Direct Etching - Targeting Commercial Photovoltaic Applications

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Abstract

A method for spatially-selective etching of dielectric layers without the use of a mask has been developed at the University of New South Wales (UNSW). This 'direct etching' method, which was first implemented using inkjet printing, is now being further developed using Optomec's Aerosol Jet Printer (AJP), in order to achieve the patterning resolution and processing throughput required for commercial photovoltaic applications. Results presented in this paper show that the use of the AJP enables etched grooves as narrow as 15-20 µm. Grooves can be etched in ~ 75 nm layers of SiO_2, SiN_x, $SiON_x$ and PECVD Al_2O_3 dielectric layers. Furthermore, the etching process can be tailored to different applications by varying processing parameters, such as the gas flow rates, platen movement speed and number of printing passes. Finally, the accurate alignment enabled by the AJP allows etched patterns to be formed in pre-patterned surfaces, a property that may find application in a number of selective-emitter solar cell designs which use aligned screen printing for metallization.

Introduction

Dielectrics are crucial to many solar cell designs; they are often used as insulators and passivation layers. The ability to pattern dielectrics accurately, at high resolution and on a large scale can greatly benefit the development of new commercially viable solar cell designs. Ideally, as an industrial process, such dielectric patterning methods would: (i) have a high processing throughput; (ii) be low cost in terms of equipment, consumables, maintenance and disposal; (iii) allow for significant automation and be easily integrated into a manufacturing line; and (iv) be reliable and robust. Direct etching with an aerosol jet printer (AJP), also referred to as aerosol jet etching (AJE), may offer an alternative patterning method that can balance the trade-offs between the robustness and fast processing rates of industrial printing methods, such as screen printing, and the high-resolution of photolithographic methods.

Direct Etching

Process Description

Direct etching allows for spatially-selective etching of dielectrics [1]. A hydrofluoric acid (HF) mixture is generated on the substrate by combining an acidic component with a fluoride component. In theory, the hydrogen and fluoride ions can combine in solution to form HF. Direct etching involves the following steps (see Figure 1):

1. An acidic, water-soluble polymer [i.e., polyacrylic acid (PAA)] is spin-coated onto the surface of the dielectric.
2. A fluoride solution is deposited onto the polymer with an AJP in a specified pattern. Hydrofluoric acid then forms on localized areas of the wafer (i.e. areas where the solution mixes with the PAA) and is able to etch the underlying dielectric.
3. Samples are then rinsed in de-ionized water to remove etch products, leaving the surface of the patterned dielectric clean and free of the PAA.

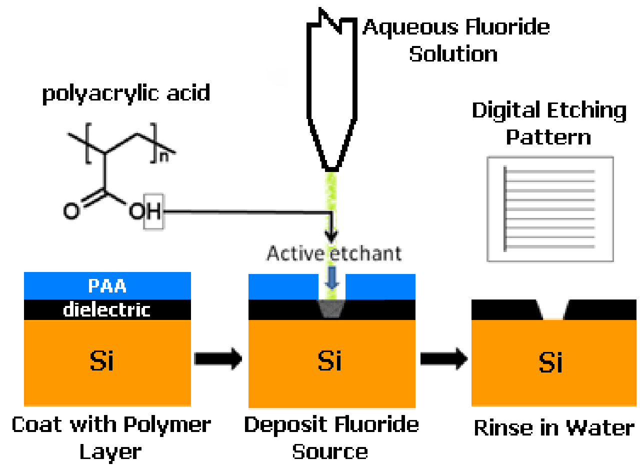

Figure 1: *A schematic of the steps involved for direct etching (adapted from [1])*

Direct etching has the potential to be low-cost and less damaging to the environment than other patterning methods which involve immersion etching in HF, largely due to the minute volumes of chemicals required for the process. It also has the added advantage of eliminating the need to apply mechanical force to the substrate. Initial trials of direct etching with an inkjet printer demonstrated etched line widths as narrow as 40 µm and laboratory cell efficiencies (on commercial-grade silicon wafers) of up to 17% [2].

