Chlorine Etching For In-Situ Low-Temperature Silicon Surface Cleaning For Epitaxy Applications

K. H. Chung, and J. C. Sturm

Princeton Institute of Science and Technology of Materials (PRISM) and Dept. of Electrical Engineering, Princeton University, Princeton, NJ, 08544, USA

Chlorine in a nitrogen ambient is used to clean silicon surfaces of impurities by etching a thin layer from the surface prior to silicon epitaxial growth. Silicon etch rates of 1-10 nm/min could be achieved for temperatures from 525^{o}C to 575^{o}C. The etching of a thin layer of silicon from the surface is also capable of removing phosphorus from the surface, which conventionally is difficult to remove. Smooth surfaces and high epitaxial quality after chlorine etching are also demonstrated.

Introduction

Oxygen-free silicon surfaces are desired for high quality silicon epitaxy. Conventionally, to achieve oxygen-free and carbon-free surfaces, it is necessary to perform in-situ cleaning steps with temperatures in the range of 760^{o}C to 850^{o}C or higher to reduce oxygen levels to below the secondary ion mass spectrometry (SIMS) resolution limit (1)(2). Cleaning temperatures less than 700^{o}C are desired, however, to minimize the diffusion of dopants in existing structures, such as would occur when using epitaxy for raised source/drain applications. In this work, we demonstrate the use of chlorine etching at 575^{o}C to produce oxygen-free surfaces and substantially reduce interface phosphorus and carbon levels before epitaxy.

Chlorine Thermal Etching

Thermal etching of silicon in-situ in epitaxial reactors is typically done using hydrogen chloride (HCl) in a hydrogen ambient. However, the etch rates using this process are very low below 800^{o}C. For temperatures less than 750^{o}C, the etch rates with HCl have been observed to be less than 1nm/min (3). Previously attempts made to use using chlorine instead of hydrogen chloride to etch silicon in a hydrogen ambient (4). It was observed that the etch rate was still negligible below 750^{o}C. The authors believed that hydrogen was reacting with the chlorine to form HCl.

In our experiments we use a nitrogen ambient instead of a hydrogen ambient for the thermal etching of silicon with chlorine. A partial pressure of 6 torr of nitrogen and 30 mtorr of chlorine was used in our experiments. The work was done in a lamp-heated cold-wall single-wafer rapid thermal chemical vapor deposition (RTCVD) reactor. Etch rates of 11nm/min, 5nm/min, and 1nm/min were achieved at 575^{o}C, 550^{o}C, and 525^{o}C respectively, based on step height measurements. For such measurements, the unetched areas were masked with silicon dioxide. A comparison of etch rates based on chlorine and HCl vs. inverse temperature is shown in Figure 1.

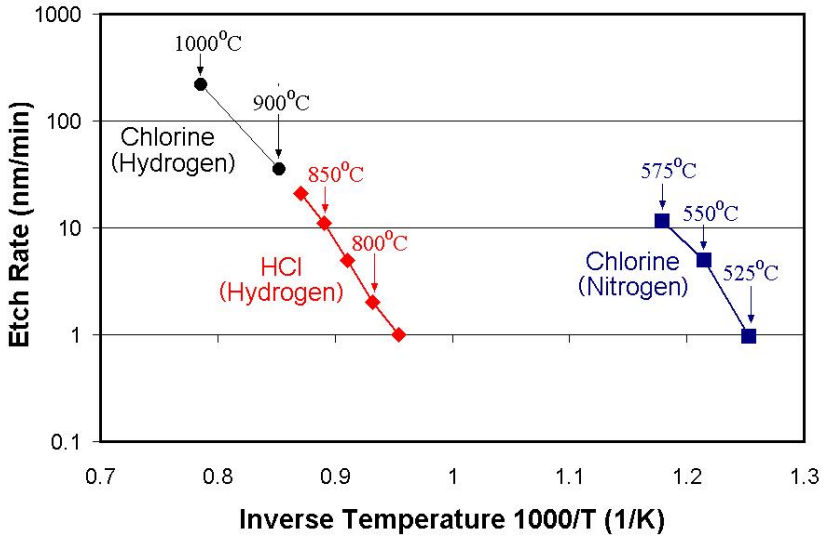

Figure 1 Etch rate of <100> silicon surface versus inverse temperature. Etch conditions using chlorine were 3 slpm of nitrogen or hydrogen flow and 15 sccm of chlorine flow at a pressure of 6 torr, for a chlorine partial pressure of 30 mtorr. HCl etch rates in hydrogen are from Ref. 3; the partial pressure of HCl is 200 mtorr with a hydrogen partial pressure of 20 torr.

