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(54) Title: LOW TEMPERATURE DEPOSITION OF SILICON OXIDE FILMS

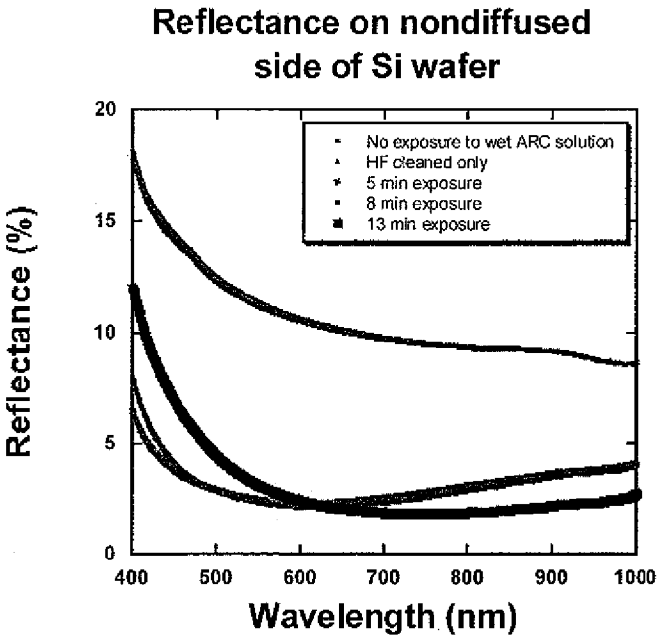

FIG. 1

(57) Abstract: Deposition of silicon oxide films at low temperature by using wet chemistry techniques. The wet chemistry solution may be a mixture of sodium hypochloride (NaOCl), tetra methyl ammonium hydroxide (TMAH) and hydrated silicate, such as silicic acid. The resulting silicon oxide films provide excellent anti-reflective coatings for solar cells and the like.

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LOW TEMPERATURE DEPOSITION OF SILICON OXIDE FILMS

FIELD OF THE INVENTION

(001) The present invention relates to methods of depositing silicon oxide films at low temperature using wet chemistry techniques.

BACKGROUND OF THE INVENTION

(002) Silicon oxide films are deposited onto silicon surfaces for use in many applications, including as masking layers for semiconductor manufacturing and as anti-reflective coatings for solar cells. There are a number of chemical vapor deposition (CVD) techniques that have been used, particularly in the semiconductor industry, to produce thin oxide films. In general, CVD processes form the oxide film by exposing the substrate to one or more volatile precursors that react with or decompose onto the substrate surface to produce the desired oxide film. The CVD processes in use differ in how the chemical reactions are initiated (e.g. activation process) and by the process conditions employed. For example, atmospheric pressure CVD (APCVD), ultrahigh vacuum CVD (UHCVD), plasma enhanced CVD (PECVD) and atomic layer CVD (ALCVD) are some of the CVD techniques used to deposit oxide films.

(003) Silicon dioxide (SiO_2) may be deposited using a CVD technique, by using any one of several source gas precursor combinations. One such combination uses silane and oxygen according to the following reaction formula.

$$SiH_4\text{ (gas)} + O_2 \rightarrow SiO_2\text{ (solid)} + 2H_2$$

A second combination uses oxygen dichlorosilane ($SiCl_2H_2$) and nitrous oxide (N_2O) according to the following reaction formula.

$$SiCl_2H_2 + 2N_2O \rightarrow SiO_2 + 2N_2 + 2HCl$$

Another possible precursor source gas is tetraethylorthosilicate (TEOS: $Si(OC_2H_5)_4$) according to the following reaction formula.

$$Si(OC_2H_5)_4) \rightarrow SiO_2 + \text{byproducts}$$

(004) The choice of source gas depends on the thermal stability of the substrate. In particular, silane deposits between 300°C and 500°C, dichlorosilane deposits at about 900°C and TEOS deposits between 650°C and 750°C. Deposition times generally last for about fifteen minutes, with the full heating and cooling cycle lasting about forty five minutes.

