

# Organic monolayers as resist layers for Cu deposition on Si (111) surfaces

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**Abstract** Organic covalently attached monolayers (CAMs) were found to be useful as resist layers for patterning Si surfaces. In the present work, we investigate selective 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) and by AFM induced scratching. 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 copper deposition by electroinduced and immersion plating on Si surfaces was investigated. A masking effect can be clearly observed, the efficiency of which depends on the type of molecule. The effect of e-beam irradiation on modification of CAMs and selective deposition of Cu in e-beam treated locations was shown. For this, the monolayers were locally irradiated using a scanning electron microscope (SEM) equipped with a lithographic tool and Cu deposition was performed under external applied potential. Selectivity of deposition strongly depends on applied e-beam dose. The results show that e-beam-modified organic monolayer can be used as a positive tone resist if treated with medium e-beam doses and as a negative tone resist if treated with high doses for both: copper immersion plating and electrodeposition. Also it was demonstrated that CAMs can be successfully used as negative tone resists for AFM induced scratching. By

optimizing the electroless deposition parameters, homogeneous deposition with a complete selectivity can be achieved, leading to a high lateral resolution of the Cu patterns.

**Keywords** Organic monolayer · Electron-beam lithography · Copper electrodeposition · Immersion plating · AFM scratching

## 1. Introduction

An important goal of contemporary surface chemistry is preparation of modified monomolecular surface films with molecular level control over structural order and composition. Within this work, the study of covalently attached monolayers (CAMs) and their applications has expanded considerably in recent years, including now a range of topics such as wetting, adhesion, electrochemistry, optoelectronics, molecular electronic devices, nanotechnological structures, bioactive surfaces and, in general, fundamental studies of molecular interface systems. CAMs bear a high potential for chemical functionalization of material surfaces and potential applications ranging from surface passivation and stabilization to development of new strategies for immobilization of either chemical or biological species on a surface. Therefore, a variety of surfaces with specific interactions can be produced with fine chemical control. The hydrosilylation mechanism is in charge for the covalent attachment of CAMs on Si surfaces, which involves insertion of an unsaturated bond into a silicon-hydride group. In 1993 Chidsey and coworkers reported for the first time an example of hydrosilylation of flat nonoxidized Si (111)-H surfaces [1–4]. The hydrosilylation mechanism involves a surface chain reaction based on R• radicals that can abstract hydrogen atoms from the

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surface and form additional highly reactive silicon radicals that react with the alkenes or alkynes molecules leading to the formation of Si–C bonds. Monolayers based on Si–OR covalent bonds on Si (111)-H surfaces have also been reported as a potential route for surface functionalization [5]. Thermal treatment [6], UV light illumination [5], catalyzed reactions or electrochemical treatment [7, 8] can be used in order to initiate both reactions. In this instance the anticipated mechanism of the reaction is either by a nucleophilic addition/hydride transfer or a radical chain mechanism via radical initiation. Both approaches lead to covalent attachment of CAMs via Si–C or Si–O bonds [9]. The fact that the properties of CAMs can be biocompatible in nature makes their applications promising in chemical and biochemical sensing. High stability of CAMs on different surfaces allows further functionalization of the substrate at the end group of the carbon chains. For instance attachment of DNA arrays was possible on Si(111) using a heterobifunctional CAM as cross-linker [10]. Recent work on nanopatterning of CAMs suggests that these systems may be applied in patterning of semiconductor surfaces and in the preparation of sensor arrays [11]. Organic monolayers have also been used successfully to build molecular switches [12, 13] and memory cells [14, 15].

The possibility to manufacture patterned CAMs offers an additional perspective for nanofeature fabrication for micro-electronic applications. CAMs can be used as resist layers for high-resolution patterning due to their typical thickness of 1–2 nm. In this framework, CAMs were successfully exploited as positive and negative resists to produce nanostructures on different surfaces. For instance, nanostructure fabrication on gold and silicon surfaces was possible by means of low energy electron beam techniques using stencil masks or direct e-beam lithography [16, 17].

