Spectroscopic and capacitance-voltage characterization of thin aminopropylmethoxysilane films doped with copper phthalocyanine, tris(dimethylvinylsilyloxy)-POSS and fullerene cages

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Abstract

We report on studies about novel 3-aminopropyltrimethoxysilane (APTMS) based hybrid composites doped by copper phthalocyanine (CuPc), [6,6]-phenyl-C\textsubscript{61}-butyric acid methyl ester and tris(dimethylvinylsilyloxy)-POSS (POSS). APTMS was used as siloxane matrix in order to produce thin layers of composite materials spin-coated onto silicon. The surface chemistry and the dielectric properties were investigated by the combination of X-ray photoelectron spectroscopy and capacitance voltage technique. We observed strong correlations between the dopant concentration and the chemical composition, homogeneity and electrical properties (permittivity, hysteresis) of the produced layers. Hence, an increase of the surfaces chemical resistance against the ambient conditions due to the POSS incorporation into the siloxane matrix was found. Furthermore, this work demonstrates that a properly chosen concentration of CuPc and POSS dopants within the siloxane matrix leads to homogenous films with an extremely low dielectric constant in the range of 1.8.

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1. Introduction

Phthalocyanines are conjugated molecules with outstanding optical and electrical properties as well as high thermal and chemical stability. The wide range of possible applications of phthalocyanines includes electrochemical devices, solar cells, gas sensors, optical switches, data-storage media and many others [1]. Metallophthalocyanines (MtPc) are considered for various technological applications like organic transistors, chemical sensors, and organic electroluminescent devices [2]. Thin organic films composed of MtPc such as copper phthalocyanine (CuPc) attracted a great scientific attention in order to design potential molecular devices [3]. The application of CuPc oligomers as high dielectric constant fillers in a polymer matrix is also reported in the literature [2,4]. According to Zhang et al., the observed dielectric constant of CuPc oligomers has been as high as $10^5$ [2]. However, the work using the theory of the local dielectric permittivity performed by Shi and Ramprasada [4] indicates that CuPc monomers do not intrinsically have a high dielectric constant, as values of around 15 and 3.4 along and perpendicular, respectively, to the CuPs plane were found. These authors attributed the high value of CuPc systems to some other extrinsic factors [4]. In our experiment CuPc has been applied as a filler into low-$k$ 3-aminopropyltrimethoxysilane (APTMS) based thin films. As revealed by our capacitance-voltage (CV) investigations the presence of the CuPc filler within the APTMS based thin films decreases the value of the effective dielectric constant of the resulting matrix.

As an additional filler of some of the low-$k$ composites described in this paper [6,6]-phenyl-C$_{61}$-butyric acid methyl ester (PCBM) was applied. PCBM was used as a source of fullerene cages that are known for its unique physicochemical properties [5]. In this paper we
incorporated PCBM into the siloxane matrix in order to decrease the dielectric constant of the
resulting material by increasing the porosity within the films [6]. Since the non-functionalized
C_{60} fullerene exhibits a low solubility and the tendency to form agglomerates in solvents [7,8],
the utilization of PCBM as its better soluble derivative realizes a better dispersion of the
fullerene species within the films.

In order to further decrease the dielectric constant by introducing porosity on the one
hand [6,9] and to increase the oxidation resistance on the other hand, some films were
additionally reinforced with incompletely condensed frameworks possessing a hybrid
inorganic–organic, three-dimensional structure cage polyhedral oligomeric silsesquioxanes
(POSS). The incorporation of this kind of molecules into the polymeric material allows the
control of the dielectric constant. Furthermore, this can lead to many substantial variations
and improvements of the final compositions ranging from the thermal stability,
hydrophobicity, refractive index, oxidation resistance, surface hardening to the optical clarity,
attracting a great research interest in the past few years [9–12].

