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Novel Germanium Surface Modification for Sub-10 nm Patterning with Electron Beam Lithography and HSQ Resist

Running title: Sub-10 nm Patterning of Germanium with HSQ Resist.

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Germanium is a promising high-mobility channel material for future nanoelectronic devices. Hydrogen silsesquioxane (HSQ) is a well known high-resolution electron beam lithography (EBL) resist, which is usually developed in aqueous based developers. However, this feature of HSQ causes troubles while patterning Ge surface as it is always shielded with native Ge oxides. GeO_2 is a water soluble oxide and since HSQ resist is developed in aqueous solvents, this oxide interferes with the patterning. After the electron beam lithography (EBL) exposure, GeO_2 is washed off during the development, lifting the patterned structures and making the high-resolution patterning impossible. To avoid this issue, it is necessary to either clean and passivate the Ge surface or use buffer layers between the native Ge oxides and the HSQ layer. In this article, a novel technique to clean the Ge surface prior to HSQ deposition, using simple “household” acids like citric acid and acetic acid, is reported. The acids are able to remove the native Ge oxides as well as efficiently passivate the surface. The acid passivation was found to hold the HSQ sturdily to the Ge surface, even during development with the aqueous salty

solvent. Using this process, Ge nanowires having widths down to 5 nm were successfully patterned on germanium-on-insulator (GeOI) substrates. To the best of our knowledge, these are the smallest top-down fabricated Ge nanostructures reported to date.

I. Introduction

Continual scaling down of semiconductor devices has led to an upsurge of sophisticated nanofabrication tools. Amongst the few extensively used techniques, electron beam lithography (EBL) is certainly the preferred tool for high-resolution patterning in research and development and small volume production. EBL is a direct-write method that requires a resist and is capable of nanopatterning even below 10 nm. The EBL radiation brings about structural changes of the resist material, such as cross-linking or chain-scission; in most cases a combination of both with one of the processes significantly prevailing over the other. To achieve a successful fabrication process, parameters like exposure voltage and dose, resist and substrate materials, developer solution, development time and temperature have to be taken into account. These parameters are interdependent and work together to give the best possible results. Hydrogen silsesquioxane (HSQ) is an inorganic high resolution, negative tone EBL resist,¹ which offers critical dimensions below 10 nm with ease. Due to physical and chemical similarity of HSQ to SiO₂, it is highly compatible with microelectronic processing.² HSQ is commonly used to pattern Si surfaces, however its application on other materials is fairly limited.^{3,4}

Currently, most semiconductor processes involve the use of Si platforms and only a fraction of them employ Ge. However, Ge is becoming a highly desirable material due to various superior qualities over Si. Ge is a carbon group (Group IV) semiconductor with a

lower effective charge carrier mass than Si,⁵ resulting in a higher electron and hole mobility (effective mass of electrons in Si = 1.06 and Ge = 0.55).⁶ Therefore, Ge-based nanoelectronic devices could offer improved performance at reduced power consumption compared to the Si electronics. However, handling Ge is more complicated than the well-established Si processing. Ge surfaces are always covered by native Ge oxides consisting of GeO and GeO₂, which form in ambient atmosphere. The latter oxide is readily soluble in water and aqueous based solvents.⁷ Development of exposed HSQ resist in tetramethylammonium hydroxide (TMAH) or aqueous NaOH solvents can dissolve the Ge native oxides. Thus, if a Ge oxide is present between the Ge substrate and the EBL exposed HSQ, the oxide will rinse off during development and so will the desired high-resolution pattern. Therefore, removal of native oxides on Ge prior to HSQ deposition and EBL exposure, or the use of non-aqueous based solvents during development, is obligatory. However, after removing the oxides new GeO_x layers have been reported to form on the surface of Ge substrates within 2 min.⁸ Moreover, non-aqueous developers of HSQ do not have the potential to yield the desired high-resolution structures.⁹ To date very few successful methods of patterning Ge with HSQ have been reported.^{10,11}

One procedure involves treating the Ge surface with halogen acids (Cl typically) which is reported to eliminate the interfacial oxides and terminate the surface with the corresponding halogen.¹² In the cited study, Ge substrates are first immersed in de-ionised water (DI) followed by 4.5 M HNO₃, to ensure removal of water soluble and uneven layers of Ge oxides. Subsequently, HNO₃ leads to the reforming of an even layer of GeO₂. The substrates were then immersed in 10 wt% HCl solution for 10 min to certify the elimination of the oxide and the termination of the Ge surface with Cl group. After this process, HSQ was spun onto the substrates and exposed by EBL. This technique yielded high resolution

structures that were well adhered to the substrate after developing with aqueous solvent. However, the process described involved several steps and is therefore, time consuming. Another reported procedure is based on the deposition of a buffer layer, such as SiO_2 , Al_2O_3 , or Si_3N_4 , between the oxidised Ge surface and the HSQ resist. The buffer layer prevents lifting of the high resolution HSQ pattern during development and can be used as a hard mask during the subsequent pattern transfer.^{11,13} In one of these studies,¹³ a 20 nm Si_3N_4 layer was deposited onto the surface of a Ge substrate by plasma-enhanced chemical vapour deposition (PECVD). Next, the HSQ film was spun on the buffer layer, exposed by EBL and developed. Subsequently, the hard mask (the Si_3N_4 layer) was first etched, followed by Ge etching to transfer the pattern into the Ge substrate. Again, although high-resolution structures were produced, this approach involves additional processing steps overcomplicating the patterning of Ge.

The present work details a novel, simple, cheap and safe method to pattern Ge with EBL and HSQ resist. The method developed has a single step, short uptime and involves using simple “household” acids, such as citric and acetic acid. The acids not only create oxide-free Ge surfaces but also help in the adhesion of HSQ resist on Ge substrates for EBL exposure by acid adsorption on the Ge surface. This process is reliable and reproducible on Ge and germanium-on-insulator (GeOI) substrates. Unlike some other acids, citric and acetic acid did not etch away the Ge substrate surface. Moreover, these acids are environment-friendly, non-hazardous to humans and cheaper than acids such as hydrogen fluoride (HF). The effects of immersion time and acid concentration on Ge surfaces are described in this work, with the aim of highlighting the best conditions for HSQ patterning.

