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Electron beam-treated organic monolayers as a negative resist for Cu immersion plating on Si

Abstract In the present work, we investigate selective immersion plating of Cu on n-type Si(111) surfaces chemically modified with different organic monolayers and subsequently directly patterned by an electron-beam (e-beam). The organic molecules (1-undecylenic acid, 1-decene and 1-octadecene) were covalently attached to a hydrogen-terminated Si surface. The use of such monolayers as masks for electroless copper deposition by immersion plating on Si surfaces was investigated. Clearly, a masking effect can be observed, the efficiency of which depends on the type of molecule. Further, the effect of e-beam irradiation to improve the masking properties of the organic monolayers was studied. For this, the monolayers were locally irradiated using a scanning electron microscope (SEM) equipped with a lithographic tool. The results show that e-beam-modified organic monolayers can be used as a negative tone resist for copper electroless plating. The selectivity of the Cu deposition at e-beam-untreated regions strongly depends on the applied e-beam dose and on the nature of organic molecules. By optimizing the electroless deposition parameters, homogeneous deposition with complete selectivity can be achieved, leading to high lateral resolution of the Cu patterns.

Keywords Electron-beam lithography · Copper electroless deposition · Organic monolayer· nanopatterning · DLC (diamond-like-carbon) · XPS surface analysis

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Introduction

Self-assembled monolayers (SAMs) have attracted a lot of research interest due to their relevance to various different fields of science and technology. SAMs can be used to chemically functionalize material surfaces, and have potential applications of this range from surface passivation and stabilization to the development of new strategies for the immobilization of either chemical or biological species on a surface. SAMs are highly ordered and oriented and can incorporate a wide range of groups both in the alkyl chain and at the ends of the chain. Therefore, a variety of surfaces with specific interactions can be produced with fine chemical control. The attachment of SAMs to Si surfaces takes place through a hydrosilation mechanism, which involves insertion of unsaturated bonds into a silicon-hydride group. The first reported example of hydrosilation of nonoxidized hydride-passivated silicon was carried out in 1993 on flat crystal Si(111)-H surfaces by Chidsey and coworkers [1, 2, 3, 4]. The mechanism is a surface chain reaction based on R· radicals that can abstract hydrogen atoms from the surface and form additional highly reactive silicon radicals that react with the alkene molecules leading to the formation of Si-C bonds. Monolayers on Si(111)-H surfaces based on Si-OR bonds have also been reported [5]. Both reactions can be initiated either by UV light illumination [5] or thermal treatment [6]. In this case, the proposed mechanism of the reaction is either via a nucleophilic addition/hydride transfer or a radical chain mechanism via radical initiation. Both approaches lead to covalent attachment of SAMs through Si-C or Si-O bonds [7]. The fact that the properties of SAMs can be biomimetic or biocompatible in nature makes their applications promising in both chemical and biochemical fields. High stability of SAMs on different surfaces allows further functionalization of the substrate at the end group of the carbon chains. For instance, it was possible to attach DNA

arrays to Si(111) using a heterobifunctional SAM as cross-linker [8]. Recent work on nanopatterning of SAMs suggests that these systems may be used in the patterning of semiconductor surfaces and in the preparation of sensor arrays [9]. Organic monolayers have also been used to build molecular switches [10, 11] and memory cells [12, 13].

In addition to the large potential that organic monolayers present for biochemistry, the possibility of manufacturing patterned SAMs offers an additional perspective for nanofeature fabrication in microelectronic applications. Due to their typical thicknesses of 1–2 nm, SAMs can be used as resists for high-resolution patterning (even using low energy electrons). In this context, SAMs were successfully utilized as positive and negative resists to produce nanostructures. For example, on gold surfaces nanostructure fabrication could be achieved by means of low energy electron beam techniques using stencil masks or direct e-beam lithography [14, 15].

Nanopatterning of surfaces requires the use of accurate lithographic tools and advanced materials as resist films. Several nanopatterning approaches have been combined with electrochemical techniques for achieving structuring of semiconductor surfaces in the sub-μm range [16, 17, 18, 19], including an e-beam writing method to produce insulating carbon layer masks on the surface [20, 21, 22]. In the present work, we explore the potential of using e-beam modified organic monolayers as a mask for a subsequent Cu plating on Si. For this, immersion plating of Cu on Si(111) covered with different organic monolayers (undecylenic acid, 1-decene and 1-octadecene) is investigated and the properties of different monolayers are discussed. Further, the organic monolayers are patterned by e-beam lithography and the masking properties are again investigated. Finally, the selectivity of the Cu immersion plating on the Si surface is discussed.