The paper is organized as follows: Based on the results of X-Ray photoelectron
spectroscopy (XPS) we discuss the chemical composition and the resistance against ambient
influences of the hybrid material films composed of CuPc, POSS and PCBM species
incorporated in various concentrations into the APTMS based siloxane matrix. The next
section describes the CV characterization of the samples. Finally, a 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 structures appearing in the spectra due to
the satellite radiation have been subtracted before the data fitting [13,14]. The peak intensities
were acquired after Shirley background removal [15]. Corrections for the energy shift were
accomplished assuming a binding energy of 103.5 eV for the Si 2p peak of the Si$^{+4}$ species
[16]. The data of atomic composition and atomic ratios were calculated using the atomic and
instrument sensitivity factors [17]. The obtained spectra were decomposed with Gaussian line
shapes into individual components of the peaks in order to obtain detailed information about
the nature of chemical interactions [18,19].

CV curves were recorded on metal-insulator-semiconductor (MIS) structures by a CV
set-up based on a LCR meter Agilent 4284A [20]. A slow ramp of 25 mV/s was used for the
DC bias, which was superposed by a 1 MHz AC signal of 25 mV (RMS). The samples were
first driven into the accumulation state, followed by biasing the semiconductor through
depletion and inversion and then backwards to accumulation. The permittivity of the
investigated layers was determined using the accumulation capacitance via the plate capacitor
approximation as described below.

Material thickness measurements were conducted by Veeco CPII atomic force
microscope (AFM) working in a non-contact mode at room temperature. Phosphorus doped
silicon cantilevers (model MPP-11123-10) with a resonance frequency of about 275 kHz and
an approximate spring constant of 48 N/m were used. The nominal tip curvatures of the
cantilevers were less than 8 nm.

2.2 Sample preparation

2.2.1 Materials and substrates

In this work we used PCBM (99.5 %), APTMS (97 %) and
tris(dimethylvinylsilyloxy)-POSS (for simplification further referred as POSS in the text)
obtained from Sigma-Aldrich. CuPc (95 %) was delivered by Alfa Aesar. Phosphorous doped
n-type silicon (100) wafers having a resistivity of 1-5 Ω cm delivered by Crystec (Berlin, Germany) were chosen as substrates for our samples.

2.2.2. Sample preparation

The schemes of all investigated samples are illustrated in Fig. 1 (the samples A, B, C contain higher dopant concentrations whereas the samples D, E, F contain lower dopant concentration). The dopant concentrations within the films were calculated in weight percent.

The Si substrates were cleaned for 10 minutes by ultrasonification in isopropanol and then in distilled water, afterwards they were dried in nitrogen stream. The wafer surfaces were hydroxylated 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 were dried afterwards in nitrogen stream. Based on this procedure, the prepared samples have a hydroxylated silicon dioxide surface (as indicated in Fig. 1) which is hydrophilic.

The hybrid materials were produced from a dispersion of PCBM, CuPc and POSS particles within the APTMS monomer. The thin films were produced by spin-coating at a speed of 6000 rpm for 15 seconds in glove box conditions under argon atmosphere.

Additionally, CV investigations were performed on the samples A, B, D, and F as these samples had very uniform thickness distributions. Silver contacts with diameters between 400 µm and 800 µm were evaporated on top of these samples (refer to Fig. 1) through a shadow mask in order to finalize the MIS structure of the samples. Results achieved previously on a pure APTMS sample [21] are included in the CV data for comparison.
3. Results and discussion

3.1 XPS investigations on the samples with higher CuPc concentration (>=0.4 %)

In this section we discuss the XPS results of the samples with higher dopant concentrations (samples A, B, and C, see Fig. 1). The sample C was additionally reinforced with POSS molecules. Fig. 2 represents the XPS results obtained for the samples A, B and C. The detailed peak analysis is listed in Table 1.

