Electrochemical Development of Hydrogen Silsesquioxane (HSQ) by Applying an Electrical Potential

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I. ABSTRACT

We present a new method for developing hydrogen silsesquioxane (HSQ) by using electric potentials and deionized water. Nested-L test structures with a pitch as small as 9 nm were developed using this electrochemical technique in saline solution without adding hydroxyl ions. Furthermore, we showed that high resolution structures can be electrochemically developed in deionized water alone. Electrochemical development is controlled by the applied voltage and may overcome several of the limitations discussed for alkaline developers, such as poor hydroxyl anion diffusion and charge repulsion effects in small trenches.

Keywords: development, resist, saline solution, electrochemical reaction, electrochemical development, electrolysis, HSQ, hydrogen silsesquioxane

II. INTRODUCTION

Hydrogen silsesquioxane (HSQ) is a negative electron-beam resist used to pattern features with high-resolution and low line-edge roughness [1]. Patterns with a half-pitch as small as 4.5 nm have been demonstrated [2]. The high etch resistance of HSQ allows it to be used as a direct write mask for patterning devices [3]. Furthermore, it has been used to fabricate molds for nanoimprint lithography [4, 5] and guiding structures for templating the self-assembly of block co-polymers [6, 7].

The unexposed portion of the HSQ layer is commonly removed by developers, which can be divided into two categories: (1) solvents in which HSQ has a natural affinity and (2) aqueous base solutions. In the first category, non-aqueous solvents like methyl isobutyl ketone (MIBK), methanol and xylenes have all been shown to develop HSQ [8]. However, no structures with nanometer resolution have been demonstrated with solvents as developer. Also, slight swelling of the remaining material has been reported [8]. The second category includes developers based on alkaline solutions like tetramethyl-ammonium hydroxide (TMAH), potassium hydroxide (KOH), or sodium hydroxide (NaOH) [9, 10, 1]. In an alkaline solution, the resist molecules undergo an ionization process comparable to an acidic reaction. The Si-H bonds present in partially and unexposed HSQ can deprotonate to form a charged, water-soluble group [11]. The net chemical reaction is described by:

$$\equiv\text{Si-H} + \text{NaOH} \;\rightarrow\; \equiv\text{Si-O}^- + \text{Na}^+ +\; \text{H}_2$$
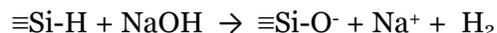
However, in aqueous base solution the created silanol groups can react further and condense to Si-O-Si bonds. This cross-linking process is unintended and needs to be avoided, since it creates a network structure that slows down further development. In general, chemical development of HSQ (development by ionization) is more aggressive due to its ability to react with partially cross-linked HSQ molecules. Thus it can resolve smaller and higher-aspect structures than physical development with non-reactive solvents.

One main challenge in fabricating high-resolution structures with HSQ is residual resist in between densely packed features. Several methods have been studied that reduce footing and increase contrast. Development in more highly concentrated alkaline solution [12], at higher

development temperatures [13, 14], and with added salts [15, 14, 10, 16], all increase the developer contrast. As described by Kim et al, the added salt ions can weaken Si-O bonds of partially cross-linked HSQ. This weakening increases the probability of partially cross-linked HSQ structures breaking up into smaller pieces. These pieces then can dissolve into solution more rapidly and so they develop faster [11].

Further, a negative charge builds up on the resist surface due to the deprotonation process of partially developed resist. This surface charge may slow down or prevent the approach of OH⁻ developer ions. The positively charged cations of the added salt screen this negative surface charge and allow developer to approach the surface more easily, especially within small trenches [17, 2].

This charge-screening effect raises the question of whether applying an external electric field may have an effect on the development of HSQ. Electric-field-assisted development of other resists has shown promising results: when used in a chemically amplified resist development system, the application of electric fields resulted in features with deeper trenches [18] and improved line-edge roughness [19]. The effects of an applied electric field on HSQ development is currently being investigated in our group.