Aerosol Jet Printing

Early experiments suggested that the AJP may enable narrower etched line widths than achieved to-date by the inkjet implementation of direct etching [3]. The AJP works by, firstly, atomizing the desired print material to produce a fine mist. A nitrogen carrier gas then transports this mist to the print head, where a second annular stream of nitrogen gas is introduced to focus the mist into a collimated beam for precise deposition (see Figure 2). The AJP is capable of: (i) printing feature sizes as narrow as 10 µm; (ii) printing materials with viscosities ranging from 1-1,000 cP; (iii) depositing material on non-planar surfaces; and (iv) processing at a maximum speed of 300 mm/s [4].

In addition to narrower etched lines, it is possible that the AJP may enable higher processing throughputs than achieved by inkjet printing. But realistically, processing throughputs would need to be significantly increased to enable the patterning of full-size commercial solar cells within a few seconds.

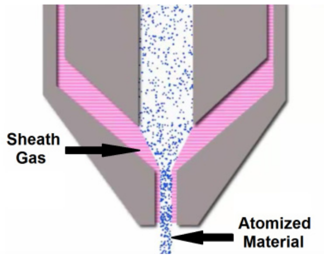

Figure 2: A schematic of atomized material exiting the deposition head opening. The Sheath Gas surrounds the material and prevents it from contacting the inner surfaces of the tip. (Optomec Inc.)

A further advantage is that the AJP can operate in a large range of ambient temperature and humidity conditions. Optomec specify an operating temperature range of 10-40 °C and a relative humidity range of 30-90% [4]. This capability suggests that the printer could be a robust manufacturing tool. The ambient temperature range for AJE is discussed later in this paper.

Experimental

Silicon samples were coated with various dielectric layers, which included SiO_2, SiN_x, $SiON_x$ and PECVD aluminium oxide. Each substrate was square with one rounded edge, of approximately 4 cm long sides. These samples were then spin-coated with a 20% w/v PAA (obtained from Sigma Aldrich) to produce a dried polymer layer 1.8 µm thick. A 10% w/v ammonium fluoride solution in de-ionized water (prepared from a 40% w/v stock solution obtained from J. T. Baker) was then deposited onto the sample using the AJP.

An ultrasonic atomizer was used for all AJE experiments described in this paper. The ultrasonic atomizer chiller temperature and voltage were kept at 25 °C and 45V, respectively. There was a thick white mist visible in the ultrasonic atomizer vial for all depositions conducted with the AJP. After rinsing, an optical microscope was used to examine the clarity of etched lines and measure feature widths.

Results and Discussion

Printing Speed

The speed at which the stage moves during deposition plays a large part in determining the amount of liquid deposited on the substrate. Faster printing speeds results in less material deposition per unit area and vice versa. Experiments were designed to explore the interdependencies between the printing speed and number of layers printed, in order to observe the effect on resulting etched line widths and clarity. Previous publications on direct etching described the effect of repeating printing patterns; the generated solution can etch deeper and the line width increases as more repetitions, or layers, are printed [1].

The results described below are for representative samples which demonstrate the trends witnessed throughout all sets of experiments. Figure 3 outlines the resulting line widths for corresponding printing speed and number of printed layers, while Figure 4 shows optical microscope images of etched lines for a particular sample. The samples were processed using: (i) a 100 µm tip; (ii) an Atomizer Flow Rate (AFR) of 15 sccm; (iii) a Sheath Gas Flow Rate (SFR) of 10 sccm; and (iv) a platen temperature of 50 °C.

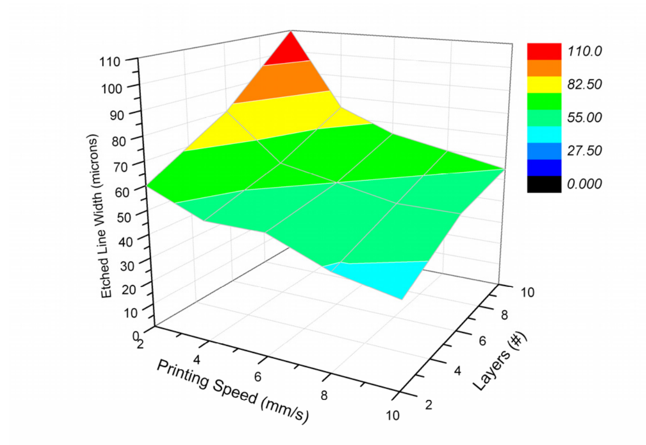

Figure 3: Contour map that describes how line width (z-axis) varies as the printing speed (x-axis) and number of printing passes (y-axis) is varied. Thinner lines result from faster printing speeds and a lesser number of layers. This sample was a textured silicon wafer with a 120 nm thick thermal oxide.