The C 1s XPS spectra of the samples B and C contain the characteristic π-π* shake-up peaks confirming the presence of fullerene cages on the surface [22,23,25] (peaks I' at around 291 to 292 eV). These features are absent in the data of the sample A where the APTMS matrix was doped only with CuPc molecules. Nevertheless, the presence of –C=C– species coming from both CuPc and PCBM molecules can also be confirmed due to shifts of the main C 1s signals (peaks III). In general, these features represent simultaneously existing sp² (graphite like) and sp³ (diamond like) carbon contributions. Since APTMS is the basic component of the analyzed films, one may presume that the main C 1s signal of the XPS spectra is dominated by the propyl groups of this substance with a corresponding signal at around 286 eV [16,34]. Thus, a shift of the center position of this feature towards lower binding energy is an evidence for the increase of the sp² contribution to the C 1s core-level spectra. The main feature in the C 1s spectra of pure fullerene and CuPc films appears around 284.6 eV-284.7 eV [25,35] suggesting a large contribution of sp³ species within the films composed of these substances. The center positions of the main feature within the C 1s data of the samples A and B are very similar (285.6 eV and 285.5 eV respectively). These binding energies are lower than those corresponding to the C 1s main feature obtained for pure APTMS films [16,34]. It suggests that the concentration of dopants including sp² carbon species (CuPc, PCBM) was high enough to shift the center position of the main feature towards lower binding energy. In contrast, the center position of the main C 1s feature of
sample C is in good agreement with the literature data of pure APTMS (286.1 eV). The small feature observed at around 284 eV may be assigned to Si–C [29] species of the POSS molecules and sp³ carbon contributions from CuPc and PCBM.

While comparing the C 1s core level spectra of the discussed samples we notice, that the feature II is the smallest in the data of sample C where POSS molecules were incorporated into the film. Taking into account that a significant contribution to these signals has been attributed to the carbon oxidized states, we suppose that the surface of the film doped with POSS molecules (sample C) is most resistant against oxidation in ambient conditions.

The conclusion regarding the higher resistance of the POSS containing sample against the interactions with ambient components can be confirmed by the N 1s core level decomposition. The area of the feature I corresponding to the NH₃⁺ species is the smallest for sample C. This protonated amino group is a product of the following reactions between APTMS and ambient CO₂ [16]:

\[
\equiv Si(CH₂)₃NH₂ + CO₂ \leftrightarrow \equiv Si(CH₂)₃NH₂⁺COO⁻ \quad (1)
\]

\[
\equiv Si(CH₂)₃⁻NH₂⁺COO⁻ + NH₂(CH₂)₃Si \leftrightarrow \equiv Si(CH₂)₃NHCOO⁻ + NH₃⁺(CH₂)₃Si \equiv \quad (2)
\]

Thus, we presume that the smallest NH₃⁺ contribution in sample C is a hint that this surface was the least affected one by the ambient.

The O 1s core level spectra of the samples A, B, C do not differ significantly from each other. While analyzing these features, we conclude that the main sources of oxygen within the analysed surfaces are the chemical groups containing oxygenated carbon and silicon oxides [24,30]. The small signals II in the O 1s spectra of the discussed samples correspond to the oxidised carbon species containing double bonds [24,31,32].

The Si 2p core level spectra of the samples A, B and C reveal one pronounced feature originating from –Si–O species [33].
A quantitative peak analysis [36] was carried out in order to determine the surface element concentrations. The spectra normalization was achieved by dividing the observed relative peak areas by the atomic and instrument sensitivity factors equal to 0.711, 0.296, 0.477, and 0.339 for O, C, N, and Si, respectively [17]. The resulting surface atomic concentrations of the films A, B and C are given in the Table 2.

The stoichiometry of the unhydrolyzed APTMS monomer (excluding hydrogen atoms) corresponds to C₆NSiO₃, whereas the “ideal” poly[(aminopropyl)siloxane] polymer has a composition of C₃NSiO₁.₅ [16]. Thus, the content of carbon and oxygen within the pure APTMS film depends on the degree of monomer condensation that takes place due to the humidity in ambient conditions. Fig. 3 describes the possible hydrolysis (a) and condensation (b) reactions of the APTMS monomer due to the presence of ambient water.

