soluble in polar solvents as expected for a branched structure with polar end groups. However, the high polarity does not allow solubility in solvents also suitable for linear high temperature stable polymers selected as matrix polymers. Therefore, an end group modification was performed to adapt the polarity and solubility and to increase the compatibility of pore forming agent and matrix polymer.

When **P1-OH** is silylated (Scheme 3, **P1-silyl**), one is able to achieve molecular mixtures with different high temperature stable polymer matrixes e.g. a fluorinated polyamideimide PAI or a thermally crosslinkable precursor polymer DVS-BCB (Scheme 3) which is available through Dow Chemicals for application in microelectronics. Figure 1 shows the AFM picture of a homogenous film prepared from PAI and **P1-silyl** (1:1 mixture). The film surface is very smooth and no phase separation can be observed on this scale. After thermal treatment or UV irradiation, surface roughness of films prepared from those mixtures did not increase significantly, however, a small decrease in the refractive index and a change in color of the film could be observed.



Scheme 3

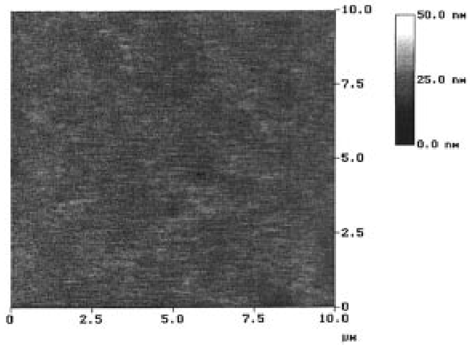
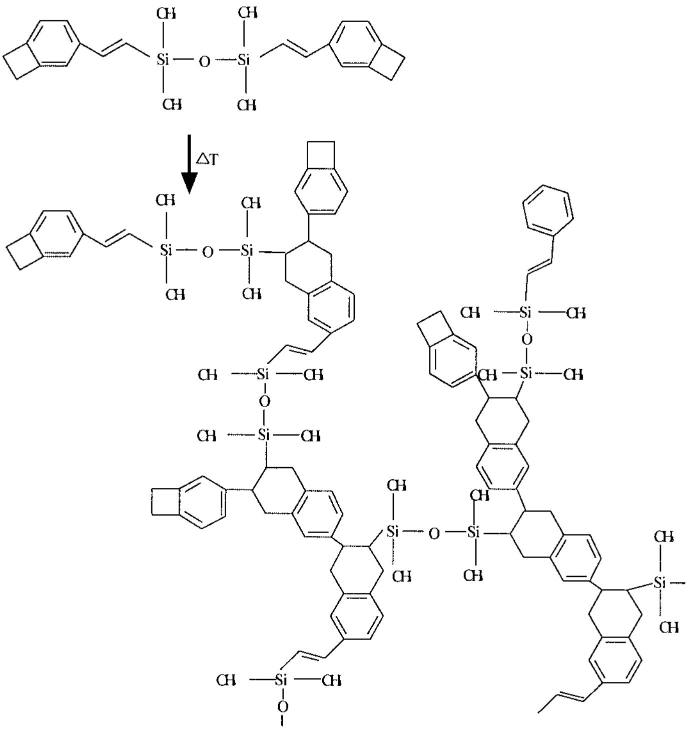


Fig. 1: AFM picture (topology, tapping mode) of PAI/**P1-silyl** 1:1, film spin coated from DMF solution (3 wt%).

DVS-BCB crosslinks thermally between 250 and 300 °C (Scheme 4). Films of DVS-BCB with 16% **P1-silyl** have been prepared on silicon wafers by spin coating, dried at 80 °C, annealed at 300 °C for 15 min. under inert atmosphere, and tested for its dielectric properties (Fig.2)[16]. For analysis, the polymer layer (0.5 to 2.5 µm) was prepared on an aluminum (1 µm) coated Si substrate. In Fig. 2 one can observe the upper Al metal layer (1 µm) which has been lithographically structured into squares of different sizes and subsequently etched. The resulting Al squares are necessary for measuring the dielectric constants.



Scheme 4

It is important to note that the crosslinked polymer layer (BCB after removal of the pore forming agent) was compatible with the lithographic process, resisted the metal etching, and showed sufficient homogeneity and adhesion to the metal layers. The second Al-layer was prepared by sputtering after rinsing the crosslinked polymer layer 10 min. with N-methylpyrrolidon. After the lithographic process the Al-etching was performed with a mixture of concentrated phosphoric acid/acetic acid 7:1.

Visually and using light microscopy one could see that the BCB layers formed without pore forming **P1-silyl** had somewhat less defects and a smoother surface. In addition, the films prepared in the presence of **P1-silyl** were thicker (2.6 μm) than pure BCB layers (1.3 μm) due to a difference of viscosity of the spin coating solutions. Both films had a reduction in film thickness of about 11 to 19% after the annealing (crosslinking and pore formation, respectively. The preparation of the resin blend BCB/**P1-silyl** was performed at a standard lab environment. The lack of a special clean room facility explains the significant increase in the defect density of the MIM devices. However the device yield was sufficiently high enough to perform the electrical measurements. Very positive was the observation that the annealed film which contained **P1-silyl** absorbed after annealing less water (< 1%) than the pure crosslinked BCB film (<1.9%). We concluded that most of the polar components of **P1-silyl** were removed from the film upon the thermal treatment.

