Polycyanurates – low-k materials approach for IC metallization

Schulze, K.[1]; Schulz, S. E.[1]; Schuldt, U.[2]; Kahle, O.[2]; Dreyer, C.[2]; Uhlig, C.[3]; Gessner, T.[1]; Bauer, M.[2]
[1] Chemnitz University of Technology, Center of Microtechnologies, Germany
[2] Brandenburg University of Technology Cottbus, Chair of Polymeric Materials, Teltow, Germany
[3] Fraunhofer Institute for Reliability and Microintegration IZM, Branch Lab Polymeric Materials and Composites in Teltow, Germany

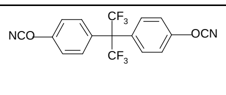
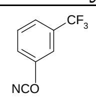
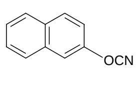
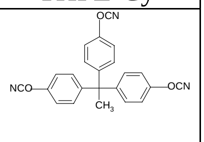
1 Introduction

Development of new low-k materials can be realized by two main attempts. One way is to decrease the dipole strength by using materials with non-polar bonds. The other approach is to decrease the dipole density, which means the reduction of the density of the material itself by introducing porosity or increasing of the free volume.

2 Experimental

For the examinations described here, polycyanurates are the basic materials. They are good candidates for low-k materials of reduced density, since annealed difunctional cyanate ester monomers yield by polycyclotrimerization a polycyanurate network of high symmetry consisting of interconnected triazine rings. The density of the polycyanurates was reduced by copolymerization of difunctional cyanate (ester) monomers with aromatic bulky trifunctional or monofunctional cyanate ester monomers. For the according structural formulas see table 1.

Tab 1:Used monomers

monomer	F10	mCF3Cy
chemical formula		
monomer	2Naphtcy	THPE-Cy
chemical formula		

Copolymerization reduces density without generation of a porous network. That offers the advantage to prevent partially from generally known integration issues of porous materials, like moisture absorption or precursor penetration during other process steps.

Polymers of different amounts of the additional introduced monomer by copolymerization were mechanically (E-Modulus, density, hardness) and electrically (k-value, field breakdown strength, leakage current) characterized. Some electrical measurement results are shown in table 2. For instance for F10, the k-value could be reduced by copolymerization from 2.91 to 2.54.

3 Results

At all the investigated films had very promising electrical properties, especially leakage current was very low and field breakdown strength fulfilled in general the required value of more than 3 MV/cm. By further examinations including curing, thermal stability and influence on k-value were tested.

Tab. 2: Electrical properties of copolymerized and non-copolymerized polycyanurates

Film composition	k	Leakage current J_{leak} [A/cm²]	E_{BD} [MV/cm]
100mol% F10	2.91	$< 5.0\cdot10^{-13}$	-
50mol% F10 + 50mol% mCF3Cy	2.88	$< 1.9\cdot10^{-12}$	7.1
33mol% F10 + 67mol% mCF3Cy	2.54	$< 5.4\cdot10^{-11}$	3.2

Patterning experiments on these polymers were done for a basic evaluation of the potential for integration in copper damascene technology. Representative for a non-copolymerized and a copolymerized material *100mol% F10* and *50mol% F10 + 50mol% mCF3Cy* were selected for these examinations. A single hard mask was used. For a better evaluation of the patterning results and possible defects a partial hard mask (see figure 1) etching was applied. That allows a strict separation of all single process steps to be done and their influence in respect to a modification or damage of the low-k films.

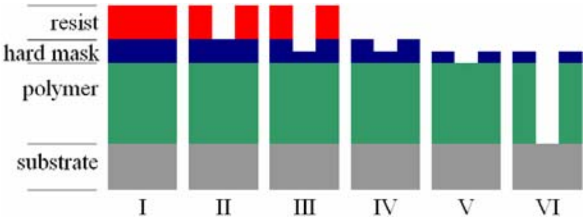


Fig. 1: Application of partial opened hard mask for patterning

After photolithographic patterning of the resist a partial anisotropic plasma etching of the PECVD SiO_2 hard mask followed. Main aspect thereby was, to avoid any breakthrough of the hard mask. This is necessary to avoid any damage or istropic etch of the polymer film by the subsequently applied O_2 plasma resist stripping. Via an additional process step, the hard mask was etched until breakthrough to the low-k material. For patterning of the polymer a new O_2 dry etching recipe was developed. In figure 2 and figure 3 SEM images of damage-free patterning results are shown.
During preparation no significant difficulties or defect mechanisms like delamination, crack or blister generation, known from other low-k materials, did occur. The quality of the generated profiles is good and comparable for both materials.

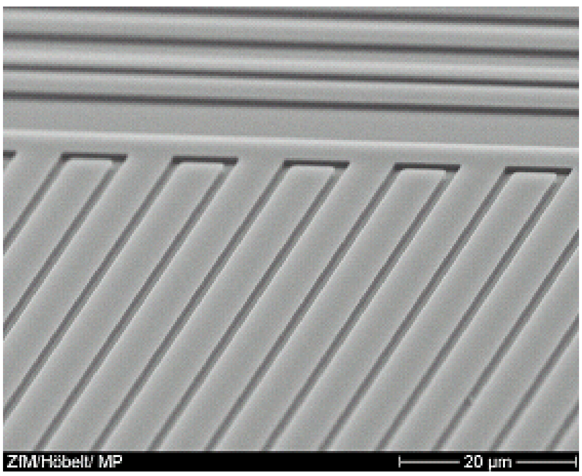


Fig. 2: SEM of patterned polycyanurate and PECVD SiO_2 hard mask on top

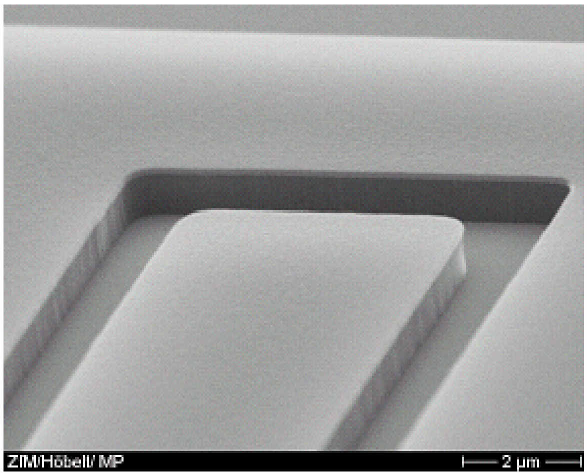


Fig. 3: SEM of patterned polycyanurate sidewalls (PECVD SiO2 hard mask on top)

Future work will be concentrated on integration of these materials in copper damascene technology, by evaluating CMP compatibility or compatibility to barrier materials. Especially mechanical properties (see table 3) are very promising for a successful Cu and barrier CMP using these low-k materials.

Tab. 3: Mechanical properties of copolymerized and non-copolymerized polycyanurates

Film composition	E-modulus [GPa]	Hardness [GPa]
50mol% F10 + 50mol% mCF3Cy	3.5	0.24
33mol% F10 + 67mol% mCF3Cy	4.0	0.21
B10	4.7	0.26
86mol% B10 + 14mol% THPE-Cy	4.1	0.27
50mol% B10 + 50mol% THPE-Cy	3.8	0.30

Acknowledgement

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