



Plasma irradiation effects in phthalocyanine films

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Abstract

Plasma irradiation effects in copper phthalocyanine films were examined. The film surface and chemical composition were characterized by means of atomic force microscopy (AFM) and secondary ion mass spectrometry (SIMS), including SIMS profiling.

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1. Introduction

A great deal of effort is going currently into extending the use of organic and/or composite materials to (opto-)electronics to replace conventional inorganic matter (e.g. III–V or Si-based semiconductors) [1]. In pursuit of the ultimate goal of this activity, which is single-molecule (nano-) devices [2], the stage of micro-technology development is often skipped over. As a result, such common and well-developed techniques as patterning, plasma, ion treatment and implantation, are much less known in the field of molecular electronics. Meanwhile, metal phthalocyanines (PcM) that feature superior chemical and thermal stability among organic substances seem to be very likely candidates for fabricating hybrid inor-

ganic/organic devices, which exploit fascinating electrical and optical activity of these complexes [3].

In the present study we report some results of plasma modification of PcCu films in the reactive ion etching (RIE) chamber. The attention was focused to the general behavior of the material exposed under ion bombardment, rather than on the changes in the electrical or optical properties of such materials. We tested O₂, He and Ar (which is of not much difference) and CCl₂F₂ since combination of such chemistries may be useful for processing of PcM-based heterostructures containing inorganic components. For instance, O₂ is often utilized for resist stripping [4], while CCl₂F₂/He(Ar) chemistries are effective for selective patterning of III–V heterostructures [5,6].

The energies of ions in a conventional RIE reactor typically correspond to tens electron volts or less [7]. This is comparable with the energies of chemical bonds in phthalocyanine molecules and by far higher than the van der Waals forces forming the molecular

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crystallites. Therefore, severe alterations both in the film composition and morphology are predictable. Contribution of a local thermal stress cannot be underestimated. In lead phthalocyanine films for example, such processes as formation of new chemical bonds, polymerization, remarkable changes in relative atomic concentration of elements in the film surface and its restructuring were detected after plasma treatment [13]. Earlier, similar effects were observed for ion beam implantation in thin polycrystalline phthalocyanine films [8], although the energy of penetrating metal ions corresponded to several tens keV, and the average projected ranges lay far in the film bulk. It is however expected that reactive or non-reactive ions and their combination will cause different effects on the film surface.

2. Experimental

Copper phthalocyanine, $C_{32}H_{16}N_8Cu$ or PcCu (pigment blue, commercial polycrystalline powder), whose molecular structure is shown in Fig. 1, was thermally evaporated onto Si(1 1 1) plates in vacuum $<10^{-3}$ Pa (VUP-5 installation). The obtained heterostructures were also used in other physical experiments [8]. The organic film thickness was equal to $0.8 \pm 0.2 \mu\text{m}$ at the deposition rate of 0.2–0.4 nm/s. The samples were stored in laboratory air prior to further processing and measurements. Plasma treatment of the PcCu films was performed in a conventional planar RIE system (Secon XPL-26) equipped with a 100 kHz rf generator. The etcher had an anodized aluminium reaction chamber with symmetric temperature controlled electrodes spaced 25 mm apart. The samples were positioned on the bottom rf-driven electrode. The gas inlet was implemented

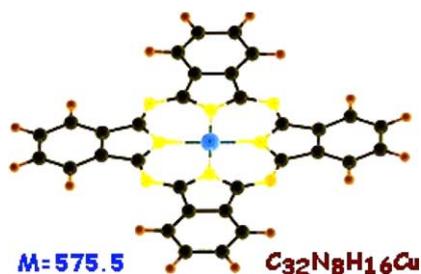


Fig. 1. Molecular structure of PcCu.

through five small orifices surrounding the cathode. The process gas pressure was monitored by a capacitive manometer in a closed loop with a downstream throttle valve and was set at 30 Pa. The applied power was always 500 W, while the process temperature ranged from 40 to 80 °C (see caption to Fig. 2). The etching gases (O_2 , He and CCl_2F_2 , or their mixtures) were supplied through stainless steel lines operated by mass flow controllers with an average flow rate of about 250 sccm.

Atomic force microscopy (AFM) measurements were done with a SOLVER P-4 (NT-MDT) microscope operating in the tapping mode with a standard cantilever (NSG111) [6]. Selected images are given in Fig. 2.

