REMOVAL OF SiO_2 FROM Si (100) BY REMOTE H_2/SiH_4 PLASMA PRIOR TO EPITAXIAL GROWTH

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ABSTRACT

This study demonstrates the cleaning of Si(100) surfaces with a remote H_2/SiH_4 plasma. The surfaces were prepared with a chemical oxide the remains after an RCA clean. The plasma cleaning process was designed to remove contaminants such as C, F, and SiO_2. The key to successful removal of the oxide is to have the plasma chemistry in a neutral deposition regime. The neutral deposition process regime is a balance between the deposition of Si by SiH_4 and the etching of the deposited Si by atomic H. During the neutral deposition mode the SiO_2 was removed without deposition of Si on the SiO_2 surface. Once the SiO_2 layer is removed, the underlying Si surface is exposed to the H_2/SiH_4 plasma and a thin epitaxial film may be deposited. The final Si surface configuration after plasma cleaning is a 2x1 hydrogen terminated surface. The characterization of the interface and epitaxial film were investigated using Auger electron spectroscopy (AES) and transmission electron microscopy (TEM).

INTRODUCTION

Various methods have been investigated for performing *in situ* cleaning prior to Si epitaxial growth. These cleaning methods include: thermally assisted cleaning [1-2], photon assisted cleaning [3], plasma assisted cleaning [4], and vapor plasma cleaning [5]. These methods have varying degrees of success in removing organic and inorganic contaminants. Some of these cleaning techniques have been developed into low temperature cleaning processes (less than 800°C). In this study our goal is to lower the temperature at which SiO_2 is removed from a Si surface by adding SiH_4 to a remote H-plasma.

The remote H_2/SiH_4 plasma process is being developed as a precleaning step prior to Si epitaxy. Previous studies have shown that a remote H-plasma is effective in removing C, O and F from the Si (100) surface [6-8] whereas high temperature cleans (> 800°C) using SiH_4 or Si_2H_6 are effective in removing SiO_2 from Si [9]. The remote rf H-plasma generates atomic H which is the primary reactive species for removing these contaminants. However, atomic H is not effective in removing SiO_2.

In this study a low temperature remote H_2/SiH_4 plasma process is described which has two main processing regimes: blanket silicon deposition and selective SiO_2 etching. In the blanket deposition regime Si is deposited on both the Si and SiO_2 regions of the wafer. In the etching regime SiO_2 is selectively etched with respect to Si. At the exposed Si regions of the surface the deposition and etching rates of Si are approximately equal (i.e., a neutral deposition process), however, in the SiO_2 regions etching of the oxide dominates. The SiO_2, as well as any Si deposited on the SiO_2, are etched off during processing in the neutral deposition regime.

EXPERIMENTAL PROCEDURES

The substrates used in this study were p-type, boron doped, 25 mm diameter Si (100) wafers with a resistivity of 0.8-1.2 Ω-cm. The Si wafers were RCA cleaned by the supplier. Prior to processing, the wafers were dipped in a 10:1 HF solution for 10 seconds to strip the oxide and hydrogen terminate the Si surface. An additional RCA clean was used to terminate the surface with a thin SiO_2 layer. Each wafer was mounted onto a molybdenum sample holder.

Mat. Res. Soc. Symp. Proc. Vol. 386 © 1995 Materials Research Society

The holder was placed into a load-lock before transferring the sample into the UHV transfer-line. The transfer-line acts as a linear wafer handler used in cluster tools. The analysis and plasma cleaning chambers are attached to the transfer-line and each chamber is isolated from the transfer-line by a gate valve. Currently there are eight stainless steel UHV chambers along the 35 ft. long transfer-line. Once a sample is placed onto the sample cart, which travels the length of the transfer-line, the sample can be moved from chamber to chamber *in situ*. The base pressure is maintained at $1x10^{-9}$ Torr through the use of Cryopumps and turbomolecular pumps.