Although the reactions presented in Fig. 3 lead to changes of the C and O amounts within the APTMS based film, this process should not influence the Si:N ratio that equals 1.

While analyzing the quantitative surface compositions given in Table 2, we notice very similar compositions of the samples A and B. Surprisingly; the surface oxygen concentration of sample A is slightly higher than this one of sample B. However, contrary to the sample B, sample A doesn’t consist of oxygen containing PCBM molecules. Thus, we attribute the highest amount of oxygen species within surface A to its relatively strong oxidation in ambient conditions. Taking into account that film A contains the highest CuPc concentration of all samples described in this paper, we suppose that this dopant accelerates the surface oxidation process.

The surface elemental composition of sample C suggests that the POSS molecules incorporation increased the surface carbon concentration to 56 %. Taking into account that this series of samples was produced and stored under the same conditions, we do not attribute this fact distinctly to the lower degree of APTMS monomer condensation. In particular this
argument is supported by the lower oxygen content within this surface compared to the samples A and B, what on the other hand may also suggest the lower degree of surface oxidation of sample C. We observe further that a relatively small amount of POSS molecules incorporated into the film C (0.3 \%) is sufficient to increase the atomic Si:N ratio, which is about 1.20 in sample C whereas it is only 0.79 to 0.89 for sample B and A, respectively. Additionally, we conclude that the surface C is the most resistant one against oxidation, since the detected surface oxygen concentration is lower than in the samples A and B, although POSS cages are a source of oxygen. Fig. 4 represents a scheme of the POSS molecule applied in the experiments described in this paper.

3. 2 XPS investigations on the samples with lower CuPc concentration (<0.1 \%)

After the aforementioned investigations of the CuPc, PCBM and POSS molecules influence onto the APTMS matrix properties, we have produced similar APTMS based films but with lower concentrations of CuPc and POSS dopants. On the other hand, in this part of the experiment we did not use oxygen-containing PCBM molecules in order to investigate the influence of POSS molecules onto the surface resistance against oxidation in ambient conditions. The samples discussed in this section are indicated as D, E and F in Fig. 1. Fig. 5 represents the XPS results obtained for these samples. The detailed peak analysis of the spectra is given in Table 3.

The application of dopants with lower concentration influenced the physical properties of the APTMS solutions providing the possibility of the preparation of thin transparent and homogenous layers in the spin-coating process (thickness in the range of 8-20 nm, see section 3.3). Its influence on the chemical properties of the APTMS layers can be estimated by XPS. The centre positions of the features III in the C 1s spectra of the samples D, E and F are in a good agreement with the literature value corresponding to the propyl group of pure APTMS
(286 eV, [16,34]). Because, contrary to the samples A, B, C, no shift of these features towards lower binding energy is observed, we suppose that either the amount of the sp\(^2\) species has not been detectable due to the low doping concentration or it has been minimized by interactions with the APTMS matrix.

While comparing the features II in the C 1s core levels, attributed to a considerable extent of carbon oxidized states, we observe also for this sample series that this signal is the weakest for the data of the POSS reinforced film (sample F). We attribute this fact, like for the thicker film C, to the smaller surface oxidation in comparison to the other samples. Moreover, also the features I in the C 1s and N 1s of sample F corresponding to the NHCOO\(^-\) and –NH\(_3\)\(^+\) species, respectively [16], are clearly smaller. Both species are formed as a result of APTMS interactions with the ambient CO\(_2\) regarding the reactions (1) and (2) [16]. These relatively weak signals suggest a higher chemical stability of the surface of sample F after air exposure. However, the decrease of the feature II in the C 1s core level spectrum of sample F in comparison to the corresponding signals of the samples D and E may be also related particularly to the smallest concentration of CuPc within the sample F.

The main contribution to the O 1s core level spectra of the samples D, E and F comes from C–O and Si–O species (signals I) [32,33]. Similarly to the spectra recorded for the samples A, B and C, the small features II are assigned to the chemical groups containing C=O bonds [32,33].