Static secondary ion mass spectrometry (SIMS) was carried out in a “Shipovnik” (NITI) installation at the bare vacuum $<7 \times 10^{-8}$ Pa [9]. The analytical conditions were as follows: primary ions: O_2^+ , differentially pumped duoplasmatron type source with a cold cathode, impact angle: 60°, primary ion energy: 10 keV using the Wien filter, beam current: 200 nA, raster size: $400 \mu\text{m} \times 400 \mu\text{m}$, beam diameter: 30 μm , working vacuum: 3×10^{-7} Pa. The positive secondary ions were detected by a quadrupole mass spectrometer adjusted to the range of 0–200 m/z . The best mass sensitivity obtained for this equipment in the given conditions was 5×10^{-6} calibrated from B^+ ions in a Si solid matrix, with the mass resolution of 0.1 m/z . The samples were analyzed without pretreatment, no charge compensation was needed for all PcCu films.

The data acquisition and treatment were performed using the software coming with the spectrometer. The program includes consecutive refinement from single-point peaks, smoothing (the procedure is based on the moving mean method) and peak deconvolution, so the vertical bar chart is finally constructed. The SIMS spectra of initial (a), sputtered (b) and variously etched PcCu films (c–e) are shown in Fig. 3. The SIMS patterns were somewhat oversaturated, we will therefore focus on the peaks with the height of ca. 10^3 and above, and on elements of particular interest. The x -axis is limited by instrumental settings. Some peak coordinates are given in Table 2.

The data are represented “as is” (without normalization [10]). Possible matrix effects and relative secondary ion yields are not taken into account here.

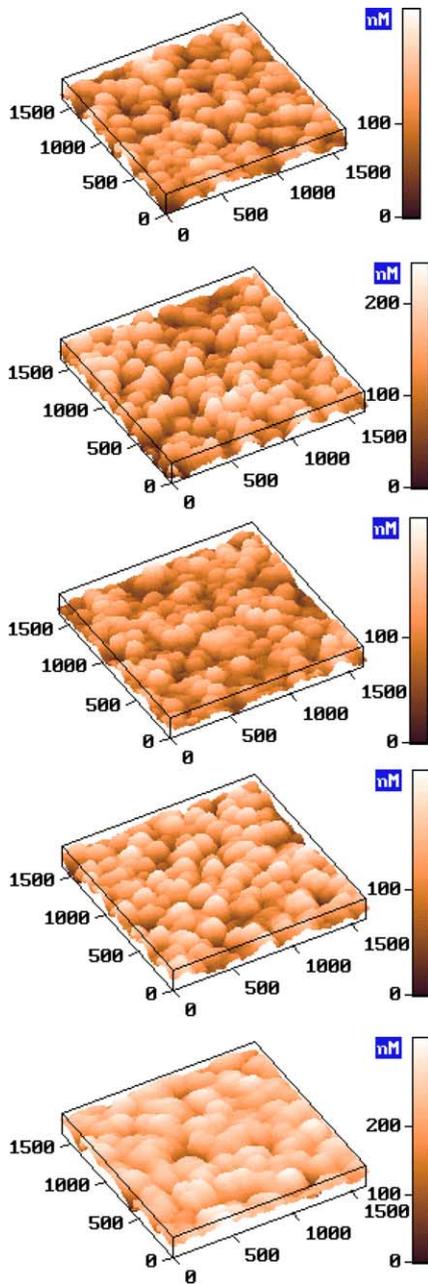


Fig. 2. AFM images of PcCu films, top to bottom: (a) intact surface, (b) etched in pure He for 1.5 min at 40 °C, (c) etched in a mixture of He:CCl₂F₂ = 1:1, (d) etched in pure CCl₂F₂ for 3 min at 80 °C, (e) etched in pure O₂ for 1.5 min at 80 °C (other conditions—see Section 2).

Although these may also affect the spectra of molecular films (see, e.g. [11]), there are no reliable literature data for correction. We are interested in the relative changes in samples and in detection of certain components within a spectrum rather than in a quantitative analysis of an organic solid with SIMS.