(005) The known oxide deposition processes have several disadvantages. These processes require high temperatures and vacuum processing before introduction of the precursor gases, particularly those that are hazardous. Further, the deposition equipment is expensive, has a relatively low wafer throughput, requires frequent cleaning and maintenance and demands highly trained operators. As a result, deposition of silicon oxide films demands substantial capital and operating expense, which increases overall device cost, for example the cost for creating anti-reflective coatings in the photovoltaic industry. Also, backside contact printing, with aluminum or aluminum/gold, is normally performed after the deposition of the oxide, and therefore requires higher temperatures for diffusion of the contacts and reduction in proper contact which could interfere with the overall efficiency of the device.

(006) There remains a need in the art for improvements to methods of depositing oxide films, such as silicon oxide films.

SUMMARY OF THE INVENTION

(007) The present invention provides low temperature methods of depositing silicon oxide films using wet chemistry.

BRIEF DESCRIPTION OF THE DRAWINGS

(008) Figure 1 is a graph showing the reflectance of p-type textured silicon wafers following processing according to the present invention.

(009) Figure 2 is a graph showing the reflectance textured silicon wafers doped with phosphor following processing according to the present invention.

(010) Figure 3 is a graph showing the reflectance of textured multi-crystalline silicon wafers following processing according to the present invention

DETAILED DESCRIPTION OF THE INVENTION

(011) The present provides methods of depositing silicon oxide films at low temperature using wet chemistry techniques. In accordance with the present invention, a wet chemistry mixture of sodium hypo chloride (NaOCl), tetra methyl ammonium hydroxide (TMAH) and hydrated silicate (such as silicic acid) is used for the low temperature oxide deposition.

(012) NaOCl is a strong oxidizing agent that ionizes in water to give hypochlorous acid (HOCl) and hypochlorite ions (OCl^-). If applied to a silicon substrate, the silicon etching rate is low because of the relative lack of availability of OH ions. However, the silicon does react with the hypochlorite ions to form SiO_2. The process of forming a SiO_2 film using a NaOCl solution alone is a slow process and the film produced is of poor quality.

Further this film does not adhere strongly to the silicon substrate. A summary of the reaction sequence is set forth below.

$$NaOCl \leftrightarrow Na^+ + OCl^- \quad (1)$$

$$2OCl^- + H_2O \leftrightarrow HOCl + OCl^- + OH^- \quad (2)$$

$$Si + 2OCl^- \leftrightarrow SiO_2 + 2Cl^- \quad (3)$$

Diluted TMAH (and other hydroxide solutions such as KOH and NaOH) exhibit strong silicon etch rates. As an initial step, the TMAH is reduced to form hydroxyl ions. This is followed by reaction of the hydroxyl ions with silicon atoms at the substrate surface to form oxidized silicates, such as $Si(OH)_2^{2+}$ and four electrons are injected from each silicon atom into the conduction band. Therefore, the overall reaction must balance the ions and the electrons. Simultaneously, water is reduced to provide more hydroxyl ions which in turn are bonded to the silicates formed in the second step. This reaction produces soluble silicic acid, with hydrogen gas as a by-product. Using the TMAH solution alone, unlike NaOCl, would result in etching of the silicon substrate rather than deposition of an oxide film. This reaction sequence is set forth below.

$$(CH_3)_4NOH \leftrightarrow (CH_3)_4N^+ + OH^- \quad (4)$$

$$Si + 2OH^- \leftrightarrow Si(OH)_2^{2+} + 4e^- \quad (5)$$

$$Si(OH)_2^{2+} + 4e^- + 4H_2O \leftrightarrow Si(OH)_6^{2-} + 2H_2 \quad (6)$$

(013) By combination of the above solutions, the deposition of an oxide can be accomplished at low temperatures. In particular, By combining dilute TMAH (or another hydroxide solution) having the capability to etch the silicon substrate, with NaOCl that is capable of forming a oxide, and silicate that provides an additional source of silicon for oxidation and deposition, in appropriate amounts, according to the present invention and applying such mixture to a silicon substrate, simultaneous etching of the silicon substrate and deposition of oxide can be accomplished at temperatures between 60°C and 90°C.