Experimental

Experiments were performed on cleaved samples from an n-type Si wafer, phosphorous-doped, (111)-oriented, with a resistivity of 2–8 Ωcm, (Wafer Net, Germany). The Si surface was first cleaned by sonication for 5 min in ethanol and propanol, and then the samples were immersed in a (H_2SO_4:H_2O_2 = 3:1) solution for 30 min at 75 °C. An ideally flat H-Si (111) surface was prepared by etching in a 40% NH_4F solution for 15 min [23]. In order to modify H-terminated surfaces with an organic monolayer, a treatment given in [24] was carried out. For this, the fresh H-Si(111) samples were dipped in undecylenic acid, 1-decene or 1-octadecene, respectively, which was previously bubbled with nitrogen for 1 h. The organic molecules were bonded to the sample surfaces under UV illumination (UV irradiation 15 W/cm) for 2 h. Finally, in order to dissolve excess (non-bound) organic solution, the samples were cleaned by sonicating

in organic solvent ($CHCl_3$) and ethanol for 5 min. Then the samples were dried under nitrogen flow. The chemicals used were ethanol, analysis grade propanol (Merck, Germany), H_2SO_4, and H_2O_2 (suprapure grade, Merck, Germany), undecylenic acid ($C_{10}H_{19}COOH$), 1-decene ($C_{10}H_{20}$), 1-octadecene ($C_{18}H_{36}$) (analysis grade, Sigma-Aldrich, Germany), and NH_4F (VLSI selectipure, Merck, Germany). For subsequent experiments, the monolayer-covered pieces were cleaved into 0.5 cm×0.5 cm square samples.

Samples were patterned using a JEOL 6400 thermionic emission SEM equipped with the lithography software Elphy Quantum. During the exposure, the pressure in the chamber was 10^{-4} Pa and the working distance was set to 16 mm. Chemical modification of organic monolayers was achieved with various electron doses using an accelerating voltage of 20 keV and 0.45 nA current.

In order to investigate copper electroless deposition, the substrates were immersed for various times in a Teflon beaker containing 1% HF + 0.5 M $CuSO_4$ solution. Then the samples were rinsed in pure water and dried with N_2.

Si surfaces modified with organic monolayers were chemically characterized by high resolution X-ray photoelectron spectroscopy (ESCA 5600 PHI). SEM images were taken with a Hitachi field emission gun 4800 SEM.

Results and discussion

In the first part of the work, the possibility of using organic monolayers as masks for the immersion plating of Cu onto Si was studied. Figure 1 shows SEM images of Cu electroless plating on Si(111) surfaces modified with different organic monolayers: (a) 1-decene, (b) undecylenic acid, and (c) 1-octadecene. Immersion time was set to 10 s, 15 s, and 20 s for each type of organic monolayer, respectively. In Fig. 1 triangular pits can be seen on the surface. The shape of the pits is attributed to etching in ammonium fluoride solution (which was used as a surface pre-treatment) that contains small quantities of oxygen [23]. Moreover, Fig. 1 demonstrates that Cu has randomly grown on the surface – no preferential deposition (for instance at step edges) can be observed. This may be due to the fact that the hydrosilation process also takes place at the steps. Therefore, organic monolayers passivate the surface and hinder Cu deposition even at preferential locations such as steps and kink sites.

Figure 1 further illustrates that the organic monolayers produced are not able to completely block the Cu deposition on the surface. It can be assumed that nucleation of Cu occurs at the defect sites of the organic layers (missing carbon chains). At the exposed defect locations, the Cu deposition reaction can occur according to an electroless deposition mechanism of Cu onto Si during immersion plating [25], and this may be described as:

Fig. 1 SEM images of silicon surfaces covered with different organic monolayers: **a** 1-decene; **b** undecylenic acid; **c** 1-octadecene. Cu was deposited by immersion plating in a 1% HF + 0.5 M CuSO₄ solution. Deposition of Cu was carried out using different immersion times: 10 s, 15 s and 20 s

$$Si + 2H_2O \rightarrow SiO_2 + 4H^+ + 4e$$
$$SiO_2 + 6HF \rightarrow [SiF_6]^{2-}$$
$$2Cu^{2+} + 4e \rightarrow 2Cu$$
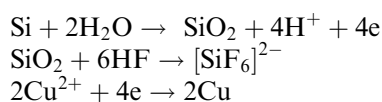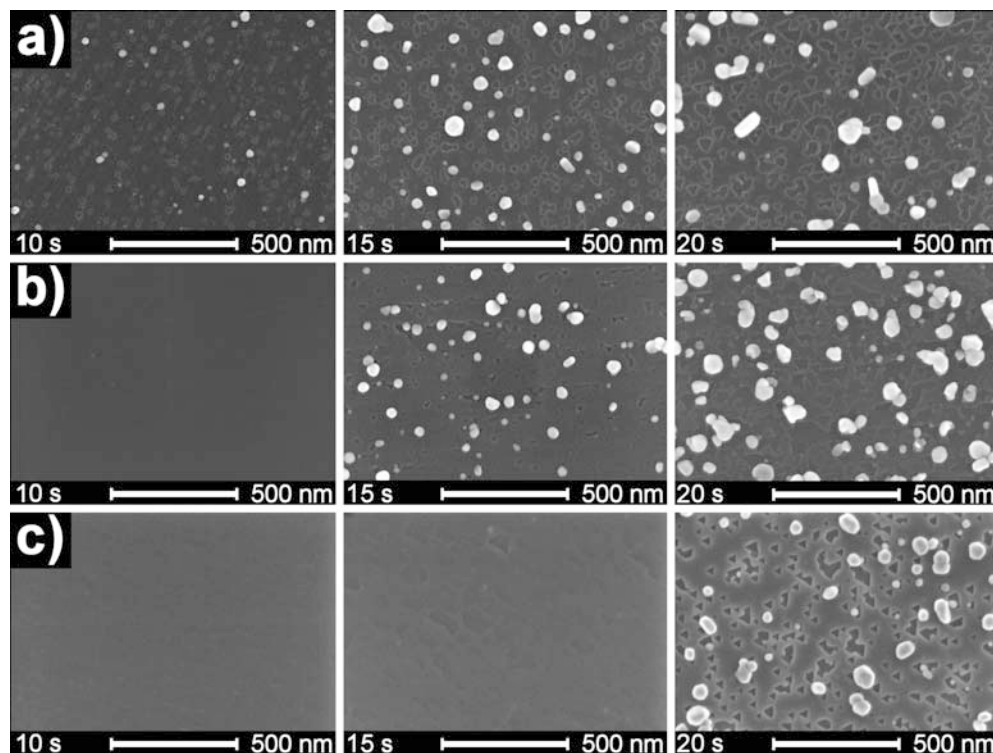
Therefore, for Si in low pH fluoride solutions, it is assumed that Cu grows on the Si surface, while dissolution (oxidation) of Si occurs. The thickness of the Cu film is limited, since the deposition process is hindered by complete coverage. As shown in Fig. 1, small particles are observed on the surface after short immersion times; over longer immersion times particle growth takes place. Figure 1 further illustrates that nucleation of Cu depends on the nature of the organic monolayers. A comparison of Fig. 1a with Fig. 1b shows that undecylenic acid-covered Si surfaces exhibit a better blocking effect than 1-decene. These molecules have the same carbon chain length but a different end group. The better blocking effect can be partially explained by the higher steric hindrance of the acidic group. Figure 1c indicates the better insulating properties of 1-octadecene layers due to their longer chain length. The surface coverage by

Cu (in %) was estimated in order to describe the Cu nuclei distribution more quantitatively. For 15 s immersion time it was found that the Cu surface coverage represents 9.3%, 7.9% and > 0.1% for 1-decene, undecylenic acid, and 1-octadecene respectively.