3. Results and discussion

3.1. The film topology

The intact film surface consists of rounded grains with the diameter (D) distribution approximately from 95 to 120 nm (Fig. 2a, Table 1). The mean peak height (Z_p) is 58 nm, while the surface roughness (Z_R) is 32 nm. These values are greater than those reported in [12] for similar systems, obviously owing to the differences in the film thickness and deposition rates. The surface roughness of initial Si-wafers prior to the deposition of organic films was less than 0.5 nm.

Treatment in He plasma led to an increase of the grain height and Z_R (see, Table 1 and Fig. 2b). As the distribution of the grain sizes is broad, it is hard to decide whether the grain diameter decreases or not. Besides, AFM measurements were made not exactly on the same area of the film surface, so possible variation in the topology along the film surface should be taken into account.

Adding dichlorodifluoromethane to the He plasma had little effect on the film surface (see Fig. 2c, Table 1). The roughness somewhat decreased in comparison with the previous two samples. A trend towards cluster association can be noticed.

The subsequent increase in the concentration of reactive etchant in plasma up to 100% was not efficient for altering the film relief. Then, the temperature

Table 1
AFM statistics

Fig. 2	D (nm)	Z_p (nm)	Z_R (nm) ^a
a	95–120	58	29
b	90–115	92	35
c	85–140	72	26
d	100–150	68	30
e	180–220	80	32

^a Calculated as $Z_R = (1/N_x N_y) \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} |Z|$, where $Z = Z_{ij} - Z_p$.

