

## MODIFIED SILICA XEROGEL AS A LOW-K DIELECTRIC WITH IMPROVED MECHANICAL PROPERTIES

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### ABSTRACT

Basing on a spin on process for preparation of ultra low k dielectric SiO<sub>2</sub> xerogel with  $k < 2.1$  the influence of a varied precursor mixture as well as of modified gelation/ aging conditions on mechanical properties was investigated. The introduction of additional small and well distributed pores should be possible by adding an Si- alcoholate with vinyl or phenyl ligand to the precursor mixture. Modified gelation/ aging conditions should result in stiffening of the network. By combination of these process modifications promising results were obtained for improved elastic modulus. The elastic modulus of a xerogel layer with shortened gelation in water containing gelation ambient was 30% higher than the reference sample while the k-value was comparable. Although the investigated processes have a potential for optimization yet, it can be concluded, that an improvement of the mechanical properties of the SiO<sub>2</sub> xerogel is possible, but not in unlimited extent. A special issue consists in adaptation of mechanical testing methods to the porous layers. Application of Nanoindentation requires a conscientious evaluation of the obtained results, because several sources of error could be identified with respect to indenter loads.

### INTRODUCTION

Recent research effort on ultra low k dielectrics with  $k < 2.1$  has been focused on porous materials. But the introduction of pores into a material offers not only the possibility to achieve ultra or extreme low k values, it lowers also the mechanical stability of the material as elastic modulus relates inversely to porosity, too. The diverse requirements for successful integration of ULK dielectrics include beside excellent electrical features the full compatibility to mechanical CMP loads during damascene processing. Thus the pore characteristic plays a key role as well as the skeleton stability for the optimization of the stiffness, while pore volume fraction has to be kept at a high level [1]. To obtain SiO<sub>2</sub> xerogel layers we have applied a typical sol gel process like described for instance in [2].

The investigations, presented here, concern the improvement of the mechanical stability of SiO<sub>2</sub> xerogels by modification of two selected processing steps of a sol gel process based on FEOS as Si-source [3]. The first issue under investigation was the introduction of additional small and well distributed pores into the network. The standard precursor component TEOS was substituted by either Vinyltriethoxysilane (VTEOS) or Phenyltriethoxysilane (PTEOS) in

several fractions. Both VTEOS and PTEOS contain a non-reactive ligand (vinyl or phenyl group) which are neither able to hydrolyse nor able to form Si-O-Si bonds as a result of polycondensation. Therefore the functionality of the network can be reduced.

The second target was the stiffening of the skeleton by modified both gelation and aging conditions. The addition of water to the standard pure solvent gelation atmosphere similar to the pore liquid supplies the hydrolysis reaction during gel formation due to excess of reaction partner H<sub>2</sub>O. An aging treatment with H<sub>2</sub>O /solvent and TEOS/solvent enhances the polycondensation reaction in principle, too. That means TEOS-monomers as well as dissolved SiO<sub>x</sub> species can move to unlinked "edges" of the network and thus contribute to a strengthening.

## EXPERIMENT

Several sols containing substituent fractions of 1, 5, 10, 20 and 30mol% VTEOS and 1 and 2.5mol% PTEOS, respectively, were prepared, following the basic sol gel process. Rheological characterization was carried out using a double cylinder rheometer to determine the spin on conditions. The layers were spun on 150 mm silicon wafers. The modification of the gelation and aging conditions was realised by varying the parameters concentration and time for the post-treatment of the wet layers after spin on in special single wafer boxes (see table 1). After drying, annealing and hydrophobization the properties of the obtained xerogel layers were characterized.

To evaluate the effect of varied precursor composition and changed gelation/aging conditions a reference layer was prepared without any changes in composition (100 % TEOS) or gelation/aging conditions.

Film thickness and surface roughness was determined by profilometry. Effective porosity was calculated from refractive index measured by Variable Angle Ellipsometric Spectroscopy (VASE) and from effective density by Laser-generated Surface Acoustic Waves spectroscopy (LSAW) [4,5]. The elastic modulus was preferentially measured by Nanoindentation and checked by LSAW, too. For the Nanoindentation a special testing regime, applying very low indenter loads in the region of 0.1..0.3mN, was developed to get more reliable results for weak porous xerogel layers.

## RESULTS

The viscosity-time relation for the sols with varied composition is changed. For small fractions of VTEOS the time until reaching gelation point is shifted to smaller values and for fractions of 10mol% and more to higher values. An untypical behaviour was detected for sols containing 5mol% VTEOS. The VTEOS and PTEOS modified samples show increased elastic moduli (see figure 1). But the k values are increased, too. Looking in detail on the relation of porosity, elastic modulus and k value to the substituent fraction VTEOS, we assume that the reason for higher elastic modulus is the reduction of effective porosity (see figure 2). That means, the main effect of introduction of a vinyl or phenyl ligand is a reduced effective porosity of the layers. This effect superposes the desired effect of additional small pores in the network. The deviation in the behaviour of sol with VTEOS 5mol% is in relation with the untypical

rheological behaviour of this sol, but it needs further investigation to give a consistent explanation.

