

HYDROPHOBISATION PROCESS FOR POROUS LOW K DIELECTRIC SILICA LAYERS

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ABSTRACT

Porous sol-gel derived silica xerogel layers were silylated using Hexamethyldisilazane (HMDS), Trimethylsilyldiethylamine (TMSDEA) or Trimethylsilylacetate (OTMSA). The results show that HMDS is the most effective silylation agent of the three chemicals compared, with respect to electrical properties. The HMDS reaction with surface silanols seems to happen at first with high reaction rate and then slowly but continuously over several hours. This can be explained by several reaction rates due to steric hindrance after the first rapid covering of the surface with TMS-groups. The long-term stability is investigated for layers stored more than 60 days in dry air and compared with the initial results.

INTRODUCTION

Low k-dielectric layers produced by a sol-gel /spin-on-process are one of the promising candidates for intermetal/ interlevel dielectrics in copper metallization. Although electrical properties like k-value, leakage current and field break down voltage of porous silica xerogel layers are regarded as excellent, they suffer in the as-deposited state from water adsorption caused by surface silanol groups. To stabilise electrical properties and to get a sufficient reliability for further integration steps layers have to be made hydrophobic.

Many investigations have been done in recent years in the field of hydrophobisation for silica by several mono- and multifunctional silanes, siloxanes and silazanes [1-3]. Especially HMDS is widely employed because of its high reactivity with silica surface silanols due to its basic nitrogen [4]. In most cases silica powders were treated for use in gas chromatography, fillers in polymers or catalyst supports. The surface characteristics of the treated samples influence significantly the hydrophobisation result, not only related with morphology, but also with chemical state depending on production history and pre-treatment at elevated temperatures. Hydrophobisation is achieved by silylation, that means surface silanol groups are reacted to yield trimethylsilyl (TMS) surface groups. An important condition for application with respect to integration issues is that the silylation process bases on chlorine-free silylating, which are able to react surface silanol groups in short time and liberate only less toxic and hazardous by-products. The next requirement consists in long-term irreversibility of the hydrophobisation effect keeping electrical properties of the layers reliable over several months. We investigated

hydrophobisation of mesoporous silica xerogel layers especially in light of their electrical properties.

EXPERIMENT

A mixture of TEOS, alcohol and acid catalyst was stirred and spin coated on silicon wafers. After gelation the coated wafers were cut and then annealed at 450°C for 1 hour under vacuum to drive out organics and water from the pores. Hydrophobisation treatment followed immediately after annealing. Hexamethyldisilazane (HMDS), Trimethylsilyldiethylamine (TMSDEA) or Trimethylsilylacetate (OTMSA) was applied in the form of saturated vapor over the liquid at room temperature in a closed container. HMDS was also applied at 70°C. The exposure time was varied. After the hydrophobisation step samples were outgassed and held under vacuum until FTIR measurement by a Bruker FT-IR-spectrometer.

²⁹Si-CP/MAS- and -HPDEC-NMR measurements were made using fine silica powder produced simultaneously from gel. Ellipsometric measurements were used to determine the relative porosity change from the porosity of untreated and treated layers from reactive index.

Electrical properties of the layers, i.e. dielectric constant (measured at 100kHz), leakage current density (measured at 1MV/cm) and field break down voltage, were determined using a mercury probe approach after about 24 hours storing in dry air.

FTIR and electrical measurements were repeated after 60 days and again after 6 months to determine the effects of water adsorption on the electrical properties.

RESULTS

Structural investigation

The pre-treatment at 450°C causes the loss of adsorbed water and formation of siloxane bridges and free silanol surface groups [5]. HMDS, TMSDEA and OTMSA can be adsorbed at the surface and one of the electrophilic Si on HMDS attacks the nucleophilic oxygen of a free surface silanol to form TMS-surface groups [4]. This S_E reaction is also believed to be true for TMSDEA and OTMSA. The scheme of the balance reactions for the different chemicals is seen in figure 1. The acetic acid is regarded as the less harmful by-product.

The HMDS attack leading to the obvious destruction of surface silanols is observable in FTIR spectra, see figure 2. Sharp absorption band at about 3750 cm⁻¹ are related to O-H-stretching vibration of free or single silanol groups. They are clearly visible in spectra of an untreated sample. While the broad absorption at 3700 cm⁻¹ is due to O-H-stretching of bonded silanols, at 3500 cm⁻¹ we find generally a broad absorption band caused by O-H-vibrations of some adsorbed water. For at room temperature HMDS treated samples it is found that already after 1 min silanols have been diminished, while C-H-vibration related absorption bands appear. At 2960 cm⁻¹ and 2906 cm⁻¹ absorption bands are related to asymmetric and symmetric C-H-stretching mode of methyl in TMS- groups, at 1260 cm⁻¹ we find absorption bands due to their bending, at 848 and 866 cm⁻¹ due to their rocking vibrational modes.

