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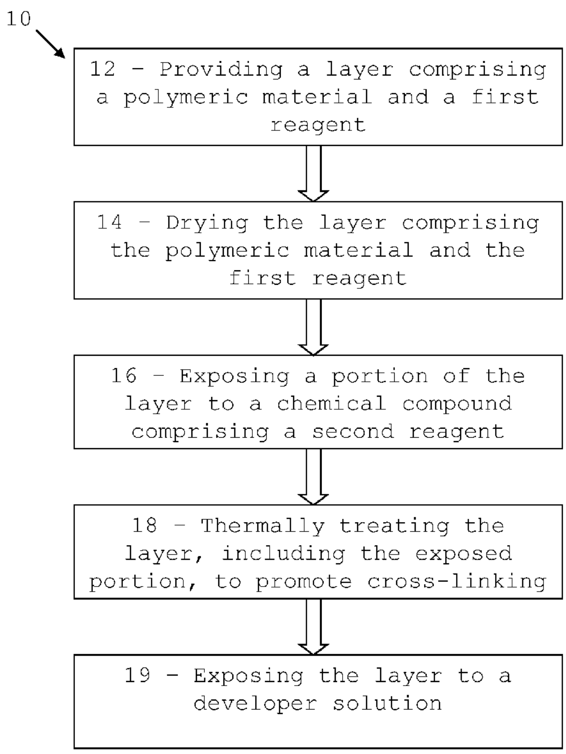

FIGURE 1

(57) Abstract: The present disclosure provides a method of patterning a polymeric layer based on the chemical reaction of two chemical compounds. One chemical compound is provided in the polymeric layer and another chemical compound is deposited on the polymeric layer by, for example, ink-jet printing. The method allows for fabrication of, for example, metallisation patterns for solar cells electronic components, integrated devices and formation of selective doped areas in solar cells amongst others.

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A METHOD OF PATTERNING A LAYER

Field of the Invention

The present invention generally relates to a method of patterning a layer, in particular the invention relates to a method of patterning a polymeric layer containing a resist material.

Background of the Invention

Patterning of polymeric layers is a crucial step in the manufacturing of microelectronic devices. For example, integrated electronic circuits are manufactured using a plurality of photolithography steps performed in sequence to form features of electronic components on chip. Each of these lithography steps involves the exposure of a polymeric photosensitive layer (photoresist) to a ultra-violet (UV) light through a chromium photomask and the chemical development of the photoresist layer. The process allows transferring a pattern from the mask to the photoresist.

This process allows creating high definition patterns in a photoresist layer which can be used, for example, to selectively deposit a metal line or implant dopant atoms. The process also allows to precisely aligning the pattern with features already present on the integrated circuit.

Photolithography steps have also been used to fabricate high efficiency laboratory solar cells, such as the PERL solar cell at the University of New South Wales, and the A300 solar cell at the University of Stanford. Despite the record results of these solar cells, photolithography is not a viable solution for the production of commercial solar cells.

The cost of photomasks and the photoresist material does not comply with the low cost requirement of the solar cell manufacturing industry. In addition, the time required for aligning the photomasks to the devices, exposing and developing the photoresist does not comply with the high throughput requirement of modern solar cell manufacturing lines.

A patterning step may be used at different stages of the solar cell manufacturing process. For example, a patterning step may be required to selective deposit a metal to form conductive fingers on a surface of a solar cell. A patterning step may be also used in many other applications, for example, the deposition of protecting coatings on glass substrates, the formation of conductive patterns on electronic boards, etc.

These applications generally do not require the resolution and alignment precision typical of the photolithography techniques used in the microelectronic industry.

There is a need for a method which can be used to pattern a polymeric layer which allows for a higher throughput and has a lower cost than conventional photolithography.

Summary of the Invention

In accordance with the first aspect, the present invention provides a method of patterning a polymeric layer, the method comprising the steps of:

providing a layer comprising a polymeric material and a first reagent;

exposing a portion of the layer to a chemical compound comprising a second reagent; and thereafter

exposing the layer to a developer solution;

wherein the first reagent of the layer reacts with the second reagent of the chemical compound to alter the chemical properties of the exposed portion of the layer in a manner such that the solubility of the polymeric material in the developer solution at the exposed portion is increased or decreased.

In embodiments, the polymeric material at the exposed portion of the layer is substantially dissolvable in the developer solution or substantially resistant to the developer solution.

The method may also comprise the step of processing the polymeric layer so that the chemical properties of a portion of the layer that has not been exposed to the chemical compound comprising the second reagent are altered in a manner such that the solubility of the polymeric material in the developer solution is increased or decreased.

The step of processing the polymeric layer may comprise the step of baking the layer at a temperature between 90˚C and 150˚C for a time between 10 seconds and 3 minutes.

Depending on the function of the baking step, in some instances, the step of processing the polymeric layer may comprise baking the layer for a period longer than 3 minutes. The duration of the baking treatment may be related to whether the layer is used as an etching mask or as a plating mask.

In some embodiments, the thermal treatment comprises blow drying the layer.

In some embodiments, the chemical compound is provided in the form of a fluid and the portion of the layer is exposed to the second reagent by depositing the chemical compound comprising a second reagent onto a surface of the portion of the layer. The chemical compound may be provided in the form of an ink comprising the second reagent and the ink may be deposited on the surface portion of the layer using an ink-jet deposition technology, an aerosol deposition technique or a screen-printing technique.

In embodiments, the exposed portion of the layer extends throughout the entire thickness of the layer and may define a pattern comprising a plurality of elongated openings in the layer. The pattern may form a solar cell metallization pattern.

