Solar Energy Materials & Solar Cells 93 (2009) 1865–1874

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Direct patterned etching of silicon dioxide and silicon nitride dielectric layers by inkjet printing

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ARTICLE INFO

Article history:
Received 1 April 2009
Received in revised form
25 June 2009
Accepted 29 June 2009
Available online 24 July 2009

Keywords:
Etch
Dielectric
Inkjet
Silicon
Solar cell

ABSTRACT

An inkjet method for the direct patterned etching of silicon dioxide and silicon nitride dielectric is described. The method involves fewer steps, lower chemical usage and generates less hazardous chemical waste than existing resist-based patterning methods (e.g., photolithography), which employ immersion etching. Holes of diameter 40–50 μm and grooves 50–60 μm wide were etched in 300 nm silicon dioxide layers. Grooves were also etched in 75 nm silicon nitride layers formed on textured silicon surfaces. The resulting patterned dielectric layers were used to facilitate masked etching, local diffusions and metal contacting of underlying silicon for solar cell applications.

1. Introduction

The patterned etching of semiconductor and dielectric materials is extensively used in semiconductor device fabrication. Patterned etching of Si-based dielectric (e.g., SiO_2 and SiN_x) layers on Si surfaces can be used to facilitate local diffusions and metal contacts to the underlying Si (e.g., in the case of silicon solar cells [1]), or to provide a mask for etching the underlying Si [2]. For many applications, including the fabrication of the world-record 25.0% efficient silicon solar cell in the laboratory [3],[1] patterned etching has been achieved using photolithography, combined with wet chemical etching processes. However, photolithography is considered too expensive to implement for commercial solar cell production and therefore alternative patterning techniques have been developed.

Methods which have been developed for commercial, or potentially commercial, patterning of dielectric layers to enable metal contact formation to silicon solar cells include: (i) screen printing of metal pastes [1,4] and corrosive etchants [5]; (ii) laser patterning as used by buried-contact cells [6] and laser-doped cells [7,8]; (iii) inkjet patterning of a resist layer [9–11] followed by wet chemical etching; and, more recently, aerosol jet printing of a seed metal plating layer [4,12,13]. Except in the case where the material responsible for the etching also contains the metal for the contact (i.e., screen printing of metal pastes), the dielectric patterning process is typically followed by an optional heavy diffusion process (for selective-emitter cells) and then a self-aligning metallization process such as metal plating.

Each of these existing dielectric patterning approaches has some limitations with respect to the resolution of the patterning (e.g., screen-printing approaches and patterning techniques which require heat to achieve the patterning), material damage to silicon due to heat or mechanical damage (e.g, laser scribing methods [14]) and high material and processing costs due to resist processing and wet chemical etching (e.g., inkjet patterning of resist). Although, it has been possible to achieve significant improvements in cell efficiency with the development of the above-mentioned patterning techniques, a commercially viable method, which has the potential to achieve a patterning resolution comparable with photolithography with no material damage, is required before high-efficiency cell structures that have been demonstrated in the laboratory (e.g. [3]) can be commercially realised.

In this paper we describe an inkjet method for the patterned etching of Si-based dielectrics, and specifically SiO_2 and SiN_x. Unlike existing photolithographic and previously described inkjet methods, wet chemical immersion etching through a patterned resist layer is not required. The patterned etching of the dielectric is achieved by inkjet deposition of a solution containing fluoride ions onto an acidic water-soluble polymer layer formed over the Si-based dielectric. The solution reacts with the polymer, at the locations where it is deposited, to form an active etchant. This

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[1] This world record was recently revised to 25.0% due to a re-evaluation of the solar spectrum. See http://www.physorg.com/news143974278.html.

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doi:10.1016/j.solmat.2009.06.028

etchant selectively etches the dielectric layer under the polymer layer to form a pattern of openings in the layer. The polymer and etch residue can then be removed easily by rinsing in water. This patterning technique is depicted schematically in Fig. 1.

Etching patterns are represented by digital images that are easily prepared and changed. The method is safer for human operators than existing dry and wet etching processes in that corrosive etchant is only formed in-situ on the device surface to be etched and therefore minimises human contact with the etchant. 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 than existing wet chemical etching processes. In some cases the fluoride waste levels of processes employing this new method can be reduced to a level of less than 5 ppm which eliminates the need to process the fluoride waste in many regions of the world [15]. Although the dimensions of features that have been etched using this method to date are larger than those achievable with photolithography, it is anticipated that significant improvements are possible in the near future through chemical modification of the surface polymer layer and refinement of the deposition method.

