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An Adhesion-based Alternative to Solvent Processing in Microfabrication

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Abstract

In the fabrication of microscale devices, organic solvents are used in a variety of processes to remove particulates from the substrate surface. The excellent solvation strength of these solvents makes them a popular method for decontaminating surfaces. However, solvent cleaning presents a risk. Without great care, solvents can volatilize without fully removing contaminants from the surface, leaving behind a residue that can hinder the performance of a device. Thus, an alternative method for surface decontamination was investigated utilizing an inert, low adhesion polymer. Chosen for its effectiveness in optical cleaning, the polymer's ability to remove organic and inorganic contaminants from microtextured features was tested against traditional solvent methods. This study's findings suggest that this polymer is more effective than traditional methods in certain microfabrication processes, at the expense of a longer processing time. This investigation also considered the application of this polymer in thin film liftoff, a microfabrication technique. Thin chromium pads were produced on substrate surfaces with results superior to those achieved by traditional acetone sonication. For film thicknesses below 30 nanometers, geometries without "fence" artifacts could be created with fewer steps than current procedures. The applications of this polymer provide alternative, low-residue pathways for microfabrication.

Keywords: Contamination control, Thin film lift-off, First Contact Polymer

1. Introduction and Background

It has long been recognized that minimizing contamination is critical to the fabrication of microscale and nanoscale devices, and even parts per million levels of contamination can modify the performance of semiconductor devices.[1] For instance, the most recent generations of microchips are created through an extreme ultraviolet lithographic process that is sensitive to even a single molecular layer of organic contamination or individual inorganic nanoparticles on the mask surface.[2] Even in a controlled environment, there is potential for contaminants to accumulate on a sample through airborne dust, process chemicals, and outgassing from storage containers.[3] Organic solvents such as acetone, ethanol, methanol, isopropanol, xylenes, and n-methyl pyrrolidone (NMP) are commonly used to dissolve and remove unwanted materials such as contaminants and residual process chemicals from the surfaces of samples, photomasks, and process chamber walls; the low cost, excellent solvation strength, and high volatility of these solvents make them popular for decontaminating surfaces.

Nevertheless, solvent cleaning comes with drawbacks, notably in the handling, storage, and disposal of large quantities of highly flammable solvents, and concerns over sample cleanliness. Also, when applied without great care, solvents can volatilize without fully dissolving contaminants from the surface, especially if the surface contains features such as ridges or cavities. Of significant concern is the fact that these processes can introduce additional contamination from solvent residues.[4] Furthermore, many of these solvents also pose handling problems due to their often toxic character.[5] While there exist numerous alternative methods to remove contamination from a surface,[6] many are prohibitively expensive for small laboratories or are too harsh for sensitive applications.

In addition to the potential risk to sample cleanliness, solvent processing can also produce undesirable effects in certain processing steps. For example, thin film lift-off is a process used frequently in microfabrication. The process is used to deposit thin metal films of desired patterns onto a substrate surface, which serve as electrodes and interconnects in microelectronic and micro-electromechanical devices. Thin film lift-off is normally a solvent-based process, and its key steps are illustrated in Fig. 1 below. These include: (i) spin coating of a sacrificial photosensitive layer, or photoresist, to the surface, (ii) selectively patterning and removing regions of the photoresist using a photomask, (iii) depositing a thin metal film across the entire sample surface, and (iv) removing the photoresist with a solvent. This process can produce undesirable artifacts called "fences" where the thin film material deposited along the sidewalls of the patterned photoresist layer remains in the final device. Additional steps, which are often cumbersome or potentially damaging to delicate samples, must be performed to remove fences and produce (v) flat films with no edge features.

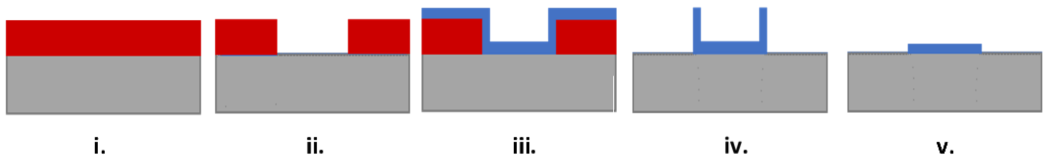

Figure 1. Process steps involved in traditional lift-off processing.