The negative charging of HSQ (creation of Si-O⁻ groups) during development is a key effect of the HSQ development process in alkaline solution. This creation of Si-O⁻ groups is driven by a chemical reaction, which is initiated by the low pH value of the developer solution. We wondered whether the generation of Si-O⁻ groups could instead be initiated by an applied negative electric potential in the absence of the low pH environment.

In this paper, we demonstrate that HSQ can be developed in an alkaline-free solution by applying a negative potential to sample. Development was observed on the negative electrode in saline solution and even in deionized water. We achieved comparable resolution to high-contrast salty alkaline developer and demonstrated pattern resolution as high as 9-nm-pitch nested-L structures using electrochemical development of HSQ.

III. EXPERIMENTS AND RESULTS

We performed a series of exposure experiments and varied the electrical potential during immersion of the sample in DI water or saline solution. Subsequently, the samples were investigated by means of SEM imaging and the resolution and pattern fidelity was analyzed.

The samples were prepared by spin coating HSQ (XR1541 1% solid, Dow Corning Co.) onto a silicon wafer (<100> P boron, 5-25 ohm cm) at 6 krpm resulting in a thickness of about 15 nm (measured on collapsed structures). A pre-exposure bake was not performed to avoid thermally induced contrast reduction. Nested-L structures with varying pitch and dose were exposed as single pixel lines (line-dose about 6nC/cm) using a Raith 150 electron-beam-lithography system at 30 kV acceleration voltage (write field 50 μm × 50 μm, step size 1 nm, aperture 20 μm, and beam current ~115 pA).

Figure 1 shows a schematic of the development apparatus. Thereby, an area of approximately 1 cm² of the sample was immersed in saline solution (mixture of 4 wt % NaCl in deionized water, with no alkaline developer component) and the sample was then connected to the positive terminal of a voltage source (current-source meter, Keithley 2400) by an alligator clip. A negative potential was applied to the sample by programming a negative voltage to the source. A platinum counter electrode was immersed into the same solution and connected to the negative terminal of the voltage source. A second platinum electrode was used as reference electrode to determine the potential of the solution without current-induced electrochemical effects on the electrode. To avoid electrochemical affects from other surfaces, sample and reference electrode were mounted in such a way that only the HSQ- or platinum-coated side was in contact to the solution.

For monitoring the change of resist-layer thickness, a small AC-voltage was added to the applied DC-signal, and the AC-voltage drop across the resist layer measured (grey parts). Figure 1 (b) shows a simplified circuit of this capacitive voltage divider. The resist layer acts as dielectric material with thickness d within the capacitor C_{resist} formed by sample substrate and solution (Figure 1 (c)). Since the capacitance of C_{resist} is inversely proportional to the thickness d, the capacitance C_{resist} increases during resist development and a decreasing AC-voltage V_{AC} was measured.
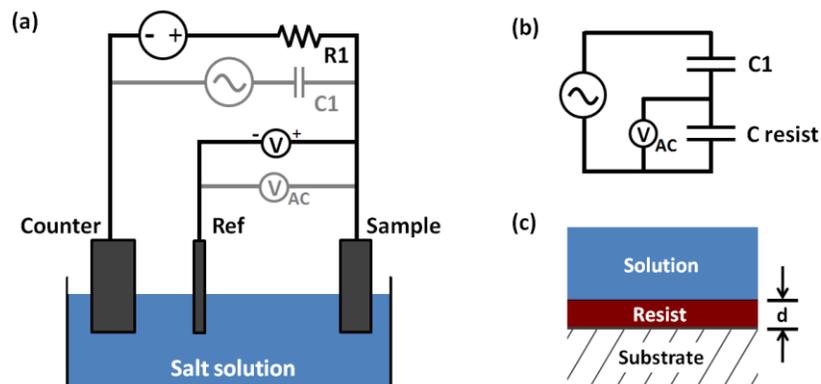
Figure 1. (a) Schematic diagram of electrical circuit designed for electrochemical development as well as for potential measurement during salty development. A DC-current/voltage was applied in between sample and counter electrode. The DC-voltage applied at the sample was measured relative to the reference electrode. By using this 3-point setup, we avoided errors due to voltage offsets occurring at the counter electrode For monitoring changes on the surface of the sample, a small AC-signal (~1 kHz, 80 mV$_{pp}$) was added to the DC-voltage and then the AC-voltage drop between sample and solution was measured (circuit elements plotted in grey). (b) Simplified sketch of the AC-circuit in (a) to monitor changes on the sample surface. The AC-circuit is a capacitive voltage divider with fixed capacitance C_1 and variable capacitance C_{resist}. (c) The resist layer acts as dielectric material with thickness d in between the substrate and the solution.

