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Removing native oxide from Si(001) surfaces using photoexcited fluorine gas

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This letter discusses the reaction between (001) oriented Si surfaces and photoexcited fluorine gas resulting in the removal of the native Si oxide. For an F_2/Ar gas system, the bulk Si was etched in areas where the native Si oxide had been completely removed. However, by using an F_2/H_2 gas system, only the native Si oxide was removed. We used this method to remove the native Si oxide in Si epitaxial growth. A high-quality single-crystal Si film surface was obtained up to a maximum temperature of 600 °C through this Si growth process. We also characterized the etching of a thermal oxide, silicon nitride, and silicon carbide.

Surface cleaning is an important aspect of wafer processing for ultralarge-scale integration (ULSI). In particular, the removal of native Si oxide is a key process for fabricating some high-performance devices, because it lowers the precleaning temperature for low-temperature Si epitaxy,¹ aiding in forming thin high-quality gate oxide, and decreases contact resistance. Silicon oxides, including native Si oxide, are stable materials, making it difficult to remove oxides from Si surfaces. Recently, hydrogen fluoride gas was used to remove the native oxide.^{2,3} We tried to remove the native Si oxide using photoexcited fluorine gas, since fluorine is the most chemically active element. In addition, photoenhanced processing is suitable for surface cleaning, since it only enhances the chemical reactivity without inducing any damage onto the surface. In this letter, we describe the reaction between the photoexcited fluorine gas and the Si surface; mainly, the removal of the native Si oxide. We discuss the usefulness of this method when applied to precleaning in preparation for Si epitaxy. We discuss the etching of a thermal oxide (SiO_2), a silicon nitride (SiN), and a silicon carbide (SiC).

The chamber used in this experiment is shown in Fig. 1. This system consists of the ultraviolet (UV) light section, the supply gas unit, and the 4 in. wafer holder. This chamber is made mainly from polymers containing fluorine. In the UV light section, low-pressure mercury lamps and two quartz windows were used. The output of the low-pressure mercury lamps at the 254 nm wavelength is 24 mW/cm² on the Si surface. Remarkably, the wavelength of the low-pressure mercury lamps matches the absorption wavelength of the fluorine molecule.⁴ For this reason, the fluorine gas is effectively excited by the low-pressure mercury lamps.

The experiments were performed at atmospheric pressure. The fluorine gas was diluted with either argon or hydrogen. For the argon gas mixture (F_2/Ar), the fluorine concentration was 1% with a total flow rate of 250 ml/min. For the hydrogen gas mixture (F_2/H_2), the flow rates of fluorine gas, hydrogen gas, and argon gas were 2.5 ml/min (0.5%), 250 ml/min (50%), and 247.5 ml/min (49.5%), respectively. The temperature of the wafer grad-

ually rose due to UV irradiation up to 70 °C, where it was stabilized for 60 min.

The Si epitaxial layers were grown by chemical vapor deposition (CVD) using disilane hydrogen as the source gases at a pressure of 3 kPa. Conventional precleaning [high-temperature (–1000 °C) thermal etching in a hydrogen ambient (0.33 kPa) which removes the native Si oxide] was done before the Si deposition. We experimented with exchanging the conventional high-temperature precleaning to the F_2/H_2 cleaning. The wafer to be exposed to F_2/H_2 was transferred to the epitaxial chamber in a vacuum or in pure nitrogen to avoid exposure to the atmosphere.

Only *p*-type Czochralski (CZ) Si(001) wafers (10 Ω cm) were used in this experiment. First, we cleaned the wafer by RCA processing, and dipped them in diluted HF (3:100) for 30 s. Then, they were boiled in HCL:H₂O₂:H₂O (1:1:4) for 10 min. The sample were thermally oxidized at 1000 °C in H₂O-O₂ gases. The SiC was a 3C polycrystal grown by CVD using disilane and acechlen as the source gases with a hydrogen carrier at 900 °C.⁵ An SiN layer was also made by CVD using dichlorosilan and ammonia as the source gases at 800 °C.

