Studies of the chemical and electrical properties of fullerene and 3-aminopropyltrimethoxysilane based low-k materials

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Abstract

Among an extremely large number of possible fullerene applications in the field of electronics, optics and photovoltaics, C\textsubscript{60}-cages are also considered as a promising dopant for low dielectric constant (low-k) materials. In this study, we incorporated C\textsubscript{60} species into a 3-aminopropyltrimethoxysilane (APTMS) based material. We prepared thin films by spin coating. Using X-ray photoelectron spectroscopy we analyzed the time-related interactions between the components of the prepared samples and the influence of the C\textsubscript{60} replacement by its better soluble derivative [6,6]-phenyl-C\textsubscript{61}-butyric acid methyl ester (PCBM) on the chemical properties of the material. We applied atomic force microscopy to investigate the surface texture and thicknesses of the obtained films. In order to obtain information concerning the electrical properties of the material we performed capacitance-voltage characterization. We have proven that the increase of C\textsubscript{60} species realized by PCBM incorporation within the APTMS-based matrix reduces the dielectric constant of the examined films while preserving its homogeneity.

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1. Introduction

The improvement of the microelectronic device performance was achieved mainly by the continuous miniaturization of the feature size what allows higher packing density [1]. However, the overall resistance-capacitance (RC) delay increases and becomes the limiting factor of the electrical and functional performance while scaling the microelectronic devices dimensions. The challenge connected with the RC delay reduction has been mitigated by the replacement of the Al/SiO$_2$ on-chip interconnect stack by Cu and low dielectric constant (low-$k$) materials. The introduction of low-$k$ materials and Cu interconnects allows moreover to reduce the power consumption and cross talk of the microelectronic devices [1–3].

Since fullerenes exhibit a number of unique properties that are valuable in many fields of science, they attract a great scientists’ attention. Therefore, big efforts have been made in order to obtain fullerene containing nano-composite materials [4, 5]. The presence of fullerenes within a low-$k$ material can improve its mechanical properties [6]. Interestingly, theoretical calculations show that the proper arrangement of C$_{60}$ structures may possess ultralow-$k$ properties [7]. In our paper we investigate the dopants influence on the chemical and electrical properties of thin hybrid films of 3-aminopropyltrimethoxysilane (APTMS) doped with fullerene cages.
In this paper, we describe our initial step leading to the preparation of ultra-low-\(k\) material including fullerene cages. The main purpose of this investigation was to characterize the chemical stability of the material after the exposure to air and to estimate the influence of fullerenes replacement by its better soluble derivatives \([6,6]\)-phenyl-\(C_{61}\)-butyric acid methyl ester (PCBM) on the dielectric constant of the films. Hence, we have prepared fullerene-based material consisting of APTMS and \(C_{60}\) molecules by spin coating. Afterwards we produced another similar sample while using PCBM instead of \(C_{60}\) in order to minimize the amount of clusters within the low-\(k\) film.

We used APTMS as the basic material for the sample preparation. The fullerene functionalization with this agent is already reported in the literature [8, 9]. The reason for using APTMS in our experiment is not only its high affinity to the fullerene molecules but also the fact that this agent functionalizes effectively the silicon surface since APTMS exhibits properties of forming self-assembled monolayer [10–15]. These properties offer the possibility to produce thin APTMS based films by spin coating. APTMS gives moreover an opportunity to introduce aminopropyl groups into the framework of the final material. At least a partial attaching of the fullerene cages to the APTMS matrix by the interaction with the aminopropyl group should lead to a better dispersion of the dopants within the film. Furthermore, removing the aminopropyl groups during the heat treatment (not investigated in this paper) ought to increase the material porosity, what is a desired feature for low-\(k\) materials [16]. The functionalization of the mesoporous silica structure with organic groups originating from organosiloxanes expands the horizon for many fields of science [17]. Thus, the investigation of the described films may prove further whether wider applications beyond the low-\(k\) field are feasible.

