# Inkjet Method for Direct Patterned Etching of Silicon Dioxide

***Alison Lennon, Roland Utama, Anita Ho-Baillie, Stuart Wenham; ARC***
***Photovoltaics Centre of Excellence, The University of New South Wales, Sydney, NSW, Australia***

## Abstract

*An inkjet printing method for the direct patterned etching of silicon dioxide is described. The method uses an inkjet device to deposit a pattern of a solution containing an inactive etching component onto a water soluble surface layer formed over the silicon dioxide. The inactive component reacts with the surface layer, where it contacts, to form an active etchant which etches the silicon dioxide under the surface layer to form a pattern of openings. The method has been successfully used to etch a front-contact finger and busbar pattern in a silicon dioxide antireflection layer of a silicon solar cell.*

## Introduction

Semiconductor device fabrication typically involves extensive use of patterned etching of both semiconductor and dielectric materials. In particular, the formation of patterns of openings in silicon dioxide dielectric layers of silicon devices is widely used because of the masking, passivating and optical effects of silicon dioxide on silicon surfaces. Patterned etching of silicon dioxide layers can be used to facilitate localised diffusions and metal contacts to underlying silicon (e.g., in the case of silicon solar cells), or in other cases, to provide a mask for etching the underlying silicon. Typically, the patterned etching of dielectric layers, such as silicon dioxide, has been achieved using photolithography or laser scribing. For applications, where material damage due to laser scribing is undesirable, photolithography is the preferred patterning method.

However, photolithography requires costly equipment (e.g., mask writers, mask aligners), expensive clean room environments, and generally many time-consuming steps. Changes in patterns require new mask sets. A typical photolithographic process for the formation of a pattern of openings in a dielectric layer requires deposition of a resist layer over the dielectric layer (usually by spin-coating), appropriately aligning a prepared mask over the resist layer, exposing the resist through the mask to UV radiation and then developing the exposed resist to form a pattern of openings in the resist. The resist with a pattern of openings is then used as a mask against etching fluid that etches the underlying dielectric layer through the openings. Fluids commonly used to etch silicon dioxide are hydrogen fluoride (HF) solutions or buffered oxide etching (BOE) solutions, both of which are highly corrosive. The surface is then rinsed to remove traces of the etchant, and finally the resist layer is removed to leave a patterned dielectric layer on the device.

More recently, inkjet methods of patterning a resist layer have been described [1,2,3]. These methods remove the need to use photolithography for the patterning step, using instead an inkjet device to deposit a solution, which creates either openings [1] or permeable regions [2,3] in the resist layer, at predetermined locations. The thus-patterned resist layer can then be used to mask the underlying dielectric layer while the inkjetted (printed) pattern provides a path for etching the dielectric when the device is immersed in the etching fluid. These inkjet methods of patterning a resist, and hence a dielectric, provide an alternative to photolithographic methods. However, like the photolithographic methods, they still involve many time-consuming steps and require the use of large quantities of chemicals, in particular resins for resist and corrosive etching solutions. Because of the need to use large quantities of corrosive solutions for the immersion etching step, many safety and environmental controls must be implemented in production environments. Therefore, advances which can reduce the number of processing steps and/or the amount of expensive and corrosive chemicals used in the patterning step are desirable. Furthermore, advances which minimise the risks to human operators when performing etching processes and reduce the amount of hazardous waste are also desirable.

In this paper we describe a method for the patterned etching of silicon dioxide that does not require a masking or resist layer and is safer than existing immersion etching methods in that the corrosive etchant is only formed in-situ on the device surface to be etched. Furthermore, because the etchant is formed only at the locations to be etched, the method requires small amounts of chemicals and produces significantly less hazardous chemical waste. The method does not require any resist chemicals and only uses small quantities of etching precursor materials.

