Silicon Nitride Surface Conversion into Oxide to Enable Hydrophilic Bonding

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Oxygen plasma was used to convert the top part of Si$_3$N$_4$ film into SiO$_2$. Surface roughness remarkably improves because of the process. SiO$_2$, at surface now allows rendering surface hydrophilic. Both effects - smoothening and conversion - are favorable for further wafer bonding. Silicon wafers with the top-reoxidized nitride film successfully bond to glass substrates. The bonding allowed layer transfer. Silicon-on-glass substrates with a barrier nitride film between the silicon and glass were fabricated.

Introduction

Ulrich Goesele was the first to successfully make silicon-on-glass and silicon-on-quarts substrates by layer transfer in 1997 [1]. In the layer transfer, hydrogen is implanted into silicon wafer thus defining a silicon film that lay above the implanted hydrogen, and a silicon bulk below the hydrogen plane. The implanted substrate is bonded to a glass sheet thus making a temporary silicon-glass assembly. The assembly is heated to induce cleavage of the silicon substrate along the hydrogen plane. Upon the cleavage, the temporary assembly divides into a leftover silicon substrate and a silicon-on-glass (SOG) substrate. The SOG substrate thus has a single crystalline silicon film covering the glass.

One of the improvements to the SOG manufacturing process is incorporating a reliable barrier between silicon and glass that would prevent contamination of silicon with glass constituents. Glasses have some metal content, including alkali metals such as sodium. Sodium is highly undesirable in silicon transistors, as it drifts in SiO$_2$ under electric field causing transistor malfunction. Other glass constituents are also generally undesirable in silicon film of SOG.

Silicon nitride is considered the most reliable barrier against drift or diffusion of impurities (including sodium) [2]. While making an SOG substrate, it is useful to incorporate the barrier nitride film between the silicon and the glass. As SOG is made by layer transfer, and layer transfer requires bonding, it is desirable to develop bonding to a Si$_3$N$_4$ surface.

However, the silicon nitride is often characterized as a non-bondable surface; see, for example, the pioneering paper by Lasky [3]. Silicon nitride, by virtue of its chemical composition - Si$_3$N$_4$ - is hydrophobic. Glass surfaces, on the other hand can be easily rendered hydrophilic, but cannot be rendered hydrophobic. Therefore, the nitride surface has to be modified to have (potentially) a hydrophilic surface. Then we can further proceed with hydrophilic type bonding. To gain hydrophilicity, the nitride can be either covered with an auxiliary SiO$_2$ film, or re-oxidized. Re-oxidation is preferable: it is a growth-type process, as opposed to deposition. The deposition tends to increase surface
roughness, while growth usually smoothes the surface. Plasma re-oxidation of the nitride is known [4]; however, its dual positive action on bonding has not yet been explored.

Additionally, the inclusion of silicon nitride thin films between the silicon and glass in a film transfer process can enable improvements in an as-transferred surface morphology.

We explore here plasma re-oxidation of near-surface area of silicon nitride. As per our best knowledge, the nitride conversion was not applied to render the nitride surface bondable. Further, it is less known that roughness of the surface of converted film can be significantly improved by properly choosing a plasma-processing condition (compared to roughness of initial nitride film). Eventually the nitride re-oxidation serves the purpose of making SOG with the canyon-less silicon film and with a reliable barrier between silicon and glass.

**Experimental**

**Glass**

Corning EAGLE XG® glass was used in this experiment. Initially, this glass has been designed for making flat panel displays with polysilicon thin-film transistors. As such, it has carefully adjusted the thermal expansion coefficient (3.18x10^{-6} °C^{-1} and 3.25x10^{-6} °C^{-1} for the glass and silicon respectively, at 400 °C). The glass also has a relatively high strain point of 666 °C, which is higher than the temperature needed to trigger exfoliation (typically around 500 °C). The ability to survive exfoliation temperature and TCE match - were main reasons to choose this glass for the layer transfer. The EAGLE XG glass is free from heavy metals and other impurities, such as arsenic, antimony, barium, that can have an adverse effect on silicon. However it contains alkaline earths which are harmful for the silicon. Even though their content is small, a barrier that prevents silicon contamination with alkaline earths is needed.

**Silicon**

Regular silicon wafers were used as donor wafers in this experiment. The wafers are 300 mm, <001> orientation, Cz grown, prime grade, p-type, boron doped, resistivity 8-12 Ohmxcem, COP free. The COPs might obstruct the film transfer process; therefore the COP free wafers were used. <001> orientation was chosen as this orientation is preferable for making thin film transistors on the final SOG. Doping type and level in the wafers was chosen to obtain desirable threshold voltages in eventual transistors made on the SOG substrates.