To determine the effect of this new development method on resolution, a sample with 20-, 12-, and 9-nm-pitch nested-L structures was developed by electrochemical development. For this purpose, the sample was immersed into 4% NaCl solution and a voltage of -5 volt applied. This voltage caused a current of approximately -300 µA. After developing for 600 s, the voltage source was switched off, the sample subsequently rinsed with deionized water, and then blown dry in a stream of nitrogen. Figure 2 shows scanning electron micrographs (SEMs) imaged at 10 kV using the same Raith 150 instrument as was used for exposure. All experiments were conducted at room temperature without agitation or stirring of the solution. A typical sample to counter-electrode separation was about 1-3 cm.
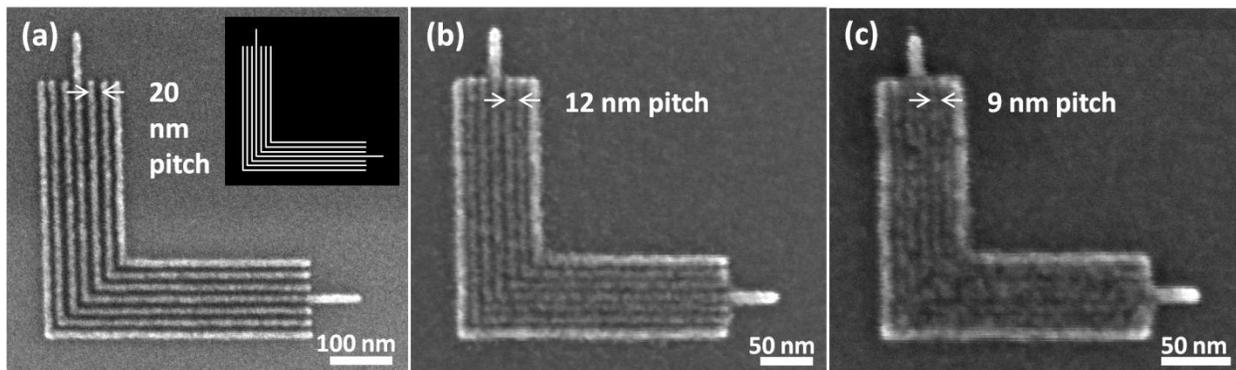
Figure 2. SEM images of (a) 20-, (b) 12-, and (c) 9-nm-pitch nested-L structures on silicon developed using electrochemical development in aqueous 4% NaCl solution at -5 V for 600 s. The structures were patterned in 15-nm-thick HSQ and exposed at 30 kV acceleration voltage as single pixel lines (~6nC/cm). Inset: diagram of lines to be patterned by electron-beam lithography.