## Overview of Etching Method

The direct etching method reduces the use of corrosive chemicals by bringing together inactive etching components at the surface location where etching is required. The components react in situ to form HF which then etches the underlying silicon dioxide. The first component is provided by an acidic, water-soluble polymer surface layer and acts as an acid source. This layer can be formed by simply spin-coating an aqueous solution of the polymer over the surface to be etched. The second component is an aqueous solution containing a fluoride source (e.g., ammonium fluoride).

The aqueous fluoride source is applied to the surface, according to a predetermined etching pattern, by an inkjet printing device. At the surface, deposited droplets of the solution first locally dissolve the polymer where they contact the polymer film, and then fluoride ions abstract protons from the acidic polymer to form HF in situ. If the solution which is inkjetted contains ammonium fluoride (as the fluoride source) then the overall reaction resembles that which occurs when silicon dioxide is immersed in a BOE solution:

$$\mathrm{SiO_2(s) + 4HF(aq) + 2NH_4F(aq)} \rightarrow \mathrm{(NH_4)_2SiF_6(aq) + 2H_2O} \qquad (1)$$

The etch product, ammonium hexafluorosilicate, has a solubility of ~130 g $L^{-1}$ at 25 °C in ammonium fluoride concentrations of ~ 10% (w/v) [4] which means that it can be readily rinsed away in water without forming solid precipitates. Although in theory, any water-soluble acidic polymer can be used, our best results have been achieved using spin-coated polyacrylic acid (PAA) films which are ~ 2-3 µm thick. We have used ammonium fluoride as the aqueous fluoride source because both it and its etch product, ammonium hexafluorosilicate, are very soluble.

Corrosive HF is only formed at the site to be etched, and therefore is not directly handled. Direct inkjet deposition of the etching solutions containing hydrogen fluoride solutions is difficult to achieve because few available printheads can tolerate the corrosive nature of the solution. Furthermore, few operators would consider it safe to deposit hydrogen fluoride-containing solutions via inkjet because of the risk of operator contact in the event of fluid leaks in an inkjet system. Although, fluoride-containing solutions, such as ammonium fluoride, are classified as toxic they can be much more safely handled than hydrogen fluoride solutions. In addition, our method only uses small quantities of fluoride ion and the fluoride ion is formulated in solutions of reasonably dilute concentration (≤ 15% (w/v)).

## Inkjet Printing

The direct patterned etching method has been developed using a FUJIFILM Dimatix Materials Printer (DMP-2831) with printhead cartridges having a nominal 1 pL drop volume. These printhead cartridges jet optimally when the surface tension and viscosity of the deposition solution are in the ranges, 28-33 mN/m and 10-12 cp, respectively [5].

The concentration of fluoride in the deposition solution can be varied depending on etching characteristics required. However, we have found that it is best to maintain the fluoride concentration in the solution below 15% and more ideally at ~ 11%. This is because at higher ammonium fluoride concentrations the solubility of the ammonium hexafluorosilicate etch product is significantly reduced [4] and may result in ammonium hexafluorosilicate precipitates being deposited on the surface being etched thus causing uneven etching of the surface.

The Dimatix cartridges have silicon fluid chambers and nozzles. We have found that the ammonium fluoride solution jets most reliably at pH values between 8 and 9. At lower pH values, firing becomes erratic and nozzles tend to block. This is believed to be due to the more acidic solutions etching the oxide surface of the silicon pumping chamber and nozzle, resulting in precipitates which may block the nozzles. However, at pH values ≥ 8, the concentrations (in the ammonium fluoride deposition solution) of the protonated species responsible for the etching of silicon dioxide, HF and $HF_2^-$ are very close to zero resulting in effectively zero dissolution of silicon dioxide [6]. In experiments reported in this paper, the pH of the deposition solution was increased to ~ 9 by addition of ammonium hydroxide. Increasing the pH beyond 9 may result in some etching of the of the silicon fluid chambers and nozzles of the DMP cartridges.