We have chosen silicon as a substrate for this experiment not only in order to realize metal-insulator-semiconductor (MIS) structures for capacitance-voltage (CV) measurements
but also because of its wide applications in the field of microelectronic devices. For that reason, there is an obvious need to understand the interactions between silicon single-crystalline substrates and the deposited thin film material [18]. The knowledge of the electronic structure of the semiconductor-organic interface is a fundamental factor that influences the device performance improvement [19]. Thus, we investigated thin films on silicon substrates in order to estimate the permittivity of the produced material and to consider its further possible application in other fields of microelectronic devices apart from low-k in the future.

The paper is organized as follow: Based on the X-ray photoelectron spectroscopy (XPS) results we discuss the stability of the hybrid material films composed of the fullerene species incorporated into the APTMS based siloxane matrix spin-coated on the silicon substrate. Subsequently, we continue with the studies of the similar material produced after the C₆₀ replacement by PCBM. In the next section, we present and discuss an example of the film thickness measurement by means of atomic force microscopy (AFM). The final part describes the electrical characterization of the samples by CV method. Finally, a summary of the relevant conclusions is given.

2. Experimental details

2.1. Measurements

XPS measurements were done using SPECS GmbH X-Ray source (Mg Kα 1253.6 eV) and energy analyzer made by Leybold-Heraeus. The structure due to the satellite radiation has been subtracted from the spectra before the data fitting [20, 21]. The acquired spectra were background corrected by Shirley background removal [22]. Corrections for the energy shift were accomplished by assuming 103.5eV binding energy for the Si 2p peak of the Si⁺⁴ species
The corrected spectra were decomposed with Gaussian line shapes in order to describe individual components and to obtain detailed information about the nature of the chemical interactions [23, 24]. Each peak was fitted using Levenberg–Marquardt least-square algorithm. The data for the atomic composition and ratios were calculated using the atomic and instrument sensitivity factors [25].

Noncontact atomic force microscopy (NC-AFM) measurements were conducted by Veeco CPII at room temperature. Phosphorus doped silicon cantilevers (model MPP-11123-10) with a resonant frequency of about 275 kHz and an approximate spring constant of 48 N/m were used. The nominal tip curvature of the used cantilevers was less than 8 nm. The AFM data were flattened by a commonly used technique in the case of steps, in which a plane is fitted to three points on one of the steps [26].

In order to determine the permittivity of our samples CV measurements were carried out on MIS structures by a homemade CV set-up basing on a LCR meter Agilent 4284A [27]. In this work, we used slow DC ramps of 25 mV/s and 25 mV (RMS) AC signals at a frequency of 1 MHz. The measurements started in accumulation, further the semiconductor was biased by the DC ramp through depletion and inversion and then back to accumulation. Using the capacitance in accumulation the permittivity of the dielectric is determined by the plate capacitor approximation.

2.2. Materials and substrates

In this work, we used C$_{60}$ (99.5 %), PCBM (99.5 %) and APTMS (97 %) obtained from Sigma-Aldrich. As a substrate for our samples preparation we have chosen Si (100). In Fig. 1 we present the schemes of all investigated samples. The C$_{60}$ and PCBM concentrations within the films were calculated in weight percent.
The Si substrates were sonicated for 10 minutes in isopropanol and then in distilled water, afterwards they were dried in nitrogen stream. The hydroxylation of the wafers was achieved by the immersion in piranha solution (a mixture of 7 : 3 (v/v) 98 % H₂SO₄ and 30 % H₂O₂) at 120 °C for 1.5 h. The substrates were then rinsed with distilled water and isopropanol several times and dried in nitrogen stream.

We produced the C₆₀ and PCBM containing materials by stirring with APTMS in glove box under argon atmosphere for 24 h. The films were deposited onto the substrates by spin-coating technique at a speed of 6000 rpm for 15 seconds inside the glove box. Here we should underline that at this stage of the investigation we did not use any external solvent. The speed of 6000 rpm is quite high. However, we realized that regarding the adjusted viscosity of our substance the spin-coated films formed at 6000 rpm were the most proper to perform AFM and CV measurements. In further progress of the experiment, one could use an external solvent like toluene in a proper concentration and this will allow the application of a lower velocity. The C₆₀ containing sample designed for the stability measurements was prepared in the similar way but in ambient conditions.