To study the influence of the electrical conductivity of the substrate, we compared nested-L structures exposed on silicon with structures exposed on a thin metal layer (10-nm chrome deposited by electron beam evaporation on silicon). The metal provides a conductive layer below the resist and avoids non-linear electrical effects caused by the silicon substrate. Each sample was UV-ozone cleaned for 5 min below a UV lamp at ambient pressure in air to prepare a hydrophilic surface before coating with HSQ. The nested-L structures were exposed in the same manner as described above. The silicon sample was developed for 600 s with a voltage of -5 V with respect to the platinum reference electrode (resulting in a current of 280 µA to 360 µA). Due to the higher conductivity of the metal-coated substrate, this sample was developed for 320 s at a voltage of -3 V (240 µA to 1 mA). For comparison, a third sample was developed in high-contrast salty developer solution (1 wt% NaOH, 4 wt% NaCl in deionized water) for 240 s without applying a potential. Figure 3 shows SEM images of 9- and 12-nm-pitch nested-L structures of all 3 samples. No obvious difference in resolution was found between development methods, except for sample 3a (9-nm-pitch structures developed with salty developer). Here, the single, free-standing, outside lines at the end of the pattern were missing. This result may have been due to an insufficient exposure-dose (i.e. a less sensitive development process).
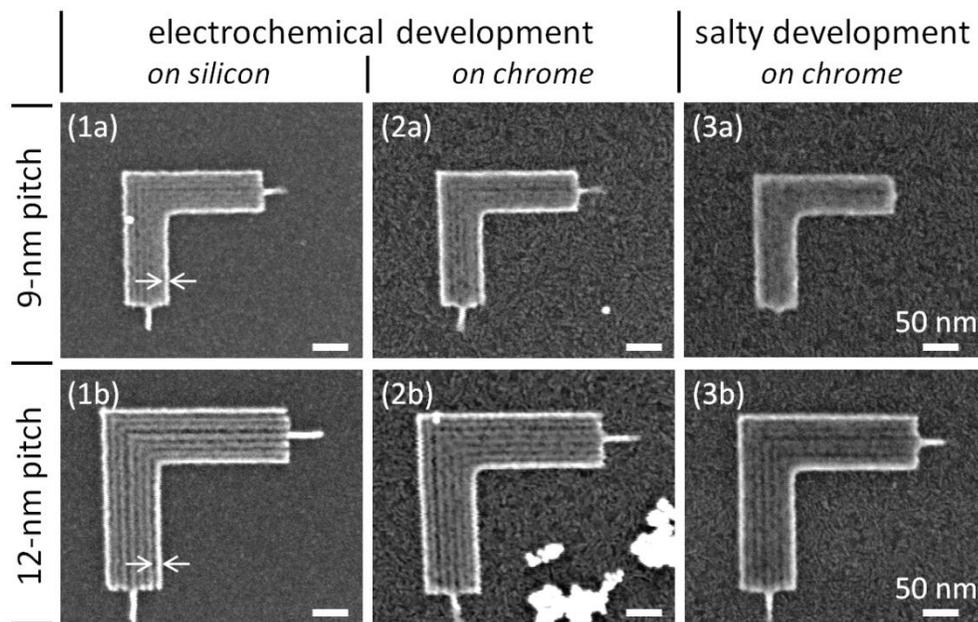
Figure 3. SEM images of (a) 9-nm-pitch and (b) 12-nm-pitch nested-L structures patterned in 15-nm-thick HSQ on silicon (1) and on 10 nm chrome on silicon (2 and 3) comparing different development methods: electrochemical development in aqueous 4 wt% NaCl solution and applied potential (images 1: HSQ on silicon substrate, -5 V for 600 s and images 2: HSQ on chrome, -3 V for 320 s) and salty developer (images 3: aqueous 1 wt% NaOH, 4 wt% NaCl, for 240 s). All structures were patterned as single pixel lines at 30 kV acceleration voltage (line dose ~6 nC/cm, 6 mm working distance). Images were taken using the same instrument at 10 kV acceleration voltage. The images show no obvious influence of the substrate on resolution comparing the different development methods and comparable resolution for electrochemical development with respect to high-resolution salty development of HSQ. The gold colloids visible in some pictures were used for electron beam adjustment before writing and probably washed into the patterning area during flushing after development with DI water. The increased brightness of the outermost features is presumed to be due to the larger secondary-electron emission-cross-section of edges during SEM imaging. The images (2 and 3) show samples with a chrome layer on the substrate (10 nm metal on silicon), which resulted in a grainy background. The metallic substrate increased the feasibility of monitoring the electrochemical development; however no influence of the increased substrate conductivity on resolution was found.

