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Cite as: Appl. Phys. Lett. **67**, 2194 (1995); https://doi.org/10.1063/1.115100
Submitted: 28 December 1994 • Accepted: 14 August 1995 • Published Online: 04 June 1998

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Morphology of Si(100) surfaces exposed to a remote H plasma

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(Received 28 December 1994; accepted for publication 14 August 1995)

This study addresses the formation of roughness and near surface defects on Si(100) surfaces that are exposed to a remotely excited H plasma. The remote H plasma processing can be employed for *in situ* wafer cleaning. Atomic force microscopy, transmission electron microscopy, and residual gas analysis are used to measure the surface roughness, the near surface defects, and the etching, respectively. For remote H plasma exposures at substrate temperatures $\leqslant$300 °C, etching is observed along with a significant increase in the surface roughness and the formation of platelet defects in the near surface region. As the substrate temperature is increased to above 450 °C, etching is significantly reduced and no subsurface defects or increases in surface roughness are observed. © *1995 American Institute of Physics.*

The hydrogen plasma exposure of silicon was studied as a potential cleaning step prior to gate oxidation or epitaxial deposition in the fabrication of integrated circuits. This process could be appropriate for an *in situ* clean in a single-wafer cluster-module system. Previous studies have shown the effectiveness of the H-plasma process to reduce the levels of contaminant species such as carbon and oxygen.[1–4] In particular, residual carbon remaining after an *ex situ* wet clean and vacuum transfer can be reduced to below the detection limits of Auger electron spectroscopy (AES). Also, residual oxygen present on the surface before plasma cleaning can be reduced to below monolayer coverage as determined by AES. Electron diffraction studies [low-energy electron diffraction (LEED) and reflection high-energy electron diffraction (RHEED)] have shown that the H-plasma cleaning is able to terminate the Si(100) surface in different phases, resulting in 1×1, 2×1, and 3×1 electron diffraction patterns, depending on the process pressure and the substrate temperature.[5–7] For H-plasma exposures from 30–200 °C, substrates exhibit the dihydride phase (1×1 diffraction). For H-plasma exposures from 300–400 °C, substrates exhibit a 2×1 diffraction pattern indicative of the monohydride reconstruction. For a plasma exposure at the intermediate temperature, 250 °C, substrates exhibit a 3×1 electron diffraction pattern, which suggests a mixture of both monohydride and dihydride phases. Several studies have now established that low-temperature (150 °C) H-plasma exposures can result in the formation of subsurface platelet defects.[8–10] Although the aspects of the surface structure can be analyzed using transmission electron microscopy (TEM) and LEED, it is difficult to completely detail the surface morphology. In this study we employ atomic force microscopy (AFM) to directly image Si(100) following exposure to an H plasma at process temperatures from 150–700 °C. TEM is used to observe the formation of near surface defects, and residual gas analysis displays the etching byproducts.

The system used for these experiments was a stainless-steel UHV chamber equipped with gas delivery and rf excitation. The plasma excitation is accomplished by coupling a 13.65 MHz rf signal to a coil wrapped around a 5 cm diam quartz tube through which molecular hydrogen flows. Atomic hydrogen is produced in the rf field region and effects the silicon surface positioned 10 cm from the downstream end of the tube. In this arrangement the system is a remote plasma system since the sample is not immersed in the hydrogen excitation region during processing. The wafers were 100 mm boron-doped Si(100) with a resistivity of 0.05 Ω cm. The AES and RHEED analysis was performed in an adjacent chamber allowing *in situ* transfer at pressures of $\leqslant 1\times10^{-8}$ Torr. The H plasma and analysis chambers were combined in one module of a multichamber cluster system.

The experiments involved *ex situ* cleaning, *in situ* plasma processing and surface analysis, and then *ex situ* analysis. The *ex situ* clean was an RCA clean to remove organic and metallic contaminants followed by an HF-acid dip to replace the RCA generated wet chemical oxide with a hydrogen terminated surface. This cleaning procedure consistently shows a 1×1 diffraction pattern with LEED or RHEED. Following the *ex situ* wet chemical cleaning, the wafers were then transferred to the load lock of the vacuum system. Each wafer was processed individually at a temperature from 150–700 °C and a plasma duration of 10 min. For all samples, the hydrogen pressure was 20 mTorr at a flow of 75–85 sccm and the rf power was 20 W.

The AFM analysis was performed with an ambient Park Scientific System with a 10 μm scanner and silicon nitride tips. The scans were obtained with a scan range of $(1\ \mu\text{m})^2$ at 128×128 points per scan. Roughness values were obtained from at least five different locations near the center of each wafer. The rms value of the surface roughness was obtained from both area and line trace statistics from the images obtained. Error bars shown were obtained by calculating the standard deviation of the measurements from the different images. In many instances, two-dimensional (2D) Fourier transforms of the scans were used to identify noise and systematic errors. This analysis accounted for variation due to multiple scans at one location, variation due to scans at multiple locations, and variation due to tip quality.