In embodiments, the first reagent is an acidic reagent with a hydrogen ion activity between 1 and 10^{-4} and the second reagent has a hydrogen ion activity between 10^{-4} and 10^{-14}. In some instances, the first reagent has a hydrogen ion activity between 1 and 10^{-2} and the second reagent has a hydrogen ion activity between 10^{-7} and 10^{-9}.

In embodiments, the hydrogen ion activity of the first reagent is selected to affect the velocity of the reaction between the first reagent and the second reagent. The first reagent may be an acidic reagent and the second reagent a basic reagent.

In embodiments, the polymeric layer comprises a photoresist material or a chemically amplified photoresist material. The chemical amplified photoresist may comprise a negative melamine formaldehyde resin (MFR). The photoresist material may be mixed with an acidic solution, which may be an organic acidic solution. The hydrogen ion activity of the solution may be between 1 and 10^{-4}.

In embodiments, the polymeric layer comprises a cross-linker molecule and a resin arranged to cross-link to each other when exposed to sufficient thermal energy.

The cross-linker molecule may comprise melamine formaldehyde and the resin may comprise a novolac polymer.

In embodiments, the chemical compound comprising the second reagent further comprises one or a combination of:

a plasticiser for improving mixing of the chemical compound through the portion of the layer;

a surfactant for improving penetration of the chemical compound through the portion of the layer; or

one or more buffering agents for controlling the PH and improve the efficiency of the reaction between the polymeric material and the second reagent.

The chemical composition of the one or more buffering agents may be such that the hydrogen ion activity of the portion of the layer exposed to the chemical compound comprising the second reagent is higher than 10^{-4} after the portion has been exposed.

Furthermore, the chemical compound comprising the second reagent may comprise an organic solvent to promote chemical reaction with the layer comprising the polymeric material and precise PH control throughout the thickness of the layer.

In embodiments, the step of exposing the layer and the chemical compound to a developer solution comprises immersing the layer in a developer solution for a time period between 1 second and 300 seconds.

In accordance with the second aspect, the present invention provides a method of forming a patterned metallic layer on a surface of a device, the method comprising the steps of:

forming a layer comprising a polymeric material on the surface of the device;

patterning a portion of the formed layer using the method in accordance with the first aspect to form one or more openings in the layer; and

forming a metallic layer onto a first portion of the surface of the device through the one or more openings formed in the layer.

In accordance with the third aspect, the present invention provides a method of selectively etching a surface of a device, the method comprising the steps of:

forming a layer comprising a polymeric material on the surface of the device;

patterning a portion of the formed layer using the method in accordance with the first aspect to form one or more openings in the layer; and

performing an etching treatment onto a first portion of the surface of the device through the one or more openings formed in the layer.

In accordance with the fourth aspect, the present invention provides a method of anodising a surface of a device, the method comprising the steps of:

forming a layer comprising a polymeric material on the surface of the device;

patterning a portion of the layer using the method in accordance with the first aspect to form one or more openings in the layer;

exposing a first surface portion of the device through the one or more of the openings to an electrolytic solution that is suitable for anodising the first surface portion when an electrical current is directed through a region of the device at the first surface portion; and

exposing a portion of the device to electromagnetic radiation in a manner such that the electromagnetic radiation induces the electrical current and the first surface portion anodises.

In accordance with the fifth aspect, the present invention provides a semiconductor device comprising a patterned metallic layer formed in accordance with the second aspect, or a surface selectively etched in accordance with the third aspect, or a surface anodised in accordance with the fourth aspect.

In accordance with the sixth aspect, the present invention provides a solar cell device comprising a patterned metallic layer formed in accordance with the second aspect, or a surface selectively etched in accordance with the third aspect, or a surface anodised in accordance with the fourth aspect.

In accordance with the seventh aspect, the present invention provides a method of forming a solar cell device, the method comprising the step of:

providing a substrate having a first polarity;

depositing a first layer having a second polarity in a manner such that the layer forms a p-n junction or a p-i-n junction with the substrate;

depositing a second layer on at least a portion of the first layer and;

forming patterned metallic layer on the second layer in accordance with the method of the second aspect.

In accordance with the eighth aspect, the present invention provides a solar cell device formed in accordance with the seventh aspect.

Advantageous embodiments of the present invention provide a method of patterning a polymeric layer which is based on the chemical reaction of two chemical compounds. One chemical compound is provided in the polymeric layer and another chemical compound is deposited on the polymeric layer by, for example, ink-jet printing. Embodiments of the method allow for fabrication of, for example, high-definition metallisation patterns for solar cells without having to use photolithography which is not a viable technique for solar cell fabrication.

Other applications of embodiments of the method include fabrication of electronic components, integrated devices and formation of selective doped areas in solar cells amongst others. The method may also be used, for example, to selectively treat or paint a surface through the openings which are formed in the polymeric layer. Generally the method can be used to replace photolithography where a very high resolution is not required and where the cost of photolithography cannot be justified. The method in fact, does not involve the exposure of the polymeric layer to UV light through a mask. This is particularly suitable, for example, to the fabrication of several types of solar cells.

Brief Description of the Drawings

Features and advantages of the present invention will become apparent from the following description of embodiments thereof, by way of example only, with reference to the accompanying drawings in which:

Figures 1 is a flow diagram outlining the basic steps required to pattern a polymeric layer in accordance with embodiments;

Figures 2A to 2G are schematic illustrations of a solar cell device at different stages of a metallisation process performed in accordance with an embodiment;

Figures 3A and 3B are microscopy images of a surface of a semiconductor wafer metallised using a method in accordance with an embodiment; and

Figures 4A and 4B are microscopy images of metal fingers of a solar cell manufactured using a method in accordance with an embodiment.