Accurate lithographic tools and advanced materials as resist films are required for nanopatterning of different surfaces. Several nanopatterning approaches have been combined with chemical and electrochemical techniques for achieving structuring of semiconductor surfaces in the sub- $\mu\text{m}$  range [18–21], including an e-beam writing method to produce insulating carbon layer masks on the surface [22–24] and AFM structuring technique for direct patterning of the surface [25]. In the present work, we explore the potential of using organic monolayers as masks for a subsequent Cu plating on Si surfaces by means of electrochemical and immersion plating techniques. For this, Si(111) surfaces covered with different organic monolayers (undecylenic acid, 1-decene and 1-octadecene) were patterned using e-beam lithography and AFM scratching technique. Electrochemical Cu deposition was performed on e-beam modified monolayers and immersion-plating technique was used for selective Cu deposition on AFM scratched surfaces. Selectivity of Cu

deposition is being investigated and the properties of different monolayers are discussed.

## 2. Experimental section

Experiments were performed on cleaved samples from a *n*-type Si wafer, phosphorous-doped, (111)-oriented, with a resistivity of 2–8  $\Omega\text{cm}$ , (Wafer Net, Germany). The Si surface was first cleaned by sonication for 5 min in ethanol and propanol successively. Before  $\text{NH}_4\text{F}$  treatment the samples were immersed in a ( $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2 = 3:1$ ) solution for 30 min at 75°C for oxidative treatment. An ideally flat H-Si (111) surface was prepared by etching in a 40%  $\text{NH}_4\text{F}$  solution for 15 min [26]. In order to modify H-terminated surface with an organic monolayer, a treatment given in Ref. [27] 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 hour. The organic molecules were bonded to the sample surfaces under UV illumination (UV irradiation 15 W/cm<sup>2</sup>) during 2 hours. At the end, in order to dissolve excess (non-bound) organic molecules, the samples were cleaned by sonicating in organic solvent  $\text{CHCl}_3$  and ethanol for 5 min. Then the samples were rinsed in ultrapure water and dried under a nitrogen flow. The chemicals used were ethanol, propanol analysis grade (Merck, Germany),  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}_2$  (suprapure grade, Merck, Germany), Undecylenic acid ( $\text{C}_{10}\text{H}_{19}\text{COOH}$ ), 1-Decene ( $\text{C}_{10}\text{H}_{20}$ ) and 1-Octadecene ( $\text{C}_{18}\text{H}_{36}$ ) (analysis grade, Sigma-Aldrich, Germany) and  $\text{NH}_4\text{F}$  (VLSI selectipure, Merck, Germany). For subsequent experiments, the monolayer-covered pieces were cleaved into 0.5 cm  $\times$  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 a 0.45 nA current.

For AFM patterning technique an atomic force microscope (Nanoscope III, Digital Instruments, Santa Barbara, CA, USA) equipped with a diamond-coated tip with a cantilever spring constant about 17 N/m (VEECO, Mannheim, Germany) was used to produce scratches through the organic layers. For scratching the *x* scan direction was disabled, the *y* scan speed was set to 4  $\mu\text{m/s}$  and a 10  $\mu\text{m}$  distance was scanned in the contact mode. Different scratches were made by 30 scanning cycles at various loads (set points). After scratching the tapping mode image showed a lot of debris on the surface particularly at the scratch edges. However, this loose debris could be removed by sonicating in

water for 5 min. After scratching the substrates were dipped in a Teflon beaker containing 1% HF solution for 40 s to remove any oxide that may have been formed in the scratches.

In order to electrodeposit Cu the samples were electrochemically polarized in a 0.1 M CuSO<sub>4</sub> + 1 M H<sub>2</sub>SO<sub>4</sub> electrolyte immediately followed by rinsing in pure water and drying with N<sub>2</sub>. For this aim the samples were pressed against a 5 mm diameter O-ring in a polymer-cell (PMMA or polypropylene). The O-ring consisted of natural butadiene rubber. Platinum gauze served as a counter electrode and an Ag/AgCl electrode ( $E = 236.3$  mV vs. SHE) was used as a reference electrode. All potential values in this work are referred to a silver/silver chloride electrode. The electrochemical cell was always placed in a black box in order to avoid any noncontrolled photochemical effects. It is well known that the light induces generation of electron-hole pairs, which have an additional contribution to the total current as a photocurrent parameter. Potentiodynamic polarization experiments were performed using Jaissle potentiostat-galvanostat (1030 DA). Various voltages and deposition times were tested in order to optimize the deposition process.

