[54] METHODS FOR PASSIVATING SILICON DEVICES AT LOW TEMPERATURE TO ACHIEVE LOW INTERFACE STATE DENSITY AND LOW RECOMBINATION VELOCITY WHILE PRESERVING CARRIER LIFETIME

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[51] Int. Cl. 6


[58] Field of Search 437/247, 235, 437/238, 937, 939, 941, 10-13

[56] References Cited

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[57] ABSTRACT

A new process has been developed to achieve a very low SiOx/Si interface state density Ditt, low recombination velocity S (<2 cm/s), and high effective carrier lifetime Teff (>5 ms) for oxides deposited on silicon substrates at low temperature. The technique involves direct plasma-enhanced chemical vapor deposition (PECVD), with appropriate growth conditions, followed by a photo-assisted rapid thermal annealing (RTA) process. Approximately 500-A-thick SiOx layers are deposited on Si by PECVD at 250° C. with 0.02 W/cm² rf power, then covered with SiN or an evaporated thin aluminum layer, and subjected to a photo-assisted anneal in forming gas ambient at 350° C., resulting in an interface state density Ditt in the range of about 1–4x10¹⁰ cm⁻² eV⁻¹, which sets a record for the lowest interface state density Ditt for PECVD oxides fabricated to date. Detailed analysis shows that the PECVD deposition conditions, photo-assisted anneal, forming gas ambient, and the presence of an aluminum layer on top of the oxides during the anneal, all contributed to this low value of interface state density Ditt. Detailed metal-oxide semiconductor analysis and model calculations show that such a low recombination velocity S is the result of moderately high positive oxide charge (5x10¹⁴–1x10¹⁵ cm⁻²) and relatively low midgap interface state density (1x10¹⁰–4x10¹⁰ cm⁻²eV⁻¹). Photo-assisted anneal was found to be superior to furnace annealing, and a forming gas ambient was better than a nitrogen ambient for achieving a very low surface recombination velocity S.

28 Claims, 6 Drawing Sheets
Fig. 1
(PRIOR ART)
Fig. 2A

Fig. 2B
Fig. 3A

C/Co(x)

PECVD oxide

QS

HF

Vg (v)

Fig. 3B

D\text{it} (cm^{-2}eV^{-1})

E-E_{v}(eV)

10^{10}

10^{11}

10^{12}
**Fig. 4**

- **PECVD only**
- **PECVD + N₂, \( \tau = 100 \mu s \)**
- **PECVD + FGA, \( \tau = 5 \text{ ms} \)**

**Fig. 5**

\[ S = 2.0 \pm 0.12 \text{ cm/s (PECVD Oxide)} \]

\[ \frac{1}{\tau_e} = \frac{1}{\tau_b} + \frac{2S}{L} \]

\[ \tau_b = 23 \pm 2.5 \text{ ms} \]
Fig. 6

Fig. 7
METHODS FOR PASSIVATING SILICON DEVICES AT LOW TEMPERATURE TO ACHIEVE LOW INTERFACE STATE DENSITY AND LOW RECOMBINATION VELOCITY WHILE PRESERVING CARRIER LIFETIME

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FIELD OF THE INVENTION

The present invention relates generally to fabrication and passivation of silicon devices, and more particularly, to a method for passivating a surface of silicon at low temperature to achieve both low interface state density $D_s$ and low surface recombination velocity $S$ at the surface, while preserving effective carrier lifetime $T_{car}$, and to a method for passivating surface and bulk defects in silicon at low temperature to achieve both low surface recombination velocity and high minority carrier lifetime within the internal region of the silicon.

BACKGROUND OF THE INVENTION

Material defects, such as dangling bonds, can reside on the surface or within silicon material. These defects can adversely affect operation of a silicon device, such as a transistor or solar cell, because electron-hole pairs recombine with the defects and are essentially lost. Accordingly, silicon surfaces and bodies are often passivated in order to tie up the defects. In this document, “passivation” means the process of tying up, eliminating, or otherwise rendering inoperative as to current flow, defects in a material.

Several different indicia are used in the industry for indicating the degree to which a surface or body is characterized by defects. “Interface state density,” or “$D_s$,” is sometimes utilized by those skilled in the art and is essentially a measure of the number of defects per unit of area. Another variable used in the industry is the “recombination velocity,” or “$S$,” which is a measure of the rate at which electron-hole pairs migrate toward the defects. The recombination velocity $S$ is mathematically proportional to the interface state density $D_s$. In other words, when the recombination velocity $S$ is low, then the interface state density $D_s$ is low, and vice versa. Furthermore, the lower the interface state density $D_s$ and/or the recombination velocity $S$ of a material, the less defects in the material.

In order to passivate a silicon surface to achieve a low interface state density and/or a low recombination velocity, an oxide layer of SiO$_x$ (where $x$ is any number) is sometimes formed over the silicon surface. In a sense, the oxide ties up the dangling bonds of the defects. Typically, a very thin (approximately 100 Å) SiO$_x$ layer is used in high-efficiency solar cells, metal-oxide semiconductor field-effect transistors (MOSFET), and advanced bipolar devices. In regard to solar cells, see M. A. Green, *High Efficiency Silicon Solar Cells*, Trans. Tech. Aedermannsdorf, 1987, and in regard to bipolar devices, see J. Ahn, et al., *IEEE Electron Device Lett.*, EDL-13, 186 (1992). However, the techniques in the industry for forming the SiO$_x$ layer on the silicon surface generally require undesirable high temperature processing steps. The thin SiO$_x$ layer is typically formed by oxidation at temperatures greater than 700° C. High temperature processing steps can limit the degree of miniaturization and can also degrade the quality of starting material.