The properties of the xerogel layers prepared with modified gelation and aging conditions are summarized in table 2. While the higher elastic stiffness of layers from Aging II and III are also in relation with a significant reduced effective porosity, the layers prepared with Aging I display a lower modulus and a higher porosity than the reference sample. Comparing the achieved layer thickness with the reference, the high porosity is explainable by smaller shrinkage during drying.

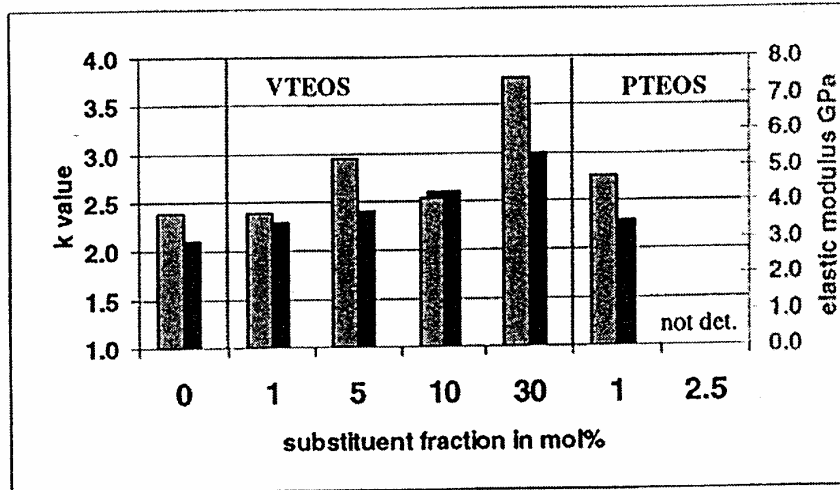


Figure 1: Elastic modulus and k value vs VTEOS and PTEOS substituent fraction

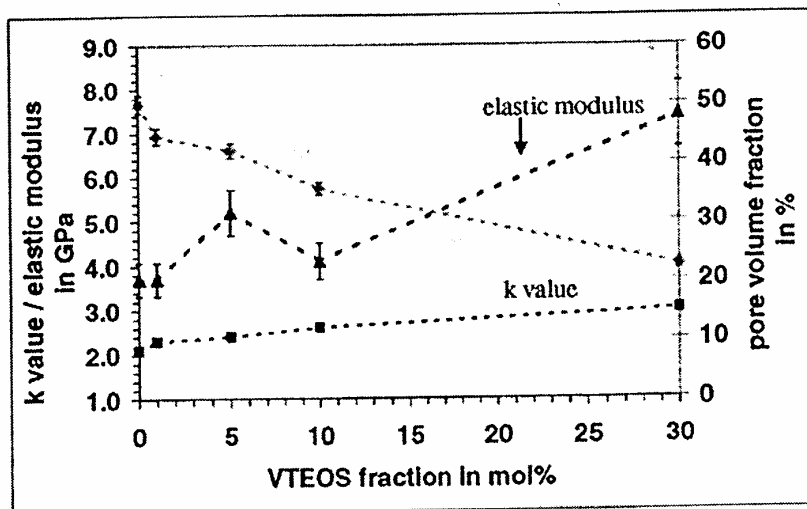


Figure 2: Elastic modulus, k value and porosity vs. VTEOS substituent fraction

After the investigation of the above described process interventions separately, we combined the two process modifications to tune the effective porosity and skeleton stiffness (see table 3). The obtained results are shown in figure 3.

**Table 1** Gelation and aging conditions applied to xerogel layers after spin on

Aging I: gelation in ambient with composition similar to pore liquid: a) 7% H <sub>2</sub> O/solvent b) 14% H <sub>2</sub> O/solvent c) 28% H <sub>2</sub> O/solvent Aging II: aging in solvent 24h Aging III: aging in TEOS/solvent 24h
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**Table 2** Properties of the xerogel layers prepared by modified gelation/ aging conditions

	$\pi_{\text{cell}}$	thickness(nm)	k	E (GPa)*
Aging Ia	58%	655 (495 <sup>o</sup> )	1.8 (2.1 <sup>o</sup> )	2.8 (3.7 <sup>o</sup> )
Aging Ib	n.d.	635 (553 <sup>o</sup> )	2.0 (2.1 <sup>o</sup> )	2.9
Aging Ic	n.d.	688 (581 <sup>o</sup> )	1.9 (2.1 <sup>o</sup> )	n.d.
Aging II	47%	546 (500 <sup>o</sup> )	2.9 (2.1 <sup>o</sup> )	3.0
Aging III	45%	424 (500 <sup>o</sup> )	3.0 (2.1 <sup>o</sup> )	5.5

\* from Nanoindentation  
<sup>o</sup> reference sample

**Table 3** Combined process modifications selected for further investigation

CP1	Aging Ia interrupted gelation
CP2	Aging Ib interrupted gelation
CP3	1mol%VTEOS combined with Aging Ia
CP4	5mol%VTEOS combined with Aging Ia
CP5	1mol%PTEOS combined with Aging Ia

## DISCUSSION

The rheological behaviour of the modified sols has been changed due to an inductive effect of vinyl and phenyl groups affecting bond strength between silicon and ethoxy groups and thus enhancing hydrolysis. With an increasing of the co-precursor fraction a steric hindrance

effect due to the vinyl groups and in particular of the more bulky phenyl groups superposes the inductive effect and leads to a retardation of the polycondensation reaction.