We obtained the reference film (sample D) by applying the sol-gel method. A basic sol solution was prepared by mixing phenyl triethoxysilane : methyl trimethoxysilane : ethanol : hydrochloric acid in molar ratio 1.00 : 1.22 : 7.77 : 1.03 × 10⁻³ respectively. Ref. [28] describes the detailed preparation procedure of this sample.

Additionally, we performed CV measurements on the samples B and C. Therefore, we prepared MIS structures by evaporation of silver contacts on top of the samples using a shadow mask. The diameters of the contact areas ranged between 400 µm and 700 µm. Two stacks corresponding to sample B were prepared for electrical measurements.

3. Results and discussion
3.1. XPS measurements

XPS is a common tool applicable for the determination of the chemical composition of the material. The peak positions in the XPS spectra in respect to the binding energy provide information concerning the chemical state of the particular atoms within the measured films [29]. The analysis of the peak intensities is used in order to perform quantitative determination of the components in the material [30].

3.1.1 Investigations on the stability of sample A

In this part we report on the influence of ambient conditions onto the material composed of APTMS and C\textsubscript{60}. Sample A was investigated twice: after 24 h of drying in air (further referred as sample A, Fig. 2(a-d)) and then after 10 days of the storage in ambient conditions (sample A’, Fig. 2(e-h)). The results of the detailed spectra analysis are summarized in Table 1. The C 1s overall signal decomposition shows that the main peak corresponding to the sp\textsuperscript{3} hybridized carbon species (signal III in Fig. 2a and 2e) appears at 285.1 and 285 eV for sample A and A’, respectively. For the pure APTMS the main feature exists at around 286 eV and corresponds to the propyl chain of the molecule [11]. Therefore, we presume that the carbon species of the fullerenes shifted the main carbon feature of the XPS spectrum. In the C 1s spectrum of the sample A (Fig. 2a) and A’ (Fig. 2e) we observe two smaller features (peaks II and III) that correspond to the C-N and C-O species, respectively. The increase of the feature III contribution to the percentage of the main peak area for the sample A’ is assigned to the reaction between the surface and CO\textsubscript{2} from the ambient. This process is confirmed by the increase of the corresponding feature of the -NH\textsubscript{3}\textsuperscript{+} group in the N 1s spectrum recorded for the sample A’ (Fig. 2f, signal I) in comparison to sample A (Fig. 2b, signal I). This observation suggests that the ambient CO\textsubscript{2} presence affects the APTMS and C\textsubscript{60} based films. The following reaction describes the details regarding the possible interactions of the APTMS based surface with the CO\textsubscript{2} from the air [11]:
\[ \equiv Si(CH_2)_3NH_2 + CO_2 \Leftrightarrow Si(CH_2)_3NH_2^+COO^- \quad (1) \]

\[ \equiv Si(CH_2)_3^-NH_2^+COO^- + NH_2(CH_2)_3Si \Leftrightarrow \equiv Si(CH_2)_3NHCOO^- + NH_3^+(CH_2)_3Si \equiv \quad (2) \]