The deposition of oxides on silicon at low temperature is extremely desirable for achieving greater flexibility in a process sequence, tight dimensional control, and preservation of minority carrier lifetime. Low temperature processing becomes increasingly important as the limits of integration or number of devices on an integrated circuit (IC) chip is increased. Low temperature processing is also crucial for discrete devices, for instance, solar cells as lower quality silicon materials are used to reduce cost of photovoltaic devices. Moreover, the use of a low temperature deposition oxide, such as SiO$_x$, would be desirable in order to maintain device dimensions within tight tolerance and reduce the process-induced degradation of bulk lifetime. Unfortunately, low-temperature processing generally produces low-quality oxides with high interface state density $D_s$ and high recombination velocity $S$. In this regard, see E. H. Nicollian et al., MOS (Metal Oxide Semiconductor) *Physics and Technology*, Wiley, N.Y., 1982.

Thus, there is currently much ongoing research in the industry in developing techniques for producing high quality oxides at low temperature. Many of these techniques utilize plasma-enhanced chemical vapor deposition (PECVD) to deposit oxides. Remote PECVD and plasma oxidation has recently produced a high quality SiO$_x$/Si interface with an interface state density $D_s$ of approximately $1.7 \times 10^{10}$ cm$^{-2}$ eV$^{-1}$, but the direct PECVD process gives $D_s$ values of approximately $5 \times 10^{10}$ cm$^{-2}$ eV$^{-1}$. These $D_s$ values are slightly higher, but nearly comparable, to thermally grown oxides at high temperatures.

Table A, which is set forth hereafter, summarizes some of the recent developments relative to PECVD oxides, along with the oxide interface formation techniques used to obtain low $D_s$ at low temperatures. In most prior art techniques using low temperature PECVD to deposit oxides, attention has been focused on the interface formation technique during the oxide growth, rather than on the post-deposition treatments.

<table>
<thead>
<tr>
<th>Ref/Year</th>
<th>Interface Formation Technique</th>
<th>$T_{pre}$ (°C)</th>
<th>Post-Anneal Condition</th>
<th>$D_s$ (cm$^{-2}$ eV$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/1988</td>
<td>Remote PECVD in situ hydrogen plasma treatment</td>
<td>300</td>
<td>400° C. in N$_2$, 30 min</td>
<td>$3.7 \times 10^{10}$</td>
</tr>
<tr>
<td>2/1991</td>
<td>Low rate plasma oxidation</td>
<td>350</td>
<td>400° C. in 10, Torr. 5 min, 30 min</td>
<td>$2.2 \times 10^{10}$</td>
</tr>
<tr>
<td>3/1992</td>
<td>Remote PECVD, wet HF etching, plasma oxidation</td>
<td>350</td>
<td>400° C. in N$_2$, 30 min</td>
<td>$1.7 \times 10^{10}$</td>
</tr>
<tr>
<td>4/1986</td>
<td>Direct PECVD, slow rate (60 Å/min)</td>
<td>350</td>
<td>400° C. in forming gas, 30 min</td>
<td>$4 \times 10^{10}$</td>
</tr>
<tr>
<td>5/1991</td>
<td>Direct PECVD, two temperature, 300–350° C. in forming gas, 30 min</td>
<td>$5.3 \times 10^{10}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
It is also important to recognize that there is a fundamental difference between deposited oxides and thermally-grown oxides. In thermally-grown oxides, the SiO₂/Si interface is formed at the end of the process and is located underneath the native oxide. In the case of deposited oxides, the deposition takes place on top of the native oxide, and the native oxide stays at the interface. Consequently, the interface property of the deposited oxides depends strongly on the native oxide. Therefore, the interface formation technique is more critical for obtaining low interface state density \( D_u \) in the PECVD oxides.

As indicated in Table A, in a known remote PECVD technique, excited species from a remote oxygen plasma interact with silane (SiH₄) in the deposition zone to avoid ion bombardment damage on the surface. In addition, the use of in situ hydrogen plasma treatment to reconstruct the silicon surface just prior to the deposition was also believed to be a key factor in obtaining low interface state density \( D_u \) of about \( 3.7 \times 10^{10} \text{cm}^{-2} \text{eV}^{-1} \).

**Low growth rate plasma oxidation of silicon in dilute oxygen/helium plasma** is another promising technique known in the art, as is indicated in Table A. In this technique, a plasma growth oxide forms a high quality interface below the original native oxide, and then the conventional PECVD oxide is deposited on top of the native oxide. Thus, the interface is dominated by a good quality plasma grown oxide rather than the native oxide or the PECVD oxide. A low interface state density \( D_u \) value of about \( 2.2 \times 10^{10} \text{eV}^{-1} \text{cm}^{-2} \) was reported using this technique in A. A. Bright et al., *Appl. Phys. Lett.* 58, 619 (1991).

