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1. Introduction

Elastomers based on PDMS are an important class of materials for the fabrication of micro-/nanoscale systems because of properties such as biocompatibility, chemical inertness, optical transparency [1–3]. The formulation of poly(dimethylsiloxane) (PDMS), its fabrication and application in soft lithographic techniques have been extensively studied and applied to develop a variety of functional components and devices for applications such as microfluidics, microelectromechanical systems (MEMS), soft robotics, and microelectronics [1,3–6].

Recently, PDMS has been used in flexible or bendable electronics as an intermediate carrier substrate to transfer Si or compound semiconductors based nano-/microstructures on to flexible substrates such as polyimide (PI) [7–9]. Termined as transfer printing, the method shown in Fig. 1(a)–(c) involves obtaining ordered arrays of micro-/nanowires and ribbons using standard top-down fabrication steps (Fig. 1(a)) and then transferring these structures to the final substrate such as PI (Fig. 1(c)), using elastomeric transfer substrates such as PDMS [Fig. 1(b)] [10–13]. Similar approach has been recently used to obtain macroscale structures such as Si membrane on flexible substrates [14–16]. The process exploits the controlled adhesion between PDMS and Si nano-/microstructures, obtained through suitable oxygen plasma exposure, to selectively pick the nano-/microstructures from bulk wafers and subsequently transfer them to flexible receiver substrates [9,17]. The adhesion between PDMS and Si micro-/nanostructures plays an important role in this transfer printing process, as the bonding strength must be strong enough to lift the Si nano-/microstructures and sufficient to allow them to stick to the PI. In other words, the bonding between PDMS and nano-/microstructures should be weaker than that between nano-/microstructures and PI. It may be noted that commonly used resists such as SU8 or PMMA (polymethyl methacrylate) could also be used for transfer of wires and other silicon structures. However, unlike PDMS it may not be possible to control the adhesion between wires and the resists and then between wires and the final receiver substrates such as PI. On other hand, the major challenge not associated with commonly used resists but with cross-linked elastomers such as PDMS in the above transfer process is to obtain the residues-free surface after the nano-/microstructures have been transferred to the final receiver flexible or bendable substrates. After transfer printing of microstructures the PDMS residues remain on the free surface, as shown in Fig. 1(d). Fig. 2 shows the profiles of two kinds of Si wires arrays after they are transferred to PI. PDMS being an insulator, its residues on the transferred Si nano-/microstructures make it difficult to realize metal connections on these structures.
The known methods for removing cured PDMS include: (a) mechanical scraping [19], (b) swelling of PDMS and peeling [2], (c) chemical–mechanical removal [2,19], and (d) dry etching [20,21]. The suitability of these methods depends very much on the target applications. For example, the mechanical scraping followed by media blast and water rinse using pressurized spray removes bulk PDMS. But, it is not suitable for nano-/microstructures due to potential surface damage, incomplete removal of PDMS, and invariable requirement of an additional cleaning operation with organic solvents, which again does not result in silicone free surface.

Another method of removing PDMS is to swell it with nonpolar organic solvents such as hydrocarbons, toluene, hexane and dichloromethane [2] or organic solvents without any reactive reagent like dimethylformamide (DMF) and then peeling it off. PDMS, like silicon dioxide, apparently requires a fluoride-based etch chemistry. The manual operation of peeling off and the swelling related mechanical stress makes this method less practical to remove PDMS from Si nano-/microstructures. Further, the solvents required in this method are unacceptable due to environmental and health issues associated to them.

The chemical–mechanical removal of PDMS employs a strongly alkaline solution (comprising NaOH, KOH, or TMAH (Tetramethylammonium Hydroxide)) in lower boiling alcohols such as methanol or isopropanol. The PDMS removal is achieved here with base induced chemical degradation of –Si–O–Si– chain surfaces. However, the low boiling solvent with strong alkali has chemical safety and flammability issues. Further, the method is not suitable for nano-/microstructures on flexible substrates such as PI foils, as TMAH is known to damage PI. The issues like chemical safety and flammability can be avoided with dry etching of cured PDMS.

Since PDMS is a Si-based polymer, the required etch chemistry is different from that of polymers consisting mainly of carbon and hydrogen. These polymers can be etched with oxygen, but the siloxane bonds –Si–O–Si– that make up the backbone of the polymer chains in PDMS are not easily broken by oxygen plasma. A problem with dry etching is that unlike chemical removal, which enables removal of PDMS also from hidden surfaces, it results in removal of PDMS from exposed surface only. Dry etching is slower (~20 µm/h [20]) and if the PDMS is on a Si substrate (as here on the Si nano-/microstructures), the plasma will begin to etch Si after it etches through the PDMS, propagating the roughness. The standard methods of using etch-stop layers such as Al or Au [22] is not desirable in this work as the metallization is done after transferring Si nano-/microstructures to flexible substrates. Further, if Si micro/nanostructures are present on flexible substrates such as PI, as here, the dry etching also removes PI, which leads to increased chances of issue such as step coverage, making it difficult to realize electrical connections.