To investigate the influence of the electrical parameters on development, four samples were developed with different development current and development time. These samples were patterned with single-pixel-line structures with a linear dose density from 3 nC/cm to 12 nC/cm, (about 1900 to 7500 electrons/nm). Three samples were developed with -150 μA (40 s, 180 s, and 620 s) and one with -500 μA (80 s). Figure 4 presents SEM images of the results arranged as matrix of exposure-dose and the product of development time × development current (equal

to a unit of development charge). With increasing development charge (left to right in figure), a larger linear exposure-dose density is necessary to make a pattern that withstands development. Under-development (insufficient development charge) was observed as development of large areas, but not of small trenches in between features (e.g. Figure 4, lines with 12 nC/cm, developed using -150 μA for 40 s). Similar behavior was also reported for under development with aqueous base [2]. The lowest dose density with successfully developed patterns (lines with 3 nC/cm) was observed for development using a current of -150 μA for 40 s.

For over-development, it was found that an increased exposure-dose density also led to patterns with good fidelity (12 nC/cm, developed -150 μA, 620 s). However, patterns exposed with lower dose withstood development only partly or vanished completely (6 nC/cm and below, developed -150 μA, 620 s). The HSQ of these patterns was less cross-linked and thus developed faster. So far, no evidence was found that development terminates after a certain time. In fact, successful development was observed for a very low development current of -25 μA and a correspondingly long development time (30 min). No distinction was found between low current combined with long development time or high current combined with short development time. At the other (positive) electrode, no development was observed in any of the experiments.
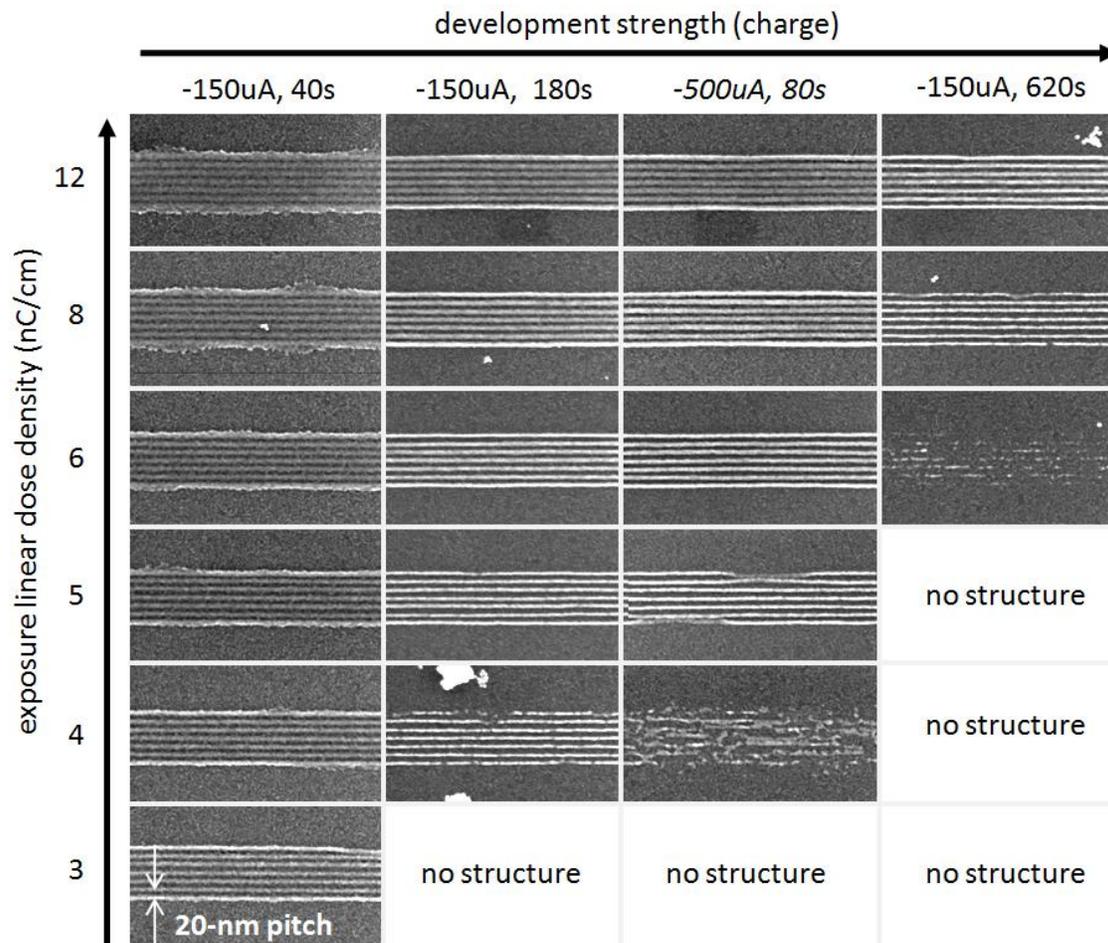
Figure 4. SEM images of line-structures with 20-nm pitch developed electrochemically. Four samples with line patterns (3 nC/cm to 12 nC/cm) were developed with different development time and current. The amount of HSQ removed increased from left to right with increased development charge (development current × development time). Structures on the top rows were exposed with higher dose density – were better cross-linked, thus withstood a more aggressive development. No HSQ structures were visible with low exposure-dose density and large development charge. Accordingly, trenches in between structures with high exposure-dose density and low development charge were not fully developed. Patterns with good fidelity have been achieved in a region between low exposure-dose density combined with low development charge and patterns with high exposure-dose density combined with high development charge. Note: no influence of development time on resolution was found. The images were arranged by development charge.