Detailed Description of Embodiments

Embodiments of the present invention relate to a method of patterning a polymeric layer. The method allows patterning a layer comprising a polymeric material using inexpensive techniques, such as ink-jet printing. The polymeric layer contains a first reagent, a portion of the polymeric layer is exposed to a chemical compound which contains a second reagent and reacts with the second reagent. The chemical reaction changes the properties of the portion of the polymeric layer which has been exposed to the chemical compound in a manner such that the solubility of this portion in respect to a developer solution is affected. For example, the exposed portion may become dissolvable in the developer solution or resistant to the developer solution.

An advantage of embodiments of the method described herein is that it does not require a UV exposure step to alter the chemical properties of the polymeric layer. A UV exposure step is used in alternative techniques, such as photolithography. In photolithography the polymeric layer contains a photosensitive layer and is referred to as photoresist. The photoresist must be exposed to the UV light through a shadowing mask. Photoresist solution can be toxic and generally have a high cost. Photolithography also requires a mask aligner and a UV source are required. This equipment has a high cost and a very low throughput.

The method described herein can be performed using less expensive equipment with a higher throughput, such as an ink-jet printer. Ink-jet printers can generally be used in a 'less clean' environment, whereas photolithography equipment is generally used in a clean room. In addition, using an ink-jet printer allows avoiding light scattering from the edge of the exposed area due to the edge of the mask.

Referring now to figure 1, there is shown a flow diagram 10 outlining a series of steps (12 to 19) required to pattern a polymeric layer in accordance with embodiments. At step 12, a layer comprising a polymeric material (polymeric layer) and a first reagent is provided. The polymeric layer may initially not contain any reagent and a regent (such as an HCl solution or citric acid with a PH ~1), may be mixed to the polymeric layer. Depending on the application, the polymeric layer can be provided on a substrate and can be patterned to gain access to selected areas of a surface of the substrate. When the method is used to metallise a solar cell surface, the polymeric material may be deposited on a surface of a solar cell by spin coating. A possible spin coating time is 30s at 1300 rpm. Other times and spinning velocities may be required for different polymeric materials. Alternatively, the polymeric material may be deposited on a substrate by, for example, dipping the substrate in a solution containing the polymeric material or applying a dry film of polymeric material onto the substrate.

The first reagent is generally added to the polymeric layer before the polymeric layer is deposited. This is done by mixing the polymeric material with the first reagent. Alternatively, the reagent may be added into the polymeric layer after the layer has been deposited.

At step 14, the layer comprising the polymeric material and containing the first reagent is dried to remove solvents. This step is optional and solvents may be removed simply by waiting for their evaporation. However, in a high throughput environment, the drying step 14 allows quicker processing. Drying step 14 can be performed, for example, by blowing air towards the polymeric layer for a period of time. Alternatively, step 14 may be substituted by a thermal treatment, such as a baking step, before the first reagent is added to the polymeric layer. In the embodiments where the polymeric material is pre-mixed with the first reagent in the fluid form, the baking step may be avoided as it may promote cross-linking of the polymeric material and affect the development step (19) of the polymeric layer.

At step 16, a portion of the polymeric layer is exposed to a chemical compound comprising a second reagent. The first and the second reagent react to change the chemical properties of the exposed portion of the polymeric layer. After the first and the second reagent react the exposed portion becomes soluble in the developer solution or resistant to the developer solution. In the first instance, after development, the area of the layer exposed to the chemical compound will have openings or grooves, depending on how deep the exposed portion extended in the layer. In the second instance the portion of the layer exposed to the chemical compound will resist the development process, while the remaining portion of the layer will be removed by the development solution. The difference between these two embodiments of the method is analogous to the concept of positive and negative photolithography.

In the embodiment described, the first and the second reagents have different hydrogen ion activity, or PH. More specifically the first reagent is an acidic reagent with a hydrogen ion activity between 1 and 10^{-4} and the second is a basic reagent with a PH of 8.6. The acidic reagent is an organic acidic solution with a volumetric concentration between 1 to 30 and 10 to 30. In some embodiments, the second reagent may be an acidic reagent with a PH between 4 and 7.

The chemical compound containing the second reagent is in the form of an ink and is deposited using an ink-jet printer onto a surface of the portion of the layer and penetrates the entire thickness of the layer. The chemical compound may be also deposited using an aerosol deposition technique or by screen-printing.

The penetration and mixing of the basic ink with the acidic polymeric material is promoted by a plasticiser contained in the ink. The plasticiser improves mixing of the chemical compound throughout the thickness of the layer. In some instance the ink may also contain a surfactant for improving penetration of the chemical compound through the portion of the layer. Further, the ink may contain one or more buffering agents for improving the efficiency of the reaction between the polymeric material and the second reagent.

At step 18, the polymeric layer is thermally treated to promote cross-linking of the portion which has not been exposed to the ink. Different temperatures and time intervals can be used depending on the chemical composition of the polymeric layer.

One of the applications of the thermal treatment is to promote the chemical crossing-linking reaction. For this application a temperature of about 110˚C is used for 1 min treatment time. Generally, temperature below 100˚C result in higher development rates of non-printed areas. Treatment temperatures higher than 140˚C may results in cross-linking of the printed areas.

At step 19, the polymeric layer is exposed to a developer solution for 1 minute and 15 seconds. The developer solution is a MIF developer solution. Different developer solutions and time intervals may be used depending on the nature of the polymeric layer.

Referring now to figures 2A to 2G there are shown schematic illustrations (200, 206, 210, 214, 218, 222, and 226) of a solar cell device at different stages of a metallisation process performed using the method 10.