Another known technique utilizes the combination of remote PECVD and plasma oxidation technique, along with wet hydrogen fluoride etching of the native oxide just prior to the deposition. This technique can produce a interface state density \( D_u \) as low as about \( 1.7 \times 10^{10} \text{eV}^{-1} \text{cm}^{-2} \), which is comparable to oxides prepared by thermal oxidation. In this regard, see T. Yasuda et al., *Appl. Phys. Lett.* 60, 434 (1992).

**TABLE A-continued**

<table>
<thead>
<tr>
<th>Ref/Year</th>
<th>Interface Formation Technique</th>
<th>( T_{dep} ) (°C)</th>
<th>Post-Anneal Condition</th>
<th>( D_u ) (cm⁻²eV⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>in situ H plasma treatment</td>
<td>60 min</td>
<td>4.0 ( \times 10^{10} \text{(n)} )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Another object of the present invention is to provide a method for passivating a surface of silicon using low temperature PECVD. Another object of the present invention is to provide a method for passivating a surface of silicon using low temperature PECVD and oxides SiO₂. Another object of the present invention is to provide a method for reducing the interface state density \( D_u \) and the recombination velocity \( S \) at a SiO₂/Si interface. Another object of the present invention is to provide a low temperature surface passivation technique that can also passivate defects in bulk silicon. Another object of the present invention is to provide a method for reducing leakage current for diffused junctions in Si devices.

The present invention provides methods for passivating silicon at the surface and in the bulk region of the silicon. The methods can be used to produce, at the surface of silicon and at low temperature, high quality oxides and nitrides having both low interface state density \( D_u \) and low surface recombination velocity \( S \), while preserving minority carrier lifetime and high recombination lifetime in the bulk. The present invention also provides for effective surface passivation of silicon emitters or diffused junctions with low leakage current.

**SUMMARY OF TEE INVENTION**

An object of the present invention is to overcome the problems and inadequacies in regard to the prior art as noted above and as generally known in the industry.

Another object of the present invention is to provide a method for passivating a surface of silicon at low temperature to achieve both low interface state density \( D_u \) and low surface recombination velocity \( S \) at the surface, while preserving high minority carrier lifetime.

Another object of the present invention is to provide a method for passivating a surface of silicon using low temperature PECVD. Another object of the present invention is to provide a method for reducing the interface state density \( D_u \) and the recombination velocity \( S \) at a SiO₂/Si interface. Another object of the present invention is to provide a low temperature surface passivation technique that can also passivate defects in bulk silicon. Another object of the present invention is to provide a method for reducing leakage current for diffused junctions in Si devices.

The present invention provides methods for passivating silicon at the surface and in the bulk region of the silicon. The methods can be used to produce, at the surface of silicon and at low temperature, high quality oxides and nitrides having both low interface state density \( D_u \) and low surface recombination velocity \( S \), while preserving minority carrier lifetime and high recombination lifetime in the bulk. The present invention also provides for effective surface passivation of silicon emitters or diffused junctions with low leakage current.

The novel method involves the following steps. Using PECVD, a thin silicon oxide layer (SiO₂) is deposited or formed over a silicon surface. The silicon may be n-doped or p-doped silicon. The SiO₂ layer is about 10 nm in thickness in the preferred embodiment and is deposited at about 250°C. The SiO₂ layer then undergoes a photo-assisted rapid thermal annealing (RTA) process in a forming gas at about 300°C to 350°C for at least 20 minutes. The forming gas preferably has hydrogen (H₂; source of H⁺) and is provided over the SiO₂ during the RTA process. The
preferred embodiment utilizes a forming gas of 90 percent ambient nitrogen (N\textsubscript{2}) and 10 percent hydrogen (H\textsubscript{2}). The hydrogen further passivates the silicon surface and bulk defects within the internal region of the silicon.

Optionally, the method may be modified to include one or more of the following steps. A thin 60 nm SiN layer is deposited over the oxide layer SiO\textsubscript{x} at preferably about 275°C, prior to the anneal, in order to further minimize interface state density \( D_{it} \) and surface recombination velocity \( S \). A thin aluminum layer is deposited over the oxide layer SiO\textsubscript{x} via an evaporation technique, prior to the anneal, in order to further minimize interface state density \( D_{it} \) and surface recombination velocity \( S \).

By using the 10 nm SiO\textsubscript{x}, the present invention gives a desirable surface recombination velocity \( S \) of less than about 2 cm/s, an effective lifetime of greater than about 5 ms, and a bulk lifetime of greater than about 20 ms maintained for high resistivity (>500 ohm-cm) float zone silicon. Moreover, very low interface state density \( D_{it} \) in the approximate range of \( 1-4\times10^{10} \) cm\textsuperscript{-2}V\textsuperscript{-1} for PECVD SiO\textsubscript{x}/Si interface has been routinely produced on 10 ohm-cm silicon by the present invention. The present invention also provides very effective emitter surface passivation, low leakage current density for phosphorus diffused junction in the approximate range of \( 4-6\times10^{-14} \) A/cm\textsuperscript{2}, depending on the surface concentration, has been achieved. Detailed analysis conducted by the inventors shows that the PECVD deposition conditions, photo-assisted anneal, forming gas ambient, the presence of an aluminum layer during the anneal, and cleaning procedure for silicon wafer and RF chamber, all contribute to the desirable properties achieved by the present invention.