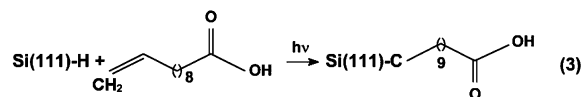
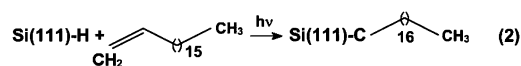
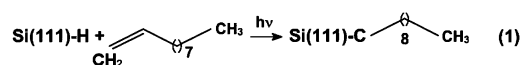
For immersion-plating technique, the samples were immersed in a 0.05 M CuSO<sub>4</sub> + 1% HF solution immediately followed by rinsing in pure water and drying with N<sub>2</sub>. The experiments were performed under normal conditions since the immersion plating is less susceptible to light because the electrons that are generated in the space-charged layer drift to the bulk due to band-bending of the energetical levels at semiconductor-electrolyte interface, and have no contribution to Cu reduction. A range of immersion times was tested for optimization of Cu deposition.

Si surfaces modified with organic monolayers were chemically characterized by high resolution X-ray photoelectron spectroscopy (ESCA 5600 PHI). Infrared spectra were obtained with a QUINOX 55 ATR-FTIR instrument. Spectra were collected in reflectance mode with 150 scans and the resolution 4 cm<sup>-1</sup>. Contact angle measurements were performed in static regime with contact angle setup from Orbisphere Laboratories. SEM images were taken with a Hitachi S-4800 field emission gun SEM and a JEOL 6400 thermionic emission SEM.

### 3. Results and discussion

The photochemical reactions of free organic species used in this work (1-octadecene, 1-decene and undecylenic acid) for grafting on Si(111)-H undergo the following reactions

(Scheme 1–3) leading to formation of well ordered, closed pack and chemically stable organic monolayers.



#### 3.1. Infrared spectroscopy

The grafting density of these monolayers was deduced from FTIR results. For this, silicon ATR crystals were treated as mentioned in experimental part and the surface reactions were monitored by ATR-FTIR analysis. Assignment of the C–H peaks observed in the IR spectra of CAMs is given in Table 1. The order in the CAMs can be assessed from position of the CH<sub>2</sub>-stretching. As shown in previous studies [28] the frequency of the CH<sub>2</sub>-stretching is characteristic of the order in CAMs of long-chains alkyls. For completely disorder structures, the frequency of the CH<sub>2</sub>-stretching is close to that of liquid alkane ( $\nu_a \sim 2924$  cm<sup>-1</sup>). For well-ordered CAMs, the frequency is shifted to lower wavenumbers and is close to that of crystalline alkane ( $\nu_a \sim 2915$  cm<sup>-1</sup>–2918 cm<sup>-1</sup>). The data of Table 1 show that, for the C<sub>18</sub>H<sub>36</sub> CAMs,  $\nu_a$  (CH<sub>2</sub>) is  $\sim 2918$ –2919 cm<sup>-1</sup>, which indicates CAMs with high degree of order. Surfaces prepared with C<sub>10</sub>H<sub>20</sub> showed less order as it was deduced from CH<sub>2</sub> stretching of  $\nu_a$  (CH<sub>2</sub>) 2921–2922 cm<sup>-1</sup>. As it was mentioned in the literature, the CAMs packing density depends strongly on carbon chain length and grafting temperature [29]. In this context longer chains show better order of closed packed methylene chains than short chains. Although C<sub>10</sub>H<sub>19</sub>COOH and C<sub>10</sub>H<sub>20</sub> molecules have the same carbon chain, the quality of C<sub>10</sub>H<sub>19</sub>COOH CAMs was found to be worse than those based on C<sub>10</sub>H<sub>20</sub>. For the CAMs with COOH terminated group CH<sub>2</sub> stretching moves even to a higher wavenumber value of  $\nu_a$  (CH<sub>2</sub>) 2924–

**Table 1** C-H IR vibrations observed for 1-octadecene, 1-decene and undecylenic acid CAMs grafted on Si(111) surface

Vibration	Peak frequency (cm <sup>-1</sup> ) in the CAM prepared from:		
	1-Octadecene (C <sub>18</sub> H <sub>36</sub> )	1-Decene (C <sub>10</sub> H <sub>20</sub> )	Undecylenic acid (C <sub>10</sub> H <sub>19</sub> COOH)
C-H			
$\nu_a$ (CH <sub>2</sub> )	2919 ± 2	2921 ± 2	2924 ± 2
$\nu_s$ (CH <sub>2</sub> )	2850 ± 2	2851 ± 2	2852 ± 2