Since XPS spectroscopy enables a quantitative determination of the elements contained in the measured sample [30], after the spectra evaluation the quantitative analysis of the investigated films was performed. The spectra normalization was achieved by dividing the observed relative peak areas by atomic and instrument sensitivity factors equal to 0.711, 0.296, 0.477, and 0.339 for O, C, N, and Si, respectively [25]. As a result of the analysis the following composition in atomic percent has been obtained: C=52.3 %, N=9.7 %, O=29.1 %, Si=8.9 % (C_5N_1O_3Si) for the sample A and C=51 %, N=9.5 %, O=29.8 %, Si=9.7 % (C_5N_1O_3Si) for the sample A’. Here we have to point out, that the calculated concentration of the atoms corresponds to the overall species present within the analysed surfaces (originating from APTMS, C_60, reaction by-products and possible contaminations as well). The stoichiometry of an unhydrolyzed APTMS monomer (excluding H atoms) corresponds to C_6NOSi, in comparison, the “ideal” poly[(aminopropyl)siloxane] polymer has a stoichiometry of C_3NOSi [11]. As reported in the literature [11, 37], the ambient humidity initiates reactions at the interface between the aminopropylalkoxysilanes based film and the air that are analogous to those taking place in aqueous solution. Thus, the decrease of the overall C amount within the film A and A’ in comparison to the unhydrolyzed monomer suggests that the APTMS monomers have partially undergone the condensation reactions during the spin coating and drying and some –CH_3 species were removed from the material. One should also take into account that the presence of fullerenes presumably increased also the detected C amount. We observed a decrease of the atomic carbon concentration within the surface after ten days of the sample storage (sample A’ in comparison to the sample A), what suggests a further progress of the condensation process. The quite high oxygen concentration may originate from by-products formed as a result of the interactions between the film and
ambient components (including for instance the reactions in Eqs. 1 and 2). This could be a hint that in order to obtain films with more stable chemical composition the samples ought to be annealed straight after the preparation. The atomic ratio of the Si and N within the described film remains close to 1 proving that the aminopropyl species were not removed from the siloxane matrix what is consistent with the expectations since the aminopropyl group is resistant against the hydrolysis [37].

3.1.2. Investigations of the samples B and C

The main aim of this part of the experiment was to estimate how the replacement of C$_{60}$ by PCBM influences the chemical composition of the final material. For this purpose, samples B [Fig. 3(a-d)] and C [Fig. 2(e-h)] have been investigated after 24 hours of the exposure to air. The results of the detailed spectra analysis are summarized in Table 2.

While analysing the C 1s XPS spectrum of sample C (Fig. 3e) one may notice the characteristic fullerene feature attributed to the $\pi$-$\pi^*$ electron transition (signal I’) [33]. In contrast, the C 1s spectrum of the sample B (Fig. 3a) reveals no characteristic C$_{60}$ shake-up features, what is the proof of very low C$_{60}$ concentration within that film. The main feature of the sample B (signal III in Fig. 3a) appears at 285.4 eV. As described in section 3.1.1, the main APTMS feature coming from the propyl group is normally placed at around 286 eV [32], what is fulfilled for the sample C where the main C 1s peak is at 286.1 eV (see Fig. 3e, peak IV). This fact supposes that the carbon main signal of the sample B placed at 285.4 eV is shifted to the lower binding energy direction due to the C$_{60}$ contribution, which was too low to distinguish a particular fullerene feature during the decomposition process.

The quantitative analysis of the film B reveals the following surface composition in atomic percent: C=51.5 %, N=9.3 %, O=29.2 %, Si=10 % (C$_{5.9}$N$_{1.1}$O$_{3.3}$Si). The atomic ratio obtained for the sample B is in good agreement with those obtained for the sample A.
Although the concentration of the fullerenes used for the film preparation equalled 2.4 % and 1 % for the sample A and B, respectively, the quantitative XPS analysis revealed that after 24 h of the exposure to air the atomic ratios for both films were almost identical. This suggests that the C_{60}-APTMS solutions used for the samples A and B preparation were already saturated and it is not possible to increase the fullerene amount within these types of films. In addition, the high spin rate applied in the preparation steps (6000 rpm) might be a limiting factor for a higher incorporation of fullerene cages into the films.

Following our earlier expertise (sample D analysis), the dielectric constant of the material ought to decrease while increasing the fullerene concentration due to the higher overall amount of pores and carbon species within the film. The sample D used in our experiment as a reference (details concerning its investigation are described elsewhere [28]) contained a high amount of carbon species and was porous what allowed to achieve its very low dielectric constant (from 2.3 to 2.5), although the C_{60} amount within the film was quite low (0.3 %). For that reason, we decided to increase the amount of fullerene species within the film further by replacing C_{60} by its better soluble derivative - PCBM (sample C). The XPS quantitative analysis revealed that after 24 h of exposure to air the composition of film C in atomic percent was the following: C=69.4 %, N=5.2 %, O=20.4 % and Si=5 % (C_{13,9}NO_{4}Si). Taking into account that in the preparation of samples B and C the identical concentration (1 %) of C_{60} or PCBM, respectively, was used, we conclude, that we achieved an increase of the amount of the C_{60} species within the film. The overall amount of the carbon species equalled 69.4% in sample C. The sample C exhibits also a higher O/Si ratio in comparison to sample B.
since the PCBM molecule is also a source of oxygen.