This investigation approached these issues in solvent-based processing through the use of First Contact Polymer (FCP), a peel off polymer emulsion. FCP has shown great success in cleaning flat, highly polished optical surfaces, such as the mirrors used in telescopes and interferometers.[7,8] We investigate the efficacy of FCP in decontaminating featured surfaces possessing corners or cavities where residue may build up during conventional processes, as well as in other solvent-based microfabrication processes such as lift-off. The adoption of this polymer would allow a reduction of solvent waste streams from laboratories and provide a potential alternative to an imperfect processing technique. This investigation has highlighted a number of such applications, as well as some drawbacks and limitations.

2. Experiment

2.1 Removal of Inorganic Contaminants

Inorganic contamination in microfabrication most often comes from suspended cleanroom dust and etch processes and can affect the properties of the substrate surface. We investigate the ability of FCP to remove inorganic contaminants from surfaces with microscale features. Silicon-100 wafers capped with a 1 µm thick low-stress silicon nitride layer were photolithographically patterned with circular and square features ranging in size from 3 µm to 320 µm. The samples were then dry etched with a CF_4 plasma in a reactive-ion etcher (RIE) to selectively remove the silicon nitride film before removing the photoresist layer. After an anisotropic etch to a maximum depth of 20 µm using hot KOH and subsequent removal of the remaining silicon nitride etch mask using a phosphoric acid solution, the samples were contaminated, cleaned, and characterized. TiO_2 nanoparticles were chosen as the contaminant, since these particles are chemically inert, are of similar size ranges to long residence time cleanroom dust, and possess a distinct signal when characterized by energy dispersive spectroscopy (EDS). Substrates were contaminated by applying a dilute aqueous suspension of the nanoparticles to the sample surface, followed by ambient drying. Each sample was observed under a scanning electron microscope (SEM) using the secondary electron (SE) and EDS detectors prior to cleaning. EDS spectra were used to confirm the chemical identity of the observed contaminants, and a qualitative claim was made through SE observation. One half of the samples were cleaned using standard solvent-based process using a 270 second sonication in acetone, followed by an isopropanol rinse. The remaining samples were treated with FCP, by applying the polymer coating over the sample, allowing the emulsion to cure, and then peeling off the cured polymer layer. After treatment, samples were once again observed under the SEM to make a qualitative comparison of the cleaning efficiencies of the two methods.

This analysis determined the range of contaminant concentrations and surface feature geometries in which the FCP process provided better results than solvent cleaning. By qualitative comparison, FCP was found to be more effective than the solvent rinse at removing inorganic particle contaminants from the shallow rectangular cavities created by plasma etching and in most pyramidal cavities generated by the anisotropic KOH etch process (Fig. 2). However, it should be noted that the curing time of FCP can take over 30 minutes, which is a notable concern given the convenience of current solvent-based methods.

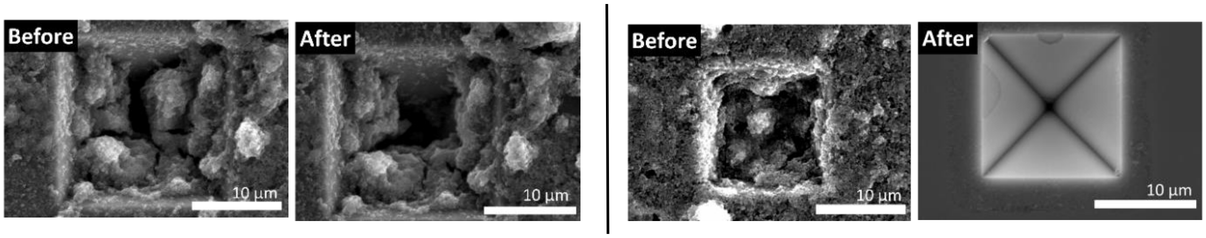

Figure 2. Removal of a high dose of titanium dioxide nanoparticles from a silicon surface textured with 20 µm wide and 14 µm deep pyramidal cavities. SEM images showing surface contamination levels before and after decontamination by traditional acetone sonication (left) and FCP (right).