Further modification of spectra is observable in the region of absorption bands caused by Si-O-vibrations. Si-O-stretching and bending vibrations of Si-O-Si-units is related to absorption

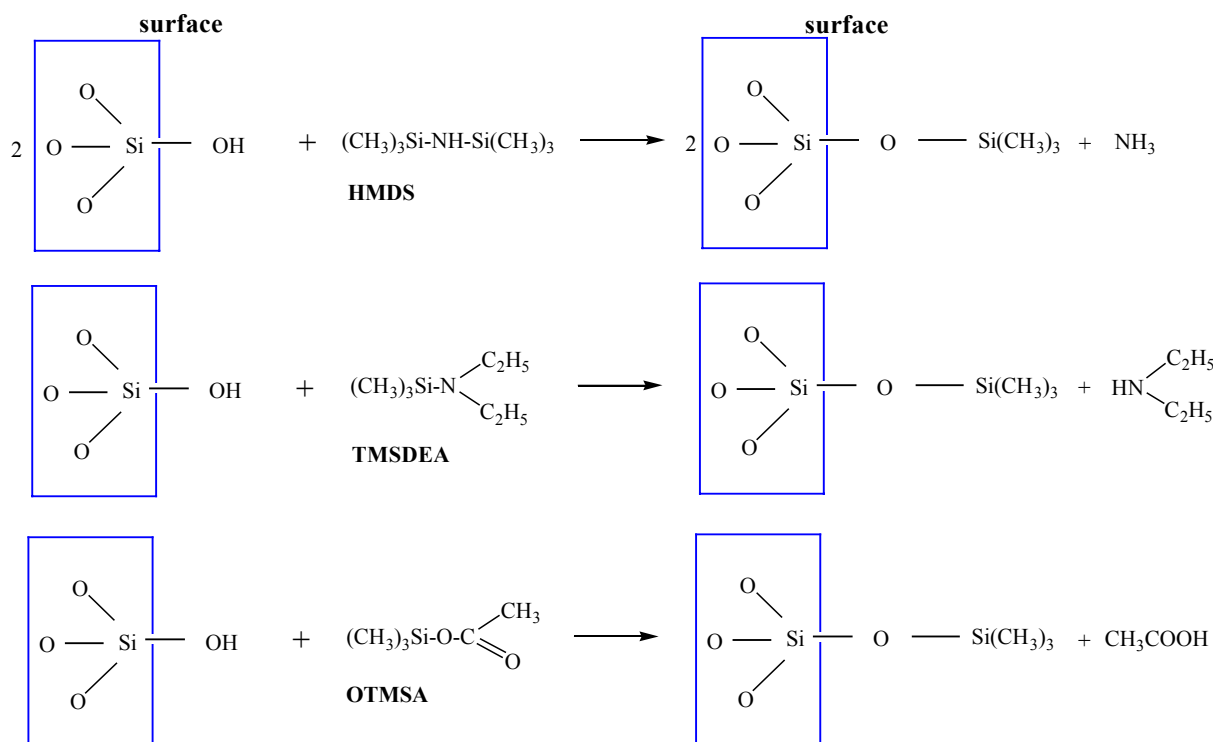


Figure 1 Silylation reaction scheme for different chemicals (balance reactions)

bands at $1000..1300 \text{ cm}^{-1}$ and 800 cm^{-1} . The shape of the broad absorption band is changed and intensity at 1100 cm^{-1} increases continuously with increasing exposure time. This change can be ascribed to an increase in number of Si-O-Si-bonds due to formation of surface TMS-groups.

That means, there should be a rapid but not full coverage of surface by TMS-groups in short time ($<1\text{min}$). The surface load by TMS-groups increases then continuously but more slowly until about 4h exposure time. The retarded reaction after initial step is also reported in literature and is explained by steric hindrance [6].