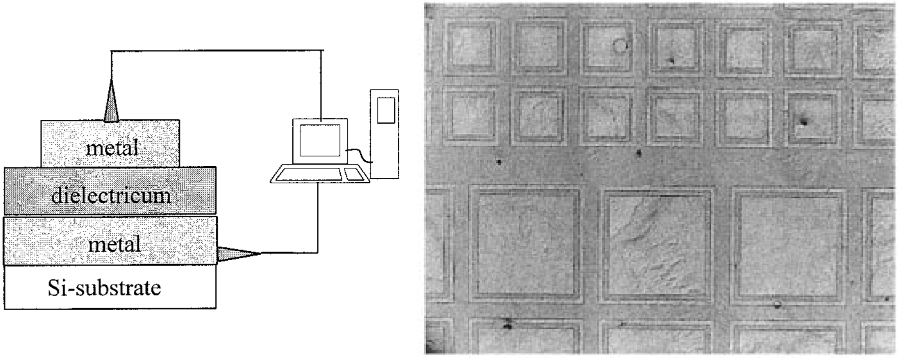


Fig. 2: Schematic representation of an MIM (metal-isolator-metal) structure for measuring dielectric behavior of polymer insulators (left) and the thermally crosslinked (300 °C, 15 min.) blend of DVS-BCB and 16 % **P1-silyl** in a MIM structure (right, Al squares on top).

In the first experiments measuring dielectric constants a significant decrease of 20 % in ε from 2.7 down to 2.2 of the thermally treated blend with the hyperbranched component compared to pure crosslinked DVS-BCB had been observed without significant changes in surface smoothness or homogeneity of the polymer film on the scale of the light microscope. This points to a successful formation of nanopores in a polymeric matrix. A further hint for some changes in the polymer film after thermal treatment can be found in the AFM pictures (Fig.3). There, a certain inhomogeneity in the cured film can be observed which might point to pores in the bulk phase of the film. In this case, a thinner film on silicon substrate had been prepared via spin coating and this film was cured for in total 90 min. between 140 to 200 °C. In Fig. 3 the topography as well as the phase sensitive AFM picture is shown. The latter differentiates between softer and harder domains and shows a granular structure with lighter domains indicating harder areas. These harder areas might be caused by increased crosslinking density, and the darker areas can be explained as a softer part of the polymer film covering an air filled pore. The size of the inhomogeneities is in the range of 8-10 nm.

In further studies also a relatively similar values for the breakdown voltage of 5×10^6 and 4×10^6 V/cm was determined for pure DVS-BCB layers and the pore containing material (DVS-BCB + 16wt% **P1-silyl**, cured), respectively. However, the properties of the polymer film are very sensitive to the temperature regime of the crosslinking/decomposition process, thus e.g. the decease of ε could not be verified when the film preparation conditions were changed slightly. A detailed study on verification of the pores and the reduction in dielectric constant as well as the mechanical properties of the new low k material is in progress.

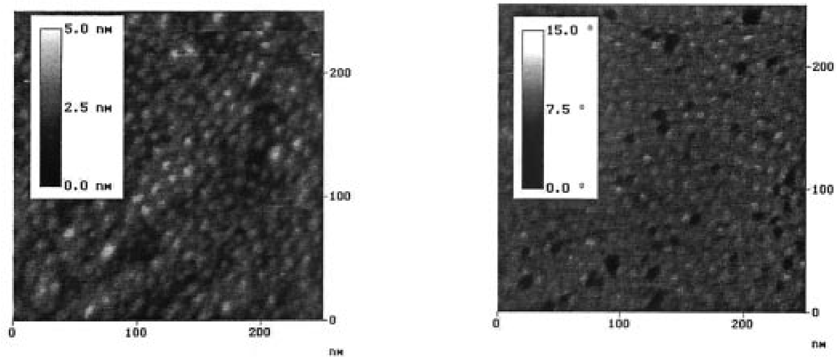


Fig. 3: AFM pictures of the cured film (200 °C, 90 min, 500 mbar) prepared from DVS-BCB + 16 wt% **P1-silyl** (left: topography; right: phase sensitive, picture: 250 x 250 nm).

Up to now, only the crosslinked BCB polymer could be successfully used as matrix for our labile poly(triazene ester) when applied in a microelectronic multilayer system. While also a homogeneous mixture of **P1-silyl** with the polyamideimide (PAI) was obtained, this blend system could not be incorporated into the lithographic process. The adhesion of PAI itself to Al was already lower than that of BCB and after thermal treatment of the blend layer PAI/**P1-silyl**, part of the polymer film fully lost contact to the substrate and measuring ε became impossible.

We can conclude that hyperbranched polymers containing labile groups in the main chain are promising substances as nanopore forming materials in a stable polymeric matrix. Choosing the right matrix and the optimum between crosslinking reaction of the matrix and thermal degradation of the hyperbranched polymer can lead to interesting polymeric dielectrica in microelectronic multilayer systems. In addition, our poly(triazene ester)s allow beside the thermal degradation also a photochemical decomposition. Thus, in case the thermal requirements from the microelectronic processes are lowered in the future, also low temperature pore forming processes are available and therefore polymeric dielectrica with lower thermal stability can be considered.

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