In addition to achieving the objects set forth previously, the present invention has many other advantages, a few of which are denoted hereafter.

An advantage of the present invention is that a SiO\textsubscript{x}/Si interface can be produced with an interface state density \( D_{it} \) which is two to four times lower than any other SiO\textsubscript{x}/Si interface produced using prior art low temperature direct PECVD techniques.

Another advantage of the present invention is that a SiO\textsubscript{x}/Si interface can be produced with a recombination velocity \( S \) of about 1 cm/second, which is very low and optimum.

Another advantage of the present invention is that a SiO\textsubscript{x}/Si interface can be produced while preserving high minority carrier lifetime in the silicon.

Another advantage of the present invention is that it can be used to passify an emitter so that the emitter saturation current \( J_0 \) is minimized.

Another advantage of the present invention is that it can be applied in solar cells, photovoltaic devices, and junction devices, such as photovoltaic devices and larger area power devices.

Another advantage of the present invention is that both surface and bulk defects can be passivated in silicon at low temperature to achieve both low interface state density and low surface recombination velocity within the internal region of the silicon. Thus, if desired, lower cost, low quality silicon having numerous defects could be utilized and could be processed in accordance with the present invention to transform the lower quality silicon to a much higher quality material having few defects.

Another advantage of the present invention is that it is simple to implement.

Another advantage of the present invention is that it is performed in a short period of time.

Another advantage of the present invention is that it has a low thermal budget.

Another advantage of the present invention is that it is a commercially viable process due to its simplicity, safety, and requisite operation time.

Another advantage of the present invention is that it is a high vacuum system is not needed.

Another advantage of the present invention is that it has a high temperature furnace is not needed.

Other objects, features, and advantages of the present invention will become apparent to one with skill in the art upon examination of the following drawings and detailed description. It is intended that all such additional objects, features, and advantages, which are not explicitly mentioned but are implicit from the discussion in this document, be included herein within this disclosure and within the scope of the present invention.

**BRIEF DESCRIPTION OF THE DRAWINGS**

The present invention can be better understood with reference to the following drawings.

**FIG. 1** is a schematic diagram of a conventional PECVD system.

**FIG. 2A** is a graph of measured high frequency (HF) and quasi-static (QS) C-V data \( C/C_{ox} \) versus \( V_g \) on MOS capacitors wherein an oxide was formed in forming gas ambient without an aluminum layer;

**FIG. 2B** is a graph of measured HF and QS C-V data \( C/C_{ox} \) versus \( V_g \) on PE MOS capacitors wherein an oxide was formed in forming gas ambient with an aluminum layer;

**FIG. 3A** is a graph of HF and QS C-V data \( C/C_{ox} \) versus \( V_g \) for a best MOS capacitor with PECVD oxide;

**FIG. 3B** is a graph of the interface state density \( D_{it} \) \( D_{it} \) versus positive charge \( E-E_F \) for the best MOS capacitor of **FIG. 3A** showing a minimum interface state density \( D_{it} \) around a midgap of \( 1.1\times10^{-10} \) eV/cm\textsuperscript{2}.

**FIG. 4** is a graph of photoconductive voltage decay transients (voltage versus transition time) for silicon samples with different treatments: (a) thin PECVD SiO\textsubscript{x} on Si; (b) PECVD SiO\textsubscript{x} on Si which is annealed in \( N_2 \) ambient using RTA; and (c) PECVD SiO\textsubscript{x} on Si which is annealed in forming gas ambient using RTA;

**FIG. 5** is a graph of \( 1/T_{sff} \) versus 1/L which gives the recombination velocity \( S \) and the bulk lifetime \( T_s \) (intercept on 1/T\textsubscript{sff} axis);

**FIG. 6** is a graph of a calculated positive charge effect (effective recombination velocity \( S_{eff} \) versus positive charge density) on recombination velocity \( S \) by a simplified model using uniform distribution of interface states;

**FIG. 7** is a graph of effective lifetime degradation (effective lifetime \( T_{sff} \) versus time) over a 2 month period for a PECVD SiO\textsubscript{x}/Si layer and a combination of a SiN layer atop a PECVD SiO\textsubscript{x}/Si layer; and

**FIG. 8** is a graph of bulk passivation (internal quantum efficiency versus wavelength) of the silicon sample during RTP when a hydrogen source is present in the forming gas.

**DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

Direct low temperature PECVD in conjunction with a subsequent photo-assisted anneal was used to achieve a record low interface state density \( D_{it} \) in metal-oxide-semiconductor (MOS)/(Al/oxide/Si) structures. The PECVD pro-
cess and systems for performing the PECVD process are well known in the art. However, for the purpose of better understanding the present invention, a typical PECVD system is illustrated in FIG. 1. As shown in FIG. 1, the PECVD system 11 has a substrate 17, preferably a silicon wafer in the front side of the wafers was mechanically polished and the back side was chemically etched. Prior to oxide deposition, the wafers were cleaned as follows: (a) Ultrasonic degreasing in solvents (TCE, acetone, methanol), followed by running de-ionized (DI) water rinse; (b) soak in HF(1):H₂O₁₀(1) for 1 min and DI water rinse; (c) boil in HCl(1):H₂O₂(1) for 1 min and DI water rinse; (d) soak in agitated HF(1):HN0₃(50) for 30 seconds followed by DI water rinse. Just before the PECVD deposition in the reactor 13 of FIG. 1, the wafers were dipped in HF(1):H₂O₁₀(1) for 1 min, rinsed in running DI water for 30 seconds, and then blown dry with N₂. This step was important for obtaining reproducible results and mitigating the undesirable effects of the native oxide on the interface. Samples were then loaded into the PECVD system 11 of FIG. 1 for pump down. The time lag between the drying to pump down was typically 1 min.