Since selective Cu deposition takes place at defect sites of the organic monolayers, such as the absence of organic molecules, immersion plating can be used as a method to test the quality of organic monolayers. In order to test this, good and poor quality organic monolayers (undecylenic acid) were anchored at Si surfaces and observed after immersion plating. Poor attachment of the organic layer was achieved by shortening the UV illumination time to 20 s. Figure 2 shows SEM images of the Si surface covered with a poor quality undecylenic acid, onto which Cu was deposited by immersion plating under the same conditions as in Fig. 1, with immersion times of 5 s, 7 s and 10 s. In this case, nucleation of Cu occurred already at short immersion times (5 s). Compared with the good quality layer, which can withstand HF/CuSO₄ electrolytes up to

Fig. 2 SEM images of a silicon surface covered with an undecylenic acid layer of poor quality (achieved by using a short UV illumination time). Cu was deposited by immersion plating under the same conditions as in Fig. 1 with immersion times of 5, 7 and 10 s
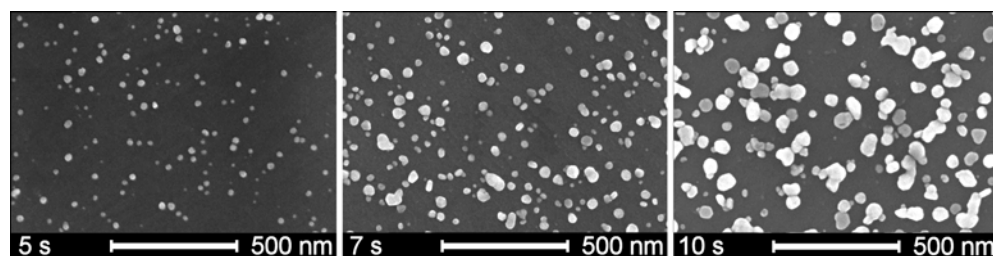
10 s (see Fig. 1b), the poor quality layers obviously contain much more defects, which lead to nucleation and growth of Cu deposits. The surface coverage by Cu of these samples was estimated to be around 30.9% after 15 s of immersion time. Nevertheless, even the poor quality monolayers show a better masking effect than silicon native oxide, since SiO_2 is rapidly dissolved in HF-Cu containing solutions, while organic monolayers consisting of alkyl chains are much more resistant to HF treatments.

Figure 3 shows the C 1s, Si 2p and O 1s XPS spectra of Si surfaces covered with undecylenic acid layers of good and poor quality. Typical compositions (atomic concentrations) were calculated from the deconvoluted C 1 s, Si 2p, and O 1s spectra and are shown in Table 1. The C 1s spectra were resolved into two characteristic peaks. The peaks at 289 eV and 284.4 eV indicate the functional groups of COO and C–C, respectively. Using a short time UV illumination treatment, there is a slight decrease in the intensity of both peaks, suggesting that fewer organic molecules were attached to the surface. The Si signal is stronger for the poor quality layer, which may be due to the non-continuous coverage of the surface. Also, for the poor quality layer the Si 2p spectrum shows a small shoulder at 102.5, which is typical of SiO_2. The O signal of the O 1s spectrum is stronger for the poor quality layers. These findings suggest that a higher SiO_2 content is present on the surface of the Si covered by a poor quality layer. Hence, a short UV illumination treatment of the surfaces leads to lower coverage by organic monolayers and subsequently to native oxide growth in air at the uncovered surfaces. With two hours of UV illumination treatment, the surfaces show a high coverage of monolayers.

Generally, organic monolayers are not defect-free and the package density of the molecules depends on the layer preparation conditions, type of organic molecules, illumination time and temperature [26]. In particular, chain ordering strongly depends on the grafting temperature. Rondelez and co-workers demonstrated the existence of a critical temperature, below which the surface energy is constant at a near-limiting value of a pure CH_3 surface, and above which the surface energy monotonically increases with increasing temperature. The reason for such behavior is that the films prepared below T_{cr} exhibit a heterogeneous structure with closely spaced islands of densely packed alkyl chains arranged almost vertically to the surface. In contrast, when prepared above T_{cr}, the films exhibit monotonically decreasing coverage with increasing temperature, and the alkyl chains show higher conformational disorder [27].