For F_2/Ar , we observed isotropic etching of the bulk Si using the etching profile generated by cross-sectional scanning electron microscope (SEM). Figure 2 shows the etching depth with time. For the first 5 min, the silicon did not etch. But after that, it was etched at a constant 12

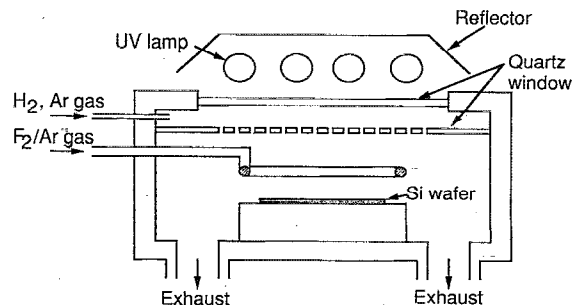


FIG. 1. Chamber used in this experiment.

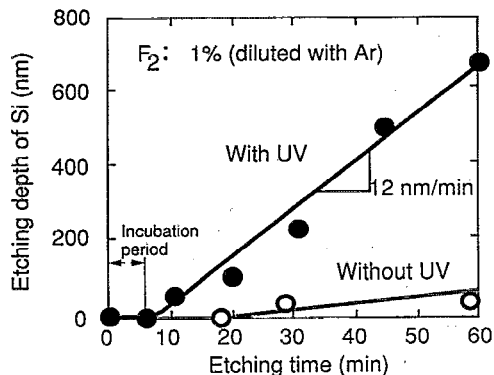


FIG. 2. Etch depth of fluorine gas varying with time.

nm/min. The passive period is assumed to be the time during which the native oxide was removed. We found that this period varied depending on the thickness of the native oxide. Using an ellipsometer, we measured the native Si oxide to be 1.05–1.45 nm, giving an etch rate of 0.2–0.3 nm/min. Without UV irradiation, only slight etching of Si was observed.

For F_2/H_2 , only the native Si oxide seemed to be removed; the bulk Si was not etched. Figure 3 shows the Auger electron spectroscopy (AES) spectra before and after 5 min of F_2/H_2 etching. We measured the post-etched spectrum without the exposing the Si wafer to air. The oxygen peak (O_{KLL}) was dramatically reduced after F_2/H_2 etching. Thus, most of the native Si oxide was removed by F_2/H_2 cleaning. The etch rate for native Si oxide was not linear, and had a maximum value over 1 nm/min as measured by AES. Even if the wafer was cleaned 1 h, little etching could be observed of the Si substrate by a mechanical step-height profiler as well as SEM observation. This is markedly different from the F_2/Ar cleaning. Since we detected hydrogen fluoride in the ambient using infrared absorption (FTIR), we deduced that the fluorine reacted with the hydrogen gas to produce residual hydrogen fluoride.

In Table I, the etching rates are listed, including those of thermal oxide, silicon nitride, and silicon carbide. It is of interest to note that SiO_2 , SiN, and SiC were etched by photoexcited fluorine gas. Both F_2/Ar and F_2/H_2 will etch the SiO_2 and SiN. But SiC is one of most chemically stable materials, and its etching suggests that photoexcited F_2/Ar has the ability to clean some hydrocarbon contaminants.

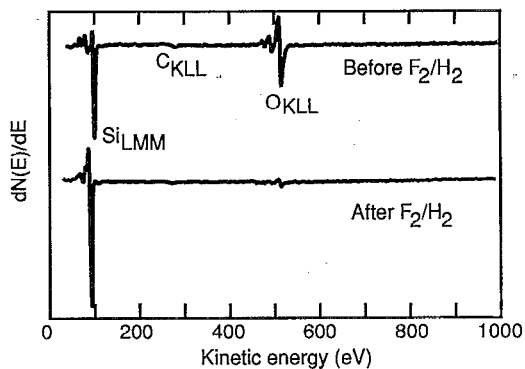


FIG. 3. AES spectra of Si surface before and after being treated by F_2/H_2 for 5 min.