The top electrode 12a was maintained at about 80°C and the temperature of the substrate 17 was kept at about 250°C. A low power level of 20 W (about 0.02 W/cm²) was used to prevent surface damage by ion bombardment. A mixture of 2% SiH₄ and 250 scm for N₂O was utilized as the gases 18 over the substrate 17. The total reactor pressure in reactor 13 was maintained at 0.3 Torr. Under these conditions the growth rate was about 100 Å/min. About 500 Å PECVD SiO₂ was deposited on the front side of the wafers followed by thermal evaporation of 2000 Å aluminum for the front gate electrode and backside contact.

The samples were then subjected to a photo-assisted thermal anneal in a rapid thermal annealing (RTA) system at a temperature of about 350°C in a forming gas ambient for approximately 20 min. RTA systems are well known in the art. The RTA system was heated by tungsten halogen lamps. Moreover, all the experiments described in this document were conducted in a class 1000 clean room.

The interface state density Dᵢ of the SiO₂/Si interface was determined by conventional high-low frequency capacitance-voltage (C–V) measurements. The high frequency C–V was measured at 1 MHz and quasistatic (QS) C–V was measured by voltage ramp method with a ramp rate of 0.1 V/s.

Three sets of samples with identical PECVD deposition, but with different post-deposition treatments, were tested to evaluate the effect of post-deposition treatments on interface state density Dᵢ. The first set of samples, which saw no treatment at all after the PECVD deposition, gave interface state density Dᵢ values of above 10¹² cm⁻² ev⁻¹. The second set of samples were subjected to a photo-assisted anneal in forming gas without the aluminum layer on top of the oxide and the aluminum gate electrode with size 0.785 mm² was evaporated after the anneal. FIG. 2A shows typical low-high frequency C–V curves for group 2 MOS capacitors which gave an average Dᵢ value of 4.0x10¹¹ cm⁻² ev⁻¹. The third set was subjected to a photo-assisted anneal in forming gas after the aluminum electrode was evaporated on top of the oxide. Typical low-high frequency curves are shown in FIG. 2B. The third set gave a typical Dᵢ value of approximately 3.3x10¹⁰ cm⁻² ev⁻¹ with the best Dᵢ value of 1.1x10¹¹ cm⁻² ev⁻¹ at midgap, which is comparable to the thermal oxides. However, the positive charge in these PECVD oxides was of the order of 10¹¹ cm⁻², which is much higher than the thermal oxides.

FIGS. 2A and 2B clearly demonstrate the beneficial effect of aluminum during the photo-assisted anneal, because it reduces the Dᵢ value by more than one order of magnitude. The merit of having an aluminum layer during the annealing process has also been reported for thermal oxides. In this regard, see E. H. Nicollin et al., MOS Physics and Technology, Wiley, N.Y. (1982). It has been suggested that the presence of Al helps to generate atomic hydrogen during the forming gas anneal, which ties up the dangling bonds and reduce Dᵢ. Our results in FIGS. A and 2B show that the PECVD oxides also respond favorably to the presence of aluminum during the anneal. It should be mentioned that there is some spread in the Dᵢ values from MOS capacitors located on the same wafer. The range of midgap Dᵢ value for the samples treated by the photo-assisted anneal with an aluminum layer was 1x4x10¹⁰ cm⁻² ev⁻¹.

FIG. 3A shows the best C–V characteristics measured on a MOS capacitor with the PECVD oxide. The near-ideal C–V curve endorses the excellent interface quality. The Dᵢ spectrum calculated from the high-low frequency curve of FIG. 3A is shown in FIG. 3B, which shows a minimum interface state density Dᵢ value of 1.1x10¹¹ cm⁻² ev⁻¹ at the midgap. This represents the lowest interface state density Dᵢ value achieved to date in the industry for PECVD oxides.

EXPERIMENT II

Samples of the silicon with SiO₂ layer were subjected to conventional furnace anneal at 400°C in the forming gas for 30 min after the PECVD oxide deposition and aluminum evaporation as described in Experiment I, which discussion is incorporated herein by reference. The Dᵢ value for these samples was found to be in the range of 4x10¹⁰ cm⁻² ev⁻¹, with the lowest value of about 4x10¹⁰ cm⁻² ev⁻¹. These values are consistent with the results reported in the reference in the fourth position of Table A. From the comparison between the furnace and photo-assisted anneal experiments, it is clear that optical effect during the photo-assisted rapid thermal anneal process is important. Some investigators have attributed the positive effects of photo-annealing to the electronic excitations which can promote additional reactions. For example, consider R. Singh, Appl. Phys. Lett., v.
oxide deposition followed by RTA in forming gas ambient. It can be seen from FIG. 4 that the annealed PECVD oxides gave a much stronger signal compared to the unannealed oxide which has very high recombination velocity S at the SiO$_2$/Si interface. FIG. 4 demonstrates that the RTA process is important for maintaining high effective lifetime, and the forming gas produces much better results compared to the N$_2$ ambient. The measured effective lifetimes were 5 ms and 100 µs for the forming gas and N$_2$ ambient, respectively. These results suggest that the presence of 10% hydrogen in the forming gas plays an important role in improving the interface.