2.2 Removal of Organic Contaminants

Organic contamination is present in all cleanrooms and is difficult to mitigate. Thus, there exist multiple processes that reduce the amount of organic contamination on a surface. One commonly used method is the Radio Corporation of America's Standard Clean-1, often referred to as an "SC1". This commonly applied process uses a heated solution of ammonium hydroxide and hydrogen peroxide to replace the native oxide layer of the silicon substrate with a new layer, removing most organic and small particulate contaminants on the sample surface. The SC1 was used as a baseline in the comparison of organic decontamination capabilities for FCP against a traditionally used solvent rinse.

Untreated Si-100 surfaces were treated with various cleaning and contamination steps to characterize the carbon residue left behind after an FCP and solvent treatment, and then to examine the ability of each method to remove a layer of solvent residue. To characterize the amount of residue that each method left on the sample surface, all samples, excluding a control wafer that received no processing, were first SC1 cleaned and then treated by different processes. Using Auger spectroscopy, the amount of carbon residue on sample surfaces was determined by comparing the spectral intensity of carbon to that of silicon. Three 50 µm by 50 µm area measurements were taken in different locations across each sample, and an average value was obtained. Chart A in Fig. 3 shows the measured carbon content when a sample had been cleaned via SC1, then treated with either an acetone and isopropanol rinse or an FCP treatment. The results of this test were indicative of the carbon residue added to the surface by each method. Chart B in Fig. 3 compares the two methods in removing contamination from a sample that had been left to improperly dry and accumulate solvent residue (SR) after washing with acetone. The results from both tests demonstrate that FCP leaves less organic residue on the surface than an acetone/isopropanol rinse, but a substrate treated with the polymer has more organic contamination than seen after an SC1.

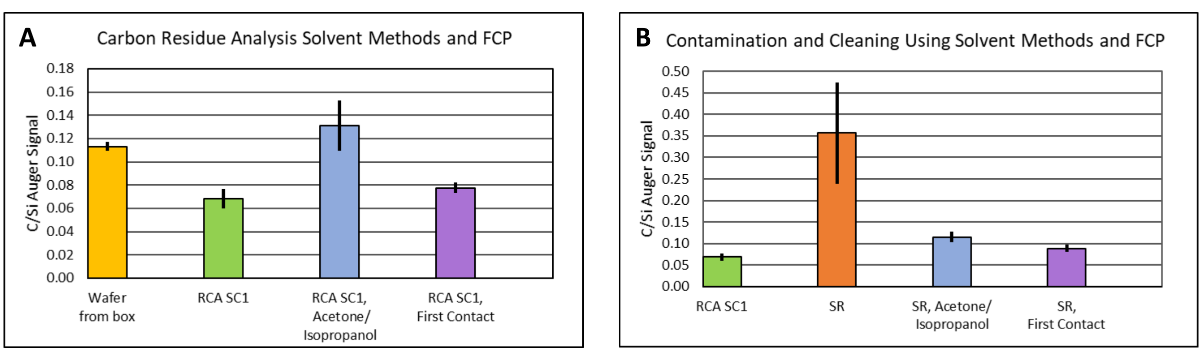

Figure 3. (A) Auger C/Si signal ratios of samples without treatment, after a SC1 clean, and after a SC1 clean in addition to solvent cleaning or FCP application, showing the carbon residue left behind after each treatment. (B) Auger C/Si signal ratios compared to the RCA SC1 clean after contaminated with solvent residue (SR) and cleaned using solvent methods or FCP application. Error bars denote one standard deviation.

2.3 Thin Film Processing with First Contact

Besides surface decontamination, this work has addressed the capabilities of FCP in photoresist removal and its implications for thin film lift-off. Through sputter deposition onto a Megaposit SPR 220-3 photoresist mask patterned with circular and square features ranging in size from 3 µm to 320 µm, thin films of chromium (commonly used as an adhesion layer in microelectronic interconnects) were applied to the surface of a silicon-100 sample. Lift-off was then attempted using a regular application of FCP onto the substrate and compared to the traditional lift-off method of sonication in acetone. The results of this experiment show that FCP lift-off was not successful on the thickest metal films, and the thin film was redeposited on the surface instead of being removed. However, on films thinner than 30 nanometers, a successful lift-off was achieved.