The remote plasma cleaning chamber has been described previously [10]. The process gases flow through a quartz tube located on top of the chamber. An inductively coupled plasma is generated using a rf power supply (13.56 MHz) and rf matching network attached to a Cu coil placed around the quartz tube. The sample is located 40 cm from the center of the rf coil. The sample is heated by a tungsten coil facing the backside of the wafer. The base pressure of the plasma cleaning chamber is $8x10^{-9}$ Torr. A point-of-use purifier/filter was located downstream of the H_2 and SiH_4 mass flow controllers. The SiH_4 gas is delivered as a mixture of 1% SiH_4 in H_2. Depending on the chamber pressure and rf power, the plasma can be maintained in the quartz tube or extended down toward the sample region. For the experiments in this study, the plasma extends down to the sample region although the plasma was excited remotely.

The samples were ramped from 150°C to 450°C at 100°C/min. The H_2 (93.9 sccm) and SiH_4 (0.1 sccm) flow rates as well as the process pressure (25 mTorr) were established prior to ramping up the temperature. The pressure was controlled by the H_2 and SiH_4 flow rates. The wafers were exposed to a 20, 100, or 400 Watt rf plasma, and the plasma was struck once the set point was reached. After the plasma exposure, the plasma, the gases, and the heater were simultaneously turned off. Once a plasma cleaning experiment is complete, a low temperature (450°C) PECVD or a (800°C) CVD epitaxial Si film was deposited in the H-plasma chamber to facilitate TEM analysis.

Auger analysis was done using a Perkin-Elmer static probe Auger system which utilizes a cylindrical mirror analyzer and a spot size less than 1 mm. The differentiated Auger spectra were normalized using the $Si_{(LMM)}$ peak at 92 eV (H_2/SiH_4 plasma cleaned wafers) or normalized using the $O_{(KLL)}$ peak at 503 eV (as-loaded RCA cleaned wafers). The LEED diffraction patterns were taken at an accelerating voltage set at 60.8 V.

TEM lattice images were obtained to determine the quality of the interface and the surface roughness. The TEM was also used to investigate the crystalline quality and the growth rate of the PECVD deposited Si film.

RESULTS AND DISCUSSION

Neutral Deposition Processes

The Auger $O_{(KLL)}/Si_{(LMM)}$ peak-to-peak ratio and TEM images were used to determine the experimental conditions that lead to a neutral deposition. The balance that is to be achieved is that Si etching from the atomic H is offset by deposition from the silane containing species. If neutral deposition is achieved on the Si surfaces then Si will not deposit on the oxide surfaces and etching can potentially be achieved. Figure 1 displays the ratio of the $O_{(KLL)}/Si_{(LMM)}$ Auger peaks versus plasma exposure for conditions of different plasma power and silane ratio. The conditions employed for the studies here were as follows: rf power varied from 20 to 400 Watts, SiH_4:H_2 ratio equal of 0.0010 and 0.0017, and a substrate temperature of 450°C. For rf powers of 100W and 400W, the underlying Si substrate is exposed in approximately 10 min. Since the RCA oxide thickness is ~20 Å, the SiO_2 etch rate is deduced to be ~2 Å/min. For the 20 Watt plasma exposure shown in Figure 1, the $O_{(KLL)}/Si_{(LMM)}$ dependence indicates that the oxide removal rate is significantly reduced, and the same low level was not achieved for the exposure times employed.

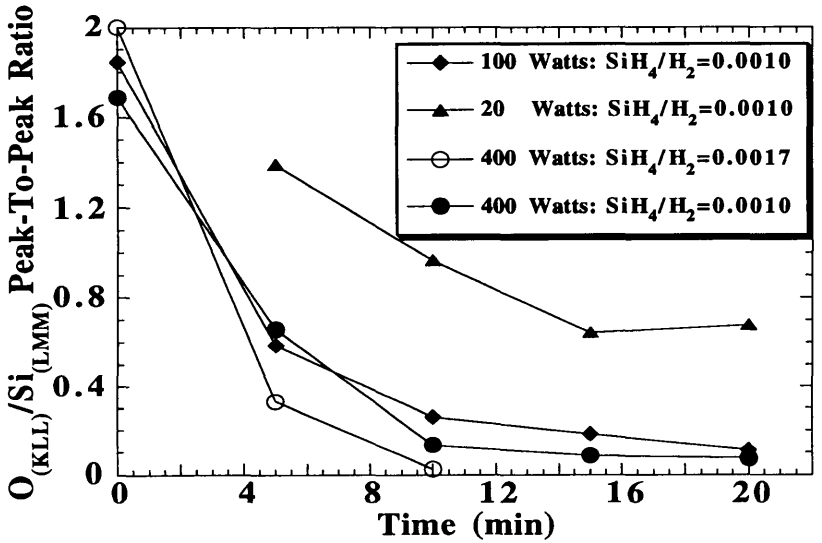

Figure 1. The Auger $O_{(KLL)}/Si_{(LMM)}$ peak-to-peak ratios of RCA cleaned Si(100) wafer after various remote plasma exposures. The results display the effect of rf power and SiH_4/H_2 ratio on the etch rate of the SiO_2 layer. The substrate temperature was 450° C.