Device 200 comprises a silicon substrate 202 and one or more layers on the substrate 202 which form a solar cell. In figure 2 these one or more layers are represented as two layers 204. The number of layers is not limited to two and the polymeric layer may be deposited on an active layer of the solar cell, a semiconducting layer, a dielectric layer or a conductive layer.

Figure 2B shows a polymeric layer 208 deposited on the top surface of device 206 by spin coating for 30 seconds at 1300 rpm. Polymeric layer 208 comprises a cross-linker molecule and a resin arranged to cross-link to each other when exposed to sufficient thermal energy. The cross-linker molecule comprises melamine formaldehyde and the resin comprises a novolac polymer. Polymeric layer 208 is pre-mixed with an acid HCl solution or citric acid with a PH 1. The solution has a volume ration of 1:30. A different PH and different concentrations may be used with different polymeric materials.

Figure 2C shows a layer of a basic ink 212 with a PH of 8.6 deposited in accordance with a predetermined pattern on the surface of layer 208. The ink layer 212 is deposited using an inkjet printer.

Upon depositing the ink layer 212 on the polymeric layer 208, the acid in the polymeric layer 208 and the basic ink 212 start reacting in a manner such that the portions of the cross-linking of the portions of the polymeric layer 208 exposed to the ink 212 is minimised. The mixing of the polymeric layer 208 and the ink 212 are promoted by a plasticiser contained in the ink. The ink may also contain a buffering agent and surfactant agents. The cross-linking of the unexposed portions of the polymeric layer 208 is promoted by baking the solar cell for 1 minute at 110 °C.

Figure 2D shows portions 216 of the polymeric layer 208 which have reacted with the ink.

Figure 2E shows device 218 after development. The device has been immersed in a solution of MIF 826 developer for 1 minute and 15 seconds. Device 218 has openings 220 in the polymeric layer 208, the openings are formed by the developer solution which has removed the portion of the polymeric layer which was exposed to the ink.

Once the polymeric layer 208 is patterned, it can be used for several applications. In the case of device 222 of figure 2F, the polymeric layer is used as a metallisation mask for a metallic layer 224. The metallic layer is evaporated across the entire solar cell 222. However, when the remaining cross-linked portion of the polymeric layer is chemically removed, portions of the metallic layer 224 are lifted-off and a patterned metallic layer 224 is left on the top surface of the solar cell, as shown in device 226 of figure 2G.

The actual steps of method 10 used to pattern polymeric layer 208 for the manufacturing of a solar cell device are shown in figures 2A to 2E. Figures 2F and 2G show device 222 when a metallic layer is applied on the patterned polymeric layer. This can be done, for example, by metal evaporation. When the polymeric layer is chemically removed, it lifts-off portions of the evaporated metallic layer, as shown in device 226. In alternative embodiments, the metallisation of the solar cell surface through the openings of the patterned polymeric layer may be performed using other methods, such as light-induced anodisation or plating. In this case the metallic material is only formed in the openings of the polymeric layer.

Further, patterned polymeric layer 208 in figure 2E may be used to selectively etch a surface of a solar cell device to create a template. This may be used, for example, to prepare the surface for further processing or to implement a light trapping technique. If an aggressive chemical etching technique is used, or a plasma etching technique, the polymeric layer 208 can be hard-baked prior to the etching step. Hard baking the polymeric layer 208 improves the bonds of the polymeric material providing a reliable masking effect for the solar cell surface.

Referring now to figure 3, there is shown a microscopy image of a series of parallel metal lines 30 realised on the surface of a semiconductor wafer using the method described above. A line width of about 20 micrometers can be achieved using the experimental parameters discussed. A detail of a single metal line 32 is shown in figure 3B. After plating and resist removal, metal lines with a width of 23 micrometers and a height of 10 micrometers are achieved.

Figure 4 shows microscopy images and of metallic lines ('fingers') 40 and 42 formed on the top surface of a commercial solar cell using the method of figure 1.

It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the invention as shown in the specific embodiments without departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.

The Claims as defined in the invention are as follows:

1. A method of patterning a polymeric layer, the method comprising the steps of:

providing a layer comprising a polymeric material and a first reagent;

exposing a portion of the layer to a chemical compound comprising a second reagent; and thereafter

exposing the layer to a developer solution;

wherein the first reagent of the layer reacts with the second reagent of the chemical compound to alter the chemical properties of the exposed portion of the layer in a manner such that the solubility of the polymeric material in the developer solution at the exposed portion is increased or decreased.

2. The method of claim 1 wherein the polymeric material at the exposed portion of the layer is substantially dissolvable in the developer solution or substantially resistant to the developer solution.

3. The method in accordance with claim 1 or claim 2 wherein the method further comprises the step of processing the polymeric layer so that the chemical properties of a portion of the layer that has not been exposed to the chemical compound comprising the second reagent are altered in a manner such that the solubility of the polymeric material in the developer solution is increased or decreased.

4. The method in accordance with claim 3 wherein the step of processing the polymeric layer comprises the step of baking the layer at a temperature between 90°C and 150°C.

5. The method in accordance with claim 3 or claim 4 wherein the step of processing the polymeric layer comprises the step of baking the layer for a period of time between 10 seconds and 3 minutes.

6. The method in accordance with any one of claims 3 to 5 wherein the step of processing the polymeric layer comprises the step of baking the layer for a period longer than 3 minutes and wherein the duration of the baking treatment is related to whether the layer is used as an etching mask or as a plating mask.

7. The method in accordance with any one of the preceding claims wherein the step of exposing a portion of the layer to a chemical compound comprising a second reagent comprises the step of depositing the chemical compound onto a surface of the portion of the layer.