^{29}Si -NMR-investigation supports this assumption, because we found a different chemical shift for Si in TMS groups after short time treatment (16min) and after long time treatment (4h) caused by different interactions between surface groups (17ppm and 14.2 ppm). Quantitative analysis of ^{29}Si -NMR-measurements gave additional information about the structural state of the xerogel bulk. A significant decrease in the ratio of Q^3/Q^4 functional units due to silylation by HMDS could not be found. This is surprisingly, because bonding of TMS-groups at the surface should consume one Q^3 -unit and produce a new Q^4 -unit. Until now we cannot explain this effect by another split reaction, because a secondary reaction of the by-product ammonia with siloxane bridges, suggested in [7], is not very likely for treatment at room temperature. We will investigate this interesting result further. An acceleration of the reaction is achieved by increasing temperature (up to 70°C) and concentration of hydrophobisation agent.

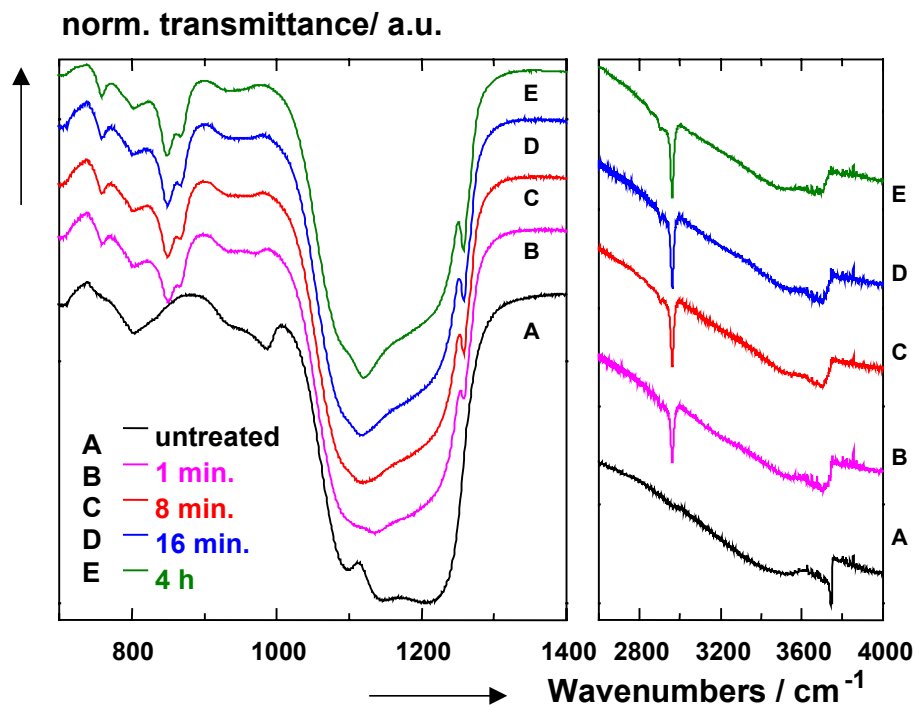


Figure 2 FTIR-spectra of untreated and HMDS treated samples

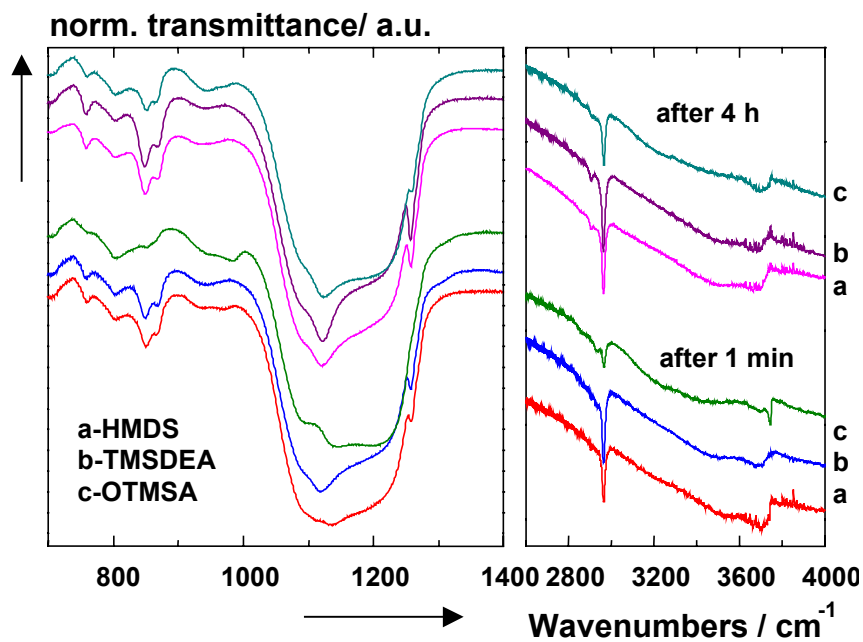


Figure 3 Comparison of FTIR spectra of samples silylated by HMDS (a), TMSDEA (b) or OTMSA (c) for 1min (bottom) and for 4 hours exposure time (top)