To study the development process in more detail, we investigated the change in mass variation of the HSQ layer by quartz crystal microbalance (QCM), and by measuring the voltage drop across the layer during development. For QCM measurements, a 96-nm-thick HSQ layer was spun on a microbalance crystal with gold surface (6% HSQ, 6k rpm). The samples were

mounted into a QCM instrument with fluidic module (Q-Sense E4 with QEM 401 electrochemistry add-on, including a gold counter electrode and Ag/AgCl reference electrode) and then flushed with 4% NaCl saline solution. As soon as a voltage or current was applied to the sample, a change in the crystal resonance frequency was observed. Using the Voight model, the measured frequency change was translated into a change in layer thickness. Figure 5 shows the change in thickness applying a constant current of -151 µA versus time. At 95 s, the current was switched off. During the time with no current, little further development was observed. After switching the current on again, the development process continued. Towards the end, the change in thickness (development process) slowed down and finally stopped, when all HSQ was fully developed.
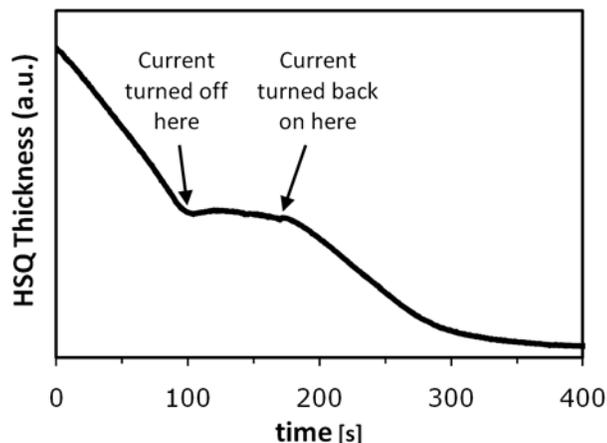

Figure 5. A Quartz Crystal Microbalance was used to monitor the thickness of a thin film of HSQ on a gold plated quartz crystal sensor. 96 nm of HSQ was spun onto the crystal before developing in 4% NaCl saline solution. A current of -151 µA was applied to the crystal from 0 to 100 s. The current was then switched off. Notice that the development stopped when the current was switched off. The current was switched on again at about 175 s and development resumed.