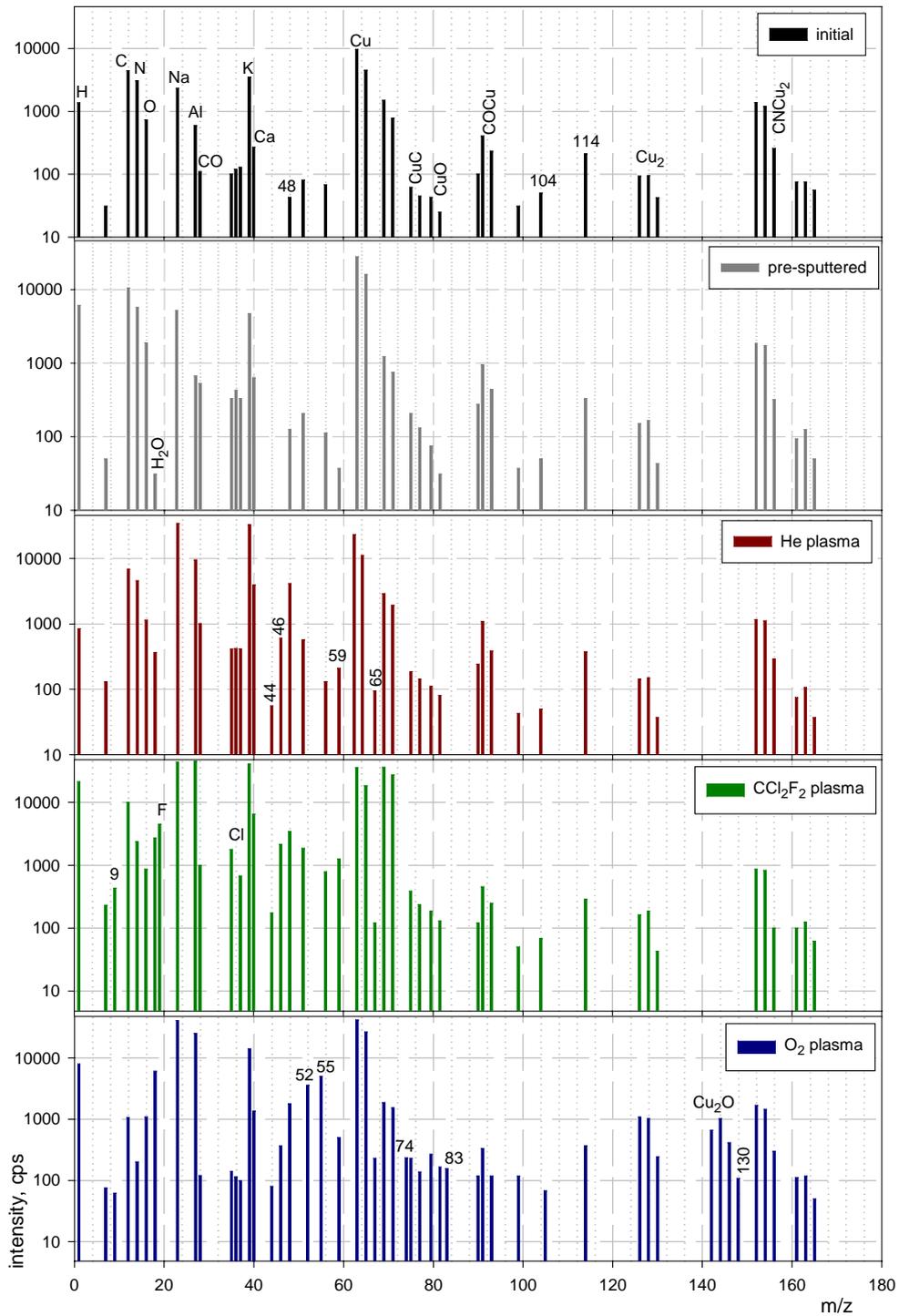


Fig. 3. SIMS spectra (top to bottom): (a) initial PcCu film (Fig. 2a), (b) pre-sputtered surface, (c) corresponds to the sample shown in Fig. 2b, (d) as in Fig. 2d, (e) as in Fig. 2e. The labeled peaks are discussed in the text, those without labels remain unexplained.

of the reaction chamber was increased to 80 °C and the films were etched in pure CCl_2F_2 for 3 min in order to attain an appreciable modification. As follows from Fig. 1d, after such a treatment the grain diameter becomes larger, but the vertical contrast is almost unaffected (Table 1). One can notice a slight faceting of the grains, which is typical for annealed PcM films [8,12].

The use of oxygen plasma under the same conditions as in the previous experiment causes most pronounced modification (see Fig. 1e). D increases 1.5 times (Table 1), while Z_p becomes equal to 80 nm. The surface roughness is virtually slightly altered, which is connected with diminution of the amount of peaks per surface area (see footnote to Table 1). In addition, the film contains deep holes (possibly up to the substrate). Etching in O_2 for 3 min results in total stripping of the organic film off the substrate.

3.2. The SIMS analysis of the surface

Common methods for investigation of modified PcMet films like XPS or FT-IR yield many useful data [10,13–16]. Nevertheless, SIMS is very appropriate because it allows observing organic molecular ions, even thermally labile, with high sensitivity on the surface and in the film bulk [17]. A decided disadvantage, especially for the already modified solids, consists in the interference of species typical of the analyzed sample, with possibly similar secondary ions produced by the primary ion impact itself [18]. Rearrangement of fragments may occur during sputtering and ionization, which complicates identification of the spectral features, too. A cautious attempt to assign the most prominent SIMS peaks is made below based on comparison with the literature data on SIMS and mass spectra of PcM [13,19–23].

First, let us discuss the initial PcCu film spectrum (see Fig. 3a). All ions of the basic elements composing the molecular formula of the parent compound, i.e., H, C, N, Cu are readily detected (Table 2), as well as common metallic impurities such as Na, K, Al, Ca, which SIMS is very sensitive to [20]. Oxygen ions are inevitably present in all spectra. They may come either from absorbed species, or from forward implantation. The latter reason determines apparently the presence of oxygen-containing positive clusters at 28 m/z , 79/81 (doublet) m/z and 91/93 (doublet) m/z , which are interpreted as CO, CuO and COCu, respectively.

Traces of organic impurities related to the sample history, such as phthalodinitrile and phthalic acid, or metal free phthalocyanine (possible metal loss, e.g. during sublimation) were not found. The peak at 104 m/z is characteristic of the mass spectra of phthalic acid (corresponds to $\text{C}_7\text{H}_4\text{O}^+$) [23], but may be due to the primary particles bombardment. The origin of the peaks at 35–37 m/z is not completely clear. Presumably, there is a contribution of chlorine, either as incidental substituent of hydrogen in Pc-ligand, or as admixture remaining after the synthesis [24].