Pore generation in xerogels happens during drying. The porosity obtained by the standard process is about 50% (determined by ellipsometric porosimetry) and the pore size distribution

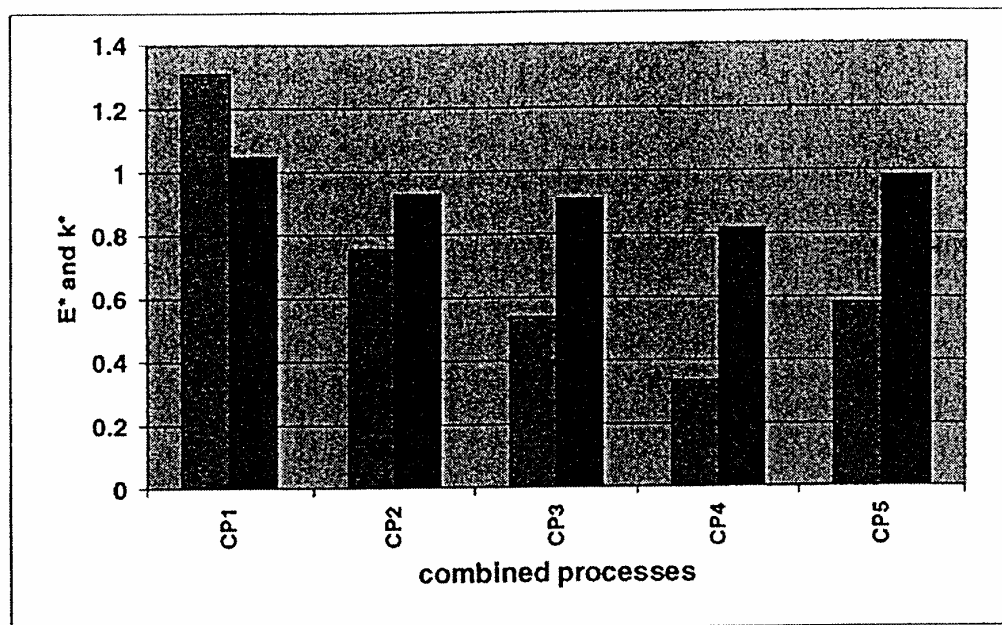


Figure 3: Normalized elastic modulus  $E^*$  and normalized k-value  $k^*$  for the xerogel layers obtained by the process combination of table 3 (related to the properties of the reference layer prepared without any changes in precursor composition and gelation/aging conditions)

limited possibilities for cross-linking, that means the more compliant the skeleton is, the smaller the effective porosity of the layer will be. Therefore the effective porosity of the VTEOS and PTEOS modified xerogel layers are inevitably smaller than that of the reference. This is connected with an increased effective stiffness of these layers. The tendency to smaller porosity with higher substituent fraction confirms this theory. On molecular scale we expect a fraction of the pores produced by these organic ligands. But this effect is superposed by the simultaneous change of the effective porosity. The differences in the pore size distribution will be investigated after further optimization of the process when the effective porosity is on the same level like for the reference layers. Finally, there is no great effect on the pore size distribution expected for small substituent fractions. The deviation for samples prepared with 5mol% VTEOS is not clear. It is interpreted as an advise, that the change in the network formation is not fully understood until now.

The effect of the second process modification is more obvious. Supplying additional water in the gelation ambient results in increased skeleton stiffness. The water of the ambient is well distributed and can diffuse to all places in the wet gel. Therefore the hydrolysis can be locally enhanced followed by polycondensation. The degree of network collapse is much less compared to the reference, which is confirmed by the higher thickness obtained for these layers as well as by the increased effective porosity.

Combination of both modifications shall give the possibility to tune the effective stiffness by tailoring of the network properties as well as the effective porosity. First promising results were obtained for combined process CPI, which displays an increase of the elastic stiffness of about 30% compared to the reference together with an  $k$  value of 2.2 (see figure 3).

Concerning determination of elastic modulus by Nanoindentation we have to mention, that the porous layers with limited thickness in the range of 300..800nm show a too high penetration depth of the Berkovich indenter. Although the loads were decreased as much as possible, the results contain an unavoidable error from substrate influence. Therefore it is necessary to compare the results from Nanoindentation by a second testing method, in our case it was LSAW. The LSAW derived elastic moduli are in general about 50% smaller.

## CONCLUSIONS

It was shown, that there is a possibility to tune the elastic modulus through process modifications (concerning precursor mixture and gelation conditions) affecting the skeleton stiffness and the overall porosity. Process CPI is the most promising candidate for further optimization.

The evaluation of CMP compatibility of layers with high porosity basing on elastic modulus obtained by Nanoindentation is counted as critical because an unavoidable error is caused by substrate influence. Further methodological effort is needed in this field to minimize this error and to get more reliable results.

## ACKNOWLEDGMENTS

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