The surface tension of an 11% (w/v) ammonium fluoride solution in $H_2O$ was measured to be ~ 70 mN/m at 25 ºC. In order to be able to reliably deposit solutions containing fluoride concentrations in the order of 10-15% (w/v) using the DMP cartridges it was necessary to reduce the surface tension of the solution. This was achieved by addition of 20% (v/v) PEG 400 to the jetting solution. Addition of the PEG 400 also served to increase the viscosity. The final surface tension and viscosity of the deposition solution were 46 mN/m and 4 cP, respectively, at the cartridge jetting temperature of 28 ºC. Although these values were outside of the optimal ranges for the DMP cartridges [5], it was possible to tune the jetting waveform to deposit well-formed drops reliably at a nozzle firing frequency in the 5-8 kHz range.

In order to etch sufficiently large volumes of silicon dioxide it is necessary to deposit many layers (e.g., 30 to 50) of an etching pattern. From Eqn (1), it can be seen that six fluoride ions are required for each silicon atom dissolved from the silicon dioxide crystal matrix. The printing of multiple layers of a pattern is easily automated using the DMP device. In addition to providing sufficient fluoride source for the required etching, it is suspected that the deposition of multiple layers of the deposition solution plays an important role in "mixing" the reaction solution at the site of etching and thus preventing etching products from occluding surfaces from further etching.

## Examples of Etched Structures

The minimum dimensions of the structures that can be etched by this process are determined by the droplet size and the contact angle of the droplets on the polymer layer surface. The PAA, used for the surface layer in this work, is reasonably hydrophilic. We have estimated (by measurement of contact angles) the critical surface tension of PAA films to be ~ 44 mN/m. When a deposition solution containing 11.2% (w/v) ammonium fluoride, 20% (v/v) PEG 400, pH 9 was deposited by inkjet (50 layers of the pattern), etched holes which are 30-40 µm in diameter resulted (see Figure 1). Clearly, the size of the etched features relies on the accurate placement of the inkjetted droplets during multi-layer printing.

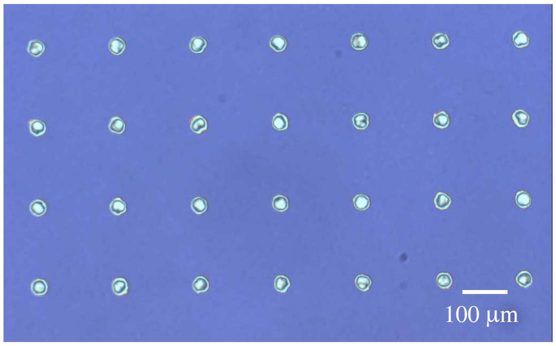

***Figure 1****. An array of hole openings etched in a 290 nm thick silicon dioxide layer, thermally grown on a polished silicon wafer. The holes were etched by depositing 50 layers of a hole pattern using a deposition solution containing 11.2% (w/v) ammonium fluoride, 20% (v/v) PEG 400, pH 9. The surface PAA layer was ~ 2.5 µm thick and the platen temperature was 45 ºC.*

As shown by the AFM contour plot shown in Figure 2A, the sidewalls of the holes etched using this method are sloped. This may represent problems for some applications, though it is possible that the slope of the sidewalls may be able to be controlled by varying the composition of the deposition solution, the printing conditions and/or the surface layer. For many applications, the sloped contour of the etched holes may enable smaller "active" etched regions to be achieved (e.g., when using the etched holes as a dielectric mask through which to diffuse or etch underlying silicon).