To more closely examine the process, TEM analysis was carried out for the wafer exposed to a 400 Watt plasma, SiH_4:H_2 ratio of 0.0010, wafer temperature of 450°C, and 15 min total exposure. A high resolution cross-section image is shown in Fig. 2. The image shows that a thin epitaxial layer has been deposited on the surface, and no defects were observed at the interface. The micrograph confirms that the oxide layer has been removed. We presume that the thin epitaxial layer was grown after the surface was oxide free. If we assume that the 50Å epi layer was deposited in the last 5 min of the process, then we deduce a rate of ~10Å per min. The slow growth of the epitaxial Si shows that the system was in a near neutral deposition mode.

When the SiH_4/H_2 ratio was increased from 0.0010 to 0.0017 for a 400 Watt plasma exposure, the $O_{(KLL)}/Si_{(LMM)}$ ratio approaches zero in a time similar to that of the more dilute processes (Figure 1). Cross-sectional TEM analysis indicated, however, that the oxide film was only partially removed and that the remaining oxide film was capped by a heavily defective crystalline Si film. This suggests that the reduction of the oxygen AES signal was a combination of oxide removal and Si deposition.

Two possible mechanisms for etching SiO_2 are ion bombardment and neutral radicals of SiH_4. To explore these effects several plasma exposures were completed with different sample bias. Experiments were carried out at a substrate bias of -25 volts (attracting ions), and in these measurements no significant change in the SiO_2 etch rate was observed. Previously, the plasma system has been characterized for H_2 gas. The atomic H concentration is 3 orders of magnitude greater than the H ion concentration [10]. Even though the plasma is remote, atomic H can react with SiH_4 in the gas phase to form SiH_x radicals [12]. We suggest that neutral SiH_x radicals in combination with the atomic H are the primary species for etching SiO_2 and not the ions. The etching mechanism of deposited Si on the SiO_2 film is by atomic H to form SiH_4. The etching of Si from the surface of the SiO_2 prevents stable Si nuclei formation which inhibits film growth on the SiO_2. A high etch rate for Si clusters on SiO_2 is likely because these deposits would be amorphous. The chemistry for the neutral deposition process is controlled by having a sufficient flux of atomic H to etch off any excess Si on the SiO_2 surface to maintain Si deposition selectivity and etching of the SiO_2.

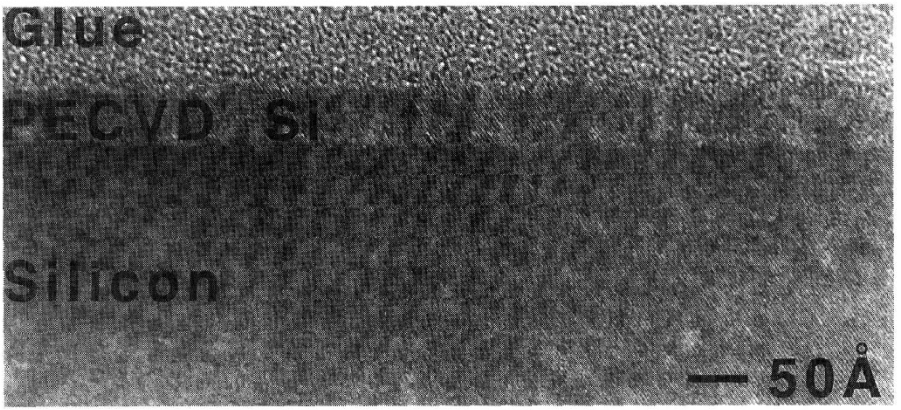

Figure 2. High resolution TEM image of a Si surface after H_2/SiH_4 plasma cleaning. The surface was exposed with a wafer temperature of 450°C, plasma power of 400W and SiH_4/H_2 ratio of 0.0010.