**EXPERIMENT IV**

A comparison is also made between the furnace-annealed and rapid-thermal-annealed (RTA) samples in forming gas ambient. Samples of the silicon with SiO$_2$ were subjected to furnace annealing and RTA, separately, to analyze the effects. The annealing temperatures and time were kept the same for both cases. The lifetime dependence on RTA temperature was studied in the temperature range of 300°C–450°C. The measured effective lifetimes for furnace and rapid-thermal-annealed samples are listed in Table B hereafter, which shows that the RTA process results in higher effective lifetime than the furnace anneal for the same temperature. The furnace anneal temperature had to be raised to come close to the RTA results. This suggests that the additional optical heating during the RTA process makes hydrogen passivation of the interface defects more efficient. The effective lifetime is sensitive to the annealing temperature because hydrogenation of the interface defect is closely related to the temperature. Table B also indicates that the RTA annealing temperature of 350°C is optimum, probably because annealing at higher temperature results in evolution of hydrogen rather than passivation of the interface.

**TABLE B**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$\tau_e$ after RTA Anneal (ms)</th>
<th>$\tau_e$ after furnace anneal (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>1.1</td>
<td>—</td>
</tr>
<tr>
<td>350</td>
<td>5.5</td>
<td>1.0</td>
</tr>
<tr>
<td>400</td>
<td>4.7</td>
<td>4.2</td>
</tr>
<tr>
<td>450</td>
<td>4.1</td>
<td>1.6</td>
</tr>
</tbody>
</table>

**EXPERIMENT V**

The effect of the oxide on the interface recombination velocity S was also explored. Interface recombination velocity S and true bulk lifetime $T_e$ were determined by measuring $T_{S}$ on the annealed oxide wafers with five different thicknesses L. FIG. 5 shows a typical 1/$T_{S}$ versus 1/L plot where the intercept of the straight line corresponds to $T_e$ and the slope gives the S value. $T_e$ and S were 23 ms and 2 cm/s, respectively, at an injection level of 5x10$^{14}$ cm$^{-3}$. The S value showed an increase from 2 to 30 cm/s when the injection level was increased from 5x10$^{14}$ to 1x10$^{16}$ cm$^{-3}$. It should be recognized that recombination velocity S is a strong function of SiO$_2$/Si interface state density $D_{it}$ positive charge density in the oxide, carrier injection level, and capture cross section for electrons and holes. See T. Warabisako et al., *Technical Digest of the International, v. PVSEC-5*, p. 583 (1990); A. G. Aberle et al., *J. Appl. Phys., v. 71*, p. 4422 (1992) and R. B. M. Girisch et al., *IEEE Trans.*

The inventors herein have developed a theoretical model to calculate the effect of these parameters on the recombination velocity S. The low S value can be either due to low-interface state density Ds, or high density of positive charge in the PECVD oxide, or a combination of both. If the positive charge density is larger than the interface state density Ds, it will cause significant downward bending of the energy band, increasing the difference in electron and hole concentration velocity, and resulting in reduced recombination at the interface. High and low-frequency C-V measurements on the PECVD oxides showed a large flat-band voltage shift with positive charge density in the range of 5x10⁻¹¹–1x10⁻¹² cm⁻², and interface state density Ds in the range of 1x10⁻¹⁰–5x10⁻¹⁰ cm⁻² eV⁻¹ at midgap. Since the C-V measurements were done on low-resistivity (0.2 Ω cm) samples, interface state density Ds may be slightly different from that for the high-resistivity samples used for S and T measurements by PCD measurements. However, the positive charge in oxides may be virtually the same for both the high and low-resistivity samples.

Model calculations in FIG. 6 demonstrate quantitatively the relationship between the recombination velocity S and positive charge at an injection level of 5x10¹⁴ cm⁻³, assuming uniform interface state density Ds with electron and hole cross sections are assumed of 10⁻¹⁴ and 10⁻¹⁶ cm⁻², respectively. See R. B. M. Girisch et al., IEEE Trans. Electron Devices, ED-35, 203 (1988). According to FIG. 6, the positive charge in the range of 1–5x10¹² cm⁻² can significantly reduce the interface recombination velocity S, if the interface state density Ds is in the range of 5–10x10¹⁰ cm⁻².

Oxide charge is undesirable for integrated-circuit devices because it affects the threshold and breakdown voltage, and the films reported here may not be good enough for complimentary MOS (CMOS) applications. However, for devices such as high-efficiency solar cells in which the surface recombination is of major concern rather than oxide charge, the positive charge of PECVD oxide can indeed be very helpful in reducing the interface recombination to improve device performance. It should be recognized that if the PECVD oxides are used in concentrator cells, where the injection can exceed 10⁶ cm⁻², the interface recombination velocity S can reach as high as 30–60 cm/s based on our experimental measurements.