II. Experimental

In order to quantify the patterning of Ge surface with HSQ resist, substrates of 10×10 mm were diced from p-doped Ge <100> and Ge-on-insulator (GeOI) wafers, purchased from Umicore and Soitec, respectively. The GeOI wafer consisted of a ~50 nm top Ge layer and a 150 nm of SiO₂ buried oxide (BOX) layer on a Si substrate. Each substrate was degreased by ultra-sonication in acetone and isopropyl alcohol (IPA) for 2 min, followed by N₂ drying. Subsequently, the chips were rinsed under flowing DI water for approximately 10 s and immediately immersed in different acid solutions for various time intervals as described in Table I.

Citric acid (Sigma) or acetic acid (Sigma) was dissolved in DI water to give various molar concentrations. As citric acid was available in solid form, whereas the acetic acid is in liquid form, the citric acid solutions were prepared by weight (w/v) and those of acetic acid by volume (v/v). Table I shows the molar concentrations and the pH of acid solutions prepared by dissolving in DI water in their particular ratios. The chips were then submerged in the appropriate solutions for time intervals of 3, 5 and 10 min. On removal of the chips from the solutions, they were dried with a N₂ gun and HSQ (XR-1541 Dow Corning Corp) resist was immediately spin-coated onto them. Ge chips immersed in 1:1 and 1:2 concentrations of either acid were rinsed with DI water for 3-5 s to remove excess acid residue that was observed on the chips. A 2.4 wt.% solution of HSQ in methyl isobutyl ketone (MIBK) was spin-coated for 33 s at 2000 rpm on the chips, which resulted in the deposition of films about 50 nm thick. The films were subsequently baked on a hot plate at 120 °C for 3 min in an ambient atmosphere. The baking step ensures removal of any excess MIBK solvent and increases the HSQ polymer size making it more sensitive to the electron-beam dose.¹⁴

TABLE I. *Preparation of dilute acids by ratio proportions in DI water with their corresponding molarities and pH.*

Concentration ratio with 1g/ml of citric/acetic acid	Citric Acid		Acetic Acid	
	Molarity (M)	pH	Molarity (M)	pH
1:1	5.20	1.37	16.52	1.77
1:3	1.73	1.45	5.55	2.01
1:7	0.74	1.64	2.35	2.19
1:12	0.43	1.76	1.387	2.31

All EBL exposures of the HSQ on Ge were carried out on Raith e-Line Plus at 10 kV. 20 and 50 nm gratings with varied pitch sizes were exposed on the chips with a base dose of $700 \mu\text{C}/\text{cm}^2$ and incrementing the dose by a factor of 0.15 in the successive patterns. Single pixel gratings were also exposed with pitch sizes ranging from 40 to 200 nm with varied doses in one set. All the sets of gratings were exposed with various electron beam doses starting from $1000 \mu\text{C}/\text{cm}^2$ at 10 kV and increased by a dose of $500 \mu\text{C}/\text{cm}^2$ for the successive set, up to $3000 \mu\text{C}/\text{cm}^2$. After the exposures, the chips were developed in a salty developer, *i.e.* by immersing them in a mixture of 0.25 M NaOH and 0.7 M NaCl for 15 s, followed by a 60 s rinse in DI water. They were lastly dipped in pure IPA for 15 s and dried with N_2 .

The substrates designated for etching were placed in Oxford Instruments Plasmalab 100 for Cl_2 -based reactive ion etching (RIE) to transfer the HSQ structures into the underlying Ge substrate. The process parameters used for the RIE included a Cl_2 flow rate of 30.0 SCCM, radio frequency power of 80 W, 10 mTorr working pressure, 20°C substrate temperature and etch time of 25 s. SEM imaging of all the resulting chips were performed on

the Raith e-Line Plus instrument at 10 kV. ATR-FTIR of acid-passivated Ge was carried out on a Thermo Scientific Nicolet 6700 FTIR spectrometer equipped with an attenuated total reflectance (ATR) accessory (Harrick Scientific). FTIR spectra were obtained by passivating the ATR Ge crystal with acid solutions. XPS spectra were collected on a Thermo Electron K-Alpha spectrometer using a monochromatic Al K α X-ray source (1486.6 eV). Spectra were referenced to the C 1s at 284.8 eV.¹⁴ The XPS spectra were processed using a Shirley background correction followed by peak fitting to Voigt profiles.¹⁵ The Ge 3d doublets were fitted to Gaussian-Lorentzian profiles with an intensity ratio of 3:2 and a spin-orbit splitting of 0.585 eV.¹⁵ The S 2p components from 100 scans were fitted to a doublet with a branching ratio of 0.5 and spin-orbit splitting of 1.2 eV.¹⁵