3.2. Thickness measurements

We used AFM to determine the thickness \( (d) \) of the deposited materials in order to calculate the dielectric constant from CV measurements (Eq. 3). All investigated materials were soft. Hence, we carefully removed a part of the investigated material by a scalpel creating a step between the material and the Si/SiO\(_2\) substrate. Afterwards, we performed the thickness measurement across this step defining the thickness of the material. We started the scan in a place where the AFM tip sensed both the substrate and the material. Fig. 4a presents a typical example of the thickness measurement for the sample \( C \). By setting the fast scanning direction perpendicular to the vertical line dividing the two regions, a clear step height difference in every measurement line was recorded (Fig. 4b). AFM thickness investigations require precise surface leveling as a small misalignment between the measuring axis and the sample axis increases the error in height measurements [40]. After the correct surface leveling, a least square line in which the slope is constrained to zero is fitted to the profiles in both scanned regions. From the fit, we rejected the edges of the image and the step, as both are prone to AFM artifacts [41, 42]. After this procedure, the difference between the individual intercepts of the lines equal to 65 nm is the thickness of the investigated material. The usage of this procedure for step height measurements is however time consuming, as one has to analyze every line independently. A good alternative for a reliable height measurement is the analysis of surface height histograms (Fig. 4c) [43]. A height histogram has the advantage of a simultaneous analysis of all the pixels of the image manifesting in turn an averaging effect in which the influences of AFM distortions are not pronounced. For a stepped surface, one can observe two well-pronounced peaks in the surface height histogram. We fitted each peak using Levenberg–Marquardt least-square algorithm, with a Gauss function and the peaks center positions were acquired from the fits. The step height equals the
difference between the peaks center positions [44, 45]. From the analysis of Fig. 4c we found the height of the deposited material to be equal to 65 nm. In general, the thickness of our films varied between 53 nm and 74 nm. For all samples, we measured the thickness at least at three different positions distributed over the surface near the evaporated contacts prepared for CV investigations. This allowed us to apply statistics and within each sample, we estimate a height percentage deviation to be of the order of ± 10 %, which is in good agreement with the capacitance fluctuation of 9 %. This is an indication that mainly the material thickness deviation causes the variation of the capacitance in accumulation. The thickness measured by AFM is the major source of error for the determination of the dielectric constant which error we assume to be in the range of ± 12 %.

As the width of the Gaussian peaks is equal to the surface height standard deviations, we may individually determine the RMS roughness of both materials [44, 46]. We obtained surface height standard deviations in the order of 3.3 nm and 1.4 nm for the substrate and 1 % PCBM in APTMS material, respectively.

3.3. CV measurements

Figs. 5a and 5b show the CV measurements of samples B and C at three different contact areas at each sample. The area capacitance in accumulation shows a relative constant value for the three contacts on both samples. Compared to our former investigations on sol-gel films (sample D, [28]) with a variation of the area capacitance in accumulation of approximately 25 %, we observe in these films prepared by spin coating an alteration of only 9 %. This indicates that the film homogeneity of our spin-coated films seems to be better than that of our sol-gel films.

However, we still observe a huge hysteresis inside the CV loop as shown in Fig. 5c which is much more pronounced in the PCBM film (sample C). At this stage of investigations, we have not yet performed annealing steps, which might lead to the avoidance
of moveable charges inside the layers corresponding to the hysteresis in the CV loops. We believe further that the investigations of annealing steps should be performed preferably at metal-insulator-metal structures (MIM) in order to avoid additional effects like charge trapping at the interface between the silicon and the dielectric, in particular sample C exhibits already a stretch out of the CV curve in the depletion state indicating interfacial states [47]. Furthermore, the MIM structure is more closely to the real configuration in interconnects. We would like to mention that we will discuss the hysteretic behavior within the CV loops on our APTMS based films in more detail in a forthcoming work. In agreement with the literature [10] we will state there, that mainly NH$_3^+$ species might be responsible for the hysteresis. In the XPS data of the films B and C reported above we observe these centers in the N 1s core level spectra in both films but more pronounced in sample C. Furthermore, a minuscule amount of impurities like absorbed water in the film may ruin the effort of low-\textit{k} integration [48] caused by the high polarity of water and consequently its high dielectric constant in the range of 80 (at room temperature and 0.1 MPa) [49] pointing out the necessity of a post deposition annealing routine.