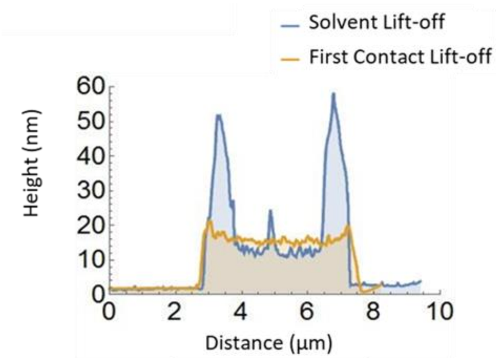

Figure 4. FCP lift-off of a thin chromium film provided features with no distinct fences, while fences were prominent when acetone sonication was used.

Upon characterization of these sputtered samples using optical and atomic force microscopy (AFM), we found that samples were lifted off using FCP had slightly different feature geometries than traditionally processed samples. Samples with lift-off performed using acetone sonication possessed moderate fences, or raised regions along the feature edges where the chromium deposited on the photoresist sidewalls persists through the lift-off process. Surprisingly, FCP-processed samples did not possess these undesirable artifacts. This is most clearly seen in Fig. 4, where fences that are several tens of nanometers tall are observed on chromium pads created by the traditional acetone lift-off process, while the chromium pads created by the new FCP lift-off process possess no discernible fences. Although the thickness of feature height is limited by this technique, this finding shows an interesting new use for FCP in microfabrication.

3. Discussion

Solvents are a valuable tool in microfabrication, despite their limitations, but the use of FCP in their stead may offer an incremental improvement in results and a new approach to achieving a more consistent thin film deposition. In this investigation, FCP was compared to traditional solvent methods in some of their most common uses: decontamination and thin film lift-off. The comparison demonstrates that FCP can more effectively remove inorganic particulates than acetone sonication, and may be more effective than a solvent rinse at removing molecular organic contamination as well. There is precedent for using FCP to decontaminate semiconducting materials. Brachmann *et al.* used X-ray photoelectron spectroscopy to characterize the capability of FCP and other common methods remove trace contaminants from silicon and $Ca_3TaGa_3Si_2O_{14}$.[9] The study used sonication in an acetone/ethanol mixture, followed by a wash in ultrapure water before drying with high purity nitrogen gas. When comparing the results of FCP versus their solvent rinse, Brachmann *et al.* concluded that FCP left more trace carbon residue on the silicon substrate than the solvent treatment. The alternative solvent treatment used in our study was chosen to mitigate effects of the high particle atmosphere this experiment was conducted in by reducing the opportunity for contaminants to solvate onto the surface via the use of more volatile solvents. Considering these results, one should note that the effectiveness of FCP in removing organic molecular contaminants may be comparable or inferior to traditional solvent treatments in certain environments.

Our experiment additionally demonstrated the use of FCP to achieve features without fence artifacts during thin metal film lift-off. This result can be otherwise obtained by polishing the deposited layer[10] or using a specialized photoresist.[11] Although these alternatives facilitate the fabrication of features with film thickness greater than 30 nanometers, they present drawbacks in terms of cost and complexity. The mechanism behind adhesion-based lift-off, particularly why it is less effective on thicker films, is not yet fully understood. We propose that during lift-off, solvent within the polymer emulsion propagates through porous areas of the film, near the top of feature cavities, causing the photoresist to gel and expand, cracking the thin metal film and allowing FCP to disperse within the photoresist. Films above 30 nanometers in thickness seem to sink to the substrate surface and adhere to the silicon before being restrained by FCP. Observations of failed lift-off samples and FCP remains corroborate these claims, showing cracking along the chrome layer retained within the polymer and a greater rate of failure in features spaced greater distances apart.

Future experiments will work to better understand the mechanisms by which FCP is able to perform lift-off and gain a more comprehensive understanding of the limitations of this polymer in decontamination. The benefits of organic decontaminating using FCP, including the removal of different types of photoresists from flat and featured surfaces is the subject of a separate investigation. The continued investigation of FCP in lithographic processes is perhaps the most intriguing, and alternative geometries are being examined to better elucidate the capabilities of adhesion-based lift-off.

First Contact Polymer presents interesting uses and a way to address many of the challenges posed by traditional solvent processing methods. There has been comparatively little literature published regarding the use of alternatives to solvents in decontamination and specific processes, and this study aims to contribute in addressing that gap. Although many of the improvements by using FCP instead of traditional methods are incremental, the discovery of a new methodology to obtain features without fence artifacts is relevant to microfabrication processes and helps lay groundwork for future studies into polymer-based lithography.

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