As has been reported previously [15], an e-beam lithographic technique can be used to chemically modify organic monolayers. Electron dose and beam energy are the main parameters that can influence the carbon chain composition, leading to different blocking behavior for Cu deposition. In this work, e-beam modification of the organic monolayers was studied, in order to improve the
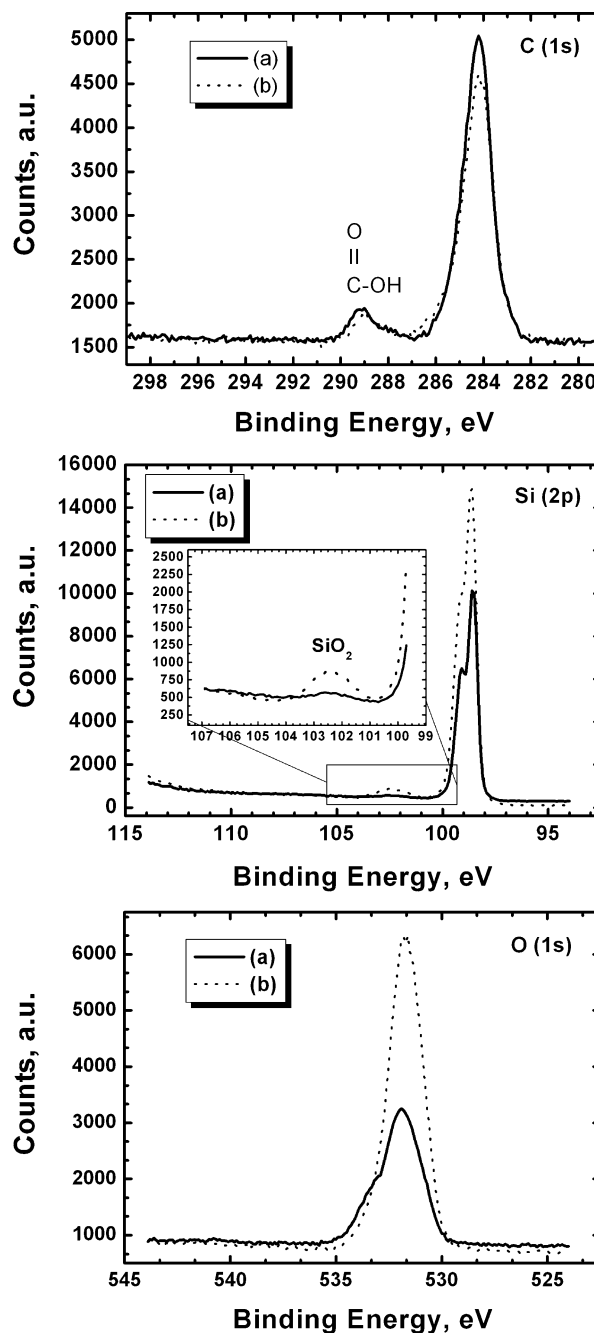

Fig. 3 XPS spectra for silicon surfaces covered with organic monolayers (undecylenic acid) of good (a) and poor (b) quality. The C graph consists of methyl group and acid group COOH signals; the Si graph shows spin-orbit splitting, indicating the presence of SiO_2 in the poor quality layer; the O graph has a shoulder in the oxygen peak corresponding to a chemical shift due to COOH (enhanced for the good quality layer)

masking properties for Cu deposition by decreasing the defect density. Figure 4 shows SEM images of Cu immersion plating of Si surfaces covered with 1-decene (a), undecylenic acid (b), and 1-octadecene (c) that were patterned using a 20 keV e-beam by applying different doses of $1.5–20 \times 10^4 \ \mu C/cm^2$. The images clearly indicate that the blocking effect for Cu deposition strongly

Table 1 Atomic concentration table for C, Si and O corresponding to the XPS data for Si surface covered with undecylenic acid of good and poor quality

Silicon surface covered with undecylenic acid of:	C 1s	Si 2p	O 1s
Good quality	34.04 a.u.	52.29 a.u.	13.66 a.u.
Poor quality	21.33 a.u.	60.94 a.u.	17.74 a.u.

depends on the applied e-beam dose. The higher the electron dose, the better blocking effect is achieved, probably due to the formation of diamond-like-carbon (DLC) in the locations modified by the e-beam. The image shows that the type of organic molecules grafted on the Si surface also determines the blocking performance obtained for identical e-beam parameters. The chain length seems to have an influence on this effect: the Si surface covered with 1-decene (Fig. 4a) shows the least masking behavior. The masking effect becomes significant at an e-beam dose of 15×10^4 $\mu C/cm^2$, while for Si covered with undecylenic acid the negative resist effect appears at 10×10^4 $\mu C/cm^2$ (Fig. 4b). The difference between these two molecules is the end group (COOH). In the case of 1-octadecene (a molecule that has eight more carbons then 1-decene), the blocking effect occurs at 5×10^4 $\mu C/cm^2$ (Fig. 4c). It is therefore apparent that the masking performance of e-beam-treated monolayers strongly depends on the e-beam dose and on the type of organic monolayer.