The Si 2p core level spectra of the samples E and F contain, contrary to that of the sample D, the substrate related feature coming from the Si\(^0\) at around 99 eV. This is attributed to the very low thickness of the deposited material (in the range of 10 nm) not exceeding the sampling depth of our XPS measurement.

Also for this sample series a quantitative XPS analysis was performed as done for the samples A, B, and C reported above. Observing the atomic ratios of the elements within the particular films, the influence of dopants on the chemical composition of the surface can be
discussed more distinctly than it would be possible by a qualitative analysis. The surface atomic concentrations of the films D, E, F are given in the Table 4.

The resulting stoichiometries are: \( \text{C}_{4.91}\text{N}_{1.09}\text{SiO}_{3.10}, \) \( \text{C}_{5.77}\text{N}_{1.13}\text{SiO}_{3.20} \) and \( \text{C}_{4.88}\text{N}_{0.96}\text{SiO}_{2.76} \) pointing out Si:N ratios of 0.92, 0.88 and 1.04 for the samples D, E, and F, respectively. For the samples D and E the slight superiority of the N in comparison to the Si is obviously caused by the contribution of the nitrogen species of CuPc, similar as it has been observed for the samples A and B. However, due to the very low CuPc dopant concentration the difference of the Si:N ratio between the pure APTMS and the analyzed films is small. For the film F reinforced additionally by Si containing POSS a slight superiority of Si in comparison to N is observable, however the Si:N ratio is lower than for sample C described above where this value equaled around 1.20.

The quite high amount of C atoms within the films D and E in comparison to the thicker aforementioned films with even higher doping concentrations may be explained by the adsorption and interactions with ambient CO\(_2\) (refer to Eq.s 1 and 2). Due to the small thickness of the films the CO\(_2\) influence could stronger affect the chemical compositions of the layers than in the samples A and B. A lower degree of APTMS condensation (see Fig. 3) of the films D and E resulting in a higher C content cannot be excluded. For the sample F we notice a lower atomic C concentration than for the sample C. This may be attributed to the lower dopant concentration within the film F. Comparing the atomic ratios obtained for the discussed films with those of the unhydrolysed ATPMS monomer and the “ideal” poly[(aminopropyl)siloxane] polymer, we confirm the conclusions deduced above that the POSS reinforced surfaces are more resistive against the ambient oxidation. The oxygen atomic concentration within the film F is only slightly lower than in sample E, but at the same time we emphasize one more time that the POSS molecule contains a considerable amount of oxygen bonded to silicon (Fig. 4). The concentration of POSS cages within the film F (0.12
turned out to be sufficient to increase the Si:N ratio within the APTMS matrix, although this material contains an additional source of nitrogen (0.04 % CuPc). Thus, we conclude that some contribution to the oxygen atomic concentration within the film F originates from POSS cages.

