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(54) Title: MOLECULAR FLUORINE ETCHING OF SILICON THIN FILMS FOR PHOTOVOLTAIC AND OTHER LOWER-TEMPERATURE CHEMICAL VAPOR DEPOSITION PROCESSES

(57) Abstract: Improved techniques for the cleaning of amorphous and microcrystalline silicon thin films used in photovoltaic applications. In greater detail, methods for the use of molecular fluorine for cleaning of thin films used in photovoltaic applications and devices formed thereby are described.



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**MOLECULAR FLUORINE ETCHING OF SILICON THIN FILMS FOR
PHOTOVOLTAIC AND OTHER LOWER-TEMPERATURE CHEMICAL
VAPOR DEPOSITION PROCESSES**

FIELD OF THE INVENTION

(001) The present invention relates to new methods for the cleaning of amorphous and microcrystalline silicon thin films for photovoltaic applications and to devices formed thereby.

BACKGROUND OF THE INVENTION

(002) Methods for the cleaning of amorphous and microcrystalline silicon thin films for photovoltaic fabrication have largely been adopted from methods used for liquid crystal display (LCD) and semiconductor devices. The manufacture of these latter devices requires chamber temperatures in excess of 280°C and typically involves the layering of several different types of thin films; for example, in addition to silicon films, SiO₂, Si₃N₄, SiO_xN_y, metal and metal oxide films may be formed. In the range of manufacturing conditions, molecular fluorine does not react quickly with the non-silicon films. Therefore, it is not convenient to clean these non-silicon films using molecular fluorine. Increasing the chamber temperatures above the manufacturing temperatures would help the reactivity, but would not be economical because of the time and energy involved.

(003) To overcome the temperature problems associated with the use of molecular fluorine, the use of fluorine radicals to remove the thin films has been carried out. The fluorine radicals are created by either *in situ* activation or external remote plasma source (RPS) activation of molecular fluorine or fluorine containing gases, e.g. NF₃ or SF₆, to generate the fluorine radicals. When using fluorine radicals, the rate at which the chamber cleaning can be accomplished is dependent upon the rate and efficiency of the

activation of the fluorine containing gases. Therefore, the cleaning step can constitute a significant fraction of the overall fabrication cycle, resulting in reduced manufacturing capacity and the requirement for excessive tooling. In addition, the equipment needed for activation of fluorine containing gases, especially RPS units, can add significant expense to the fabrication process and are known to be troublesome points-of-failure, which reduce the effective uptime for the manufacturing process.

(004) Moreover, fluorine radicals produced by either *in situ* or RPS activation are very reactive and not very selective, thereby causing damage to seals, RF generators, and other important equipment inside or associated with the fabrication chamber. Also, RPS and *in situ* activation necessarily occurs at limited sources, with the distribution of fluorine radicals being highly anisotropic. This results in the requirement for so-called “overetch”, i.e. a time period of radical generation well in excess of the stoichiometric requirement for cleaning, in order to clean the harder to reach places in the reaction chamber.

(005) US patent number 6,880,591 (Goto *et al.*) recognizes that molecular fluorine can be used for chamber cleaning of silicon processes, but is focused on high-temperature regimes and is intended for LCD display processes. In particular, Goto *et al.* suggests temperatures for use of molecular fluorine well in excess of the temperatures used for LCD production; i.e. between 280°C and 400°C, and preferably about 450° C. It is believed that these high temperatures are chosen to compensate for the low partial pressures of fluorine allowed by the Goto *et al.* process, e.g. less than 1 mbar. It is noted that Goto *et al.* found cleaning with molecular fluorine was not completely effective and needed to be coupled with either *in situ* and/or RPS activation.

(006) It is also noted that Fluorine containing gases other than molecular fluorine, such as NF_3 , SF_6 , and C_xF_y compounds, are not effective cleaning agents for silicon films at

temperatures below 500°C, and for commercial applications, at temperatures below 900°C.