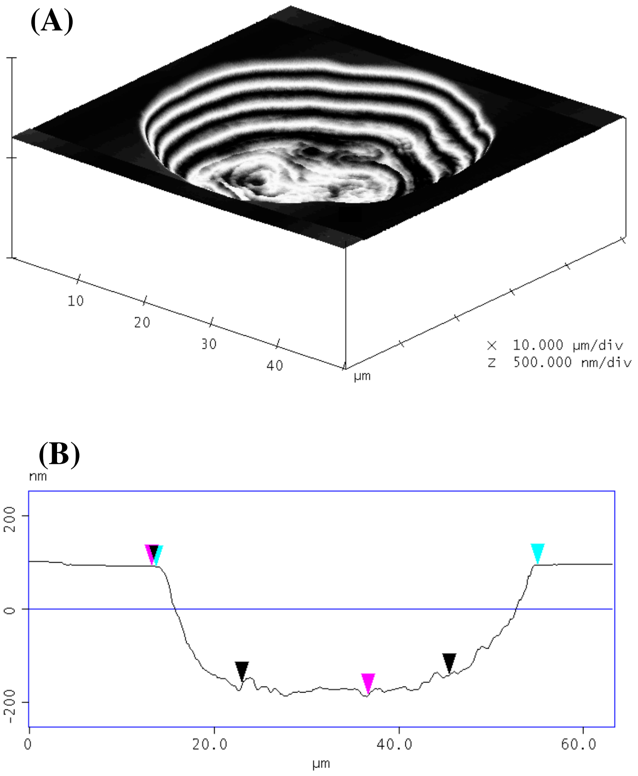

***Figure 2****. An AFM contour plot (A) and section profile (B) of one of the etched holes shown in Figure 1.*

Grooves have also been etched using the method. Figure 3 shows 390 nm deep grooves etched in a silicon dioxide layer thermally grown on a polished silicon wafer. The grooves were 50-60 µm wide at the surface. A Dektak profile of the one of the etched grooves in Figure 3 is shown in Figure 4. Figures 3 and 4 show, that like the edges of the etched holes, the edges of the grooves are sloped, thus enabling a smaller "active" groove width for subsequent processes such as etching, diffusing or metallisation. The number of layers required for the etching of groove structures depends on how closely the adjacent drops are placed. The grooves depicted in Figure 3 were etched by depositing 50 layers of a deposition solution comprising 11.2% (w/v) ammonium fluoride, 20% (v/v) PEG 400, pH 9, with a drop spacing of 25 µm. Fewer layers are required if the drop spacing is reduced, however reducing the drop spacing too much results in wider etched structures.

Grooves are etched more cleanly if a surfactant is present, in low concentration, in the PAA surface layer. This can be achieved by adding the surfactant to the PAA solution before spin-coating. We have incorporated the fluorosurfactant Novec 4200 (obtained from 3M) at concentrations of 0.5 to 0.8% (v/v) into the PAA solution to form the surface films. Novec 4200 was developed by 3M for use in reducing the surface tension of BOE systems. We believe that the surfactant acts by reducing the surface tension of the local etching solution and thus improving the wettability of the surface being etched. Although, it also reduces the critical surface tension of the PAA surface, contact angle measurements suggest that this effect is relatively minor. The addition of surfactant to the PAA is especially advantageous when etching silicon dioxide grown on planar and textured wafers.

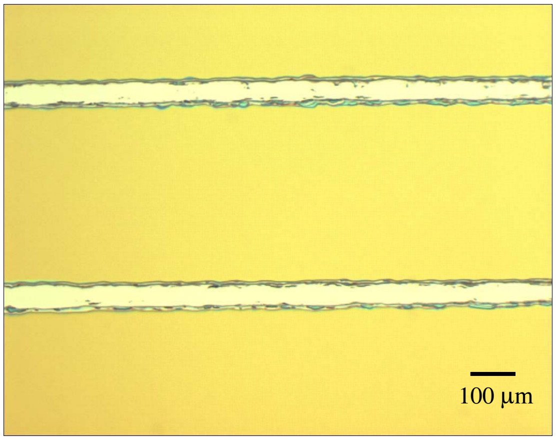

***Figure 3****. Etched grooves in a in a ~400 nm thick silicon dioxide layer, thermally grown on a polished silicon wafer. The grooves were etched by depositing 50 layers of a groove pattern where the individual droplets were spaced 25 µm apart. The deposition solution comprised 11.2% (w/v) ammonium fluoride, 20% (v/v) PEG 400, pH 9 and the surface PAA layer was ~ 2.5 µm thick. Novec 4200 surfactant was added to the PAA solution (0.6% (v/v)) before spin-coating. The platen temperature was maintained 45 ºC.*