8. The method in accordance with claim 7 wherein the chemical compound is provided in the form of a fluid.

9. The method in accordance with claim 8 wherein the chemical compound comprises an ink comprising the second reagent.

10. The method in accordance with claim 9 wherein the step of depositing the chemical compound onto a surface of the portion of the layer is performed using an ink-jet deposition technology.

11. The method in accordance with claim 8 or claim 9 wherein the step of depositing the chemical compound onto a surface of the portion of the layer is performed using an aerosol deposition technique.

12. The method in accordance with claim 8 or claim 9 wherein the step of depositing the chemical compound onto a surface of the portion of the layer is performed using a screen-printing technique.

13. The method in accordance with any one of the preceding claims wherein the portion of the layer extends throughout the entire thickness of the layer.

14. The method in accordance with any one of the preceding claims wherein the portion of the layer defines a pattern comprising a plurality of elongated openings in the layer.

15. The method in accordance with claim 14 wherein the pattern in the layer forms a solar cell metallization pattern.

16. The method in accordance with any one of the preceding claims wherein the first reagent is an acidic reagent with a hydrogen ion activity between 1 and 10^{-4} and the second reagent has a hydrogen ion activity between 10^{-4} and 10^{-14}.

17. The method in accordance with claim 16 wherein the first reagent is an acidic reagent with a hydrogen ion activity between 1 and 10^{-2} and the second reagent has a hydrogen ion activity between 10^{-7} and 10^{-9}.

18. The method in accordance with claim 16 or claim 17 wherein the method further comprises the step of selecting the hydrogen ion activity of the first reagent to affect

the velocity of the reaction between the first reagent and the second reagent.

19. The method in accordance with any one of claims 1 to 18 wherein the first reagent is an acidic reagent and the second reagent is a basic reagent.

20. The method in accordance with any one of claims 16 to 19 wherein the layer comprises a photoresist material or a chemically amplified photoresist material.

21. The method in accordance with claim 20 wherein the chemical amplified photoresist comprises a negative melamine formaldehyde resin (MFR).

22. The method in accordance with claim 20 or claim 21 wherein the step of providing a layer comprises the step of mixing the photoresist material with an acidic solution.

23. The method in accordance with claim 22 wherein the acidic solution is an organic acidic solution.

24. The method in accordance with claim 23 wherein the organic acidic solution has a hydrogen ion activity between 1 and 10^{-4}.

25. The method in accordance with any one of claims 16 to 24 wherein the layer comprises a cross-linker molecule and a resin arranged to cross-link to each other when exposed to sufficient thermal energy.

26. The method in accordance with claim 25 wherein the cross-linker molecule comprises melamine formaldehyde.

27. The method in accordance with claim 25 or claim 26 wherein the resin comprises a novolac polymer.

28. The method in accordance with any one of claims 16 to 27 wherein the chemical compound comprising the second reagent further comprises a plasticiser for improving mixing of the chemical compound through the portion of the layer.

29. The method in accordance with any one of claims 16 to 28 wherein the chemical compound comprising the second reagent further comprises a surfactant for improving penetration of the chemical compound through the portion of the layer.

30. The method in accordance with any one of claims 16 to 29 wherein the chemical compound comprising the second reagent further comprises one or more buffering agents for controlling the PH and improve the efficiency of the reaction between the polymeric material and the second reagent.

31. The method in accordance with claim 30 wherein the chemical composition of the one or more buffering agents is such that the hydrogen ion activity of the portion of the layer exposed to the chemical compound comprising the second reagent is higher than 10^{-4} after the portion has been exposed.

32. The method in accordance with any one of the preceding claims wherein the chemical compound comprising the second reagent further comprises an organic solvent to promote chemical reaction with the layer comprising the polymeric

material and precise PH control throughout the thickness of the layer.

33. The method in accordance with any one of the preceding claims wherein the step of exposing the layer and the chemical compound to a developer solution comprises immersing the layer in a developer solution for a time period between 1 second and 300 seconds.

34. A method of forming a patterned metallic layer on a surface of a device, the method comprising the steps of:

forming a layer comprising a polymeric material on the surface of the device;

patterning a portion of the formed layer using the method in accordance with anyone of claims 1 to 33 to form one or more openings in the layer; and

forming a metallic layer onto a first portion of the surface of the device through the one or more openings formed in the layer.

35. A method of selectively etching a surface of a device, the method comprising the steps of:

forming a layer comprising a polymeric material on the surface of the device;

patterning a portion of the formed layer using the method in accordance with anyone of claims 1 to 33 to form one or more openings in the layer; and

performing an etching treatment onto a first portion of the surface of the device through the one or more openings formed in the layer.

36. A method of anodising a surface of a device, the method comprising the steps of:

forming a layer comprising a polymeric material on the surface of the device;

patterning a portion of the layer using the method in accordance with anyone of claims 1 to 33 to form one or more openings in the layer;

exposing a first surface portion of the device through the one or more of the openings to an electrolytic solution that is suitable for anodising the first surface portion when an electrical current is directed through a region of the device at the first surface portion; and

exposing a portion of the device to electromagnetic radiation in a manner such that the electromagnetic radiation induces the electrical current and the first surface portion anodises.

37. A semiconductor device comprising a patterned metallic layer formed in accordance with claim 34, or a surface selectively etched in accordance with the method of claim 35, or a surface anodised in accordance with the method of claim 36.

38. A solar cell device comprising a patterned metallic layer formed in accordance with the method of claim 34, or a surface selectively etched in accordance with the method of claim 35, or a surface anodised in accordance with the method of claim 36.