As follows from the SIMS patterns in Fig. 3a–e, copper ions and clusters play a dominant role in the chosen spectral range. One explanation could be a higher relative yield of secondary ions, which is, for pure matrix materials, by more than 1.5 order of magnitude greater for Cu^+ than for light ions C^+ , N^+ , O^+ . In addition to a well-resolved doublet at 63/65 m/z (intensity ratio 7:3) typical of Cu^+ with natural isotopic abundance, an intense triplet was detected in the range of 152–156 m/z (Fig. 2a). It was identified as a positive cluster CNCu_2 . Similar clusters (CNCu_2^+) were observed in the SIMS spectra of PcCo powders [20]. The presence of CNCu^+ ions is not so evident as there are other peaks in this region (see Fig. 3a). Furthermore, the triplet at 126–130 m/z can be

Table 2
Intensities (cps) of some peaks corresponding to element constituents of a PcCu molecule (see, Fig. 1)

Sample in		Figs. 2a and 3a	Fig. 3b	Figs. 2b and 3c	Fig. 2c	Figs. 2d and 3d	Figs. 2e and 3e
Positive ion	Cu(63)	9600	25100	23100	22800	35800	41800
	N(14)	3100	5800	4600	2200	2400	300
	C(12)	4500	10500	6900	7700	10000	1100
	H(1)	1400	6100	900	5100	21100	7900

attributed to Cu_2^+ . If the triplet at 161–165 m/z in the right part of Fig. 3a–e also corresponds to a particle composed of two copper atoms, then the organic residue must correspond to 35 m/z , that is difficult to interpret. The nearest known case would be a positive ion with a structure $[\text{1/4Pc} + \text{metal} - \text{CN}]^+$ giving a doublet at 165 m/z [22]. Finally, a less intense doublet at 75/77 m/z is associated with CuC^+ (CuO^+ and COCu^+ are mentioned above).

Speculation on the relative intensities (isotopic ratios) of neighboring maximums in these multiplets is generally complicated because of a diffuse nature of the peaks and mutual overlapping. For example, the peak at 128 m/z in the Cu_2^+ triplet is relatively more intense than the others (Fig. 3a–e). This can be thought to be due to the contribution of the phthalodinitrile ion ($\text{C}_8\text{H}_4\text{N}_2^+$, $M = 128$), which is often reported for SIMS [25] and MS patterns of PcM [22]. It may originate from the charged shiver of phthalocyanine organic ligand (1/4Pc—see, Fig. 1) or, as a molecular ion, from an admixture.

There is also a strong doublet at 69/71 m/z , whose position and relative intensity visually match the Ga^+ ion. It is an unexpected impurity even for the material of technical grade. Other techniques (X-ray photoelectron spectroscopy [8]) did not reveal this element in remarkable amounts. Additionally, by comparing between the samples (Fig. 2a–d) one can see that the intensity of these peaks is essentially not constant.

The peak at 114 m/z is attributed to benzopyrrole (*izo*-indole) fragments of the PcCu molecule. They can be formed by symmetrical breaking of a four-leaf organic ligand with detachment of bridging (outer) nitrogen atoms (Fig. 1). Since this peak was not observed in conventional mass spectra of PcM, we assume that such fragmentation is caused by the primary ion impact. Note that this peak is stable whatever the sample.

The Pc-ligand has a high carbon content (32 of 56 atoms), so the peak at 48 is assumed to relate to C_4^+ . Perhaps, such peaks with small m/z numbers (e.g. 51, 56) may also be due to multiply charged or dehydrogenated ions.

As shown elsewhere [20,22,26], positive mass and SIMS spectra of metal phthalocyanines usually exhibit peaks corresponding to variously charged molecular ion, detached metal, secondary and quaternary molecular fragments 1/2Pc and 1/4Pc, and ions

formed by the loss of the nitrile group. With the exception of clusters containing metal atoms, which are clearly distinguishable by isotopic distribution, all these ions have even mass numbers, when singly charged. Peaks with odd mass numbers would be expected for metal free phthalocyanine, where, similarly to the indole or pyrrole derivatives, loss of hydrogen or HCN group is characteristic [27]. Hence, the detected peaks at 7, 51, 59, 99 and some others are most likely associated with re-arranged or multiply ionized clusters.

Next, the SIMS spectrum of the initial PcCu film was recorded once again from the same raster area after the first scan (i.e., from the pre-sputtered surface) (Fig. 3b). Basic relative ratios of ions and clusters in this case are approximately similar to those from the uppermost layer (Table 2). Appearance of a weak signal of H_2O^+ ion and overall increase of the peak intensities (Fig. 3b, Table 2) are registered. As the high vacuum was not broken at these stages, the former feature implies that the water ions are indeed formed by forward implantation of oxygen. The latter feature points towards a better yield from the pre-sputtered surface.