(007) The manufacture of MEMS devices has also provided guidance for the thin film photovoltaic industry. In general, in MEMS manufacturing, the aim of using molecular fluorine is to release devices fabricated from compounds like SiO₂ and Si₃N₄ from a matrix of silicon. In particular, by etching with molecular fluorine at low temperatures, *e.g.* room temperature, and relatively high pressures, *e.g.* 250 mbara, the silicon film making up the matrix can be completely removed without any deleterious reactions of the molecular fluorine with the device components. However at higher temperatures, the selectivity of fluorine for silicon over the other compounds decreases, and therefore, the usefulness of molecular fluorine is diminished at elevated temperatures. (see Arana et al., “*Isotropic etching of silicon in fluorine gas for MEMS micromachine*”, J. Micromech. Microeng., vol 17, 384-392, 2007).

(008) There remains a need in the art for improvements to apparatus and methods for the cleaning of amorphous and microcrystalline silicon thin films for photovoltaic applications.

SUMMARY OF THE PRESENT INVENTION

(009) The present invention provides improved techniques and apparatus for the cleaning of amorphous and microcrystalline silicon thin films used in photovoltaic applications. In greater detail, the present invention provides methods and apparatus for the use of molecular fluorine for cleaning of thin films that overcome the disadvantages noted above.

DETAILED DESCRIPTION OF THE INVENTION

(010) The present invention relates to the use of molecular fluorine for etching of silicon thin-films for photovoltaic applications. The disadvantages noted above with respect to LCD and MEMS processes can be avoided. In particular, the processes for production of thin-film photovoltaic devices are conducted at lower temperatures than the processes for thin-film transistor LCD devices. For example, photovoltaic processes are typically carried out between 50°C and 300°C. Molecular fluorine reacts well with silicon in this temperature range. In accordance with the present invention, the use of molecular fluorine at the deposition temperature and at partial pressures between 1 mbara and 1000 mbara, accelerates cleaning and thereby improves productivity. Pressures below those used for MEMS production can be employed effectively.

(011) Because, photovoltaic processes involve only the deposition of lightly doped silicon films and do not require deposition of films that are poorly etched by molecular fluorine at lower temperatures, the cleaning and etching processes can be carried out effectively. In particular, there is no need for activation to form fluorine radicals, because the non-silicon films are not present. This means that there is no requirement for activation equipment to produce the fluorine radicals, which reduces the cost of capital equipment, and thereby reduces the cost of production for the photovoltaic panels.

(012) The methods of the present invention can be carried in a number of ways. In one embodiment, the fluorine is introduced to the chamber at an initial static partial pressure in stoichiometric excess of the silicon in the thin film to be cleaned. The excess fluorine allows the cleaning to go to completion in a finite, and commercially desirable, time. In another embodiment, the fluorine is introduced to the chamber at an initial static partial pressure approximately equal to the stoichiometric amount required to fully clean the thin film. In this embodiment, the thin-film can be greatly reduced in thickness, which is often acceptable in order to allow for another deposition cycle. When using this