III. RESULTS AND DISCUSSIONS

A. Germanium Patterning with Acid Treatment

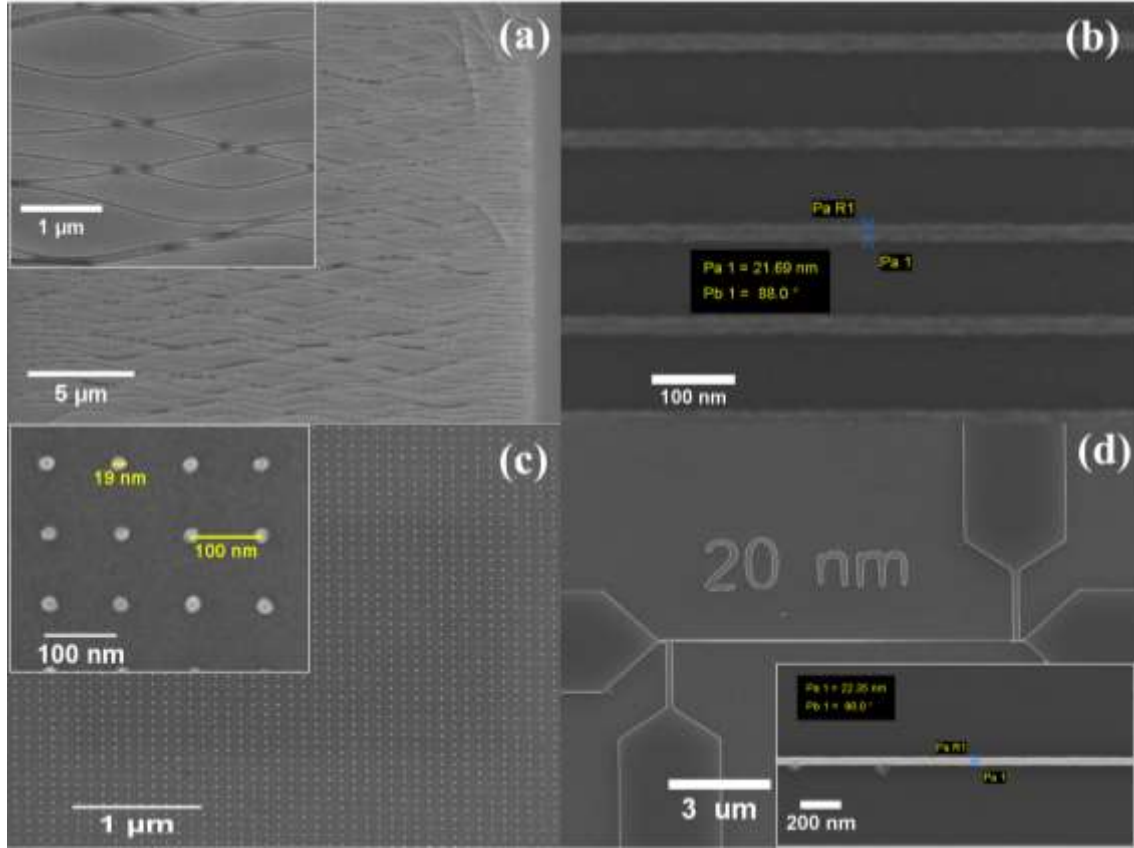


FIG. 1. (Color Online) SEM micrographs of (a) HSQ gratings on a Ge substrate with no prior surface treatment, (b) 20 nm wide HSQ gratings with 120 nm pitch on a Ge chip pre-treated with citric acid, (c) an array of 20 nm dots with 100 nm pitch etched into acetic acid-treated GeOI through the HSQ mask and (d) four probe resistance measurement test structure with a 20 nm nanowire patterned on GeOI with HSQ resist. All insets are higher magnification SEM images.

Figure 1(a) shows a scanning electron microscopy (SEM) image of an untreated Ge substrate after HSQ deposition, EBL exposure and subsequent development. Although the

HSQ lines were resolved with the desired linewidth of 50 nm (inset), the adhesion of the HSQ to the Ge substrate was immensely poor. The Ge substrate was not treated with any acids and was only degreased with acetone and IPA and rinsed with DI water prior to HSQ resist deposition. The native oxides on the Ge surface were, therefore, not removed and hence during the development with the aqueous solvents they were washed away, resulting in the lifting of the overlaying HSQ lines. Figure 1(b) displays the SEM image of HSQ gratings on Ge substrate treated with citric acid. The Ge chip was immersed in 1.73 M citric acid solution in DI water for approximately 5 min, rinsed with DI water for 2-3 min and then nitrogen dried before spin-coating with the HSQ resist. Figure 1(b) shows that HSQ lines as narrow as 20 nm adhered very well to the Ge surface. The quality of the structures was not compromised even though the EBL exposure dose was kept the same as for the untreated Ge surface. Moreover, the size of the pitch (the distance between the edges of two lines) did not affect the adhesion to the Ge surface. This observation shows that citric acid efficaciously removed the Ge native oxides prior to the HSQ resist deposition. Hence, a strong aqueous base, such as NaOH, could also be used for the development of high-resolution HSQ structures. Figure 1(c) shows an array of nanodots patterned on a GeOI substrate treated with 2.35 M concentration acetic acid. The inset in Figure 1(c) shows the critical dimensions of the nanodots, which are as small as 20 nm, spaced ~80 nm apart (100 nm pitch). Similar results of good adherence of HSQ structures to Ge surfaces were observed with diluted solutions of both citric and acetic acids, i.e. 0.43 for citric acid and 1.38 for acetic acid. Figure 1(d) illustrates a Ge nanowire with a width of 20 nm and a 10 μ m length between four Ge contact pads. The inset of Figure 1(d) shows the critical dimension of the nanowire which is 21 nm. Nanowires ranging from 1000 to 20 nm were fabricated using 1.74 M citric acid on GeOI substrates and subsequently etched into the top Ge layer by reactive ion etching (RIE). All images shown in Figure 1

prove that the novel acid treatment of Ge surface is capable of competently producing high-resolution HSQ structures.

B. XPS Analysis

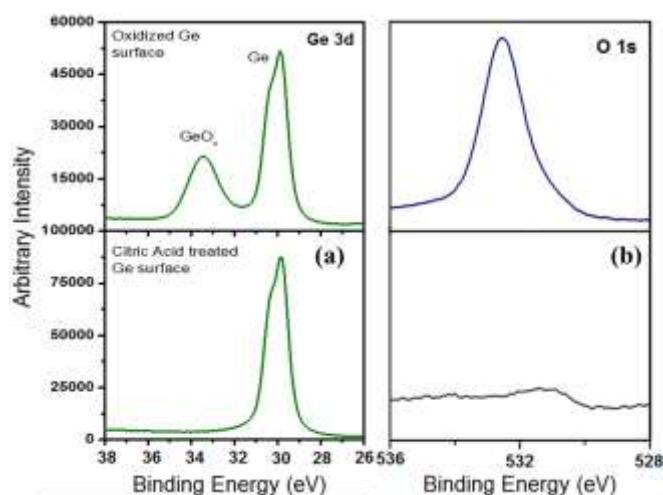


FIG. 2. (Color online) XPS spectra of (a) Ge 3d core-level and (b) O 1s of a Ge surface before (upper spectra) and after (lower spectra) treatment with 0.74 M citric acid for 60 s. The GeO, GeO₂ and O 1s peaks are eliminated after citric acid treatment.