Second, let us discuss the changes in the SIMS pattern occurring after plasma irradiation of PcCu films. Several distinctive features should be mentioned here. For all etched samples H_2O^+ species were detected. This means that the surface of these films exposed to air from the etcher before SIMS measurements intensively adsorbs water. As in the AFM images no important increase in the surface area is seen (Fig. 2, Table 1). The retention of water is possibly related to the chemical activity of the modified surface. None of the peaks typical of the intact PcCu film surface disappeared (Fig. 3c–e, Table 2) or significantly changed relative to each other (except etching in oxygen). We therefore assume that the film surface is still composed dominantly of phthalocyanine molecules.

On the other hand, SIMS patterns for etched PcCu films are richer, especially in the small m/z numbers domain. Appearance of new peaks at 44 (possibly, CO_2^+ [21]), 46, 59, 65 m/z was detected, while the intensity of peaks at 18, 27, 48, 56, 69, 71 m/z increased. Higher intensity of the Al^+ signal (Fig. 3c–e) can reasonably be attributed to possible contamination from the walls of reaction chamber. For the film etched in CCl_2F_2 (Fig. 3d) the well-resolved

chlorine isotopic doublet at 35/37 m/z and the peak of fluorine ions at 19 m/z were detected together with a rise of a relative C/N ratio. However, the peaks expected for a dichlorodifluoromethane molecular ion or its fragments were not found. This implies that atoms (or groups) of dichlorodifluoromethane are chemically bound to phthalocyanine molecules. In the case of oxygen treated films the situation is more complicated. The Cu^+ signal is most intense in this case, whereas C and N signals are very weak (compare Fig. 3, Table 2). A new strong multiplet at 142–146 m/z was detected, which can be assigned to Cu_2O^+ . Although oxygen was used as a primary ion, these peaks were missing in all other samples (Fig. 3a–d). The presence of a copper oxide on the surface of the organic film stands for destruction of PcCu molecules. Further etching in thicker films can be slowed by the growing inorganic by-product. Besides, occurrence of a multiply ionized molecular ion $\text{PcCu}/+4$ in this range can also be hypothesized.

3.3. The SIMS profiling

In the final stage, the SIMS profiling of the studied samples has been carried out. The total sputtering time required to reach the substrate (checked by abrupt increase of Si signal and simultaneous drop of the intensity of other peaks) was ca. 1.1×10^{-3} s for the initial PcCu film. Nearly the same time was used for profiling of the film treated in the He plasma. The substrate boundary was degraded in the latter case, which correlates with the increased surface roughness of this sample (compare Fig. 2b) [28]. For both initial and etched samples the distribution of C^+ , N^+ and Cu species was homogeneous all through the film. Meanwhile, the profiling of the film etched in dichlorodifluoromethane was considerably longer—ca. 1.5×10^{-3} s. This suggests hardening of the film by plasma irradiation. The content of Cu in the uppermost layer was higher than in the bulk of the film. The profiling of the PcCu films treated in oxygen plasma took ca. 6×10^{-2} s, whereas the residual film is two times thinner (by interferometry and AFM). The derived etching rate is about 5 nm/s.¹ Again, the surface is enriched with copper atoms.

¹ For comparison, the rate of 5 nm/min for plasma etching of PcCu in 100% O_2 was reported in [15] (150 W rf power).

4. Conclusion

As known, the structural perfection of PcM molecules makes them very stable to fragmentation under various impacts [29]. The bombardment with energetic particles leads to destruction of the molecules, up to carbonization of the layer [30]. It is assumed that stable intermediate fragmentation of PcM molecules may occur when chemical bonds are broken under moderate irradiation [8,13,15,20]. Appearance of “new” structural species (subunits) detected by SIMS, would mean that the fragmentation is definite. However, treatment both with non-reactive (He) and reactive etchant (CCl_2F_2) revealed good withstandability of thin sublimed PcCu films. Effect of oxygen plasma is stronger, which is displayed in both quick removal of the film and chemical degradation of organic material. This opens opportunities for application of this method to fabrication of complex PcM-based heterostructures by means of plasma processing technology.

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