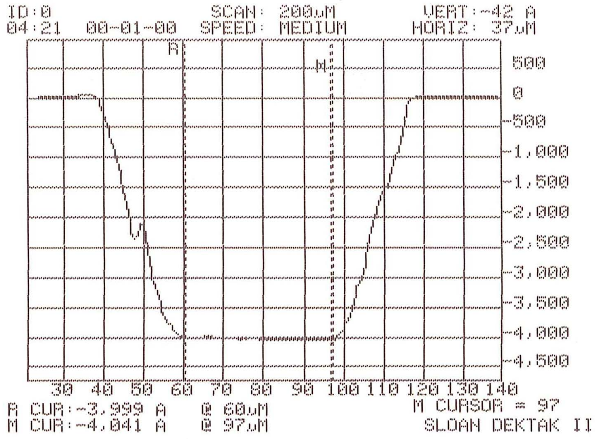

***Figure 4****. Dektak profile of one the grooves from Figure 3.*

The dimensions of etched structures also depend on the platen temperature. Smaller holes and narrower grooves can result if the platen is heated to temperatures greater than 45 ºC (the temperature used for the experiments described in this paper), however the etching can be less even across a structure such as a groove at higher platen temperatures, necessitating the deposition of more layers of the deposition solution. It is possible that smaller areas are etched at higher platen temperatures because water evaporates from the jetted solution during deposition thus resulting in smaller droplets contacting the surface.

Grooves have also been patterned in silicon nitride layers (see Figure 5) which have been deposited on textured wafers using plasma enhanced chemical vapour deposition (PECVD). Although, our work to date, has focussed on the patterned etching of silicon dioxide surfaces, the ability to pattern silicon nitride layers is important for solar cell fabrication where silicon nitride is routinely used for antireflection layers in commercial silicon solar cells.

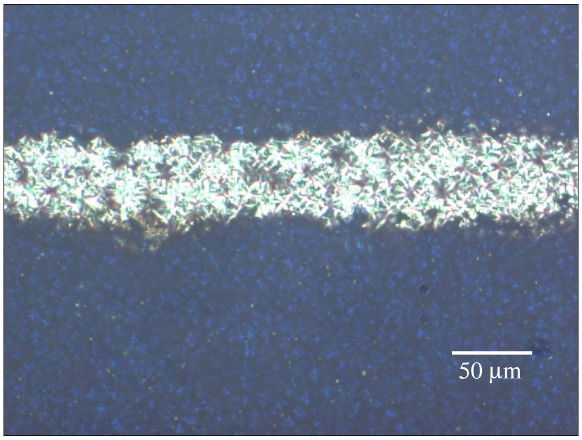

***Figure 5***. *Etched groove in a 75 nm silicon nitride layer deposited by PECVD on a textured silicon wafer. The groove was etched by depositing 50 layers of a groove pattern where the individual droplets were spaced 25 μm apart. The deposition solution comprised 11.2% (w/v) ammonium fluoride, 20% (v/v) PEG 400, pH 9 and the surface PAA layer was ~ 2.5 μm thick and the platen temperature was maintained 45 ºC.*

## Application to Silicon Solar Cell Fabrication

### *Overview*

The direct patterned etching method has the potential to replace the role of photolithography in high efficiency silicon solar cells and therefore make higher cell efficiencies commercially possible. To demonstrate the applicability of the method for commercial silicon solar cell production, a selective emitter solar cell design, as shown in Figure 6, has been fabricated.