Similar behavior was also observed when investigating the applied electrical signals during electrochemical development. For that purpose, a 3-point measurement setup was used as shown in Figure 1. Applying a fixed current facilitated monitoring. Figure 6 displays a recorded voltage vs. time trace for developing a 160-nm-thick HSQ layer on chrome. Initially, a voltage of -2.45 V had to be applied to achieve the desired current of -150 µA. The voltage reduced as the

HSQ developed. After 150 s, a nearly constant value was reached, indicating that the development was complete.

To monitor changes in the thickness of layers on the sample surface, a small AC-voltage was added to the DC signal and the voltage drop between sample and solution (across the resist layer) measured. So, a change in the resist layer thickness was reflected in an alteration of the AC-voltage. The circuit diagram in Figure 1 shows the additional elements used for the AC-voltage in gray. The frequency of the AC-voltage was experimentally determined in a reference experiment applying low (Hz) and high (MHz) frequencies to samples with and without HSQ layer and measuring the voltage drop between sample and solution. The measured voltage was most sensitive on the surface coating of the sample when a low frequency was applied (Hz to a few kHz). For the experiment, a frequency of about 1 kHz was chosen. A resistance of 5 kΩ and capacitances of 10^4 nF were added to the circuit to decouple the AC and DC signals as indicated in the circuit in Figure 1. Neither a change in the measured DC-potential was observed when switching the AC signal on or off, nor was development observed with the applied AC-voltage only.
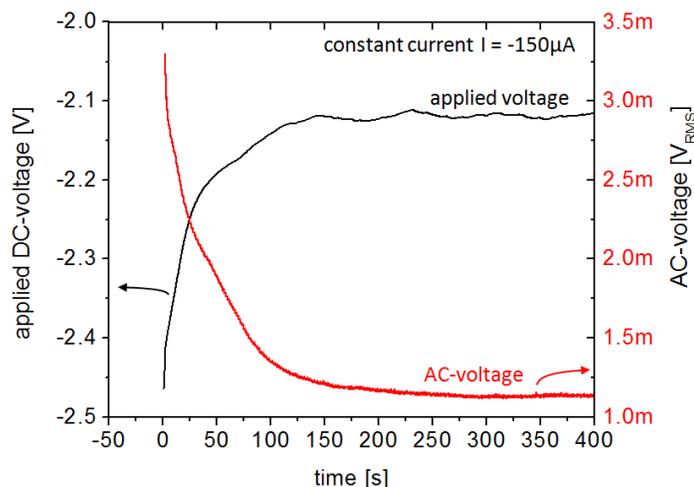

Figure 6. Plot of applied potential and measured AC-voltage versus time. The voltage was adjusted to drive a constant current of -150 μA. At the beginning, the HSQ acted as high resistive layer on the sample surface, thus a higher potential had to be applied to gain the desired current. During this time, also a larger AC-voltage was measured than at the end. As development proceeded, the applied potential decreased until the resist was removed from the entire surface and a steady current value reached. This process was correlated to the observed change of the measured AC-voltage.

IV. DISCUSSION

As previously proposed by Kim et al. [11], the HSQ development reaction in basic saline solution might be expressed by

$$\equiv Si\text{-}H + NaOH \rightarrow \ \equiv Si\text{-}O^- + Na^+ + H_2.$$
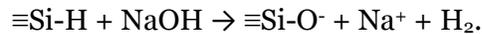
The Si-H bond of HSQ is oxidized by the developer to Si-OH, which further deprotonates to Si-O$^-$ due to basic pH value of the solution. The development process is initiated by the charge imbalance caused by the low proton concentration in the basic developer solution and the energetically less favorable configuration of silicon in $HSiO_{3/2}$.