The oxide coatings produced according to the present invention have the proper texture and properties to serve as anti-reflective coatings for solar cells. The thickness of the oxide coating can be adjusted by changing temperature or chemical exposure times to obtain optimal coatings that have low reflectance of visible light. This results in the ability of devices with these coatings to capture the appropriate solar spectrum with increased efficiency of the solar cell.

(014) The present invention will be described in greater detail with reference to the following examples. Initially, a single crystal Si (100) wafer may be textured using either KOH+IPA, TMAH+IPA or acid solutions such as nitric acid mixed with hydrofluoric acid. The native oxide of the wafer is first removed in a 4% HF solution for several minutes. The wafer is then exposed in accordance with the present invention to a solution of NaOCl, TMAH and extra dissolved Si or added silicic acid. This exposure results in a coating of hydride silica (Polymerized) which when dry heated forms silica having an index of refraction close to SiO_2; i.e. about 1.45.

(015) Figure 1 shows the reflectance properties of p-type silicon wafers as a function of exposure at 75°C to the solution mixture according to the present invention described above. As can be seen, reflectance is significantly reduced with as little a five minutes exposure, while even better results are achieved with thirteen minutes of exposure. In simulations, the average oxide build-up is 63 nm for five minutes exposure, 93 nm for eight minutes exposure and 120 nm for thirteen minutes exposure.

(016) Wafers that were phosphor-diffused using $POCl_3$ were treated according to the present invention using the solution mixture noted above, i.e. a solution of NaOCl, TMAH and extra dissolved Si or added silicic acid. The results are shown in figure 2. In particular, while the high doping concentration slowed the deposition rate, the significant reduction in reflectance was still achieved. The rate of deposition on highly phosphor doped substrates was reduced by a factor of up to two compared to deposition rates on low boron doped (p-type) substrates.

(017) In a similar manner multi-crystalline (mc-Si) silicon surfaces were treated according to the present invention with a solution of NaOCl, TMAH and extra dissolved Si or added silicic acid. Figure 3 compares the reflectance properties of the mc-Si surface prior to treatment and after exposure for ten minutes at 80°C. The reflectance properties shown in Figure 3 are averaged over a few grains orientation. However, it appears the value does not change appreciably with the location on the wafer. These results suggest that the deposition rate of oxide coating is weakly dependent on the crystalographic orientation of Si wafer exposed. Therefore, it is believed that the coating method of the present invention can be applied to mc-Si as well a single crystal silicon substrates.

(018) The present invention of depositing silicon oxide coatings by exposure to wet chemical solutions, has several advantages of the CVD deposition techniques used in the prior art. In particular, the present invention can be carried out at low temperatures and provides faster deposition rates. In addition, the pressent invenition is a simpler process and requires less expensive equipment and fewer utility costs. Moreover, the present invention does not requires any hazardeous gaseous precursur chemicals. The results of the using the present invention are lower reflectance in the high energy wavelength band of natural light and overall reduced light reflectance when integrated across the light spectrum of 400nm to 1000 nm. The present invention is particularly advantageous in solar cell application, where the deposition of oxide anti reflective coating by wet chemistry can be carried out before as well as after contact print film deposition. The solutions used in the present inventino do not significantly etch either the aluminum or gold used for contacts. This results in better contact between the Al or Al/Ag contacts and the dopped silicon and therefore improves the electrical properties of the solar cell.

(019) It will be understood that the embodiments described herein are merely exemplary and that one skilled in the art may make variations and modifications without departing from the spirit and scope of the present invention. All such variations and modifications are intended to be included within the scope of the invention as described above. Further, all embodiments disclosed are not necessarily in the alternative, as various embodiments of the invention may be combined to provide the desired result.