Chlorine etch rates versus chlorine flow rates are plotted in figure 2. The etch rate is still increasing with the flow rate, indicating that even faster etch rates may still be achievable. Etch rates were also measured with our system using chlorine in a hydrogen ambient. At high temperatures 900°C and 1000°C, the silicon etch rate was 35nm/min and 220nm/min respectively. However, for temperatures below 700°C the etch rates were negligible, consistent with the earlier work.

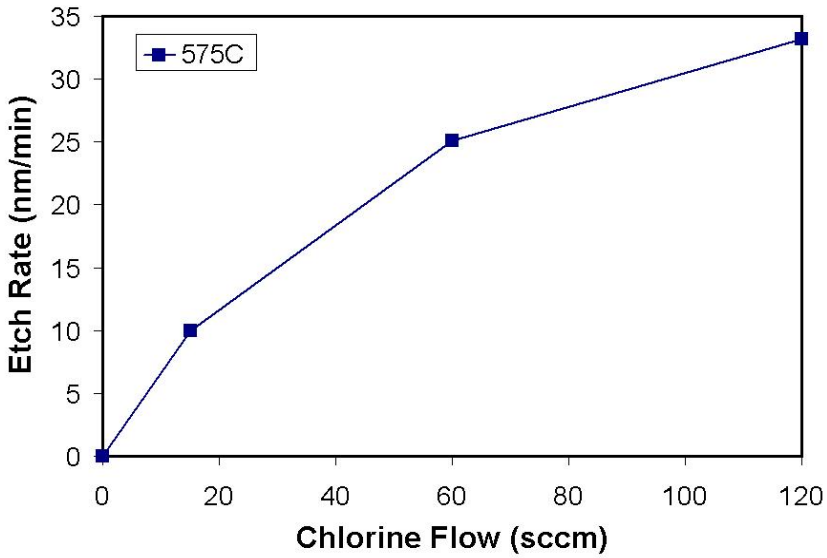

Figure 2 Etch rate of <100> silicon surface versus chlorine flow rate at 575°C. The pressure was 6 torr with 3 slpm of nitrogen flow.

Furthermore, as inferred from Figure 2, silicon etching with chlorine at 575^{o}C in nitrogen ambient has roughly the same etch rate as with chlorine at 900^{o}C in hydrogen ambient. This is consistent with the belief that hydrogen reacts with the chlorine to form HCl.

The roughness of the surfaces was measured by atomic force microscopy (AFM) after etching with chlorine at 575^{o}C (Fig. 3). A RMS roughness of ~1nm over an area of 50x50 microns was found, showing that the etching results in smooth surfaces.

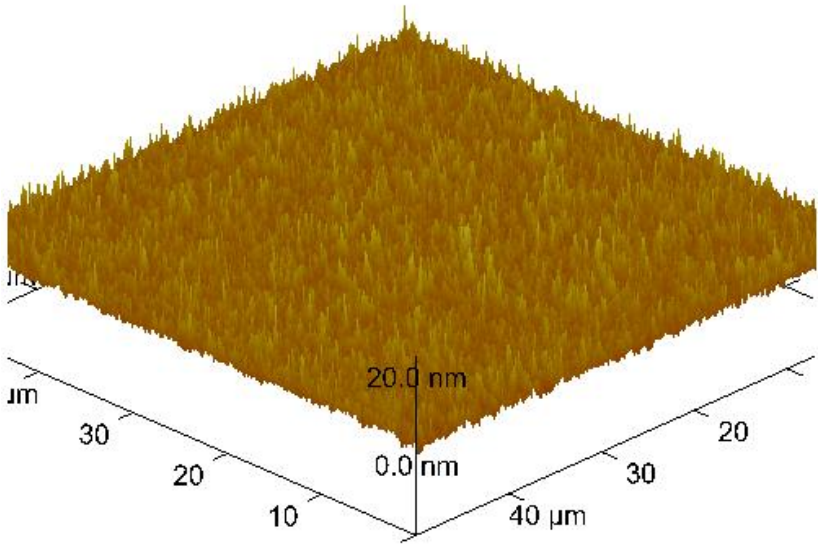

Figure 3 AFM image of silicon surface after etching of 20nm of silicon at 575^{o}C and a pressure of 6 torr with a flow of 15 sccm of chlorine.