**Table 2** Advanced contact angle measurements for 1-octadecene, 1-decene and undecylenic acid CAMs grafted on Si(111) surface

Advance contact angle in (°) for CAM:		
1-Octadecene (C <sub>18</sub> H <sub>36</sub> )	1-Decene (C <sub>10</sub> H <sub>20</sub> )	Undecylenic acid (C <sub>10</sub> H <sub>19</sub> COOH)
1102	942	582

2925 cm<sup>-1</sup>. The justification of the partial loss of chain order could be due to the bigger volume of acid COOH group in comparison with that of methyl CH<sub>3</sub> group.

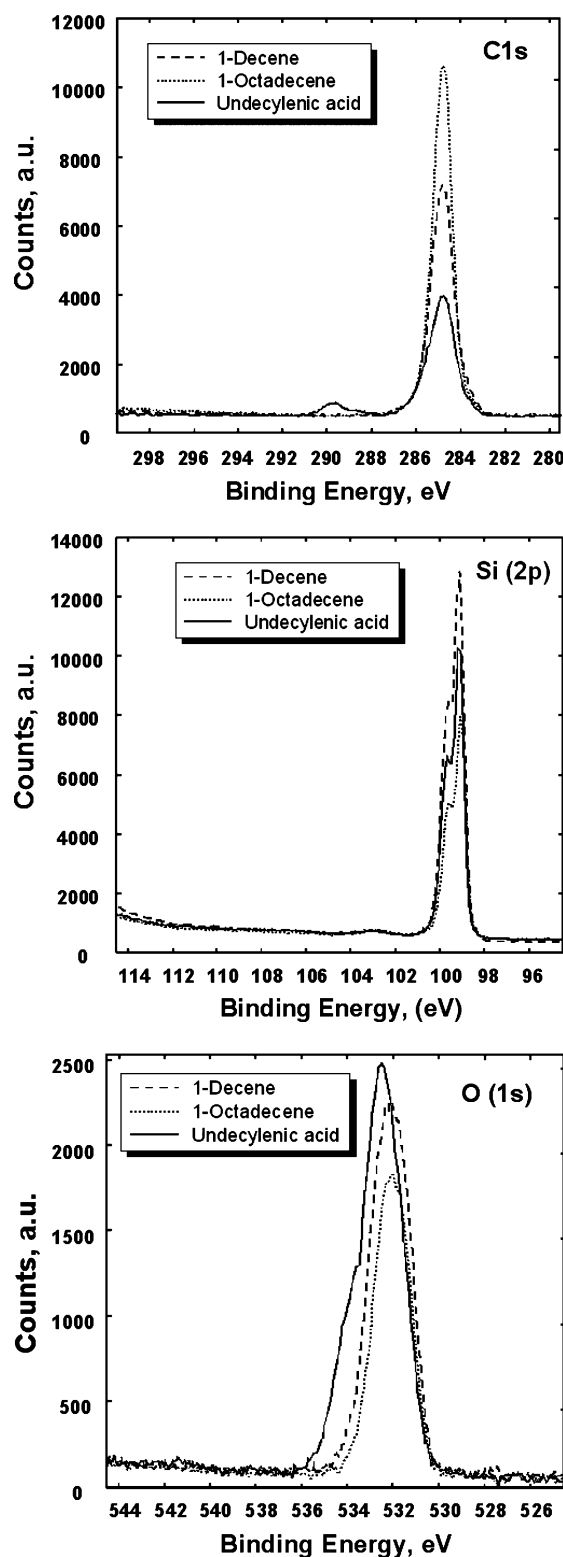
### 3.2. Contact angle measurements

Contact angle measurements were performed for qualitative deduction about package order of CAMs and are presented in Table 2. For 1-octadecene CAMs, advance angle was measured to be in the order of 110 ± 2°, which is in a good agreement with the formation of densely-packed monolayers with a uniform surface of pure methyl character [30]. 1-Decene CAMs show smaller contact angles of 94 ± 2° suggesting less order of carbon chains that is in accord with FTIR data. Si samples covered with undecylenic acid illustrate much smaller contact angles in the order of 58 ± 2°. For this type of molecules there are two effects that could influence the wettability of the surface: one is the hydrophilic nature of acid COOH group due to the charge separation and the second one is the loss of closed-packed chains due to voluminous acid group.