CLAIMS

What is claimed is:

1. A method of depositing a silicon oxide film comprising:

exposing a silicon wafer to a wet chemical solution of sodium hypochloride, tetramethylammonium hydroxide and a hydrated silicate to form a layer of hydride silica on the surface of the wafer; and

dry heating to form a silicon oxide film.

2. The method of claim1 wherein the hydrated silicate is silicic acid.

3. The method of claim 1 wherein the deposition is accomplished at temperatures between 60°C and 90°C.

4. The method of claim 1 wherein in the wafer is a solar cell wafer and the silicon oxide film is an anti-reflective coating.

5. The method of claim 1 further comprising adjusting the thickness of the silicon oxide film by changing temperature or exposure time.

6. The method of claim 1 wherein the wafer is a single crystal Si (100) wafer.

7. The method of claim 1 wherein the wafer is a multi-crystalline wafer.

8. The method of claim 1 wherein the wafer is a phosphor doped wafer.

9. The method of claim 1 further comprising exposing the wafer to the wet chemical solution contact print film deposition is performed on the wafer.

10. A silicon oxide film deposited by the method comprising

exposing a silicon wafer to a wet chemical solution of sodium hypochloride, tetramethylammonium hydroxide and a hydrated silicate to form a layer of hydride silica on the surface of the wafer; and

dry heating to form the silicon oxide film.

11. The silicon oxide film of claim1o wherein the hydrated silicate is silicic acid.

12. The silicon oxide film of claim 10 wherein the wafer is a solar cell wafer and the silicon oxide film is an anti-reflective coating.

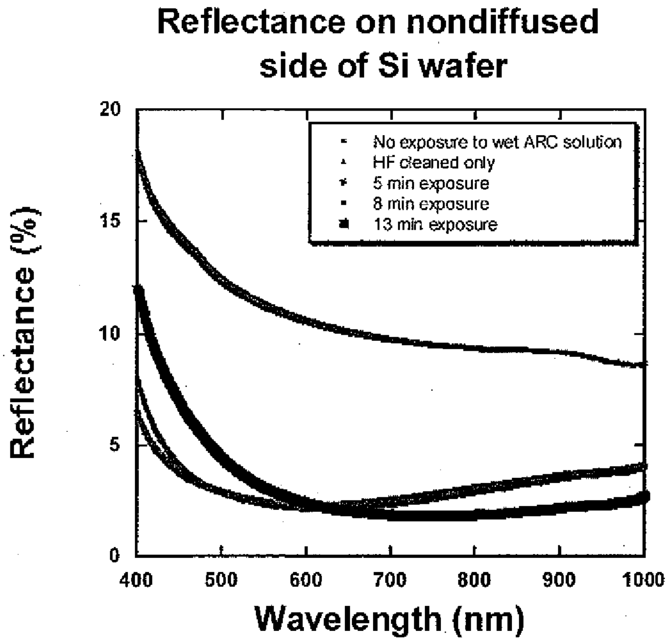
13. The silicon oxide film of claim 10 having a thickness of 63 nm to 120 nm.

14. The silicon oxide film of claim 10 wherein the wafer is a single crystal Si (100) wafer.

15. The silicon oxide film of claim 10 wherein the wafer is a multi-crystalline wafer.

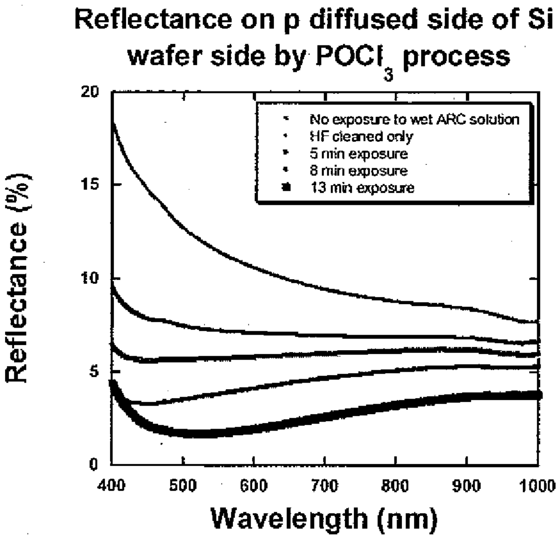
16. The silicon oxide film of claim 10 wherein the wafer is a phosphor doped wafer.