EXPERIMENT VI

The stability of the thin PECVD SiO₂/Si interface was investigated because the increase in interface recombination velocity S with UV light exposure has been reported for high-quality thermal oxides. In this regard, consider P. E. Gruenbaum et al., Appl. Phys. Lett. 52, 1407 (1988). Some investigators have also shown that the presence of moisture near the interface increases not only negative charges in oxides but also the recombination center density at the interface. For example, see E. H. Nicollian, J. Vac. Sci. Technol., v. 14, p. 1118 (1977), and E. H. Nicollian et al., MOS (Metal Oxide Semiconductor) Physics and Technology, Chapter 11, Wiley, N.Y. (1982). Therefore, a protective layer on top of the oxide, such as a metal contact in MOS devices or antireflection coating in solar cells, can have a significant impact on the stability. When the unprotected PECVD oxide was exposed to the air for several days the effective lifetime was found to decrease with time, as shown in FIG. 7. The exact reason for this decay is not fully understood at this time. However, the role of moisture cannot be ruled out, since thinner oxides showed faster degradation. It is also important to note that the reduced effective lifetime can be fully restored by reannealing the oxides.

An attempt was made to prevent this degradation by depositing a PECVD SiN layer on top of the oxide. FIG. 7 shows the variations in Teff with time for a duration of 2 months, for the unprotected thin SiO₂ as well as SiN-protected SiO₂. In the case of unprotected SiO₂, Teff decreased from 7 to 3.7 ms in 3 days and to 1.5 ms in 1 month before stabilizing. In contrast, thin SiO₂ capped with SiN was found to be extremely stable and showed virtually no degradation for the period of 2 months. The SiN layer, which is known to block the moisture from reaching the interface, may therefore contribute to the stability improvement. It is interesting to note that the SiN layer not only successfully prevents the degradation but also gives a higher effective lifetime (>10 ms) and very low S (≤5 cm/s). A large amount of hydrogen in the PECVD SiN films, detected by Fourier transform infrared (FTIR), along with the additional positive charge in the SiN (≥10²⁵ cm⁻³) may be responsible for such a low S and high Teff. FTIR is described in A. Rohatgi, Z. Chen, W. A. 20 Doolittle, J. Salami, and P. Sana, Final Technical Report to National Renewable Energy Laboratory, March 1992. In addition, the value of the recombination velocity S in the SiN-capped PECVD oxide only went up to 15 cm/s at the injection level of 10¹⁰ cm⁻³.

In conclusion, Experiments III–VI show that for the first time direct PECVD SiO₂ deposition at 250°C followed by RTA at 350°C can result in a high effective lifetime (>5 ms) and very low recombination velocity S (≤2 cm/s). Such a low temperature process retains the true bulk lifetime which was found to be 23 ms after the PECVD and RTA processes. MOS measurements coupled with model calculations confirmed that the high effective lifetime and low surface recombination velocity S results from the combination of low-interface state density Ds (approximately 5x10¹⁴ cm⁻² eV⁻¹) and relatively high positive charge density (5–10x10¹¹ cm⁻³) in the PECVD oxide. Some degradation in the effective lifetime was observed in the thin PECVD oxides, but the PECVD SiN layer cap was found to be very effective in preventing this degradation and enhancing Teff. The annealing studies showed that the forming gas ambient is superior to nitrogen, and that the RTA is better than the conventional furnace anneal for achieved low interface recombination velocity S and high effective lifetime.

EXPERIMENT VII

In addition to passivating surface defects, as described previously with respect to Experiments I–VI, bulk defects in the internal region of the silicon substrate 17 can be passivated at low temperature to achieve both low interface state density and low surface recombination velocity S within the internal region of the silicon. The bulk defects which can be passivated include vacancies, grain boundaries, and dislocations, which terms are well known in the art. Thus, if desired, lower cost substandard silicon having numerous defects could be utilized and could be processed in accordance with the present invention to transform the substandard silicon to a much higher quality material having few defects.

In order to demonstrate the bulk defect passivation effect due to the present invention, internal quantum efficiency (IQE) was measured on solar cells. The cells were made on
low-cost p-type Edge-defined Film-fed Growth (EFG) sheet silicon material. The cells were simple n+pp+ structure, in which n+ was formed by phosphorus diffusion on front surface, and p+ was formed by Al diffusion on back surface of wafers. Thin layer PECVD SiOx (10 nm, n=1.45) was deposited on the front surface. Then PECVD SiN (59 nm, n=2.27), and SiOx (95 nm, n=1.45) were deposited on the top of the thin SiOx layer, respectively. The thin SiOx (10 nm) coupled with SiN (59 nm) was used as passivation, and SiOx (95 nm) was used for antireflection. After PECVD depositions, the solar cells were photo-assisted annealed in a lamp-heated rapid thermal process (RTP) system at 350° C. in forming gas or in nitrogen ambient for 20 min. The IQE measurements were conducted by Optronic 764-428 system. A typical IQE of these EFG solar cells is shown in FIG. 8. The IQE was measured before the PECVD deposition, after PECVD deposition, after N2 anneal (N2 RTP), and after forming gas anneal (FG RTP). The improvement of IQE in short wavelength (<700 nm) due to the PECVD deposition and RTP anneal shows the surface passivation effect, while the increase of IQE in long wavelength (>800 nm) represents the bulk defect passivation effect due to the PECVD coating and photo-assisted anneal.