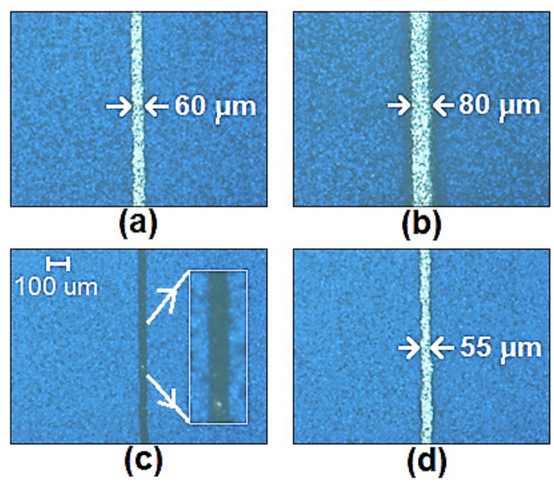

Figure 4: Line width and clarity vary with printing speeds and layers. The processing parameters are: (a) 2 layers at 2 mm/s; (b) 10 layers at 2 mm/s; (c) 2 layers at 10 mm/s; (d) 10 layers at 10 mm/s. All other experimental parameters were kept constant. Incomplete etching had resulted with 2 layers at a speed of 10 mm/s. This sample was a textured silicon wafer with a 75 nm thick PECVD SiN_x.

In general, the line width increases with slower printing speeds and for increasing numbers of layers. Consequently, line widths can be tailored to suit individual applications by simply varying the printing speed and layers. One application where this may be useful is in the case of realigning to previously etched or patterned regions. By varying the processing speed and layers, a thinner etched feature may be realigned to a wider feature, as shown in Figure 5.

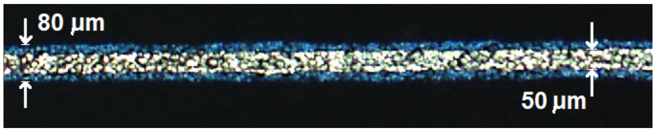

Figure 5: The thin white line (~50 µm wide) has been etched through a 75 nm SiNx layer and was realigned to a ~80 µm wide planarized groove. The groove was printed at a speed of 4 mm/s with three layers and the thinner etched line was printed at a speed of 16 mm/s with four layers; all other processing parameters were kept constant.

Platen Temperature

The temperature of the platen largely determines the temperature of the etching solution generated on the substrate. This in turn determines the characteristics of the etching reaction. Figure 6 illustrates how the platen temperature can be controlled in order to minimize etched line widths; all other experimental parameters were kept constant.

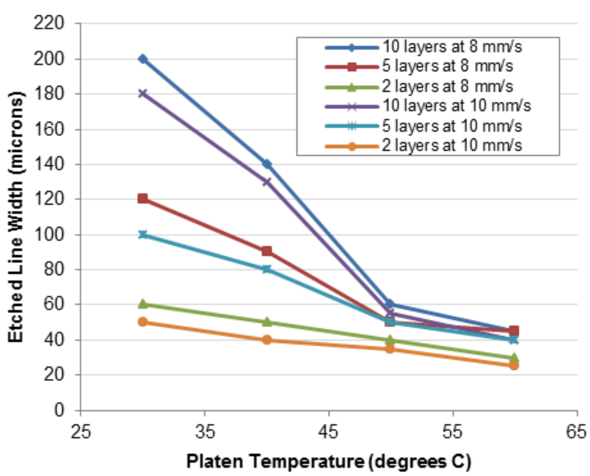

Figure 6: Etched line width graphed as a function of platen temperature. For all experiments the tip size, AFR and SFR were maintained at 100 µm, 15 sccm and 10 sccm, respectively.