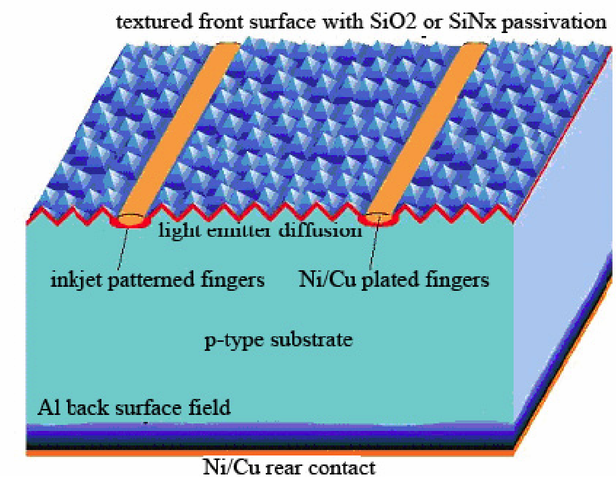

***Figure 6***. *Schematic of selective emitter solar cell structure fabricated using the direct patterned etching method. In the cell fabricated the front surface was not textured (as shown in the figure).*

The solar cell structure is similar to a laser-doped solar cell structure previously reported [7] with the exception that direct patterned etching method is used instead of a laser to define the metal contacts on the front surface of the solar cell.

### *Experimental*

An FZ 1 Ωcm p-type (non-textured) silicon wafer was first diffused to form an n-type emitter layer (~ 130 Ω/□) and then thermally oxidised to form a silicon dioxide layer of ~ 310 nm thickness on both surfaces of the wafer. A film of PAA was then formed on the front surface of the wafer by spin-coating a 25% (w/v) PAA solution containing 0.6% (v/v) Novec 4200 surfactant, at a spin-speed of 7500 rpm for 30 s, onto the front surface. The resulting film was air-dried.

A finger-busbar pattern was then etched in the front-surface oxide by depositing 50 layers of a finger-busbar pattern using a deposition solution containing 11.2% (w/v) ammonium fluoride, 20% (v/v) PEG 400, pH 9.0. The PAA film, containing etch residue, was then removed by rinsing in deionised water.

The exposed silicon (through the etched grooves in the oxide) was heavily diffused to allow low resistance ohmic metal contacts to be formed while leaving the rest of the front surface lightly doped to allow maximum collection of photo-generated carriers [8]. A back-surface-field was created by depositing and then alloying an ~ 1 μm thick layer of aluminium.

Nickel was then electrolesssly plated onto both the back-surface and front-surface grooves followed by sintering to form ohmic metal contacts to the cell. Finally, copper was electrolessly plated to further reduce the resistance of the metal contacts. The cell was completed by thinning the front surface oxide to ~ 100 nm so it would act as a rudimentary antireflection coating.

### *Results*

The width of the plated metal lines was ~ 75-80 μm (see Figure 7) due to some plating over the edges of the ~ 50 μm etched grooves.

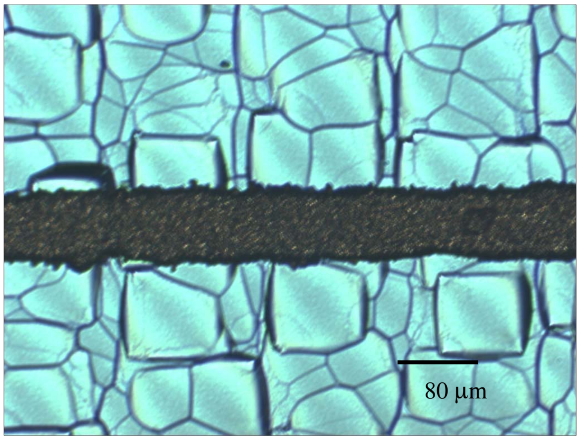

***Figure 7***. *Optical image of an etched finger groove plated with copper. The width of the plated groove was 75-80 μm.*

The current-voltage curve of the resulting 8 cm$^2$ cell is shown in Figure 8. The efficiency of the initial cell is 15.0%. The fill factor (FF) of 0.78 for the cell is better than the equivalent laser-doped cell reported in [7]. Inkjet patterning (for metal contacts) is expected to result in higher fill factors than laser patterning methods because the inkjet process does not result in the material damage evident with laser patterning [9].