17. The silicon oxide film of claim 10 wherein the oxide film is deposited after contact print film deposition is performed on the wafer.



Reflectance on nondiffused side of Si wafer

FIG. 1



Reflectance on p diffused side of Si wafer side by $POCl_3$ process

FIG. 2

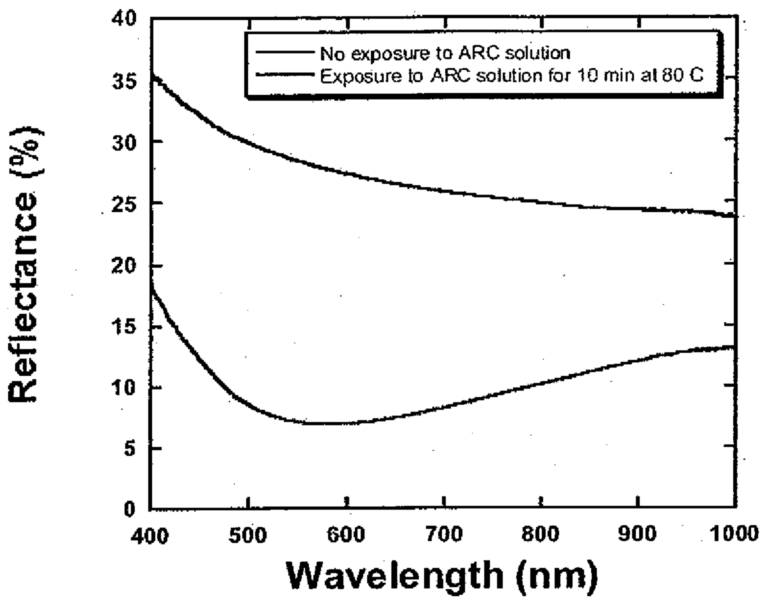

40
35
30
25
20
15
10
5
0
Reflectance (%)
400
500
600
700
800
900
1000
Wavelength (nm)
No exposure to ARC solution
Exposure to ARC solution for 10 min at 80 C

FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 12/31122

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - H01L 23/00 (2012.01)
USPC - 106/287.34; 257/646; 257/760

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) - H01L 23/00 (2012.01)
USPC - 106/287.34; 257/646; 257/760

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)
PubWEST (PGPB, USPT, EPAB, JPAB); Google: Silicon, wafer, substrate, solar cell wafer, single crystal, polycrystalline, multicrystalline, n-doped, p-doped, silicon oxide, coating, film, deposition, wet chemical etching, wet chemical, wet chemical oxidation, passivation, TMAH, tetramethyl ammonium hydroxide, sodium hypochlorite, hypochlorite, silici

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2003/0047111 A1 (Niume et al.). 13 March 2003 (13.03.2003); para [0009], [0012], [0048], [0050], [0055].	1-17
Y	US 5,445,698 A (Takano et al.). 29 August 1995 (29.08.1995); col. 2, ln. 42, 42-43, 42-49, 47-49; col. 3, ln. 26-41; col. 4, ln. 11-18, 34-37, 34-51, 51-55; col. 5, ln. 47; col. 7, ln. 4-9, 7, 8.	1-17
Y	US 2009/0183776 A1 (Kwag et al.). 23 July 2009 (23.07.2009); para [0013], [0028], [0032], [0083].	4, 6-8, 12-16
Y	US 7,671,001 B2 (Skee). 2 March 2010 (02.03.2010). col. 5, ln. 8-11, 45-47; col. 7, ln. 26-29; col. 11, ln. 15-17, 21-22, 51-62.	9, 17

☐ Further documents are listed in the continuation of Box C. ☐

* 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
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"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

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Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774