Nevertheless, the improved homogeneity of the spin-coated films allows a plot of the normalized capacitance taken in accumulation ($C_{acc}$) versus the contact area ($A$) as depicted in Fig. 6. We applied the plate capacitor approximation in order to determine the $k$-value of the films. Writing

$$C_{acc} \frac{d}{\varepsilon_0} = k A,$$  

where $d$ is the film thickness, and $\varepsilon_0$ is vacuum permittivity, it can be seen easily that the dielectric constant $k$ of the film can be calculated directly by the slope of a linear fit to the data. In Eq. 3 we applied the thickness determined near each related contact used for the CV measurements on the samples. The lower slope of the fit to the data of sample C containing 1
% of PCBM shows that this sample exhibits a smaller $k$-value equal to 3.4, in contrast to sample $B$ where we obtained $k = 4.1$. Here we have to mention that on the Si substrate a residual SiO$_2$ layer was still existent after the cleaning procedure as revealed in the XPS investigations (not shown). Assuming a SiO$_2$ thickness of 1 nm to 2 nm as a typical value of a native oxide the resulting influence on the permittivity value of our layers is in the range of 1.6 % to 3.2 %. Therefore, we neglected a probable SiO$_2$ layer in the calculations.

Concerning these results, we can conclude that the usage of a film containing the better soluble fullerene derivative PCBM is leading to lower $k$-values compared to films produced by solutions of pure C$_{60}$.

Conclusions

We synthesized and investigated APTMS based low-$k$ material including fullerene cages by means of the spin-coating method. With XPS spectroscopy, we performed an analysis of the time-related chemical processes within the prepared films exposed to ambient conditions. It was confirmed that the fullerene containing APTMS monomer spin-coated on the substrate partially undergoes a condensation reaction loosing $–$OCH$_3$ and $–$CH$_3$ species and forming a Si-O-Si network. However, the quantitative XPS analysis of the described samples reveals that the ratio of the N and Si atoms within the films remains close to 1. This result proves that the aminopropyl groups still exist in the siloxane matrix. The 1 % C$_{60}$ APTMS solution is already saturated, and the films prepared by spin coating contain about 51 % of the carbon species. This value increased up to about 69 % by the replacement of C$_{60}$ with PCBM molecules. CV measurements showed that the increase of the overall carbon species amount within the film reduces the dielectric constant of the prepared material. Large hysteresis of the CV curves suggest the presence of movable charges and trap centers within the film that may be by-products of the chemical reactions between the components. In agreement with our XPS data, NH$_3^+$ species may act as trap centers modifying the hysteresis. We cannot exclude
the adsorption of small water amount and other impurities that could influence the dielectric properties (permittivity and probably the hysteresis).

Summarizing, a significant homogeneity improvement of the films was obtained due to the spin-coating preparation, in comparison to films prepared previously by the sol-gel method (sample $D$, see also [28]). At the same time, the fullerene species concentration was significantly increased. The prepared thin film material has a low dielectric constant. Further improvements (water elimination, replacing fullerenes by its derivatives, additional dopants application) are still necessary to obtain high quality ultra-low-$k$ films. The influence of the fullerene dopants onto mechanical and dielectric degradations of the hybrid material has to be studied further since they can weaken the elastic modulus of the material [4] as well as they may act as a percolative path of defects resulting in the breakdown of the dielectric [50].
Acknowledgement

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References

Fig. 1. The schemes of the investigated samples: A) 2.4 % C$_{60}$ solution in APTMS spin-coated on the Si surface (referred in the text as sample A), B) 1 % C$_{60}$ solution in APTMS spin-coated on the Si surface (sample B), C) 1 % PCBM solution in APTMS spin-coated on the Si surface (sample C), D) low-$k$ film obtained by the sol-gel method used as a reference sample (sample D).