### 3.3. XPS analysis

Figure 1 shows the C 1s, Si 2p and O 1s XPS spectra of Si surface covered with 1-octadecene, 1-decene and undecylenic acid. Clearly the XPS C1s spectra shows the attachment of organic molecules and has a higher carbon signal for 1-octadecene covered surface than that of 1-decene and undecylenic acid which is in a good agreement with the number of carbon atoms in the molecule chain. For undecylenic acid the C1s spectra were resolved into 2 characteristic peaks. The peaks at 289.5 eV and 284.4 eV indicate the functional groups of COO and C–C, respectively. The Si signal illustrates a very narrow oxide peak indicating that almost no silicon dioxide formation has taken place. However XPS O1s spectra showed more oxygen present in 1-decene and undecylenic acid layers suggesting that some oxide formation at the Si-CAM interface could occur.

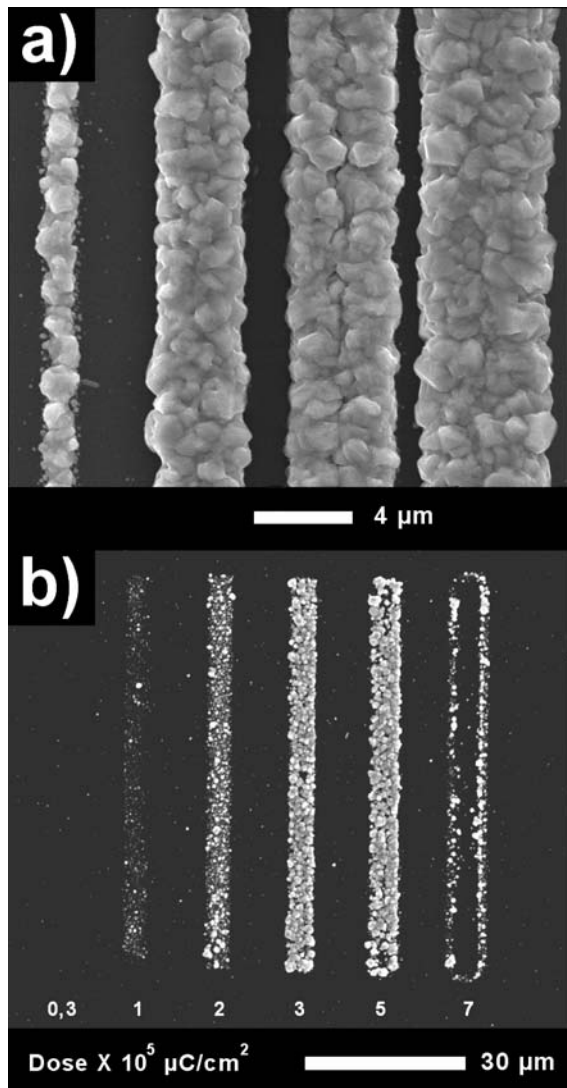
In this framework it was achievable to use well-ordered CAMs for patterning of Si(111) surface using two techniques: e-beam lithography and AFM scratching technique. Both approaches showed the possibility to obtained well-defined structures with high degree of selectivity.



**Fig. 1** XPS spectra for silicon surfaces covered with free organic monolayers: 1-octadecene, 1-decene and undecylenic acid. C graph consisting from C signal coming from methylene group and carbon peak that corresponds to acid group COOH for undecylenic acid; Si signal with spin-orbit splitting, indicating almost no presence of SiO<sub>2</sub>; O signal with the shoulder in the oxygen peak for undecylenic acid corresponding to chemical shift due to COOH