39. A method of forming a solar cell device, the method comprising the step of:

providing a substrate having a first polarity;

depositing a first layer having a second polarity in a manner such that the layer forms a p-n junction or a p-i-n junction with the substrate;

depositing a second layer on at least a portion of the first layer and;

forming patterned metallic layer on the second layer in accordance with the method of claim 34.

40. A solar cell device formed in accordance with the method of claim 39.

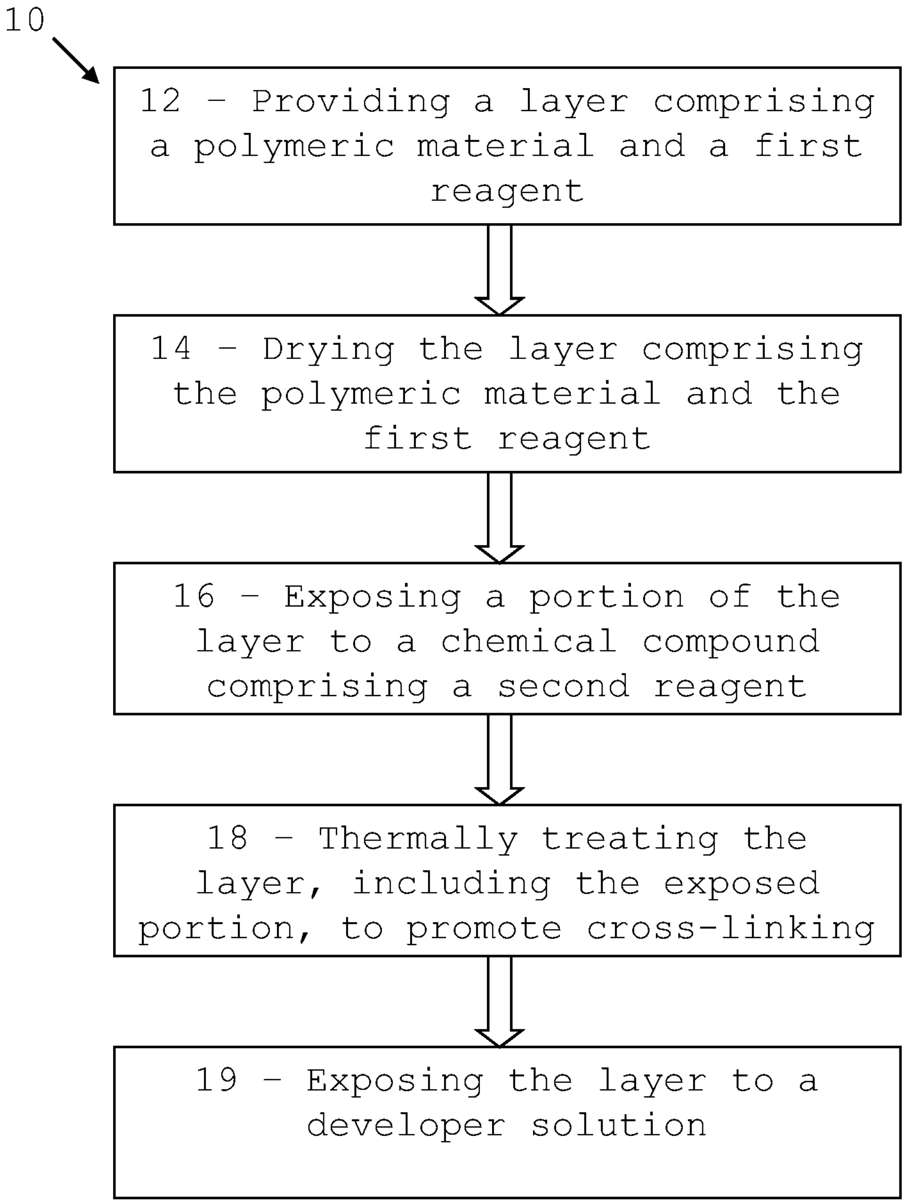
10
12 – Providing a layer comprising a polymeric material and a first reagent
14 – Drying the layer comprising the polymeric material and the first reagent
16 – Exposing a portion of the layer to a chemical compound comprising a second reagent
18 – Thermally treating the layer, including the exposed portion, to promote cross-linking
19 – Exposing the layer to a developer solution