We now hypothesize that an applied negative potential can provide sufficient energy to split HSQ in the surrounding of water into a negative, water-soluble ion and hydrogen with the following proposed chemical reaction (HSQ-olysis) :

$$\equiv Si\text{-}H + H_2O + e^- \ \rightarrow \ \equiv Si\text{-}O^- + 1.5H_2$$
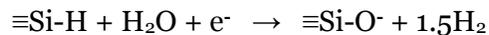
We speculate that HSQ-olysis is possible at an applied potential lower than the minimum required voltage for electrolysis (-1.23 V), because development was already observed for an effective applied voltage of about -1.0 V. However, electrolysis of water in basic solution produces OH$^-$ ions at the negative electrode (cathode). Thus, if a potential larger than -1.23 V is applied both effects contribute to development. Note: for both processes, the electrochemical reaction happens directly at the sample surface, where the HSQ is developed. No sample charging or low concentration of developer can prevent development, e.g. within small trenches.

The effective applied voltage was calculated from an actual applied voltage of -1.4 V (sample against reference electrode) and a potential offset (-0.4 V) taking the difference between material of the sample and the reference electrode into account. The potential offset was experimentally determined by measuring the voltage that must be applied to the system (sample versus reference electrode) to achieve zero current. A direct determination of the offset potential by measuring the open circuit potential was not possible due the insulating behavior of the HSQ layer.

At the sample (cathode), the formation of gas bubbles was observed in some cases during the experiments. However, the generation of gas (hydrogen) is inherent to the development process

of HSQ and also to electrolysis. Thus HSQ-olysis and electrolysis cannot be distinguished by this observation.

We also tried to develop the HSQ in a strong acidic solution (acetic acid : DI-water = 1:10, pH ~1) both with and without an applied potential. Electrochemical development did not occur at either the positive or negative electrode. We hypothesize that the overflow of H_3O^+ ions prevented the generation of negatively charged HSQ ions and thus development. This hypothesis is consistent with the fact that no development of HSQ has been reported in an acidic solution – HSQ itself acts acidic during development. Further, no development was found for a sample immersed in a simple saline solution without applied potential.

Since extremely slow development showed good results, we assume electrochemical development is not limited by the rate of development; i.e. no stopping of electrochemical development in saline solution was observed. Thus, the resolution is likely not influenced by the electrochemical development rate. This observation is in contrast to aqueous base developers for HSQ, where it has been suggested that a high initial development rate might be necessary to achieve high resolution structures [2]. Also, the required exposure-dose density for electrochemical development seems to be lower than that required for salty developer. High-resolution patterns with a dose density of only 3 nC/cm were successfully developed (Figure 4).

Due to the direct influence on the development process by the applied potential, electrochemical development allows more control of the process itself. Electrochemical development can be switched on and off on purpose and controlled in its rate and intensity by the applied voltage or current. Even more interesting, by investigating the applied signals, real time monitoring of the development progress is possible.

Further work may include the investigation of development localized to certain areas of the sample by using structured electrodes (e.g. conductive AFM). One may even think about patterning the substrate by this process i.e. by using a patterned field without exposing the resist beforehand. We hypothesize further, that the electrochemical approach would also be beneficial with other saline solutions and would develop other acid-like resists.

V. CONCLUSION

We have demonstrated that HSQ can be developed in non-alkaline saline solution (4% NaCl in DI-water) with the application of a negative potential. Thereby, comparable resolution to salty development was achieved and pitches for nested-L structures as small as 9-nm were demonstrated. Since development was observed only at the negative electrode, we hypothesize that the unexposed resist was either directly reduced to negatively charged HSQ ions by the transfer of electrons (HSQ-olized) or water was electrolyzed and thereby developer produced locally to the resist.

VI. ACKNOWLEDGMENT

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