For F_2/H_2 , selective etching of Si oxide was achieved between native oxide and thermal oxide. Selective etching of Si oxides occurs in a F_2/H_2 gas system due to the ionic reaction through the intermediate H_2O .⁶ In addition, the amounts of H_2O on Si oxide surfaces are different for native oxide and thermal oxide. For F_2/Ar , since the fluorine directly reacts with the Si oxides, other compounds do not affect the etch. Therefore, selective etching does not occur.

We found from attenuated-total-reflection (ATR) spectroscopy in the infrared region that the dangling bonds of the Si surface after F_2/H_2 etching were mainly terminated with hydrogen. We deduced that the surface remained crystalline since the $Si-H_x$ ($x = 1-3$) absorption peak from the ATR spectroscopy was not broad as the amorphous Si film. This surface structure is desirable for Si epitaxy.

We applied photoexcited cleaning to Si epitaxy. Figure 4 shows the reflection high-energy electron diffraction (RHEED) pattern of the grown films with and without precleaning using F_2/H_2 . We kept the temperature below 600 °C throughout the epitaxy process. Polycrystalline Si film was deposited by conventional CVD, when the F_2/H_2 cleaning had not been performed [Fig. 4(a)]. However, when the F_2/H_2 treatment had been performed, a good single-crystal Si film was grown [Fig. 4(b)]. Thus, the temperature of the preclean for single-crystal Si films can be lowered to 600 °C. This temperature was 150 °C lower than that of any other conventional CVD method.

We have discussed the reaction between the Si surface and the photoexcited fluorine gas. The removal of the na-

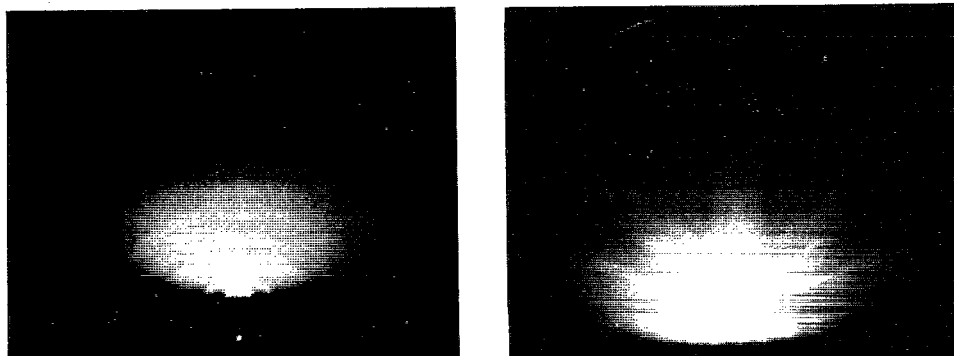


FIG. 4. RHEED pattern of the Si films (a) deposited by the conventional methods and (b) after treating with F_2/H_2 . During the epitaxy process, the maximum temperature was 600 °C.

TABLE I. The etching rates of the Si compounds by the photoexcited fluorine gas.

	Si	native oxide	SiO ₂	SiN	SiC
F ₂ /Ar	12	0.2-0.3	0.2-0.7	2	0.03
F ₂ /H ₂	0	> 1.0	0.01-0.4	2	0

tive Si oxide was observed. When the fluorine was diluted with argon gas, the Si substrate was etched after the native Si oxide had been removed, while fluorine gas diluted with only hydrogen gas, only the native Si oxide was removed.

We conclude that surface cleaning using the photoexcited fluorine gas is one of most attractive candidates for

precleaning in various processes such as the low-temperature Si epitaxy.

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