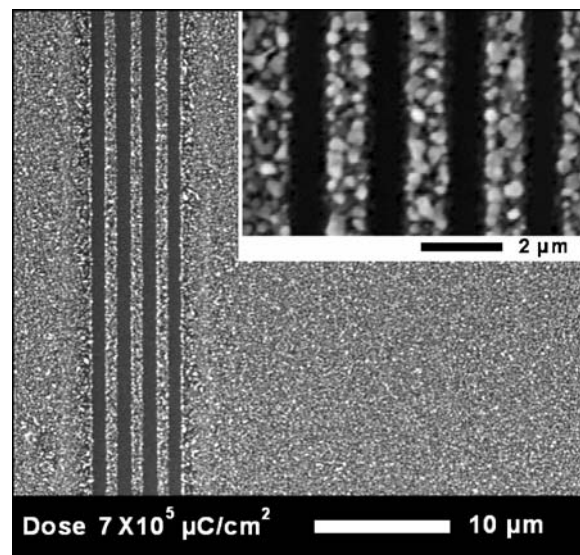
### 3.4. Electron-beam modification

In the first part of the work, the possibility to use organic monolayers as masks for electrochemical and immersion plating of Cu on Si was studied. Figure 2(a) shows SEM image of Cu electrodeposition on Si(111) surfaces modified with 1-Decene with four e-beam modified patterns that are around 1, 2, 3 and 4  $\mu\text{m}$  width with decreasing the space among them from left to right by 3, 2, 1  $\mu\text{m}$  respectively. E-beam doses were set to  $3 \times 10^5 \mu\text{C}/\text{cm}^2$ . Copper has been selectively electrodeposited in a 0.1 M  $\text{CuSO}_4 + 1 \text{ M H}_2\text{SO}_4$  electrolyte by applying the optimal potential for electrode-



**Fig. 2** SEM images of silicon surfaces covered with 1-decene. CAMs were patterned using (a)  $3 \times 10^5 \mu\text{C}/\text{cm}^2$  e-beam dose in four locations that are around 1, 2, 3 and 4  $\mu\text{m}$  width with decreasing the space among them from left to right by 3, 2, 1  $\mu\text{m}$  respectively. (b) different e-beam doses: from  $0.3 \times 10^5$  to  $7 \times 10^5 \mu\text{C}/\text{cm}^2$ . Cu was selectively electrodeposited in e-beam treated locations in a 0.1 M  $\text{CuSO}_4 + 1 \text{ M H}_2\text{SO}_4$  electrolyte by applying the potential of  $-340 \text{ mV}$  for 3 min

position that was found to be around  $-340 \text{ mV}$  and optimal deposition time 3 min. For a longer deposition time, overgrowth of Cu in the patterns took place. In contrast, for shorter times randomly distributed Cu nuclei are formed within the patterns. In case of lower cathodic potentials no deposition is observed, whereas for high cathodic potentials Cu nuclei start to grow randomly on the whole surface. This may be ascribed to dielectric breakdown of C-layer. The selectivity of copper deposition further strongly depends on the applied e-beam dose. Figure 2(b) shows Si sample covered with 1-decene that was patterned with different e-beam doses: from  $0.3 \times 10^5$  to  $7 \times 10^5 \mu\text{C}/\text{cm}^2$ . It was found that enhancement of copper deposition increases with increasing e-beam dose. However, at high doses ( $>7 \times 10^5 \text{ C}/\text{cm}^2$ ) a blocking effect of copper deposition is observed. The optimal electron dose for selectivity of this process was found to be in the order of  $3 \times 10^5 \mu\text{C}/\text{cm}^2$ . The previous XPS studies [17] confirmed that at these doses the scission of C-chain occurs, which is the likely reason for copper selective deposition in the e-beam treated locations. The same source showed that for high doses, formation of diamond-like-carbon (DLC) could take place [31]. In earlier work this was confirmed by corresponding Raman spectra [32]. Hindrance effect of Cu deposition on samples treated with high e-beam doses was found to be efficient also for immersion plating technique. Figure 3 illustrates this effect on Si samples coated with 1-decene that were e-beam modified with  $7 \times 10^5 \mu\text{C}/\text{cm}^2$  dose and submitted to immersion plating in 0.05 M  $\text{CuSO}_4 + 1\% \text{ HF}$  solution for 2 min. Cu deposition took place on the e-beam untreated locations. Auger studies confirmed no Cu deposition on e-beam modified surfaces. This is in line with earlier work and with

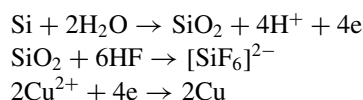


**Fig. 3** SEM images of Si samples covered with 1-decene patterned with high e-beam doses ( $7 \cdot 10^5 \mu\text{C}/\text{cm}^2$ ). Cu was selectively deposited outside e-beam modified locations by immersion plating in a 1% HF + 0.05 M  $\text{CuSO}_4$  solution during 2 min