Surface Cleaning by Chlorine Etching

The effectiveness of the chlorine etching for cleaning a silicon surface prior to epitaxy was examined. SIMS was done to compare the interface impurity concentration after silicon epitaxy that had no in-situ clean step with that after epitaxy that had a 575^{o}C chlorine etch step. Prior to silicon growth in both steps, the sample was cleaned with a conventional ex-situ wet clean of H_2SO_4/H_2O_2 and a dilute HF dip (5). Silicon was grown in this experiment at 700^{o}C at 6 torr chamber pressure using dichlorosilane (DCS) as the silicon source. A 2.5-nm boron doping marker was used to indicate the start of silicon epitaxy in both cases. Both experiments were performed on a single wafer so data could be obtained with a single SIMS measurement. After the first wet cleaning the sample was loaded into the reactor in a hydrogen environment. The temperature was raised to 700^{o}C and approximately 150 nm of silicon was grown, without any cleaning steps such as a high temperature hydrogen bake. The wafer was then taken out of the reactor and exposed to air for 12 hours. Now the sample was chemically cleaned again as described earlier. After loading, 20 nm of silicon was etched back using chlorine in nitrogen ambient at 575^{o}C prior to epitaxy. After etching, the ambient was switched to hydrogen, the temperature was then raised to 700^{o}C and 50 nm of silicon was grown. From the SIMS shown in Figure 4, we observed an interfacial spike in both oxygen and carbon levels for the growth with no cleaning step and no interfacial oxygen above the SIMS background was visible in the case of the chlorine etching. The interfacial spike in carbon level is also significantly smaller in the latter case.

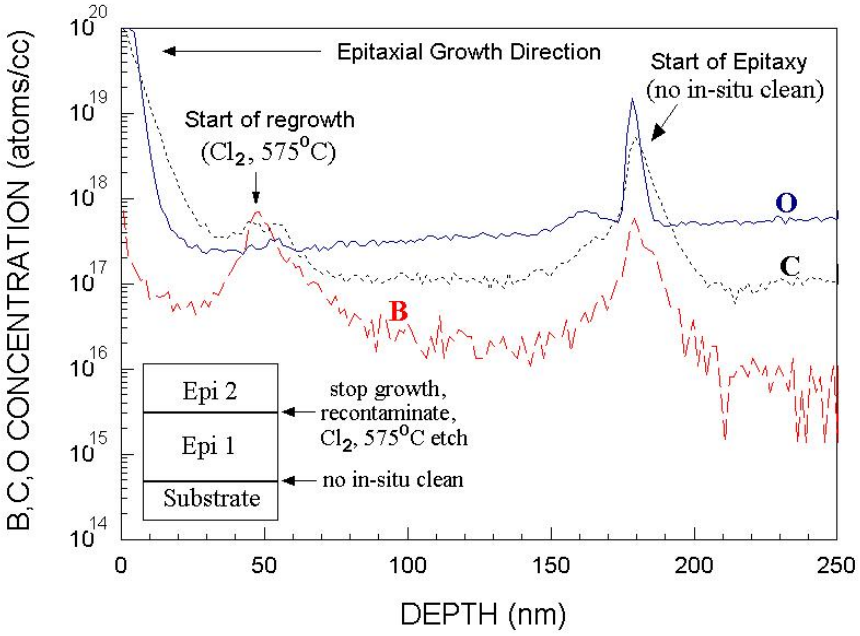

Figure 4 Secondary Ion Mass Spectrometry plotting depth versus impurity concentration for B (dashed), C (dotted), and O (solid). No in-situ cleaning was done at the start of epitaxy as indicated on the plot. After the first silicon epitaxy step, the wafer was removed from the reactor, exposed to air for 12 hours, and reloaded after wet cleaning again. 20nm of silicon was etched back using chlorine at 575°C prior to the second epitaxial step. No oxygen spike and a clear reduction of carbon impurities demonstrate the effectiveness of chlorine in cleaning silicon surfaces. The inset depicts the structure of the sample.

The carbon and oxygen levels were integrated at both growth interfaces and the results are summarized in Table 1. There is more than an order of magnitude decrease of both surface oxygen and carbon after chlorine surface etching.

TABLE I. Integrated carbon and oxygen levels for both the no in-situ clean and chlorine cleaning at 575°C

In-Situ Clean	Integrated Oxygen Concentration	Integrated Carbon Concentration
None	$8x10^{12}$ atoms/cm^2	$3x10^{12}$ atoms/cm^2
575°C Cl_2 etch	$< 10^{11}$ atoms/cm^2	$< 2x10^{11}$ atoms/cm^2

Experiments were done to test the ability of chlorine surface etching steps to remove other surface impurities, specifically phosphorus. A thermal desorption step at 800°C, a chlorine surface cleaning step by etching at 575°C, and no in-situ cleaning were compared. Silicon was grown in this experiment at 700°C at 6 torr chamber pressure using dichlorosilane (DCS) as the silicon source in hydrogen ambient. The growth was halted and a 0.5 sccm phosphine dose was injected into the chamber with 3 slpm hydrogen flow at a temperature of 700°C at 6 torr chamber pressure for 5 minutes to coat the surface with phosphorus.