2. Etching method

Wet chemical etching of SiO_2 typically involves immersion of substrates in hydrofluoric acid (HF) solutions or buffered oxide etching (BOE) solutions [16]. The latter solutions, which comprise a mixture of HF and NH_4F, are often preferred because of their more stabilised etching rate and protection of resist against attack by HF [17]. Silicon nitride can be similarly etched; however, the etch rate for the SiN_x is typically much slower than that of SiO_2 in solutions containing HF, and depends on the specific Si–N composition of the layer and the method by which it is deposited [18]. In the direct patterned etching method described in this paper, the requirement for immersion etching is eliminated by bringing together the fluoride and acid components required for etching at the surface location where etching is required. The acid component is provided by an acidic, water-soluble polymer layer which can be formed by spin-coating an aqueous solution of the polymer over the surface to be etched. The fluoride source is then applied to the surface according to a predetermined digital etching pattern by an inkjet printing device.

At the surface where the fluoride ions are deposited the polymer is locally dissolved, and the fluoride ions abstract protons from the polymer to form the HF-based species responsible for the etching of the SiO_2. If NH_4F is used as the fluoride source, then the overall etching reaction for SiO_2 resembles that which occurs when SiO_2 is immersed in a BOE solution [17]:

$$SiO_2(s)+4HF(aq)+2NH_4F(aq)\rightarrow(NH_4)_2SiF_6(aq)+2H_2O. \quad (1)$$

The etch product, $(NH_4)_2SiF_6$, has a solubility of $\sim 130\,g\,L^{-1}$ at 25 °C in 10% (w/v) NH_4F solutions [17], 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. Ammonium fluoride is used as the aqueous fluoride source because both it and its etch product, $(NH_4)_2SiF_6$, 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 HF is difficult to achieve because few available inkjet printheads can tolerate the corrosive nature of the solution. Furthermore, few operators would consider it safe to deposit HF-containing solutions via inkjet because of the risk of operator contact in the event of fluid leaks. Although, fluoride-containing solutions, such as NH_4F, are classified as toxic they are more safely handled than HF solutions.

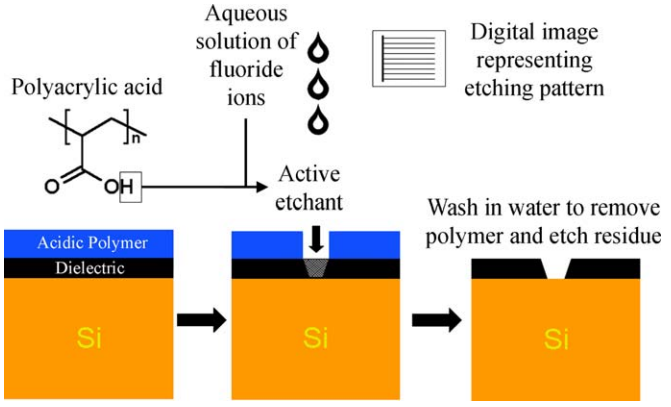

Fig. 1. Schematic showing the use of the direct etching method to form a pattern of openings in a dielectric layer formed on a silicon wafer.

3. Experimental

Silicon dioxide layers were thermally grown on Si wafers using a combination of dry oxidation (30 mins) at 1030 °C, wet oxidation at 980 °C, followed by a final dry oxidation step (30 mins) at 1030 °C. The thickness of the SiO_2 layer was varied by varying the duration of the wet oxidation step. Silicon nitride layers, with refractive indexes of ~2.1, were formed using plasma-enhanced chemical vapour deposition (PECVD). The polished surfaces wafers used were ⟨1 0 0⟩ CZ n-type wafers with a bulk resistivity of 2–9 Ω cm. The textured surfaces used were ~300 μm thick, 1 Ω cm p-type ⟨1 0 0⟩ CZ wafers [provided by Suntech Power Co. Ltd (China)].

Acidic, water-soluble polymer layers were formed on the surfaces to be etched by spin-coating a 25% (w/v) aqueous PAA solution (MW 90,000; obtained from Polysciences, Inc.) onto the surface and then air drying the surface layer for at least 2 h. The thickness of the dried PAA layer was controlled by the spinning speed. A 2.3 μm thick layer, for example, was obtained by spin-coating silicon wafers at 7000 rpm for 30 s. In experiments involving etching of grooves, a fluorosurfactant (Novec 4200 from 3 M) was added to the PAA solution at a concentration of 0.6% (v/v) before spin-coating to ensure lower surface tension at the local etching sites and therefore, more uniformly etched structures.

The direct patterned etching method has been developed using a FUJIFILM Dimatix Materials Printer (DMP-2831) with silicon MEMS inkjet 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 [19]. The DMP device operates by moving the printhead assembly across a platen, which can be heated to temperatures up to 60 °C, depositing individual droplets according to a digital pattern. The jetting process is achieved by applying an electrical pulse (defined by a jetting waveform) to piezo actuators located on the walls of the pumping chamber.

The concentration of the NH_4F in the deposition solution was varied between 10% and 15% (w/v). At higher NH_4F concentrations, the solubility of the $(NH_4)_2SiF_6$ etch product is significantly reduced [5], and may result in $(NH_4)_2SiF_6$ precipitating on the surface being etched thus causing uneven etching of the surface.