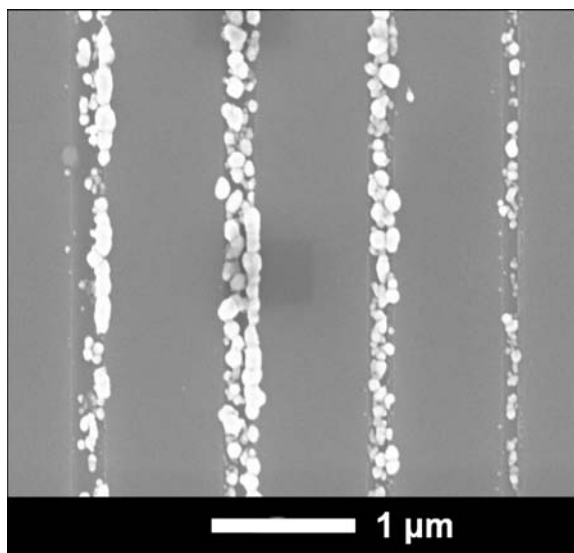
the Auger profiles showing an increase in carbon signal at the patterns treated with high e-beam doses. As DLC layers are highly insulating, this explains the hindrance of copper deposition in the patterns treated with such high doses.

### 3.5. AFM induced scratching

Figure 4 shows an SEM image of a silicon surface covered with 1-octadecene with four AFM scratches that are 10  $\mu\text{m}$  long and about 1  $\mu\text{m}$  apart. Cu was selectively deposited in the scratch locations by immersion technique. At the exposed defect locations, the Cu deposition reaction can occur according to an electroless deposition mechanism of Cu on Si during immersion plating [33] and may be described as:



Hence, for Si in low pH fluoride solutions, it is assumed that Cu grows on the Si surface, while dissolution (oxidation) of Si occurs. Different electrolyte concentrations and immersion times were tested in order to optimize the deposition. A clear relation between electrolyte concentration and Cu nuclei was found: a lower copper concentration results in deposition of smaller features while an increase of HF concentration leads to an increase of nucleation site density and deposition rate. Within tested parameters, 0.05 M  $\text{CuSO}_4$  + 1% HF electrolyte and 15s immersion time were found to give satisfactory results. Figure 4 depicts clearly well-defined deposition lines. The width of the lines was measured to be in the order of 150–200 nm. Selectivity of this



**Fig. 4** SEM image of the Cu deposition in AFM induced nanoscratches on Si sample covered with 1-octadecene. Cu was electroless deposited in 0.05 M  $\text{CuSO}_4$  + 1% HF for 15s

technique was tested with different CAMs. As it was shown in previous studies [19] the best hindrance effect for Cu electroless deposition showed 1-octadecene layers. These CAMs have illustrated the highest degree of selectivity while those based on 1-decene and undecylenic acid have showed a few crystallites on the coated surface treated under the same conditions. Nevertheless it was demonstrated that these CAMs can be successfully used for AFM scratching technique and Cu immersion plating deposition as negative resist layers.

## 4. Conclusions

The present work investigates use of organic monolayers as resist layers on Si (111) surfaces for Cu selective deposition. The results show that organic monolayers presented on Si can be used as masks on *n*-type Si (111) surfaces for e-beam writing and AFM induced scratching. It was demonstrated that these CAMs can be successfully used for Cu electroless plating and electrodeposition technique. The efficiency of the masking effect depends strongly on the type of molecule. The effect of e-beam irradiation on modification of CAMs and selective deposition of Cu in e-beam treated locations was shown. The results illustrate clearly that e-beam-modified organic monolayers can be used as positive tone resists after being exposed to small e-beam doses and as negative tone resists if treated with high doses. The effect of e-beam dose on Cu deposition is applicable for both: copper immersion plating and electrodeposition technique. It was also demonstrated that CAMs can be successfully used as negative tone resists for AFM induced scratching. Using this technique high-resolution patterning in nm scale of Si surfaces can be produced. Organic monolayers, in contrast to silicon oxide layers, show a good blocking effect against immersion plating taking place in HF containing solutions and represent ultrathin resists, which may have applications in high-resolution nanopatterning of Si surfaces.

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