3.3 CV measurements

Next we discuss the CV investigations done on the CuPc (samples A and D), CuPc/PCBM (B) and CuPc/POSS (F) incorporated APTMS films. On all samples the CV measurements were performed at four to five contacts with different diameters distributed over the surface of the sample, while the CV dependencies on one contact of each sample are presented in Fig. 6a and 6b. The data are normalized to the contact area (A_C), the measurements shown in Fig. 6 were performed on the smallest contact area of each sample. The thicknesses (d) of the samples were determined on different positions on the surface of the samples by AFM height histogram analysis as we described recently [38], where 167 nm, 190 nm, 20 nm, and 8 nm were evaluated as the thickness of the samples A, B, D, and F, respectively (see table 5). In Fig. 6a the CV data of the thicker samples are compared. Although the sample B consists of a thicker dielectric in comparison to sample A, it exhibits a higher accumulation capacitance (C_{acc}). Therefore, as according to the plate capacitor approximation the capacitance depends inversely on the thickness, we can conclude that the dielectric constant (k) of sample B should be higher compared to sample A. In Fig. 6b the CV data of the thinner layers are depicted. Here, the thinner layer of the sample F exhibits a higher C_{acc} value in comparison to the sample D. However, the thickness of the sample F is smaller by a factor of 2.5 than the thickness of sample D. Hence, as the C_{acc} value is not higher by this factor, a smaller k-value of the layer F compared to the film D can be concluded qualitatively. In order to determine the permittivity of the films quantitatively we plotted the normalized C_{acc} values in dependence of the area according to
where \( \varepsilon_0 \) is the vacuum permittivity. Fitting the data with respect to Eq. 3, the permittivity can easily be determined by the slope of the linear approximation. This is illustrated in Fig. 7 where the normalized accumulation capacitance values of the samples \( A, B, D, \) and \( F \) as well as of a pure APTMS reference sample [21] are depicted. The results regarding the \( k \)-values of the samples investigated in this work are overviewed in Table 5. The error connected to the \( k \)-value determination via the linear approximation was in the range of 1 % to 8 %. A probable additional interfacial SiO\(_2\) capacitive contribution has not been taken into account. The samples \( A \) and \( B \) are relatively thick; therefore an influence on the permittivity is below 1 %, when a SiO\(_2\) interfacial layer of 1 to 2 nm, as a typical value of the native oxide, is assumed. However it should be pointed out, that in the samples \( D \) and \( F \) the deviation of the permittivity is then in the range between 4 % and 13 %. Nevertheless, we observe a distinct decrease of the dielectric constant compared to the pure APTMS layer in all samples. While the relative dielectric constant of our pure APTMS film is 4.1 [21], it reaches values of 2.6, 3.4, 3.3, and 1.8 for the samples \( A, B, D, \) and \( F \), respectively. Discussing first the thicker layers, we state that in particular the incorporation of CuPc of sufficient concentration into the APTMS film is effective for the permittivity decrease. In sample \( A \) only CuPc is incorporated into the APTMS and the CuPc content is higher (1.3 %) compared to sample \( B \) (0.7 %) where also PCBM (0.5 %) was added. Moreover, we realized a dielectric constant in the same range like for sample \( B \) when 1 % PCBM without CuPc was incorporated into APTMS [38]. But, if we include also the thinner layers into the discussion, we realize that an incorporation of only CuPc with a concentration lower than 0.1 % into the APTMS (sample \( D \)) matrix does not lead to such a strong decrease of the permittivity. However, the further addition of POSS molecules in a relatively low concentration (0.12 %) into the matrix\(_x\) while keeping the CuPc concentration in a similar range (sample \( F \)), delivers an outstanding value of the dielectric
constant of the resulting APTMS based film. We argue that the additional incorporation of POSS molecules into the matrix induces the required porosity into the film. In our previous work [21,38] we observed a similar behavior in the PCBM/POSS/APTMS system where also the combination of PCBM and POSS led to the best results in terms of the dielectric constant. However, there the amount of POSS monomers within the produced layers was overloaded leading to fractal patterns within the film surfaces [21].

We have to note that we have not yet investigated heat treated films by CV. Products formed due to the hydrolysis and condensation reactions (see Fig. 3) of the APTMS like –OH residual groups or water may still be present at the surface or within the film [21,38–40]. These species have strong permanent dipoles which may contribute to a higher overall polarizability of the final material and, hence, give rise to an increased dielectric constant [39,41,42]. Nevertheless, comparing the results of this work to our previous investigations [21,38] we conclude that a CuPc/POSS material combination in a range as used in sample F in this work is most successful in order to reduce the final dielectric constant of APTMS based films incorporated by PCBM and/or POSS and/or CuPc molecules and might be a potential candidate for an ultra-low-k material.