Platen temperatures in the range of 50-60 °C have shown consistent results and clear etching. This value is slightly higher than the optimal 45 °C quoted for direct etching experiments performed on an inkjet printer [1]. There are, however, side-effects of significantly increasing the platen temperature, as the deposited mist tends to dry more prior to contacting the substrate. For platen temperatures higher than 60 °C there was an increasing tendency for deposition tips to clog whilst printing. Although it's preferable not to have to use higher platen temperatures, this effect requires further investigation.

Gas Flow Rates

The AFR partially determines the resulting volume of material deposited onto the substrate. By varying the AFR, the line widths and clarity of etching can be controlled. However if the AFR is too low then an insufficient source of fluoride ions will be deposited on the surface and features may not be etched all the way through the dielectric, as shown in Figure 4c. Figure 7 summarizes the effect of varying the AFR on the width of lines etched in a 75 nm thick SiN_x layer deposited onto a textured silicon wafer. Optical microscope images of some of the etched lines are shown in Figure 8. A 100 µm tip was used and the platen temperature and SFR were maintained at 50 °C and 10 sccm, respectively, for all experiments.

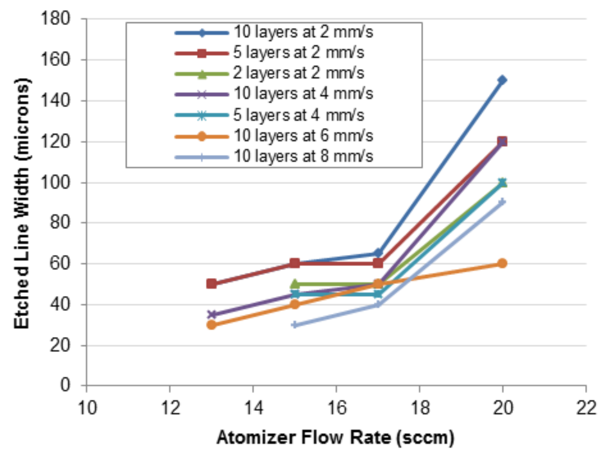

Figure 7: Etched line width graphed as a function of AFR. Some values are not shown for AFRs of less than 13 sccm because incomplete etching resulted.

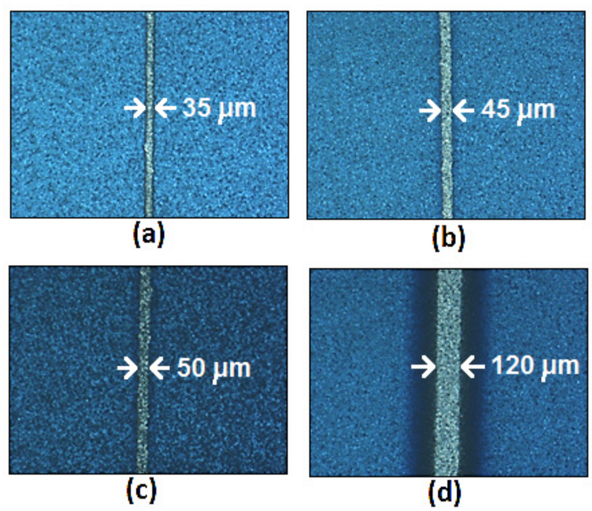

Figure 8: Optical microscope images showing lines which were etched using different AFR values. All four samples were processed with the same experimental parameters, with the exception of the AFR which were: (a) 13 sccm; (b) 15 sccm; (c) 17 sccm; (d) 20 sccm.

Etched line widths increase with larger AFRs most likely due to the spreading of the dissolved polymer region when more fluoride aerosol is deposited. These results indicate that etched line width can be controlled and minimized by varying the AFR.

Alternative Dielectrics

In addition to SiO_2 and SiN_x layers, recent trials have also demonstrated that $SiON_x$ and PECVD aluminum oxide layers can also be patterned with direct etching. The images in Figure 9 are examples of etched lines through these latter two materials. In fact, one of the narrowest etched lines demonstrated so far was etched through a 75 nm $SiON_x$ layer; it was measured at approximately 20 µm wide.