Figure 2 illustrates the X-ray photoelectron spectroscopy (XPS) spectra from a Ge surface before and after treatment with citric acid for 60 s. The upper plots in Figure 2 highlight the Ge surface before any treatment, whereas the lower plots are representative of the surface after treating the Ge surface with 0.74 M citric acid for 60 s. Figure 2(a) shows the Ge 3d core-level and Figure 2(b) shows the O 1s spectra under both conditions. The obvious observation from Figure 2(a) is the elimination of peaks denoting the presence of oxides. In Figure 2(a), prior to the citric acid treatment, wide peaks are observed at 33.75 and at 33 eV due to contributions from GeO and GeO₂, respectively. These two peaks were completely absent on the XPS spectra after treatment with citric acid for 60 s. Similarly, in the O 1s spectrum of an untreated sample (Figure 2(b)), a clear peak is observed at 532 eV, which was

completely eradicated post citric acid treatment. Thus, the given data supports the fact that native oxides on the Ge surface are successfully removed after acid treatment. Due to the exclusion of the interfacial oxides between Ge and HSQ, it was possible to fabricate high-resolution structures on Ge with the HSQ resist after acid treatment, as shown in Figure 1.

C. FTIR Analysis

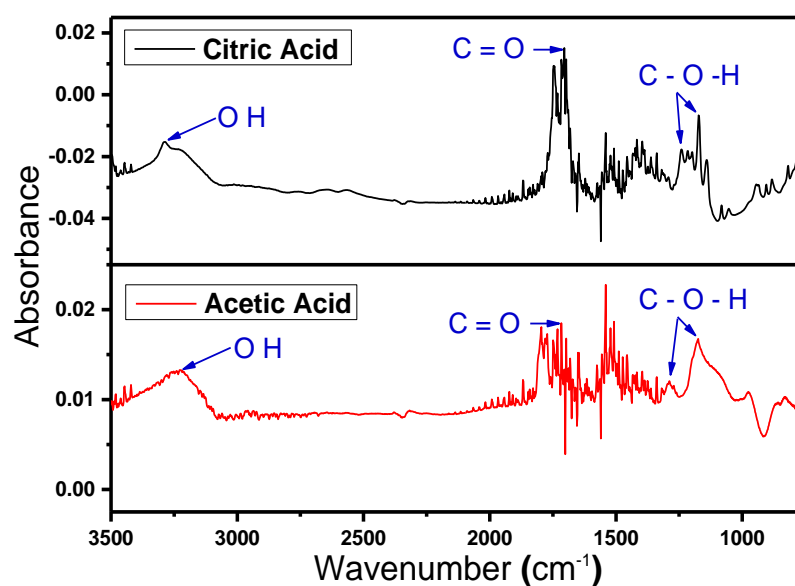


FIG. 3. (Color online) FTIR spectra of a Ge composed ATR crystal treated with citric acid and acetic acid for 60 s each. The presence of characteristic peaks shows the passivation of the Ge by the acids.

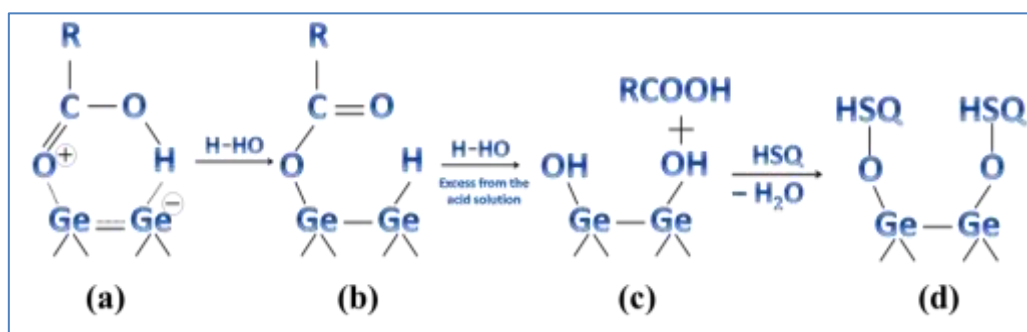
Fourier transform infra-red (FTIR) spectroscopy was employed to detect changes on the surface of Ge substrates after treating with citric and acetic acid. Due to the nature of the attenuated total reflectance (ATR) crystal (a pure Ge crystal globe), it was not feasible to obtain any measurements from the Ge chips. Therefore, the flat arc of the ATR crystal in the FTIR instrument itself was passivated with the acids to obtain IR data. A drop of the required acid was placed on the ATR crystal for approximately 60 s. Excess acid was absorbed onto

blotting paper until the crystal was almost dry before being left in air for another 3 to 5 min for the remaining moisture to completely dry out. The crystal was then carefully placed in the FTIR instrument and measurements taken.

Figure 3 shows FTIR spectra obtained from a Ge ATR crystal passivated with citric and acetic acids. The spectra obtained were generally noisy due to contributing IR signals from water molecules, since the measurements were undertaken in an ambient atmosphere. The wide peaks in both plots at 3200 cm^{-1} denote the high availability of -OH groups from the acids as well as moisture. Strong C=O peaks, a characteristic stretch of a carboxylic group, were also revealed around 1700 cm^{-1} in both the spectra. Peaks positioned at $1250\text{--}1150\text{ cm}^{-1}$ can be assigned to C-(OH) stretching and C-O-H bending modes from the acids.¹⁶ The IR spectra suggested that the Ge surface could be functionalised by citric acid and acetic acid.