A remark is necessary regarding the diminished surface silanols in FTIR spectra after a 1 min treatment. Haukka et al have described in [7] that single OH groups can also form hydrogen-bonds to neighbouring methyl of TMS-groups, so that a part of the free silanols are shifted in the absorption region for H-bonded silanols. That makes the definition of a reaction grade basing on the intensity of absorption bands related to single OH-groups uncertain. But looking at the changes above described in the FTIR-spectra relating to C-H-vibrations and Si-O-vibrations, an estimation of the reaction grade basing on comparison seems to be possible.

The most important difference between the selected silylating agents is expected to be in their reactivity. Figure 3 contains FTIR-spectra comparing HMDS, TMSDEA and OTMSA treated samples at room temperature. Single surface silanols are only visible in spectra of the OTMSA treated sample (1min). From spectra in figure 4 it is obviously, that the reaction rate for TMSDEA should be higher than for HMDS and for OTMSA. This is also confirmed by ²⁹Si-NMR-studies for TMSDEA. The jump related with structural changes between untreated samples and short time treated samples is generally bigger than can be observed between short time treated samples and long time treated samples.

Morphological changes

The loading of the xerogel surface by TMS-groups is accompanied by a significant reduction in porosity. Pores smaller than 2 nm are closed during the hydrophobisation treatment and the pore volume shrinks [8]. The porosity data are summarized in table 1. Porosity is calculated from refractive index measured by ellipsometry using an effective medium approximation, for details see [8]. This porosity decrease is assumed to be caused mainly by pore filling or covering by TMS-groups in agreement with results published by Fuji et al [9].

Former assumptions about further reactions like condensation were not confirmed. Change in porosity is stronger for TMSDEA than for HMDS and OTMSA. Assuming for the three different chemicals the same effect for porosity reduction we can conclude, that the above deduced assumption of higher reactivity of TMSDEA is supported.

Exposure time/min	pore volume/ initial pore volume in %		
	HMDS	TMSDEA	OTMSA
0.5	88.0	not determ.(n.d.)	n.d.
1	87.9	82.1	95.4
2	85.8	n.d.	n.d.
4	83.8	n.d.	n.d.
8	81.8	79.0	94.9
16	81.8	79.8	93.4
240	n.d.	78.0 / 77.7	89.1/ 92.7

Table 1 Porosity decrease of xerogel layers vs. exposure time for different chemicals

Electrical properties

Silylation leads to a decrease of dielectric constant and of leakage current density with increasing exposure time, see figure 4 and 5. From our structural investigation, especially FTIR, we can conclude that this effect is caused by a continuously increasing number of TMS-groups on the xerogel surface and its raised hydrophobicity. Leakage current density follows an exponential time law and is obviously related with silylation rate. K-value change is more difficult to explain, because two opposite tendencies are superposed. Hydrophobisation prevents water adsorption. Influence of the high k-value of water is thus limited by effective volume of adsorbed water. But k-value depends also strongly from absolute initial pore volume of the xerogel layer. Therefore it would be better to discuss only a relative k-value change, but it is not possible to measure the initial value of the untreated samples because of too high leakage currents. The scatter is mainly caused by small differences in initial sample porosity. HMDS treated samples reach the desired limit of 10^{-9} A/cm² at shorter exposure times than TMSDEA and OTMSA treated ones. K-value change is stronger for TMSDEA treatment and scatters for OTMSA are without clear tendency. A possible explanation is that the partially silylated surfaces have different capability to adsorb water, and HMDS treated samples have the lowest capability. The k-values reached at 4 hours exposure time of about 2.15 are comparable for HMDS and TMSDEA, but higher for OTMSA.