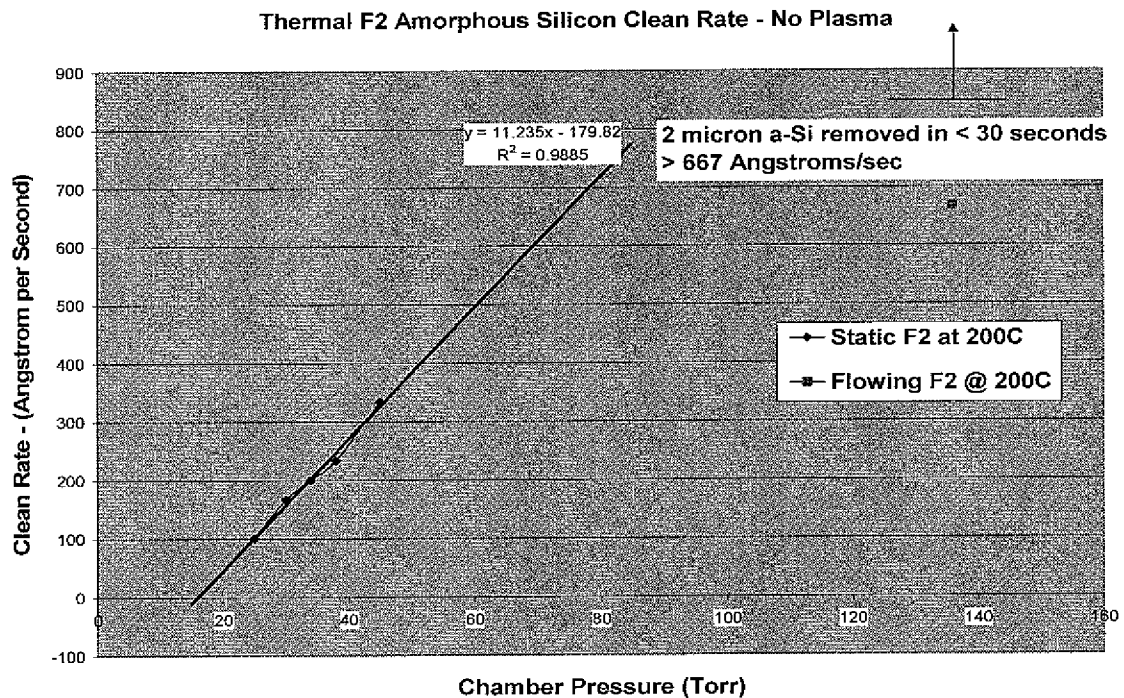
embodiment in repetitive cycles, a steady state cleaning is created with the lowest fluorine use that is still commercially viable with respect to cycle time. In a further embodiment, the fluorine is introduced to the chamber at an initial partial pressure and additional fluorine is added at a steady or varying rate. A vacuum pump may be used to keep the chamber at the constant or varying pressure. With this embodiment, the reaction rate can be varied in accordance with the user specified recipe, because the reaction rate will vary at a fixed temperature with changing partial pressure of available molecular fluorine. Alternatively, this embodiment allows a relatively high and constant partial pressure to be maintained while the cleaning takes place, thereby accomplishing a constant cleaning rate.

(013) Experiments have been carried out according to the present invention. Data was collected and results are shown in the graph below. The experiment comprised cleaning a 2 micron sample of silicon using molecular fluorine at 200°C. The 2 micron silicon film was deposited on an aluminium under layer, which is not appreciably etched by molecular fluorine at 200°C below 1000 mbara. A portion of the silicon thin film sample was covered by a sapphire disk, which is also not appreciably etched with molecular fluorine at 200°C below 1000 mbara. The experiment consisted of exposing the silicon films to molecular fluorine at various partial pressures at 200°C, after which the silicon film samples were removed from the reaction chamber. The sapphire disk was removed and the height difference of the etched and unetched surfaces were measured by profilometry in order to calculate the etch rate.

(014) The gathered data is shown in the graph below, wherein it is clear that increasing chamber pressure corresponds to increased cleaning or etch rate at 200° C. Comparing the results for the present invention to known cleaning methods proves the superiority of the present method. For example, some commercially available silicon-based thin film photovoltaic processes operate at or near 200°C, and use a recipe having an average device thickness of 2 µm. In these processes, the process chamber is cleaned after each

substrate deposition, with cleaning time taking from 5 to 20 minutes to complete. The data of the method according to the present invention shows that an etch rate of $8.54 \text{ \AA} / \text{sec} - \text{mbar}$ can be achieved, which means that a $2 \text{ }\mu\text{m}$ film can be successfully cleaned in 60 seconds using molecular fluorine held at a constant partial pressure of 39 mbar and a temperature of 200°C . The cleaning rate according to the present invention is therefore 5 to 20 times faster than currently available cleaning recipes relying on *in situ* or RPS activation.

(015) In a further example, some commercially thin-film processes clean only daily after depositing silicon films at comparable rates to the example above. This cleaning stage can take from 100 to 240 minutes to complete. The results of the experiments according to the present invention indicate that a film of $100 \text{ }\mu\text{m}$ thickness can be successfully cleaned in 20 minutes using molecular fluorine held at a constant partial pressure of 100 mbar and at a temperature of 200°C . This etch rate is 5 to 12 times faster than the currently available cleaning recipes relying on *in situ* or RPS activation.