**Pad oxide**

A silicon nitride film was deposited onto the silicon wafers over a native oxide film. The native oxide film was intentionally left on the silicon surface. The reason to use the additional oxide is to ensure low defect density on an interface between the silicon film and the substrate in the final SOG. Alternatively, the silicon surface can be oxidized before the silicon nitride deposition; thermal, plasma, or chemical oxidation can be used. The oxide under the nitride is called pad oxide. As the oxide is a low elastic modulus
material, the excessive thickness of the oxide will lower the stiffening effect of the hard nitride film. If the thickness of the oxide is much smaller than the thickness of the silicon film to be transferred, it does not deteriorate the stiffness. Typically, 200 nm silicon films are transferred. Therefore, the thickness of the pad oxide has to be 10 nm or less.

Nitride Deposition

LPCVD technique was used for the nitride deposition. The deposition was performed in a standard LPCVD tool using an argon-diluted silane and ammonia mixture, 40 sccm total gas flow rate, 3:1 ratio of silane and ammonia, at 800°C and 1 mTorr pressure in the chamber. This resulted in a deposition rate of about 2 nm/minute. 100-nm-thick silicon nitride film has been deposited.

Surface roughness of the deposited silicon nitride film has been analyzed. The low roughness surface is required for subsequent bonding to the glass. The roughness was measured with atomic force microscopy (AFM) and with an optical technique using a Zygo tool. Both methods had shown the surface roughness in the range of 4 to 8 Ångstrom r.m.a. For substrates with such roughness, the bonded assembly often has defects on bonding interface (voids). Roughness under 3 Ångstrom r.m.a is needed to get high-yield defect-free bonding. Therefore, additional smoothening of the film surface before the bonding, is required to ensure the defect-free bonding.

As mentioned above, the surface of the nitride is hard to render hydrophilic and thus make bondable. An auxiliary film over the nitride can be used to achieve bondability. This results in oxide-nitride-oxide (ONO) structure of the film on the silicon surface. The top oxides in the ONO structure is called a cap oxide.

Conversion of nitride surface into oxide

The silicon wafers with a 100 nm nitride film having 4 – 8 Ångstrom r.m.a roughness, was processed in a low frequency (30 kHz), capacitively-coupled type plasma chamber in a Technics plasma tool. The processing conditions were as follows:

incoming gas: oxygen,
oxygen flow: 2 sccm,
pressure in the chamber: 30 mTorr,
plasma power: 700 W,
process time: 20 minutes.

To determine process windows, samples were plasma treated by applying varying conditions: pressure in the chamber ranged from 30 to 300 mTorr, plasma power ranged from 100 to 700 W, and process duration spanned from 0.5 to 50 minutes.

Results

SIMS profiling was used to characterize the obtained ONO films. The SIMS profile in Fig. 1 shows that about 20 nm of the Si₃N₄ which is converted into SiO₂, and the top 7 nm of the film, are completely free of nitrogen, i.e., the top 7 nm is a pure oxide, not
oxynitride; i.e., plasma results in complete conversion of the nitride into oxide. The complete removal of nitrogen in the converted region ensures the surface can be rendered hydrophilic and, further, proper bondability of the new film surface to the glass.

![Figure 1](image1.png)

**Figure 1.** Nitrogen (1), Oxygen (2), and Silicon (3) concentration profiles from the surface down to 60nm in the plasma processed Si₃N₄ film.

A set of SIMS profiles in Fig. 2 show elemental profiles for various processing times in plasma. The profiles indirectly indicate the smoothening effect of plasma. A slope of the oxygen curve depends (among other parameters) on surface roughness. Lower slope corresponds to rougher surface. The SIMS curve for short plasma time, 0.5 minute in this case, has a slope which is mostly determined by initial roughness of the nitride film. It can be seen that SIMS profiles for 1 minute- and 2 minute-long plasma processing have about the same slope as the 0.5 min profile. However, profiles for 5 minute- and 10 minute-long processing have a steeper slope. This means that film surface and nitride-oxide interface are smoother than the roughness of the surface of the initial nitride film. With smoothening, we achieve better bondability.

The roughness of the film surface before and after plasma processing has been analyzed with AFM. AFM images in Fig.3 show that the peak-to-valley roughness improves plasma processing by about an order of magnitude: from 12 nm to 1.4 nm, and rms roughness improves almost 3 times: from 0.32 nm to 0.13 nm.