For the first cleaning step, we attempted to remove the phosphorus from the surface by etching with chlorine at 575°C. Silicon was then grown and a thin SiGe layer was then grown to reduce the surface concentration of phosphorus prior to the next phosphine dose,

followed by a second phosphine exposure. After the second phosphine dose, we attempted to remove the phosphorus via desorption by heating the surface to 800°C for 10 minutes. Silicon was then grown followed by a thin SiGe layer to reduce the surface concentration of phosphorus prior to the next phosphine dose, followed by a final phosphine exposure. After the last phosphine dose, no cleaning step was performed and more silicon was grown. At no time was the chamber opened or the sample removed during this experiment. A SIMS measurement of dopants and impurities vs. depth is shown in Figure 5.

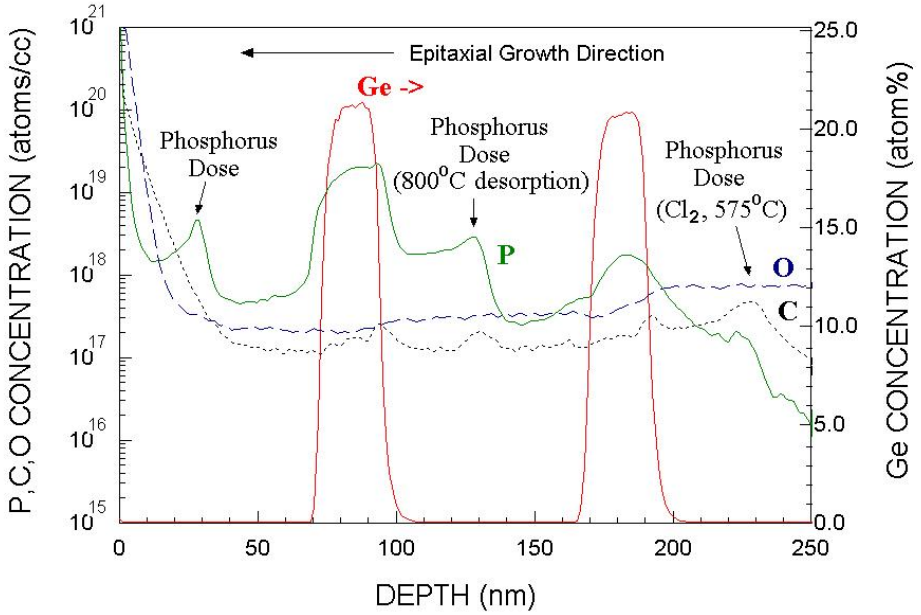

Figure 5 Secondary Ion Mass Spectrometry plotting depth versus impurity concentration for P (solid), C (dotted), and O (dashed). Growth was halted to cover the surface with phosphorus by injecting phosphine into the chamber at 3 different times during the growth. After the first two phosphine doses, different techniques were used to attempt to remove the phosphorus from the surface. SiGe layers were grown in between phosphorus doses to reduce the surface phosphorus concentration.

No phosphorus spike was observed at the interface treated with the chlorine etching step, indicating that chlorine etching removed all of the phosphorus from the surface prior to growth. A phosphorus spike at the growth interface after 800°C thermal treatment was still observed showing that the treatment was less effective than the etching. The surface desorption of the remaining phosphorus led to a high concentration in the top SiGe layer. (The spreading of the phosphorus in the first SiGe layer is due to the annealing step at 800°C). The last phosphorus spike, without any cleaning step, is used as the control for comparison. The phosphorus levels were integrated and are summarized in Table II.

TABLE II. Integrated phosphorus levels for no in-situ clean, chlorine cleaning at 575°C, and 800°C desorption.

In-Situ Clean	Integrated Phosphorus Concentration
None	3×10^{12} atoms/cm^2
575°C Cl_2	$< 10^{11}$ atoms/cm^2
800°C desorption	2×10^{12} atoms/cm^2

No significant reduction in phosphorus concentration was observed from the 800°C desorption technique, which produced a decrease from $3x10^{12}$ atoms/cm^2 to 2 $x10^{12}$ atoms/cm^2, while the Cl_2 etching step reduced the phosphorus concentration significantly from $3x10^{12}$ atoms/cm^2 to less than 10^{11} atoms/cm^2. This indicates that the chlorine etching of the silicon surface also etched away the phosphorus atoms that were adsorbed onto the surface.