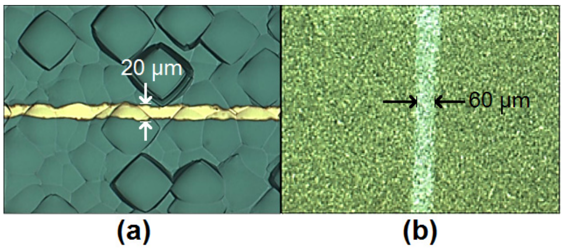

Figure 9: *(a) A groove etched through a 75 nm thick $SiON_x$ layer on a planar silicon surface with an average line width of ~20 µm. (b) A groove etched through a 75 nm thick PECVD aluminum oxide on a textured surface with an average line width of ~60 µm. Both samples were etched using a 150 µm tip, SFR of 25 sccm, AFR of 15 sccm and platen temperature of 50 °C.*

Ambient Temperature

Experiments were designed to examine the performance of direct etching in varying ambient temperatures, the results of which are shown in Figure 10. Samples coated with 75 nm thick $SiON_x$ layers were prepared and were then etched at different ambient temperatures, whilst keeping all other printing parameters equivalent. A digital thermometer placed inside the AJP was used to measure the ambient temperature of the process for each printing run.

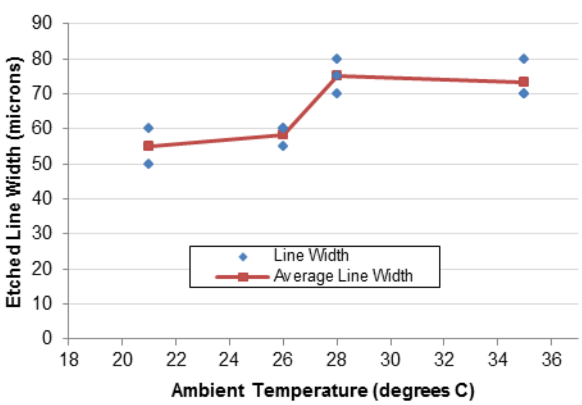

Figure 10: *Etched line width as a function of ambient temperature. All samples were etched using a 150 µm tip at a printing speed of 8 mm/s for 10 layers. The platen temperature, AFR and SFR were 50 °C, 15 sccm and 25 sccm, respectively.*

Although these results demonstrate that AJE can be performed at ambient temperatures of up to 35 °C, there appears to be some variability in the width of etched lines at different temperatures. This could be due to increased drying of aerosol particles at higher temperatures so that they are not as effectively constrained by the sheath gas flow. This issue will be examined more closely in future work.

Conclusion

The presented results demonstrate that grooves as narrow as 20 µm can be etched using AJE in 75 nm thick dielectric layers. The method can be used to etch grooves in ~ 75 nm layers of SiO_2, SiN_x, $SiON_x$ and PECVD Al_2O_3. Processing parameters, such as the gas flow rates, platen movement speed and number of printing passes, can be varied to 'tune' the method for particular etching requirements. Finally, the high positional accuracy of the AJP enables the ready alignment of etching to previously patterned regions, a property that may find application in a number of recently-developed selective-emitter solar cell designs which currently use aligned screen printing for metallization [5,6]. Aerosol Jet Etching is currently being applied to innovative solar cell designs under development at UNSW and will likely continue to be a catalyst for more novel and innovative solar cell research.

Future work will look more closely at developing etching processes for high throughput processing in order to suit the requirements of commercial solar cell manufacturing. More specifically, examining the stability of the process over longer periods of operation will be required. And although AJE has been demonstrated to operate over a reasonably wide range of ambient temperature, etched lines were observed to be wider at higher temperatures. This variability in etching performance needs to be understood and addressed.

Acknowledgements

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Author Biography

John Rodriguez is a PhD student currently enrolled at the University of New South Wales in Sydney, Australia. His PhD topic, based around novel fabrication techniques for crystalline silicon solar cells, is being conducted under the supervision of Dr. Alison Lennon and Prof Stuart Wenham, at the School of Photovoltaics and Renewable Energy Engineering.