FIGURE 1

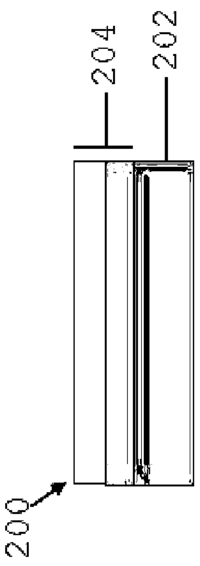

FIGURE 2A

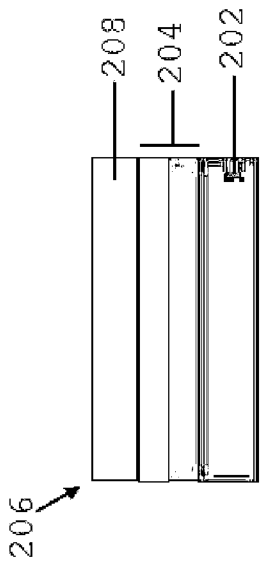

FIGURE 2B

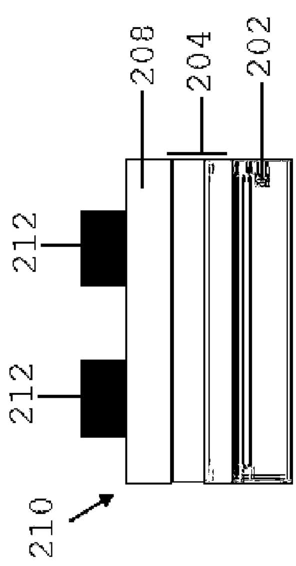

FIGURE 2C

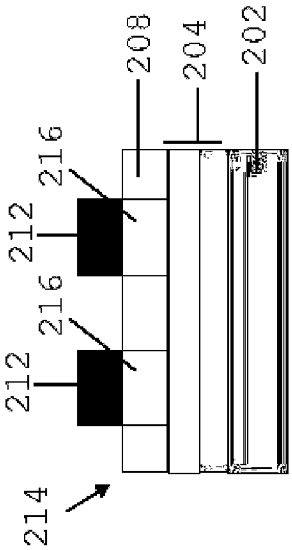

FIGURE 2D

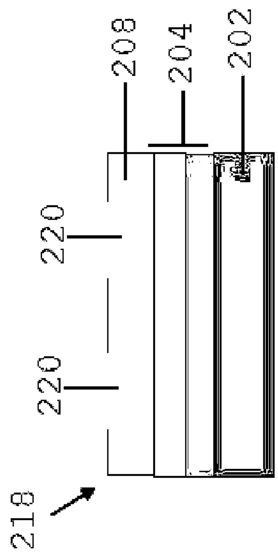

FIGURE 2E

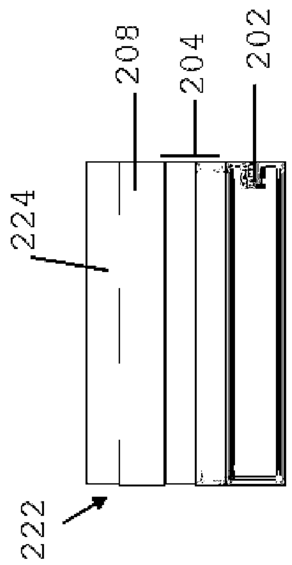

FIGURE 2F

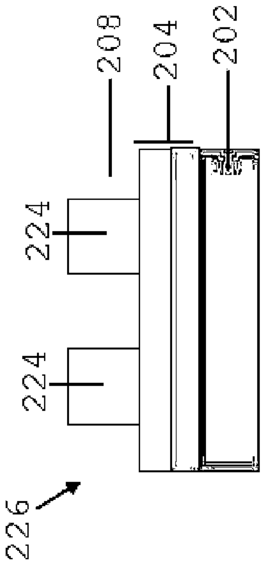

FIGURE 2G

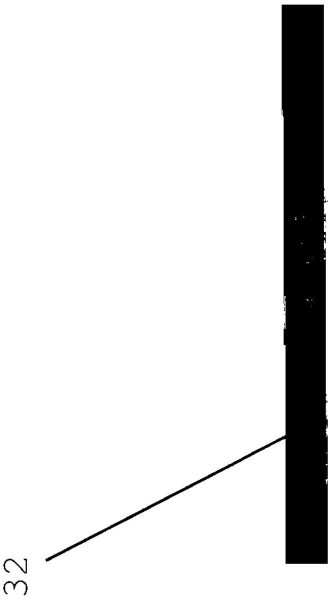

FIGURE 3B

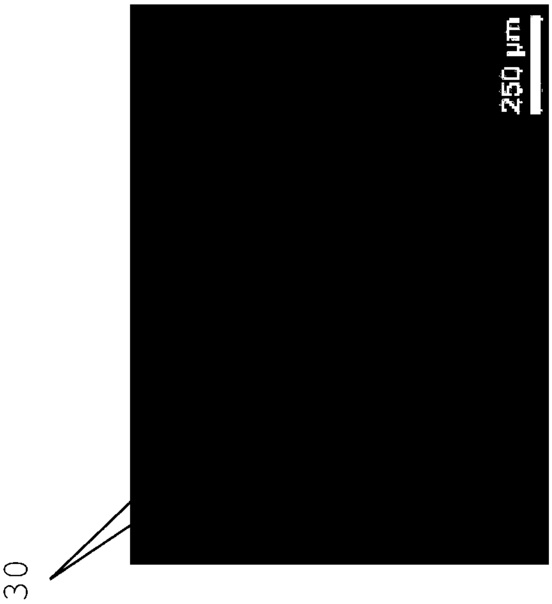

FIGURE 3A

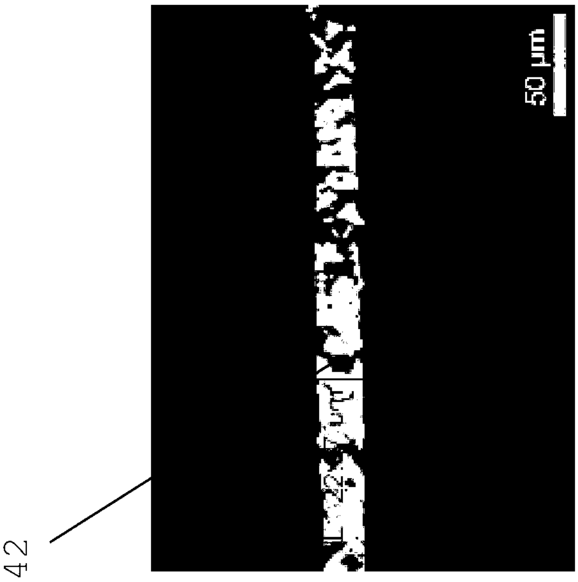

FIGURE 4B

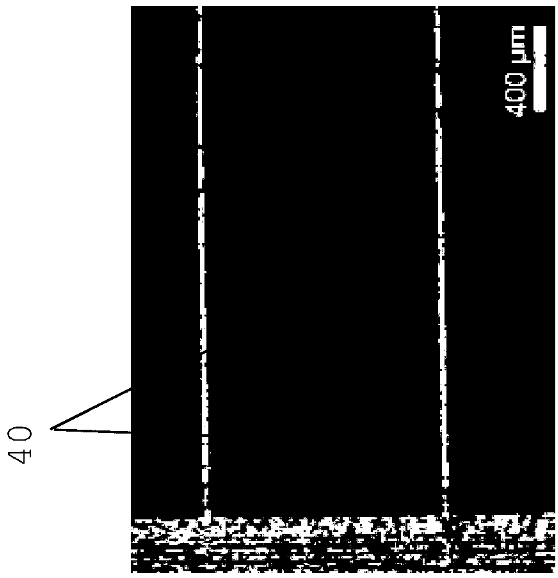

FIGURE 4A

INTERNATIONAL SEARCH REPORT	International application No. PCT/AU2015/000602

A. CLASSIFICATION OF SUBJECT MATTER

G03F 7/20 (2006.01) H01L 29/06 (2006.01) H01L 21/76 (2006.01) G03F 7/40 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Databases: WPIAP, EPODOC and Keywords: microelectronic, semiconductor, silicon, solar, photovoltaic, patterning, lithographic, resist, photoresist, chemical, reactant, reagent, crosslink, additive, cure and like terms.
Internet searching: Databases: ESPACENET, GOOGLE PATENTS and GOOGLE SCHOLAR. Keywords: Patterning, resist, photoresist, mask, chemical, reagent, reaction, semiconductor, solar cell, photovoltaic, etching, metallization, anodising, anodizing and like terms.
Applicant and Inventor searching on database ESPACENET. Applicant: Newsouth innovations and Keyword: resist or photoresist. Inventor: Li or Lennon and Keyword: patterning and solar.
ESPACENET/GOOGLE PATENTS: Cited/citing most relevant prior art documents and their family members.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	

[X] Further documents are listed in the continuation of Box C   [X] See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
17 December 2015	17 December 2015
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustralia.gov.au	**Authorised officer** Graeme Evans AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. 0262832822

INTERNATIONAL SEARCH REPORT	International application No.
C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT	**PCT/AU2015/000602**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2007/0007627 A1 (YOUNG et al) 11 January 2007 Abstract, paragraphs 1, 4-10, 12, 32-34, 36	1-40
X	US 2010/0047721 A1 (WENHAM et al) 25 February 2010 Abstract, Paragraphs 4, 9-35, 85, 94	1-40