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 0003-6951/95/67(15)/2194/3/$6.00

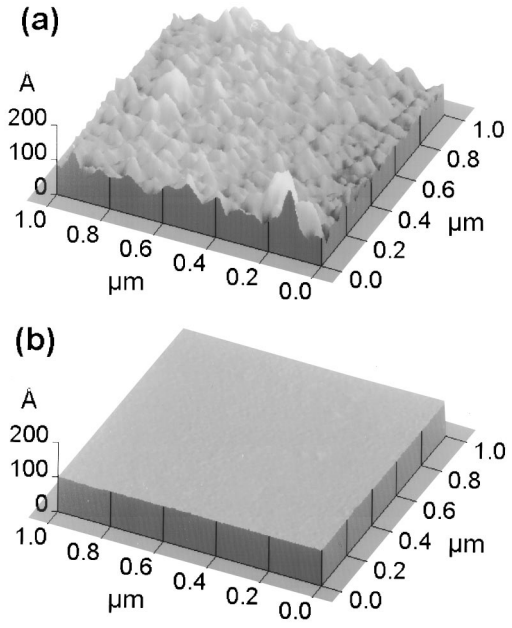

FIG. 1. AFM 3D renderings of silicon surfaces treated with a 10 min H-plasma exposure with a substrate temperature of (a) 150 °C and (b) 450 °C. These surfaces have relative rms roughnesses of 23±5 and 2±1 Å, respectively.

The initial surface of the silicon following the *ex situ* cleaning and the sequential stripping of the residual oxide exhibited an rms roughness of 2±1 Å. Following an H-plasma exposure for 10 min at 150 °C, the rms roughness increased to 23±5 Å; Fig. 1(a) is a 3D rendering of the AFM data. Shown in Fig. 1(b) is a 3D rendering of the AFM data for the surface following a plasma exposure of 10 min at 450 °C. The rms roughness of the silicon surface showed no significant increase over that of the starting surface. Additionally, the rms roughness of a surface treated for 10 min at 700 °C increased only slightly to 4±1 Å. These results are compared in Fig. 2 in the graph of relative rms roughness versus substrate temperature during processing. Samples processed at temperatures of 450 °C and above resulted in a sample morphology that was essentially unchanged, with rms roughness values comparable with the roughness prior to plasma exposure. In contrast, samples exposed to an H

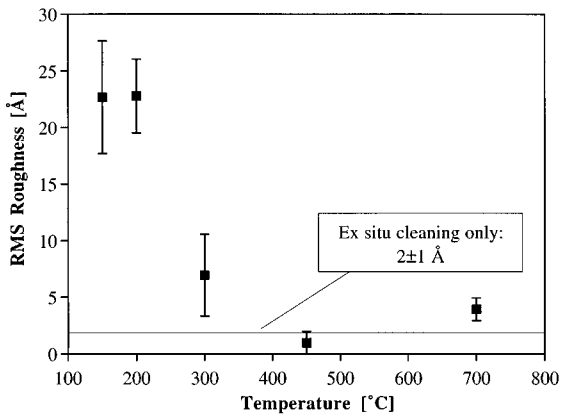

FIG. 2. Relative rms roughness of the silicon surface vs temperature following H-plasma treatment.

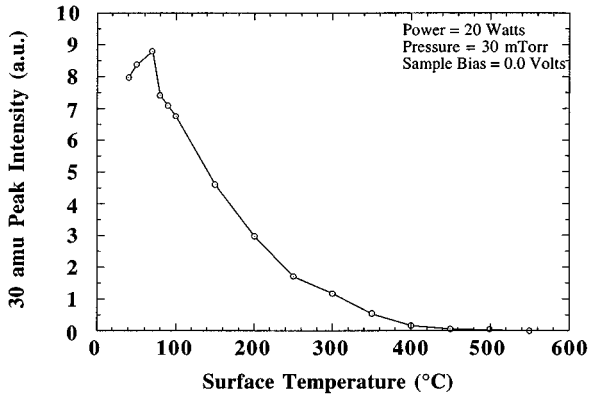

FIG. 3. Relative partial pressure of the 30 amu signal ($Si–H_2$) vs substrate temperature for H-plasma exposure. The signal is attributed to a fragmentation of the SiH_4 molecules.

plasma for times of 10 min at temperatures from 150 to 300 °C show significant roughening. We note that roughening is often associated with surface etching processes.