A combination of wet and dry etching of PDMS has also been reported to overcome issues related to the surface roughness and to attain faster etch rates [21]. However, due to smaller dimensions

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**Fig. 1.** Transferring printing of Si wires from bulk wafers to flexible PI substrate. (a) Wire on Si wafer realized using standard lithography; (b) Si wires peeled off from wafer using PDMS as carrier; (c) Si wires on the receiver substrate; and (d) the transferred Si wires (w = 50 µm; t = 2.5 µm) on PI.

**Fig. 2.** The PDMS residues on the Si wires, after they were transferred to flexible PI: (a) 8 µm wide Si-wire (inset) with 8 µm spacing between the wires; (b) 20 µm wide wires (inset) with 10 µm spacing. The images in the inset and the plots were obtained with mechanical profilometer. The x-axis shows the horizontal position of wires on the substrates and the y-axis shows the thickness of wires with and without PDMS residues.
it is challenging to use these methods for Si nano-/microstructures, especially when these structures are present on flexible substrates. For example, the dry etching step will also etch the flexible substrate.

The complete removal of PDMS residues from nano-/microstructures requires methods that: (a) do not involve manual scrubbing; (b) are swelling neutral, and (c) compatible with the various substrates such as polyimide (PI), inorganic materials, and metals used in the fabrication of electronic components from nano-/microstructures. In this regard, organic reactive reagents based chemistry such as quaternary ammonium fluoride (QAF) (e.g. TBAF (Tetrabutylammonium Fluoride)) in low solubility solvents such as di-substituted amides (e.g. N-Methylpyrrolidinone (NMP), dimethylformamide (DMF)) or tetrahydrofuran (THF) are interesting, as they have been found to yield satisfactory results [23,24]. These solutions cause rapid disruption/disintegration of the PDMS polymer matrix, and mostly remove the residues by dislodging it from the surface and, to a large extent, by dissolving PDMS residues by breaking Si–O bonds and forming Si–F bonds, which is similar to the etching of glass in hydrogen fluoride [23,24]. A similar chemistry, with dilute solution of TBAF (1% weight concentration) in hydrophobic non-hydroxylic aprotic solvent propylene glycol methyl ether acetate (PMA), has been used in this paper. This solution is compatible with the flexible PI substrate and the Si micro-/macrostructures used in this paper, as evident from the results given in the following section.

3. Experimental results

3.1. Fabrication and transfer of micro-/macrostructures

The procedure for transferring wires from Si wafer to the flexible PI substrates using PDMS as carrier is shown in Fig. 1. In this work the wires of different dimensions were realized on a SOI (Si on insulator) wafer using top-down approach involving standard photolithography and etching steps (Fig. 1a) [9]. With some additional fabrication steps bulk Si wafers can also be used for obtaining microstructures, as in [25]. However SOI wafers have been this paper as it is easy to obtain wires with uniform geometry. The top-down fabrication has been adopted in this work as it also has good control over geometry (thicknesses, widths, and lengths of wires), crystallinity, and doping levels. Whilst the dimension of wires used in this work are of micron scale (width (w) – 8, 20, 50 μm, length (l) – 100, 200, 1000 μm and thickness (t) – 2.5 μm) with suitable technology such as Electron Beam Lithography (EBL) they can be scaled down to nanoscale. By placing plasma exposed PDMS carrier substrate (6 mm thick) over the wires (Fig. 1a) a weak siloxane bonding is allowed to develop between wires and the PDMS [9]. Peeling off the PDMS at this stage (Fig. 1b) results in the transfer of ordered wires from the wafer to PDMS. The wires are then transferred again from PDMS to flexible PI substrate (Fig. 1c) and at this stage the PDMS residues are left on Si wires (Fig. 1d), making it difficult to realize the electrical connection and hence using the wires to develop electronic devices. Similar issue is faced for the cm-scale flexible chips realized on flexible PI using the transfer-printing process [14,15]. The PDMS used throughout the study was Sylgard 184 mixed in a 10:1 ratio with its curing agent.

3.2. Removal of PDMS residues

A dilute solution of TBAF (1% weight concentration) in hydrophobic non-hydroxylic aprotic solvent propylene glycol methyl ether acetate (PMA) was used to remove the PDMS residues from the Si wires. The solution containing TBAF causes rapid disruption/disintegration of PDMS polymer matrix and removes it by dislodging it from the surface and, to a large extent, by dissolution of the PDMS residues. A key feature of the chemistry used here is the compatibility of etchant with the flexible PI substrate. The sample was immersed in the solution which was stirred continuously. The solution was maintained at a temperature of 50 °C throughout the cleaning process as this temperature results in faster etching. The cleaning action was performed for a period depending on the amount of polymer residues. In general an etching rate of 1–1.5 μm/min was observed and an immersion time of about 10 min was sufficient to remove PDMS from the samples. After the first etching step, the sample was transported to the first solvent rinse bath comprising of preheated (50 °C) PMA solvent.