However, the short circuit current, 30.6 mA/cm$^2$, of this initial cell is low due to (i) the lack of surface texture to reduce front reflection; and (ii) the shading loss from the 75-80 µm wide metal fingers (which are wider than the 40 µm fingers of the laser-grooved cells reported in [7]). In the future, we plan to trial the direct-etching method on solar cells using commercial-grade CZ textured wafers. In addition, ways of reducing the etched groove width will be investigated.

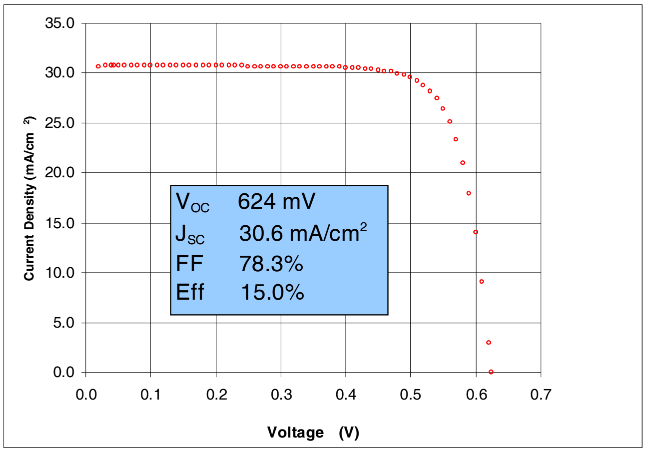

***Figure 8**. Measured current-voltage curve for the initial direct-etched 8 cm$^2$ silicon solar cell under ~100 mW/cm$^2$ illumination at 25 ºC.*

## Conclusions

The inkjet method for directly etching dielectrics, such as silicon dioxide and silicon nitride, is a novel, low-cost, low-waste process that can be implemented more safely than existing immersion etching processes. The method uses routinely available chemicals, though it is possible that additives, such as surfactants, may be valuable when optimising the process for different etching surfaces.

We have demonstrated that the method can be successfully used to open up regions in dielectrics for localised diffusion and the subsequent formation of metal contacts to silicon solar cells. However, it is also anticipated that the method of etching dielectrics such as silicon dioxide and silicon nitride, may have general application in the fabrication of other semiconductor and microelectromechanical systems (MEMS) devices.

Finally, the general technique of printing an inactive etching component onto a receptive surface layer may be applicable to the etching of other materials, including metals and semiconductors. The ability to provide an acid source to an etching system in the form of an acidic polymer layer can be applied to the etching of semiconductors, such as silicon, and metals such as aluminium, copper and chromium. All these materials are routinely used in semiconductor fabrication processes.

## Acknowledgements

This work has been jointly supported by Suntech Power Co. Ltd in China and the Australian Research Council's Photovoltaics Centre of Excellence. The authors would also like to thank Ms Katie Levick (from the Electron Microscope Unit at the University of New South Wales) for her assistance with AFM imaging.

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## Author Biography

*Alison Lennon holds a B.Sc. in Chemistry and Biochemistry and a PhD in Biochemistry from the University of Sydney. She worked for ten years as a research scientist for Canon Information Systems Research Australia and is currently enrolled in a PhD degree at the School of Photovoltaic and Renewable Energy Engineering at the University of NSW. Her current research is focussed on the use of inkjet technology for silicon solar cell fabrication.*