This result correlates with a study of reactions of carboxylic acids on Ge surfaces, where it was reported that on treating Ge with various acids, these acids could be adsorbed onto a Ge surface.¹⁷ This adsorption was also confirmed by the dissociation of O-H groups of the carboxylic acid. A stable intermediate carbonyl oxygen dative-bonded state was formed, which is a phenomenon also reported in other studies of organic reactions on Ge surfaces.¹⁸ The final product reported in the cited study, which was formed by O-H dissociation, was Ge-O-COR on the Ge surface. However, it should be noted that in the referenced work the acids used were undiluted with DI water. In the present work the acids were diluted with DI water to obtain different acid concentrations. However, the absence of a Ge-O bond in the Ge 3d XPS spectra (Figure 2(a)) suggests that citric acid was not attached to Ge surfaces with a Ge-O-C linkage. This kind of behaviour was also reported in a study on the passivation of Ge surfaces for thiol functionalization.¹⁹ Moreover, a Ge-H bond was also not present in the

FTIR spectra which should have been observed at around 2070 cm^{-1} .²⁰ The most plausible explanation could be that since the acids used were diluted, the product formed after OH dissociation of the carboxylic acid may further undergo hydrolysis in the solution to give Ge–OH linkage on the Ge surface. This process must be rapid and hence the Ge–O–C bond was undetected by both FTIR and XPS analysis. When HSQ resist is deposited on the passivated Ge surface, the Ge–OH group can readily react with the silanol groups present in the HSQ to give Ge–O–Si bonding. The silanol groups from the HSQ were previously reported to react with Ge–OH via a condensation reaction during pre-bake and electron beam exposure.⁶ The reactions is summarized in Scheme 1.



SCHEME. 1. (Color Online) Proposed reaction pathway of Ge surface functionalisation with carboxylic acids and subsequent bonding with HSQ resist.

Of note, the presence of water was necessary for the process to work. When Ge substrates were treated with pure acetic acid solution, the HSQ structures did not remain on the surface. Scheme 1 shows that water is necessary to form the Ge–OH linkage on the surface which forms the strong linkage site with HSQ. The different concentrations of the acids did not affect the resolution of HSQ but they only affected the adhesion behaviour of HSQ on Ge. At higher concentration, such as undiluted acetic acid or 1:1 concentration of citric acid, the adhesion of critical HSQ features was not regularly observed. It can be

supposed that at lower water content in the acid solutions, lesser –OH binding sites on Ge are generated for the HSQ–O–Ge bond formation (Scheme 1 reaction). Whereas, the solutions with lower acid concentration, i.e. 1:10 and below, excess water content might be preventing the initial adsorption of the carboxylic group on the Ge surface. Thus, the adhesion of the HSQ structures was affected. The optimum concentrations for both the acids were found to be between 1:3 and 1:6.

Ge surfaces terminated with Cl groups are hydrophilic in nature.²¹ Cl termination of Ge substrates, as mentioned previously, has been successful for patterning HSQ on Ge by EBL.¹⁰ Similarly, from our results the removal of oxides and then carboxylic passivation makes the Ge surface hydrophilic and suitable for adhesion of HSQ. The contact angle measured on citric acid treated GeOI substrate was 54.7°/57.2° (left/right angle) and that measured for acetic acid treated GeOI was 50.3°/52.1°, depicting that acetic acid makes the surface slightly more hydrophilic than citric acid (1:3 concentrations) (contact angle of untreated GeOI is 59.6°/60.3°). As reported previously, the age of HSQ resist plays an important role in its adhesion to any surface,⁶ as also noticed in our study. When the resist was used beyond its shelf-life on acid passivated substrates, the exposed structures did not adhere to Ge surfaces after development. A possible explanation for this is that when the HSQ polymer ages, the Si–H bonds start to cross-link instead forming a network within the resist. This process releases hydrogen gas, reducing the Si–H sites in the HSQ to bond with a surface. This consideration indicates that Si–H groups in HSQ are the sites of cross-linking to acid-treated surfaces as uprooting of exposed structures was observed when aged HSQ resist were used.

D. Lithographic Quality

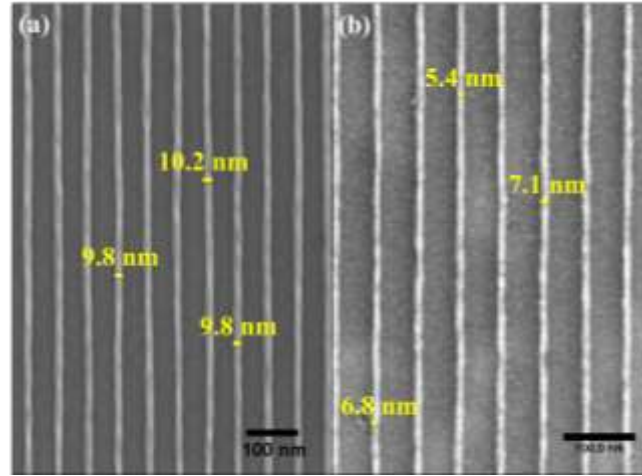


FIG. 4. (Color Online) Sub-10 nm HSQ lines with 60 nm pitch size on GeOI treated with (a) 0.86 M citric acid and (b) 2.75 M acetic acid.