(016) The present invention provides many advantages over the prior art. In particular, because the rate of reaction of molecular fluorine with silicon films at any set temperature is dependent only upon the partial pressure of fluorine in the chamber, the partial pressure can be adjusted to achieve cleaning rates that are orders of magnitude faster than *in situ* or RPS cleaning with fluorine containing gases. Further, molecular fluorine is less reactive and more selective to the etching of silicon films than fluorine radicals and therefore causes less damage to seals, RF generators, and other important equipment associated with the fabrication chamber. Also, molecular fluorine is completely isotropic in its distribution within the chamber, and therefore can be reacted stoichiometrically.

(017) It is anticipated that other embodiments and variations of the present invention will become readily apparent to the skilled artisan in the light of the foregoing description, and it is intended that such embodiments and variations likewise be included within the scope of the invention as set out in the appended claims.

CLAIMS

What is claimed:

1. A method of etching a silicon thin film for use in photovoltaic devices comprising using molecular fluorine as the etching agent.
2. The method of claim 1 wherein etching is performed at a temperature between 50°C and 300°C and a partial pressure between 1 mbara and 1000 mbara.
3. The method of claim 1 wherein the molecular fluorine is introduced to an etching chamber at an initial static partial pressure in stoichiometric excess of the amount needed to etch the silicon thin film.
4. The method of claim 1 wherein the molecular fluorine is introduced to an etching chamber at an initial static partial pressure equal to the stoichiometric amount required to etch the silicon thin film.
5. The method of claim 4 wherein repetitive cycles of etching are performed to achieve steady state cleaning and use the lowest amount of molecular fluorine that is commercially viable.
6. The method of claim 1 wherein the molecular fluorine is introduced to an etching chamber at an initial static partial below the stoichiometric amount required to etch the silicon thin film and additional molecular fluorine is added at a steady or varying rate.
7. The method of claim 1 wherein etching is performed at a temperature of 200°C and a partial pressure between 1 mbara and 1000 mbara.

8. The method of claim 7 wherein the partial pressure is between 1 mbara and 350 mbara.
9. The method of claim 8 wherein the partial pressure is 39 mbara.
10. The method of claim 8 wherein the partial pressure is 100 mbara.
11. The method of claim 1 wherein the etch rate is greater than $8 \text{ \AA} / \text{sec} - \text{mbara}$.
12. The method of claim 1 wherein the silicon thin film has $2 \text{ }\mu\text{m}$ completely removed in less than 60 seconds.
13. The method of claim 1 wherein the silicon thin film has $100 \text{ }\mu\text{m}$ film completely removed in less than 20 minutes.
14. The method of claim 1 wherein partial pressure of the molecular fluorine is adjusted during the etching to control the etch rate of the silicon thin film.
15. A silicon thin film that has been etched using molecular fluorine as the etching agent.
16. A photovoltaic device having a silicon thin film that has been etched using molecular fluorine as the etching agent.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2009/069581

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B08B 7/00 (2010.01)

USPC - 134/22.100

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)

IPC(8) - B08B 7/00, B08B 7/04 (2010.01)

USPC - 134/22.100, 134/2, 134/28

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)

MicroPatent, Freepatentsonline, Google, Google Scholar

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 6,544,345 B1 (MAYER et al) 08 April 2003 (08.04.2003) see entire document	15 --- 1-14, 16
Y	WO 2007/116033 A1 (PISCHTIK et al) 18 October 2007 (18.10.2007) see entire document	1-14, 16
Y	US 6,124,211 A (BUTTERBAUGH et al) 26 September 2000 (26.09.2000) see entire document	2-10, 14
A	US 6,620,256 B1 (ARNO et al) 16 September 2003 (16.09.2003) see entire document	1-16
A	REICHE et al. Modification of Si(100)-Surfaces by SF6 Plasma Etching –Application to Wafer Direct Bonding. Crystal Research Technology (2000) Vol 35, 6-7, pg 807-821. see entire document.	1-16

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“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

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