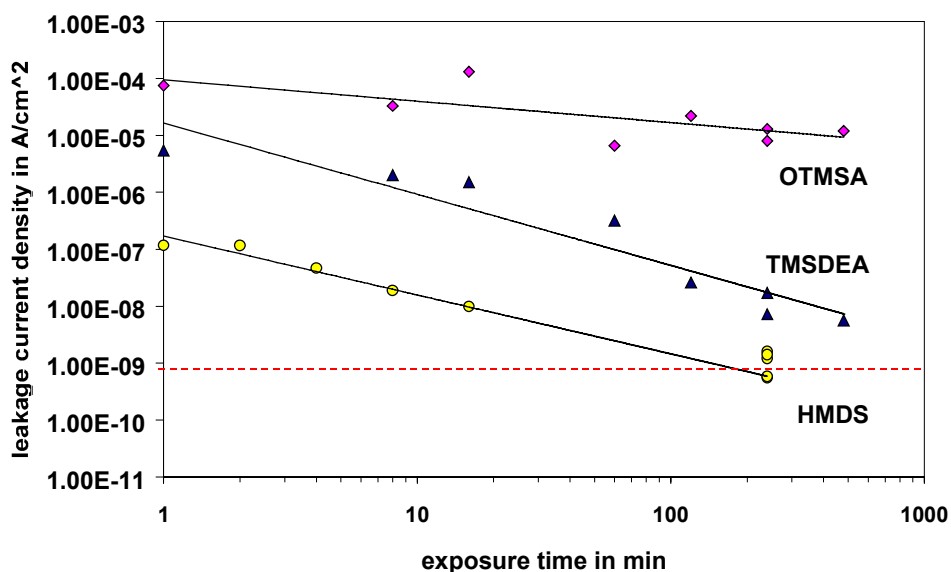


Figure 4 Leakage current density vs exposure time for HMDS, TMSDEA and OTMSA treated samples

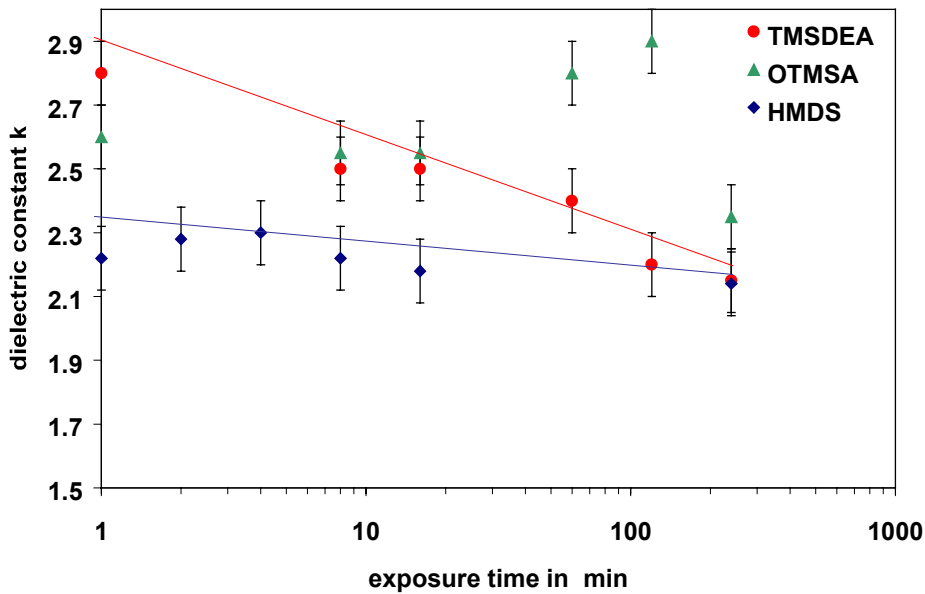


Figure 5 k-value vs exposure time for HMDS, TMSDEA and OTMSA treated samples

While structural investigation lead to the assumption, that TMSDEA is more reactive, the results of electrical measurement show, that HMDS treated samples are more stable against water adsorption related especially with leakage current.

Field break down voltage raises for the three selected chemicals from about 1.5 MV/cm up to 3 MV/cm over a treatment time of 4 hours.

Long-term stability

Long-term stability is studied for HMDS treated xerogel layers regarding effects due to water adsorption. The deterioration of k-values and leakage current densities measured after 60 days compared to those after 1 day is obvious. The adsorption of water is visible in increased absorption band intensity in FTIR spectra. The longer the treatment was performed the weaker is the deterioration of the electrical film properties. Samples treated more than 4 hours did not show any degradation of electrical behaviour due to water absorption. This was also proved after more than 6 months.

CONCLUSIONS

From structural studies we can undoubtedly conclude that TMSDEA is the more reactive hydrophobisation agent compared to HMDS and OTMSA. The relation between reactivity determined by structural effects on the xerogel layer and leakage current density is not explainable by the available experimental data and so will be the object of further investigation. We could show that for all three selected chemicals an exposure time of more than 4 hours is necessary to achieve the desired specification for leakage current density ($1 \cdot 10^{-9} \text{ A/cm}^2$), k-value (2.0) and field break down voltage (3MV/cm). After storing for half a year there was no degradation of electrical properties measured for samples treated more than 4 hours in HMDS.

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