In order to test the effectiveness of the acids in removing surface oxides on critical patterning, single pixel lines (SPLs) were exposed on GeOI substrates treated with 1:7 concentrations of both acids. The SPLs were exposed at 10 kV and 1000 pC/cm by varying the dose factor of the pattern. The gratings exposed had pitch sizes of 40, 60, 80, 100 and 200 nm. Nanodots of 30, 50 and 100 nm were also exposed with a basic dose of 1000 $\mu\text{C}/\text{cm}^2$ and varying dose factors. The SEM images of high resolution gratings are shown in Figure 4. Sub-10 nm lines, down to as low as 5 nm, could be fabricated very conveniently with HSQ on both acid treated Ge surfaces. Figure 4(a) illustrates the critical resolution attainable with citric acid, which was 9 nm with 60 nm pitch sizes, whereas Figure 4(b) shows the critical dimension of ~ 5 nm width achievable with acetic acid. The smallest linewidth resolved on citric acid treated GeOI substrates was slightly wider, *i.e.* 9 nm, as lower doses resulted in under-exposed features. To the best of our knowledge, this is the first time that ~ 5 nm top-down fabricated structures have been presented on a Ge surface. Moreover, the thickness of

the resist used was 50 nm, so a good aspect ratio of 1:10, with respect to the linewidth, was obtained with the resist. Previously reported smallest features, 4.5 nm, achieved with HSQ resist were on Si surface and with ultrathin resist films of 10 nm.²² 7 nm HSQ lines have also been reported on Si using, yet again, a 10 nm thin resist film, exposed at 100 kV and developed with TMAH developer.²³ Thus acid treatments developed in this study not only create an oxide free Ge surface but also positively passivate the Ge surface, resulting in strong adhesion of HSQ resist to Ge substrates during EBL exposure and development, irrespective of dimensions. Acid concentrations as low as 0.74 M for citric acid and 2.35 M for acetic acid were able to successfully bind HSQ structures onto Ge surfaces.

The high resolution structures were then etched into the top Ge layer of the substrates to quantify the pattern transfer process as well as the stability of acid treatment under chlorine RIE. The acid treatment did not interfere with the etch process which can be seen in the SEM images in Figure 5.

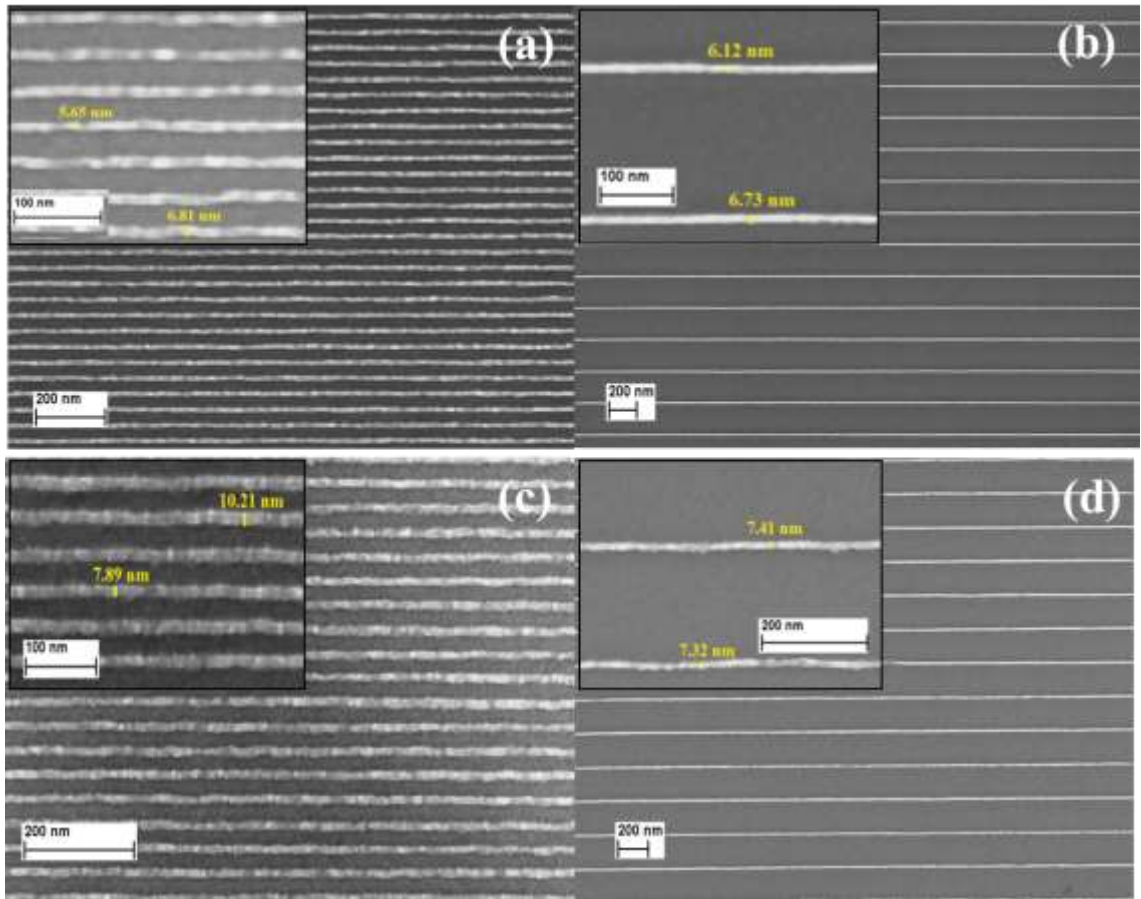


FIG. 5. (Color Online) SEM images of Ge nanowires etched by RIE with Cl_2 chemistry into the ~ 50 nm thick top Ge layer of GeOI substrates: (a) and (b) are generated on acetic acid treated surfaces having 40 and 200 nm pitch sizes, respectively; (c) and (d) are generated on surfaces treated with citric acid having 40 and 200 nm pitch sizes, respectively. All insets show the critical dimension values.

Figure 5 shows that patterns were successfully transferred into the 50 nm thick Ge layers of GeOI substrates. The inset of Figure 5(a) shows the highest resolution Ge nanowire of 5.7 nm width. All of the Figure 5 insets show sub-10 nm wide and about 50 nm high Ge nanowires that were transferred successfully without causing collapse of the nanostructures. The aspect ratios (ratios between height and width) of all the nanowires produced were between 6 and 10.

IV. Applications

The simple passivation methods described above were employed to pattern Ge and GeOI substrates for varied applications, such as (i) HSQ guides for the directed self-assembly (DSA) of block copolymers (BCPs) and (ii) the fabrication of four-probe test device structure (Figure 1(d)).