FIG. 8 is a graph of bulk passivation (internal quantum efficiency versus wavelength) of the silicon sample during RTP when a hydrogen source is present in the forming gas. This graph shows that defects are tied up in the bulk of the silicon. It is believed that during RTP, hydrogen ion H+ migrate into the upper surface of the SiOx layer and then into the bulk of the silicon to the defects, thereby passivating the defects. It will be obvious to those skilled in the art that many modifications and variations may be made to the experiments and embodiments described above without substantially departing from the principles of the present invention. It is intended that all such modifications and variations be included herein within the scope of the present invention, as set forth in the following claims.

Wherefore, the following is claimed:
1. A method for passivating a surface of crystalline silicon, comprising the steps of:
forming an oxide layer over said crystalline silicon using a plasma enhanced chemical vapor deposition process; and
lowering an interface state density associated with said silicon by heating said oxide layer and said silicon with a light radiating source after said plasma enhanced chemical vapor deposition process.
2. The method of claim 1, wherein said silicon is n-type silicon.
3. The method of claim 1, wherein said silicon is p-type silicon.
4. The method of claim 1, wherein said oxide layer is formed below about 250 degrees Celsius.
5. The method of claim 1, wherein said heating step is performed at between 300° and 450° C.
6. The method of claim 1, wherein said heating step includes the step of utilizing a forming gas having hydrogen so that hydrogen migrates to and passivates defects within said silicon.
7. The method of claim 1, further comprising the step of forming a nitride layer over said oxide layer.
8. The method of claim 1, wherein said plasma enhanced chemical vapor deposition process uses a plasma containing silane (SiH4) and nitrous oxide (N2O).
9. The method of claim 1, further comprising the step of forming an aluminum layer over said oxide layer.
10. The method of claim 1, further comprising the step of producing an integrated circuit.
11. The method of claim 6, wherein said forming gas comprises about 90 percent nitrogen gas and 10 percent hydrogen gas.
12. A method for passivating surface and bulk defects in crystalline silicon, comprising the steps of:
forming an oxide passivating layer over said crystalline silicon using a plasma enhanced chemical vapor deposition process;
lowering an interface state density associated with said silicon by heating said passivating layer and said silicon with a light radiating source after said plasma enhanced chemical vapor deposition process; and
exposing said passivating layer to a hydrogen-containing forming gas while said passivating layer is being heated so that hydrogen migrates to and passivates said surface and bulk defects within said silicon.
13. The method of claim 12, wherein said defects comprise dislocations.
14. The method of claim 12, wherein said defects comprise grain boundaries.
15. The method of claim 12, wherein said defects comprise vacancies.
16. The method of claim 12, wherein said silicon is n-type silicon.
17. The method of claim 12, wherein said silicon is p-type silicon.
18. The method of claim 12, wherein said passivating layer is formed below about 250 degrees Celsius.
19. The method of claim 12, wherein said heating step is performed at about 350 degrees Celsius.
20. The method of claim 12, wherein said plasma enhanced chemical vapor deposition process employs an electromagnetic plasma excitation signal having a frequency of about 13.7 megahertz.
21. The method of claim 12, wherein said plasma enhanced chemical vapor deposition process uses a plasma containing silane (SiH4) and ammonia (NH3) to produce atomic hydrogen during film deposition.
22. The method of claim 12, wherein said plasma enhanced chemical vapor deposition process uses a plasma containing silane (SiH4) and nitrous oxide (N2O) for producing atomic hydrogen to passivate defects.
23. The method of claim 12, further comprising the step of producing a solar cell.
24. The method of claim 12, further comprising the step of producing an integrated circuit.
25. The method of claim 12, wherein said forming gas comprises about 90 percent nitrogen gas and 10 percent hydrogen gas.
26. A method for passivating a surface of crystalline silicon, comprising the steps of:
forming an oxide layer over said crystalline silicon using a plasma enhanced chemical vapor deposition process; and
heating said oxide layer and said silicon to a temperature of about 350° C. with a light radiating source after said plasma enhanced chemical vapor deposition process so that an interface state density associated with said silicon is lowered.
27. A method for passivating a surface of crystalline silicon, comprising the steps of:
forming an oxide layer over said crystalline silicon using a plasma enhanced chemical vapor deposition process; and
heating said oxide layer and said silicon to a temperature approximately between 300° and 450° C. with a light radiating source after said plasma enhanced chemical vapor deposition process so that an interface state density associated with said silicon is lowered.

28. A method for passivating a surface of crystalline silicon, comprising the steps of:

forming an oxide layer over said crystalline silicon using a plasma enhanced chemical vapor deposition process;

forming an aluminum layer over said oxide layer; and

achieving an interface state density associated with said silicon at least as low as $1.1 \times 10^{10} \text{ cm}^{-2} \text{ eV}^{-1}$ by heating said oxide layer and said silicon with a light radiating source after said plasma enhanced chemical vapor deposition process.