Interestingly, we observe in the thick APTMS layers mixed with CuPc (samples A and B, Fig. 6a) much lower hysteresis inside the CV measurements in comparison to our former investigations, where C$_{60}$, PCBM or POSS species were incorporated into siloxane based films [21,38,43]. In [21] we have discussed a probable mechanism related to a filling and defilling of NH$_3^+$ charge trapping centers within the APTMS based films, where the trapping centers are caused by the interaction with ambient CO$_2$ (see also Eq.s 1 and 2), which is in agreement with other findings in literature [44]. We have further stated that these centers are mainly due to the APTMS itself [21]. If we compare the N 1s core level spectra in Fig. 2 with that one of our previous work, we find a clear reduction of the NH$_3^+$ related contribution (peak I) within the signals of the samples A and B. While the contribution of the NH$_3^+$ species
to the N 1s signal was over 11 % in our previous work [21], in the samples A and B it equals around 4.1 % and 7.4 % respectively. Although the CuPc molecule reveals an insignificant Lewis acidity [45], the XPS spectra show that CuPc in an adequate concentration (above or equal 0.7 %) within the APTMS seem to interact with the NH$_3^+$ centers resulting in a relatively low signal contribution of NH$_3^+$ species to the N 1s core level spectra. Contrary, the films with very low concentrations of CuPc (below 0.1 %, samples D, E, F) exhibit much stronger NH$_3^+$ signals (see Fig. 5) which we observed also for the pure APTMS reference sample [21]. Moreover, the small remaining hysteresis in the CV data of the samples A and B is observed in the opposite direction compared to our previous investigations in [21,38,43]. Therefore, we conclude that in the layers A and B NH$_3^+$ trapping centers are not the reason for the observed hysteresis. According to the direction of the hysteresis we propose here a charge injection coming from the Si substrate [39]. Probably both mechanisms are coexisting in all samples, but in the CuPc incorporated APTMS films the charge injection from the substrate is more prominent in contrast to the pure APTMS films as well as to the APTMS films mixed with C$_{60}$, PCBM and/or POSS, where the charge injection into the NH$_3^+$ centers is dominating. This fact is further supported by the hysteresis found in CV data of the thin layers D and F (Fig. 6b). As discussed above, the NH$_3^+$ contribution within the N 1s signal is much higher for these samples compared to the samples A and B. In agreement with this finding, we observe the same kind of hysteresis in the CV data of sample F like in the pure APTMS films or in the APTMS films added with C$_{60}$, PCBM or/and POSS molecules [21,38]. However, in the CV measurement of sample D, we found the hysteresis in the other direction. But here we observed additionally a time dependence of the hysteresis, where at the beginning it was appearing in the same direction like in sample F, but then it changed to the opposite direction like it is shown in the example curve in Fig. 6b. This might be caused by a negative charging of the whole sample, as we found a positive shift of the CV curve with time (inset in Fig. 6b). This effect was not observed in all other samples. Due to the fact that annealing steps have not
yet been performed, moveable charges (Si–OH, water) might contribute to the hysteresis too [21,40,41].

Additionally, we observe a positive shift of the flatband voltage with respect to the voltage axis for the samples A, B, and F (sample D is not further discussed here because of the above mentioned charge injection with time). According to our previous report the ideal flatband voltage originating from the work function difference between the silver metal and the semiconductor should be in the range of -0.2 V to 0 V for these samples [21]. The measured flatband voltage of these samples is in the range between 0.74 V and 0.81 V for the samples A and B and between 0.96 V and 1.01 V for sample F corresponding to negative fixed oxide charges in the range of $5.7-7.7 \times 10^{10}$ cm$^{-2}$, $7.2-9.7 \times 10^{10}$ cm$^{-2}$, and $1.2-1.5 \times 10^{12}$ cm$^{-2}$ for the samples A, B, and F, respectively [46]. Recently, we discussed carbamate (NHCOO$^-$) species in our APTMS based films originating from interactions with ambient CO$_2$ [21,38] which might be responsible for the flatband voltage shift in positive direction [21]. Also in the C 1s core level spectra of the samples A, B and F we observe NHCOO$^-$ species (peak I in the related signals in Fig.s 2 and 5). Because the film F is not exhibiting a higher NHCOO$^-$ contribution inside the C 1s data compared to the samples A and B, we propose that an additional charge injection leading to negative fixed charges took place in the beginning of the measurement due to the low thickness of the film.