![AFM Image](image2.png)

**Figure 3.** AFM images showing improvement in roughness before and after plasma processing.

Fig. 4 to Fig. 6 show kinetics of nitride re-oxidation in plasma as a function of plasma power, chamber pressure, and processing time, respectively.
Figure 2. Oxygen, and Silicon nitride concentration profiles from the surface down to 20 nm in the plasma processed Si₃N₄ film at various plasma processing times, from 0.5 to 10 minutes.
Figure 3. AFM of as-deposited Si$_3$N$_4$ film (top) and after plasma (bottom).

Figure 4. Thickness of SiO$_2$ film (nm) converted from Si$_3$N$_4$ as a function of plasma power (W). Time and pressure are fixed: 2 min, 30 mTorr.
Figure 5. Thickness of SiO$_2$ film (nm) converted from Si$_3$N$_4$ as a function of chamber pressure (mTorr). Time and power are fixed: 2 min, 700 W.

Figure 6. Thickness of SiO$_2$ film (nm) converted from Si$_3$N$_4$ as a function of processing time (minutes). Pressure and power are fixed: 30 mTorr, 700 W.

**Discussion**

Plasma polishing effect was noticed elsewhere [5], where rms roughness was improved from 0.2 to 0.15 nm by oxygen plasma and from 0.22 to 0.12 nm in argon plasma. As per our best knowledge, the remarkable 3x plasma polishing effect we observed has not been previously described. The positive effects of plasma activation on bonding are widely known and are considered well investigated [5]. However, useful plasma effects on bonding were explained as being due to micro-roughening, increase of OH concentration available at the surface, etc., [6] but not by plasma polishing. We have
shown a different bonding improvement mechanism due to the plasma. The study of smoothening as a function of time in the plasma shows a wide process window of 5 to 20 minutes. Longer times result in surface erosion. Complete conversion of the nitride into oxide is another distinctive feature of our process.

Chemical mechanical polishing can be used to improve the roughness. However, the nitride is a hard film, and polishing of such a film is an expensive operation. Also, the polishing itself is not enough to make the nitride surface bondable. Silicon dioxide is a bondable material as its surface can be easily rendered hydrophilic. Deposition of the SiO$_2$ film over the nitride film is possible, but not preferable, as it results in a further increase of surface roughness. Conversion of nitride surface into oxide by thermal oxidation is possible, but not preferred either, as it requires high temperatures.

In general, a film on a substrate can be obtained by one of two opposites processed – either by growth or by deposition. Smoothening is an attribute of film growth processes. Plasma conversion and thermal oxidation are examples of growth processes. The film is growing down when reactive species diffuse through the film and extend the film at the interface between a substrate and the grown film. Oppositely, an attribute of deposition processes is an increase of the surface roughness. Here we have initially, a very smooth silicon surface, a rougher surface after nitride deposition, and a smoother surface again after plasma processing.

Plasma also has some sputtering action, and at long plasma processing times the roughening due to sputtering become significant. We observed that roughening became noticeable for plasma processing times that were longer than 30 minutes. Conversion of the nitride surface into oxide is not limited to a low-frequency plasma tool. RF, microwave, and other types of plasma can be successfully used as well.

Nitride bonding to silicon (and/or silicon dioxide) is still a controversial topic. Hydrophobic bonding of these surfaces should be possible, and it was reported for example, in [7]. However, as hydrophobic bonding requires much better roughness of mating surfaces compared to hydrophilic type bonding is not suitable for mass production. Many authors notice that bonding of re-oxidized nitride is generally successful (bonding strength is sufficient), but they indicate non-continuous bonding: there were many bubbles on the bonded interface [5, 8, 9, 10]. Our plasma conversion process results in void-free bonding.

Using low-frequency plasma, we have successfully obtained very smooth and bondable silicon dioxide surfaces. The thickness of the converted film, 20 nm, is higher than expected. Other experiments were done using 13.56 MHz RF plasma, which resulted in only 7 nm of converted film. Also, smoothening by RF plasma was not as remarkable as in the case of low-frequency (30 kHz) plasma. Thus, using low frequency plasma is preferable, as it will improve quality and yield of the bonding step. Incorporation of a desirable nitride barrier into silicon-on-glass is thus made possible.
Conclusion

Processing of silicon nitride in room temperature oxygen plasma results in (1) complete conversion of the top part of Si₃N₄ film into SiO₂, and (2) an improvement in surface roughness. Both effects are favorable for bonding the resulting surface to glass or other hydrophilic substrates.

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References