To characterize the epitaxial quality on layers grown after etching with chlorine, a Si/SiGe/Si quantum well was grown after chlorine etching. The silicon layers were grown with DCS, and the SiGe layers were grown with DCS and germane for both samples. The photoluminescence (PL) intensity of silicon is very sensitive to the rate of non-radiative recombination, and thus to the defect density. Photoluminescence measurements were taken comparing a reference Si/SiGe/Si quantum well with a 1000°C hydrogen thermal clean step before growth of the Si/SiGe/Si quantum well to one grown after chlorine etching (Figure 6).

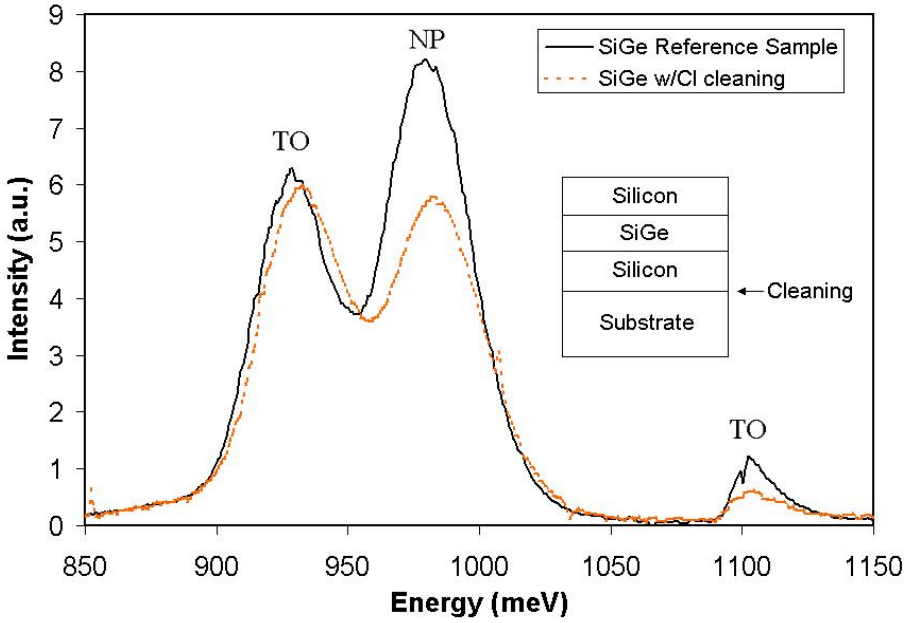

Figure 6 Photoluminesence intensity vs. photon energy at 77°K. Indicated on the plot are the TO (transverse optical phonon replica) for Si and SiGe and the NP (no phonon) peaks for SiGe. Photoluminesence for a reference SiGe quantum well with a 1000°C bake in hydrogen instead of a Cl_2 etching step is compared with the structure with Cl_2 etching of the substrate.

The SiGe layers were grown after the chlorine etch step. If chlorine etching had a detrimental effect on the subsequent epitaxy, then all the layers after chlorine etching would be of a poor crystalline quality. The comparable photoluminesence intensities of SiGe and Si indicate high-quality defect-free silicon epitaxy growth on a chlorine-etched surface.

Summary

Crystalline silicon can be etched with chlorine from 525^{o}C- 575^{o}C in a nitrogen ambient. The method can be used in-situ to produce oxygen-free silicon surfaces prior to the start of epitaxial growth. The technique of etching a thin silicon layer with chlorine is also capable of removing phosphorus impurities from the surface. No detrimental effects from chlorine etching were observed. Smooth surfaces were observed after etching and high-quality Si/SiGe/Si epitaxy was attained after chlorine etching.

References

1. M. K. Sanganeria, M. C. Ozturk, K. E. Violette, G. Harris, C. A. Lee, D. M. Maher, *Appl. Phys. Lett*., **66** 1255 (1995).
2. K. Oda and Y. Kiyota, *J. Electrochem. Soc*., **143** 2361 (1996).
3. Y. Bogumilowicz, J. M. Hartmann, R. Truche, Y. Campidelli, G. Rolland, and T. Billon, *Semicond. Sci, Technol.*, **20** 127 (2005)
4. K. E. Violette, P. A. O'Neil, M. C. Ozturk, K. Christensen, and D. M. Maher , *J. Electrochem. Soc*., **143** 3290 (1996)
5. M. S. Carroll, J. C. Sturm, and M. Yang, *J. Electrochem. Soc*., **147** 4652 (2000)