The RGA measurements were employed to determine the conditions at which the hydrogen plasma would induce etching of the Si surface. This experiment was performed in a prototype chamber of similar design to the cluster module chamber. The system has been described elsewhere.[11] Our premise is that during steady-state operation of the H plasma, an etch reaction of the silicon surface would produce SiH_4. The RGA signal of the SiH_4 would exhibit SiH_x fragments (x=1,2,3), and the spectra that we obtained exhibited the expected relative peak concentrations. The 30 amu peak was monitored to avoid contributions from O_2, N_2, and CO that occur at the other masses. With no wafer present, no signal was detected. Shown in Fig. 3 is a plot of the 30 amu (SiH_2) peak intensity versus substrate temperature. Each data point is the steady-state relative partial pressure after at least 10 min of plasma exposure. These data indicate that SiH_4 production due to the H plasma is substantially reduced for Si wafer temperatures >350 °C. This reduction in etch rate with an increase in temperature is consistent with the experiments of Carter *et al.*[12] and Gates *et al.*[13]

A portion of two different wafers were analyzed using plan-view and cross-sectional TEM.[8–10] As shown in Fig. 4 there is a significant difference in Fig. 4(a) the sample treated for 10 min at 250 °C and Fig. 4(b) the sample treated for 10 min at 450 °C. The 250 °C sample shows a high density of subsurface platelet-type defects induced by the H-plasma exposure. These defects were analyzed using high-resolution TEM (HTEM) and found to be the hydrogen-induced platelets studied by Johnson *et al.*[9,14,15] Our TEM results also indicate that the defects had a compressive type strain field and, therefore, are interstitial in nature and were found to have a habit plane of type {111}. The density of these defects is greater than 10^9 cm^{-2}. The diffraction conditions used in the plan-view mode revealed that approximately 90% of the defects are within 250 Å of the plasma treated surface. This corresponds to one-quarter of the extinction distance (ξ_g) for the reflecting **g** vector, 220. The 450 °C case shows not only an atomically flat surface, as confirmed by AFM, but exhibits no evidence of the subsurface defects.

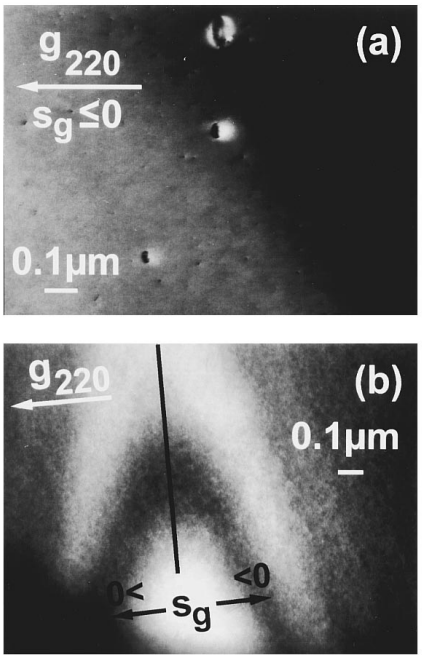

FIG. 4. Plan-view TEM images of surfaces treated with a 10 min H-plasma exposure with a substrate temperature of (a) 250 °C and (b) 450 °C during processing.

The results presented here indicate a significant change in the surface morphology and the near surface defect structures for surfaces exposed to an H plasma. At temperatures from 150 to 300 °C, etching is observed along with roughening and near surface defect formation. At and above 450 °C etching is significantly reduced along with the defects and roughening. These results appear contrary to many etching or chemical processes in which the rates increase with increasing temperature. The effects suggest that the surface interactions are changing in the temperature range studied here (i.e., 150–450 °C). The interactions of atomic H with a Si surface can involve several complicated processes that include a balance of adsorption and desorption. It is interesting to note that the H termination of the surfaces varies significantly in the same temperature range. A monohydride surface is obtained for temperatures greater than 300 °C while a mixed and dihydride surface is obtained at temperatures less than 300 °C. This indicates a significant change in the surface H concentration for processing in this temperature range. At this time we can only speculate as to whether the surface H-concentration change is the most significant effect in changing the etching and concomitant roughening processes.

In summary, AFM measurements indicate that exposures of silicon to a H plasma at temperatures from 450–700 °C produce no observable changes in the surface rms roughness. However, for temperatures of 300 °C and lower there is significant roughening of the surface. Plan-view TEM showed that the H plasma in the high-temperature regime did not create any detectable subsurface defects while the low-temperature case showed a substantial defect concentration in the near surface region (100 Å). Residual gas analysis indicates that surface etching decreases for increasing temperatures and reaches detection limits at substrate temperatures $\geqslant$450 °C. The effects reported here demonstrate a new processing regime for *in situ* H-plasma cleaning of Si(100). This process could prove suitable for cleans prior to gate insulator formation, contact epi or metallization, presilicide clean, or following reactive ion etching.

This work has been partially supported by the National Science Foundation Engineering Research Centers Program through the Center for Advanced Electronic Materials Processing (Grant No. CDR 8721505).

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