Conclusions

In the present work we have investigated Cu immersion plating on Si(111) surfaces that have been coated with organic monolayers. The results show that organic monolayers present on Si can be used as a mask on n-type Si(111) surfaces and can completely block Cu deposition for up to 10 s of immersion time. The onset time for Cu nucleation strongly depends on the type of organic monolayer. For long alkyl chain monolayers, Cu deposition occurs at longer immersion times, whereas for short alkyl chain monolayers Cu is formed at shorter times. The end group also plays a role in the nucleation of Cu. 1-Decene shows a weaker blocking effect for Cu deposition than undecylenic acid, although these two molecules have the same alkyl chain length.

A total blocking effect is hindered by the presence of defects, such as missing carbon chains, in the monolayers, leading to Cu deposition at the exposed locations. The immersion plating process can therefore be used as a quality check for the monolayers.

E-beam modification of the monolayers, in order to improve the blocking nature, was also explored. The e-beam treatment was found to lead to the creation of defect-free layers, which can even withstand up to 2 min of immersion plating. The masking effect of the e-beam treated layers strongly depends on the applied dose and
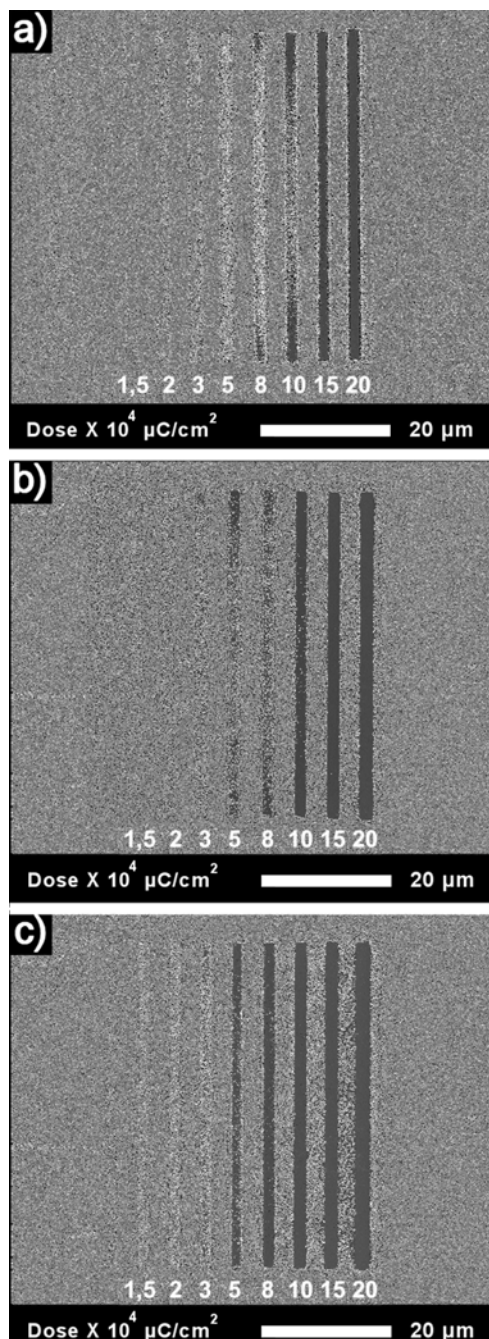

Fig. 4 SEM images of Si samples covered with **a** 1-decene, **b** undecylenic acid, and **c** 1-octadecene patterned with different e-beam doses ($1.5–20 \times 10^4$ $\mu C/cm^2$). Cu was deposited by immersion plating in a 1% HF + 0.5 M CuSO$_4$ solution for 2 min

on the type of organic molecules grafted onto the surface.

Organic monolayers attached to Si surfaces therefore represent ultrathin resists, which in contrast to silicon oxide layers show a good blocking effect against immersion plating in HF-containing solutions. Using e-beam treatment of the organic monolayers, defect-free coatings can be produced that may have applications in high-resolution patterning of Si surfaces [15].

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