**Conclusions**

Based on the collected spectroscopic data we observe that even low concentration of CuPc and POSS dopants (in the range of 0.04 % - 1.3 %) influences the Si:N ratio within the APTMS layers sufficiently to be detected by XPS quantitative analysis. XPS revealed that the POSS containing layers were the least affected ones by ambient influence while at the same time the CuPc molecules accelerate the surface oxidation process.
The CV measurements indicated a distinct decrease of the dielectric constant of all composite APTMS based films described in this paper compared to the pure APTMS layer. The incorporation of POSS and CuPc dopants in a proper concentration (0.12% POSS and 0.04% CuPc) into the APTMS matrix results in a relative dielectric constant of 1.8. Although up to now CuPc oligomers have been applied mainly as high dielectric constant fillers in a polymer matrix [2,4], our investigation demonstrates that an appropriate chosen CuPc/POSS dopant combination seems to deliver a successful reduction of the final dielectric constant of APTMS based films. Moreover, CuPc molecules seem to decrease the hysteresis inside the CV measurements of the investigated samples probably due to an interaction with NH$_3^+$ trapping centers.

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References


Table 1. Peak decomposition of the XPS spectra of the samples A, B, and C.
Table 2. Atomic concentrations of the samples A, B, and C.
Table 3. Peak decomposition of the XPS spectra of samples D, E, and F.
Table 4. Atomic concentrations of the samples D, E, and F.
Table 5. Initial compositions and thicknesses of the electrically investigated samples and relative dielectric constant deduced by fits according to Eq. 3.

Fig. 1. (Color online) Schemes of the investigated samples prepared by spin coating onto Si substrates: A 1.3 % CuPc solution in APTMS (referred in the text as sample A), B 0.7 % CuPc and 0.5% PCBM solution in APTMS (sample B), C 0.4 % CuPc, 0.3% PCBM and 0.3% POSS solution in APTMS (sample C), D 0.09 % CuPc solution in APTMS (sample D), E 0.05 % CuPc solution in APTMS (sample E), F 0.04 % and 0.12% POSS solution in APTMS (sample F)

Fig. 2. (Color online) XPS spectra of the samples A (top row), B (middle) and C (bottom row). The following core level spectra are drawn in the same order for every sample: C 1s, N 1s, O 1s, Si 2p. The insets within the C 1s spectra show the magnified signals I´.

Fig. 3. Scheme of the hydrolysis (a) and the condensation (b) reactions of the APTMS molecule.
Fig. 4. Scheme of the POSS molecule applied as a dopant into the APTMS matrix. R’ indicates the cyclopentyl groups.

Fig. 5. (Color online) XPS spectra of the samples D (top row), E (middle) and F (bottom row). The following core level spectra are drawn in the same order for every sample: C 1s, N 1s, O 1s, Si 2p.

Fig. 6. CV characteristics of samples A (part a, open triangles, solid line), B (part a, filled circles, dotted line), D (part b, open stars, gray line), and F (part b, filled rectangles, dashed line). The capacitance values were normalized to the contact areas. The measurement direction is indicated by indexed arrows. The inset in part b shows repeated measurements from accumulation to inversion for sample D.

Fig. 7. Normalized accumulation capacitance versus the contact area of the samples A (open triangle), B (filled circles), D (open stars), F (filled rectangles), and a reference sample of pure APTMS taken from our previous investigation (open squares [21]). The data are normalized corresponding to Eq. 3. Linear fits to the data are performed according to Eq. 3 (A: thick solid line, B: dotted line, D: gray line, F: dashed line, reference sample: thin solid line). The results of the fits are discussed in the text and displayed in Table 5.
### Table 1

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Figure 1

Figure 2
Figure 3

Figure 4
Figure 5

Figure 6
Figure 7