A. Directed Self Assembly of Block copolymers

Block copolymers have lately been an area of increasing interest for nanofabrication due to various potentials such as molecular scale pattern precision, ultrafine line edge roughness (LER), and low-cost processing.^{24, 25, 24} However, due to the spontaneity of the micro-phase separation the ordering of the BCP domains is random, which limits the potential of this technique. Graphoepitaxy is one of the keys to order the BCP nanostructures by pre-defining the substrates with a template using top-down techniques like EBL. DSA on Si and a few other materials have been demonstrated in the past.^{27,28} However, DSA on Ge has very recently been reported for the first time with poly (styrene-*b*-4 vinyl pyridine) (PS-*b*-P4VP) BCP systems.²⁹

To act as guidance for the BCP, arrays of 50 nm HSQ lines with various spacing between the lines were patterned with EBL on Ge substrates after the citric acid treatment. Figure 6 illustrates the DSA of the PS-*b*-P4VP BCP system on Ge substrates. Figure 6(a) shows the BCPs that phase-separate to form long lamellar domains, which are arranged in a “finger-print” formation. When HSQ trenches are introduced, the lamellar structures arrange parallel to the HSQ lines. It can be seen that as the trench size increases from Figure 6(b) to (d), the number of the BCP lines contained in the HSQ trenches have increased. Thus, the pattern density is increased by the simple DSA of BCPs within top-down fabricated guiding

patterns. A Fe_3O_4 hardmask was subsequently formed on the BCP structures, which was then used to transfer the pattern into the Ge substrate via RIE. Figure 6(e) shows the Ge fins achieved successfully by pattern transfer. To conclude in brief, the surface passivation with citric acid or acetic acid for the HSQ exposure was successful and did not interfere with the phase-separation and self-assembly of the BCP in the later processing steps.

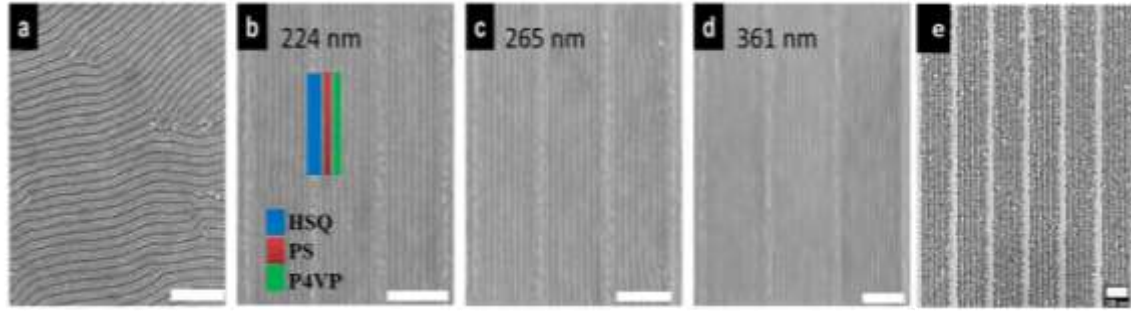


FIG. 6. (Color Online) Graphoepitaxy with the PS-b-P4VP BCP system on Ge surface. (a) Top-down image of BCP on un-patterned area. Graphoepitaxial alignment of the BCP within HSQ trenches of sizes (b) 224 nm, (c) 265 nm and (d) 361 nm. (e) Parallel arrays of pattern transferred Ge nanofins in trench widths of 361 nm (Scale bar 250 nm)²⁹

B. Four-Probe Test Device Structures

The four probe test device structures, as shown in Figure 1(d), were patterned on GeOI substrates, after citric acid treatment, in two lithography steps. In the first lithography, the high resolution nanowires of varying linewidths from 1 μm to 20 nm with the small contacts were exposed. The substrates were then developed in the salty developer and again immersed in 0.74 M citric acid for 5 min and then the resist was spun on the same substrates to pattern the large contact pads, *i.e.* the next lithography step. The results show that the acid treatment does not adversely affect the high-resolution HSQ patterns. These device structures were initially fabricated using the Cl-termination in a study demonstrating a non-destructive dopant-infusion method by Metalorganic Vapour Phase Epitaxy (MOVPE) process into Ge

nanowires to measure the reduction in access resistance across the nanowires.³⁰ Another study was conducted on similar test structures where the doping process was changed to Molecular Layer Doping (MLD). The Ge structures for this study were fabricated using citric acid treatment as described above. The SEM images in figure 7 shows the four-probe test device structure (Figure 7a) and a 10 μm long Ge nanowires having 30 and 20 nm width (Figure 7b and 7c, respectively).