X	US 2006/0292821 A1 (YOUNG et al) 28 December 2006 Abstract, Paragraphs 1, 3-9, 29, 31	1-40
A	EP 2709160 A1 (ATOTECH DEUTSCHLAND GMBH) 19 March 2014 Abstract and Paragraph 8	14-15
A	US 6576394 B1 (XU et al) 10 June 2003 Abstract, Columns 3-4	20-26
A	US 6362079 B1 (IWATA et al) 26 March 2002 Abstract, Claim 1	36

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/AU2015/000602**

This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document/s Cited in Search Report		**Patent Family Member/s**	
Publication Number	**Publication Date**	**Publication Number**	**Publication Date**
US 2007/0007627 A1	11 January 2007	US 2007007627 A1	11 Jan 2007
		US 7585781 B2	08 Sep 2009
		AU 2004271225 A1	17 Mar 2005
		AU 2004271225 B2	21 Jan 2010
		CN 1853257 A	25 Oct 2006
		EP 1665346 A1	07 Jun 2006
		JP 2007505487 A	08 Mar 2007
		WO 2005024920 A1	17 Mar 2005
US 2010/0047721 A1	25 February 2010	US 2010047721 A1	25 Feb 2010
		US 8398877 B2	19 Mar 2013
		AU 2008210253 A1	07 Aug 2008
		CN 101636829 A	27 Jan 2010
		EP 2109882 A1	21 Oct 2009
		KR 20090125078 A	03 Dec 2009
		TW 200847273 A	01 Dec 2008
		WO 2008092186 A1	07 Aug 2008
US 2006/0292821 A1	28 December 2006	US 2006292821 A1	28 Dec 2006
		US 7446051 B2	04 Nov 2008
		AU 2004271223 A1	17 Mar 2005
		AU 2004271223 B2	18 Feb 2010
		CN 1849702 A	18 Oct 2006
		EP 1665353 A1	07 Jun 2006
		JP 2007505485 A	08 Mar 2007
		WO 2005024927 A1	17 Mar 2005
EP 2709160 A1	19 March 2014	EP 2709160 A1	19 Mar 2014
		CN 104620394 A	13 May 2015
		PH 12015500543 A1	04 May 2015
		US 2015349152 A1	03 Dec 2015
		WO 2014040818 A1	20 Mar 2014
US 6576394 B1	10 June 2003	US 6576394 B1	10 Jun 2003
		CN 1436324 A	13 Aug 2003
		EP 1297386 A1	02 Apr 2003
		EP 1297386 B1	27 Dec 2006
		JP 2004503830 A	05 Feb 2004

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/AU2015/000602**

This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document/s Cited in Search Report		**Patent Family Member/s**	
Publication Number	**Publication Date**	**Publication Number**	**Publication Date**
		JP 4799800 B2	26 Oct 2011
		KR 20030076229 A	26 Sep 2003
		KR 100790412 B1	02 Jan 2008
		TW 567403 B	21 Dec 2003
		WO 0196960 A1	20 Dec 2001
US 6362079 B1	26 March 2002	US 6362079 B1	26 Mar 2002
		EP 0987743 A1	22 Mar 2000
		JP H10340885 A	22 Dec 1998
		WO 9856036 A1	10 Dec 1998

End of Annex

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.