Fig. 3. Removal of PDMS residues from Si wires on PI foils. (a) The array of Si wires (w – 50 μm; t – 2.5 μm) with PDMS residues (dark color) on them; (b) The optical image of wires at an intermediate stage. The etching solution causes rapid disruption/disintegration of PDMS polymer matrix and removes it by dislodging it from the surface and, to a large extent, by dissolution of the PDMS residues. The images were taken after cleaning and drying the samples; (c) The image of wires after final removal of PDMS; (d–f) SEM images at various stages of PDMS removal. The wires shown in SEM image are same as those in (a)–(c). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
with agitation and kept there for about 15 min. This was followed by another solvent rinse in preheated (50 °C) PMA solvent for about 10 min. After this, the sample was immersed from solution from time to time and examined under the optical microscope and SEM. The various stages of PDMS removal are shown in Fig. 3.

The above method was also used to remove PDMS residues from the flex-chips on PI substrates [14,15]. The I–V measurements recorded with probe station connected to semiconductor parameter analyzer, as shown in Fig. 4 with the ultra-thin chip conforming to cylindrical surface in the inset, confirm the complete removal of the PDMS from the contact pads of the metal lines on flex-chips.

It is difficult to determine with optical microscope the complete removal of PDMS. Therefore, to prove the efficiency of the cleaning process, we also used X-ray photoelectron spectroscopy (XPS) to analyze the surface of a SiO₂ coated Si sample before deposition of the PDMS layer (as a reference), after deposition of the PDMS layer, and finally after removal of the PDMS layer. XPS spectra were recorded with a KRATOS AXIS UltraDLD instrument equipped with a hemispherical analyzer and a monochromatic Al Kx (1486.6 eV) X-ray source. The survey, the valence band (VB) and the core lines were recorded at 80, 40 and 20 eV respectively. In particular, the core lines (C1s, O1s, Si2p) at 20 eV pass energy lead to an energy resolution of ~0.4 eV. Compensation of the surface charging was performed by bombarding the samples surface with an electron flood gun during the analyses. After a Shirley-type background subtraction, the spectra were fitted using a non-linear least-squares fitting program adopting a Gaussian–Lorentzian peak shape.

Fig. 5 presents the detailed deconvolution of the C1s, O1s and Si2p core lines for the three different surfaces. For the bare SiO₂ surface, the spectra are displayed in Fig. 5 (panels a.1–3). Since the deposited films were exposed to air, the C1s peak may include a significant amount of carbon due to ambient contamination. After deconvolution of the C1s core line the main peak corresponding to hydrocarbon contamination was used as internal reference (setting it at the binding energy of 285.0 eV) to calibrate all the spectra and correct the binding energy (BE) shift due to surface charging, either under flood electron gun application or without. Looking at the C1s, O1s and Si2p regions acquired on the PDMS surface (Fig. 5, panels b.1–3) we observe that the main components appear at 284.4, 532.0 and 101.9 eV respectively, which is consistent with the typical C–Si and Si–O bonds in the PDMS polymeric chain [26]. The measured O/Si and C/Si ratios are consistent with those expected on the base of the PDMS monomer composition, where C:Si:O = 2:1:1, as reported in Table 1. The minor component in the Si2p peak at 103.3 eV (assigned to O–Si–O bonds), as well as its correspondent O1s peak at 532.8 eV in the O1s spectrum are
Table 1

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<th></th>
<th>O1s BE [eV]</th>
<th>Si2p BE [eV]</th>
<th>C1s BE [eV]</th>
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<td>103.6</td>
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<tr>
<td>O–Si–O</td>
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<td>1.1</td>
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<tr>
<td>PDMS</td>
<td>532.8</td>
<td>103.7</td>
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<tr>
<td>Wafer after PDMS removal</td>
<td>532.8</td>
<td>103.7</td>
<td>O–Si–O</td>
<td>1.9</td>
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**Fig. 6.** XPS valence band regions acquired on a simple SiO2 substrate, on the same substrate after the deposition of a PDMS layer and after the removal of the PDMS by chemical etching.

The method reported in this paper results in complete removal of PDMS residues that are left on the surface of Si macro-/microstructures during their transfer to the flexible substrates. Even if the size of the demonstrated PDMS residues free transferred structures is not in nanoscale, the chemistry to remove PDMS would still work as long as the solution is not attacking the silicon wires. From the results presented in this paper it is clear that the silicon is not attacked by the presented chemistry to remove PDMS. Though the method has been demonstrated on Si macro-/microstructures the utility of the approach on nanostructures such as nanowires (NWs) and in other areas such as soft lithography and microfluidics are evident. For example, the presented chemical etching method could be used to pattern the PDMS to develop microdevices. Currently, micromolding techniques such as replica molding [28], microtransfer molding [29] and micromolding in capillaries [30] are used for this purpose. Similarly, the method could be used to remove PDMS from hidden or non-exposed surfaces and in MEMS applications.

**References**