Fig. 2. XPS spectra of the sample A. Top row (a-d) represents the sample A measured 24 h after the preparation (sample A), bottom row (e-g) depicts the same sample measured 10 days after the preparation (sample A').

Fig. 3. XPS spectra of the samples B and C. Top row (a-d) represents the sample B, bottom row (e-g) depicts the sample C. The inset in (e) shows the magnified region I.

Fig. 4. NC-AFM thickness measurement on the sample C at a randomly chosen position. (a) Surface topography of two regions: Si/SiO$_2$ substrate (dark color), and 1 % PCBM in APTMS spin-coated surface (light color). (b) Typical profile of the step with linear fits to both regions. (c) Surface height histogram of the whole image with two Gaussian fits.

Fig. 5. CV measurements recorded at 1 MHz on the samples B and C. Figure part (a) depicts the measurements on sample B at three different contacts with various diameters as given in the legend, while figure part (b) shows the same for sample C. Part (c) pictures the hysteresis during the measurement on both samples. The arrows illustrate the measurement direction.

Fig. 6. Normalized accumulation capacitance versus contact area of samples B and C and linear fits performed according to Eq. (3).

Table 1

Peak decomposition of the XPS spectra of sample A: obtained after 24 h (sample A) and ten days after the preparation (sample A') respectively.

Table 2

Peak decomposition of the XPS spectra of samples B and C
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<th>Region</th>
<th>Peak Number</th>
<th>Position [eV]</th>
<th>Percentage of the main peak area [%]</th>
<th>Assignment</th>
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<td>Sample A'</td>
<td>Sample A</td>
<td>Sample A'</td>
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<td>-NH₄⁺ [11, 18] -NH₄⁺ [11, 18]</td>
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<td>N 1s</td>
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<td>400</td>
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<td>-NH₄⁺ [32] -NH₄⁺ [32]</td>
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<td>II</td>
<td>533.2</td>
<td>533.7</td>
<td>-C-O [34], -Si-O [35] -C-O [36]</td>
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<tr>
<td>O 1s</td>
<td>II</td>
<td>531</td>
<td>531</td>
<td>N-C=O [34] ---------</td>
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<tr>
<td>Si 2p</td>
<td>I</td>
<td>103.5</td>
<td>103.5</td>
<td>O-Si-O/Si-OH [35] O-Si-O/Si-OH [35]</td>
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</tbody>
</table>
Figure 1
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2.4% C\textsubscript{60} in APTMS spin-coated

1% C\textsubscript{60} in APTMS spin-coated

A

B

1% PCB in APTMS spin-coated

the reference low-k material

C

D
<table>
<thead>
<tr>
<th>Sample</th>
<th>Element</th>
<th>Binding Energy [eV]</th>
<th>Counts</th>
<th>Figure</th>
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<tr>
<td>A</td>
<td>C 1s</td>
<td>-292 to -280</td>
<td></td>
<td>(a)</td>
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<tr>
<td></td>
<td>N 1s</td>
<td>-108 to -100</td>
<td></td>
<td>(b)</td>
</tr>
<tr>
<td></td>
<td>O 1s</td>
<td>-408 to -400</td>
<td></td>
<td>(c)</td>
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<tr>
<td>A'</td>
<td>C 1s</td>
<td>-292 to -280</td>
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<td>(e)</td>
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<td></td>
<td>N 1s</td>
<td>-108 to -100</td>
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<td>(f)</td>
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<td></td>
<td>O 1s</td>
<td>-408 to -400</td>
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Fig. 3

(a) sample B  
(b) sample B  
(c) sample B  
(d) sample B  
(e) sample C  
(f) sample C  
(g) sample C  
(h) sample C
Figure 5
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Figure 6
Click here to download Figures (if any): fig6.eps