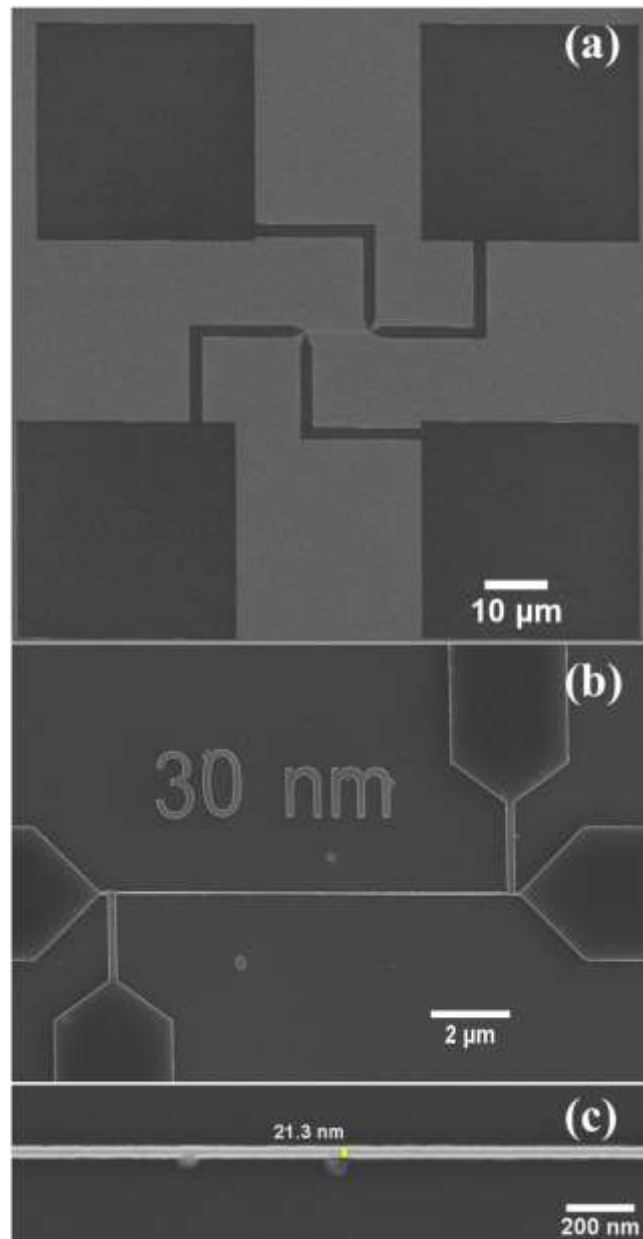


FIG. 7. (Color Online) SEM images of (a) Ge four probe test structure fabricated using 0.74 M citric acid passivation; (b) 30 nm wide and 10 μm long Ge nanowire suspended between two electrodes; (c) magnified image showing the 21 nm dimension of another Ge nanowire.

V. SUMMARY AND CONCLUSIONS

A novel, simple, effective, safe and environment-friendly process to fabricate nanoscaled patterns on Ge surfaces with EBL using the negative tone resist HSQ has been developed. The chemical nature of the untreated Ge surface does not allow competent EBL patterning with this high resolution resist. The treatment with “common” acids to clean and passivate Ge surfaces makes them favourable for good adhesion of HSQ resist after EBL exposure and salty solution development processes. Two acid solutions, citric and acetic acid, have been shown to successfully remove native Ge oxides and further passivate Ge surfaces with carboxylic groups. Thus, the passivation helped in better adhesion of the HSQ resist to Ge surfaces after EBL exposure and development in aqueous based developer. The efficacy of this route was also validated on GeOI substrates. The proposed process is simpler, faster and cheaper than previously used methods and is non-hazardous in all manners. Using this process, Ge nanowires with widths down to 5 nm and heights of 50 nm have successfully been patterned on GeOI substrates. To the best of our knowledge, these are by far the smallest top-down fabricated Ge nanostructures reported to date. There was no obvious difference observed in the adhesion behaviour of HSQ in respect to the acid with which the Ge surface was treated. However, in the case of resolution, acetic acid treatment was able to produce smaller sized HSQ structures as compared to citric acid treatment. Moreover, the application of this Ge patterning process to fabricate nanodevices also proves its compatibility with semiconductor nanofabrication. The removal of native Ge oxides presented here can also aid other studies and processes that require working with oxide-free Ge surfaces.

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TABLE

TABLE I. *Preparation of dilute acids by ratio proportions in DI water with their corresponding molarities and pH.*

Concentration ratio with 1g/ml of citric/acetic acid	Citric Acid		Acetic Acid	
	Molarity (M)	pH	Molarity (M)	pH
1:1	5.20	1.37	16.52	1.77
1:3	1.73	1.45	5.55	2.01
1:7	0.74	1.64	2.35	2.19
1:12	0.43	1.76	1.387	2.31

FIGURE CAPTIONS

FIG. 1. (Color Online) SEM micrographs of (a) HSQ gratings on a Ge substrate with no prior surface treatment, (b) 20 nm wide HSQ gratings with 120 nm pitch on a Ge chip pre-treated with citric acid, (c) an array of 20 nm dots with 100 nm pitch etched into acetic acid-treated GeOI through the HSQ mask and (d) four probe resistance measurement test structure with a 20 nm nanowire patterned on GeOI with HSQ resist. All insets are higher magnification SEM images.

FIG. 2. (Color online) XPS spectra of (a) Ge 3d core-level and (b) O 1s of a Ge surface before (upper spectra) and after (lower spectra) treatment with 0.74 M citric acid for 60 s. The GeO, GeO₂ and O 1s peaks are eliminated after citric acid treatment.

FIG. 3. (Color online) FTIR spectra of a Ge composed ATR crystal treated with citric acid and acetic acid for 60s each. The presence of characteristic peaks shows the passivation of the Ge by the acids.

FIG. 4. (Color Online) Sub-10 nm HSQ lines with 60 nm pitch size on GeOI treated with (a) 0.86 M citric acid and (b) 2.75 M acetic acid.

FIG. 5. (Color Online) SEM images of Ge nanowires etched by RIE with Cl_2 chemistry into the ~50 nm thick top Ge layer of GeOI substrates: (a) and (b) are generated on acetic acid treated surfaces having 40 and 200 nm pitch sizes, respectively; (c) and (d) are generated on surfaces treated with citric acid having 40 and 200 nm pitch sizes, respectively. All insets show the critical dimension values.

FIG. 6. (Color Online) Graphoepitaxy with the PS-b-P4VP BCP system on Ge surface. (a) Top-down image of BCP on un-patterned area. Graphoepitaxial alignment of the BCP within HSQ trenches of sizes (b) 224 nm, (c) 265 nm and (d) 361 nm. (e) Parallel arrays of pattern transferred Ge nanofins in trench widths of 361 nm (Scale bar 250 nm) ²⁹

FIG. 7. (Color Online) SEM images of (a) Ge four probe test structure fabricated using 0.74 M citric acid passivation; (b) 30 nm wide and 10 μm long Ge nanowire suspended between two electrodes; (c) magnified image showing the 21 nm dimension of another Ge nanowire.

SCHEME. 1. (Color Online) Proposed reaction pathway of Ge surface functionalisation with carboxylic acids and subsequent bonding with HSQ resist.