The chemical processes for the etching of the SiO_2 are not established at this time. Previous studies have indicated that the remote H-plasma did not etch the SiO_2. However, oxide has been removed from Si by exposure to a Si flux in MBE systems at temperatures of ~750°C. In these experiments it was presumed that the excess Si allowed the formation of SiO which is volatile at these temperatures. We suggest that the combination of SiH_x and excess atomic H allows the formation of molecules or radicals that are volatile at the lower temperatures employed in this study.

Surface Characterization

The Auger analysis was also used to monitor the level of oxygen and carbon contamination after each process step as shown in Figure 3. The AES scans in Figure 3 depict the carbon remaining after the RCA clean (as-loaded condition) and after removal of the SiO_2 film by the H_2/SiH_4 plasma. After an RCA clean some carbon is detected on the SiO_2 surface (Figure 3a). The carbon peak is reduced below the detection limits of AES after H_2/SiH_4 plasma cleaning. Previous studies of H-plasma cleaning have indicated that the carbon is removed from the wafer surface through the interactions of atomic H with the carbon contaminants.

LEED was used to investigate the surface structures from the as-loaded RCA cleaned surface to a PECVD Si surface due to the H_2/SiH_4 plasma exposure. There was no LEED pattern for the as-loaded wafer due to the amorphous SiO_2 film (15-20 Å)., and this is consistent with the AES scan (also indicating oxide) for the wafer in Figure 3a. In contrast, the 400 Watt plasma cleaned surface exhibits a 2x1 reconstructed surface which is similar to the LEED pattern for H-plasma cleaning of Si above 300°C [10]. The streaked 2x1 LEED pattern of the H_2/SiH_4 plasma cleaned surface is consistent with a hydrogen terminated monohydride configuration.

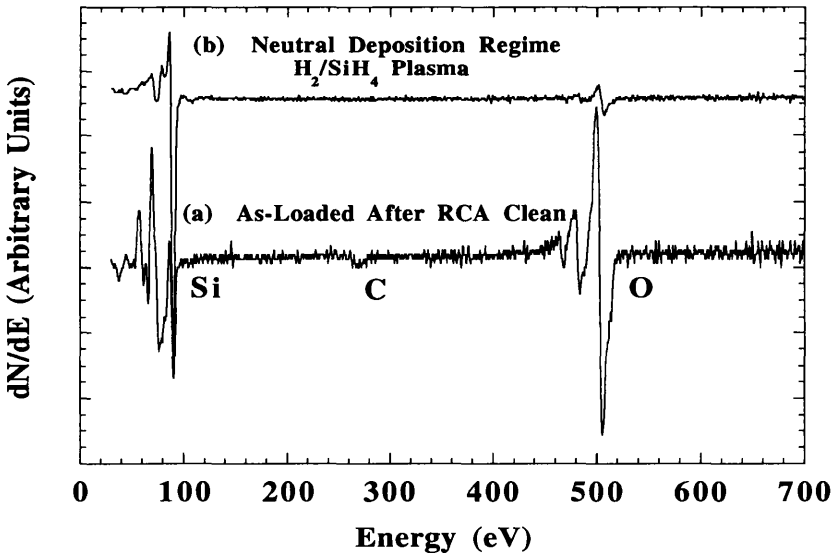

Figure 3. Auger spectra of Si (100) surfaces after (a) RCA clean and (b) H_2/SiH_4 plasma clean.

SUMMARY

This study has established that the remote H_2/SiH_4 plasma removes an SiO_2 film from a Si surface at an etch rate of approximately 2 Å/min. The trace amount of SiO_2 that remained after the plasma clean was insufficient to prevent a high quality PECVD Si epitaxial film from being deposited. For the neutral deposition process regime, the experimental conditions for removing SiO_2 was 450°C, 25 mTorr, 100-400 Watts of rf power, and a SiH_4:H_2 flow ratio equal to or less than 0.0010. Future studies will explore methods to enhance the etch rate without damaging the surface.

ACKNOWLEDGMENTS

This work has been supported by the NSF Engineering Research Centers Program through the Center for Advanced Electronic Materials Processing (Grant CDR 8721505).

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