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Very Low Defect Remote Hydrogen Plasma Clean of Si (100) for Homoepitaxy

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We discuss a remote hydrogen plasma cleaning technique which is effective at removing carbon, nitrogen and oxygen from a silicon surface that has been pretreated with a wet chemical clean and a final dilute HF dip. It has been found that for best results, air exposure of the wafer after the HF dip must be minimized, as the ability of the H plasma clean to remove oxygen seems to be reduced on wafers which have been exposed to air for several hours. The atomic H supplied by the clean also results in different hydrogen terminated surface reconstructions depending on the substrate temperature. We observe a (1 × 1) RHEED pattern at clean temperatures below 190° C which is believed to be due to disordered silicon monohydride and dihydride termination, a (3 × 1) pattern between 200 and 280° C, corresponding to ordered monohydride and dihydride coverage, transitioning to a (2 × 1) pattern around 300° C due to monohydride termination. A dilute HF dip produces a (1 × 1) pattern due to disordered (3 × 1) cells, *i.e.* disordered monohydride and dihydride coverage. The passivating effects of the dilute HF dip and of the remote hydrogen plasma clean have also been discussed. The two processes have been found to result in similar hydrogen coverage of the wafer surface which in turn results in similar surface passivation. Both the dilute HF dip and the *in situ* remote H plasma clean have been found to protect the wafer from contamination for up to 15 min in ambient air and for an indefinite period under vacuum.

Key words: Si homoepitaxy, hydrogen plasma clean, hydrogen passivation

INTRODUCTION

It is well documented that proper cleaning of the silicon surface prior to growth is required for successful epitaxy.[1,2] A typical method of wafer preparation consists of a wet chemical treatment prior to loading substrates into the epitaxial reactor followed by a second clean which is performed *in situ* to remove any remaining contamination. It is important to minimize recontamination of the surface between cleans since the *in situ* clean is often effective at removing only certain contaminants. In conventional silicon epitaxy, a protective oxide is grown after the *ex situ* clean to prevent recontamination. The oxide is then removed *in situ* using a high temperature HCl bake. A similar technique has been used in silicon MBE where a 10–50Å oxide is formed using a boiling $NH_4OH:H_2O_2:H_2O$ mixture and subsequently removed using a 1–10 min 840–1240° C *in situ* bake.[3,4] These high temperature cleans leave the wafer surface extremely clean and highly reactive. In such cases, growth must begin immediately after cleaning to prevent recontamination.

A high temperature *in situ* clean would be unacceptable for multilayer heteroepitaxy where there is a thermal expansion mismatch between dissimilar materials, a consideration for future applications to novel device structures. If a substrate contains materials other than silicon, the clean temperature may be limited by the maximum temperature at which the interface between the two materials is stable. Therefore, in order to develop a true low-temperature epitaxial growth process, one must also develop a low-temperature *in situ* cleaning technique. We have developed a remote hydrogen plasma clean at 250° C which effectively removes carbon, nitrogen and oxygen from a pre-treated silicon surface,[5] and produces a hydrogen terminated surface with very few crystalline defects. Subsequent to the remote H plasma clean we have achieved homoepitaxial silicon growth via Remote Plasma-enhanced Chemical Vapor Deposition (RPCVD) for deposition temperatures ranging from 150 to 480° C. An important benefit of the remote hydrogen plasma clean is that hydrogen termination of the Si surface acts as a barrier to recontamination. In this paper we will show that the remote H plasma clean leaves the surface H terminated, and that such a surface is protected from recontamination for short durations in air (~15 min) and for indefinite periods under vacuum.

EXPERIMENTAL PROCEDURE

These experiments have been performed in an RPCVD system. This Ultra-High Vacuum (UHV) system consists of three interconnected chambers: a load lock chamber for wafer loading and storage, a surface analysis chamber which is equipped with Auger Electron Spectroscopy (AES), and a deposition chamber equipped with Reflection High Energy Electron Diffraction (RHEED), where deposi-

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tion and cleaning processes are performed. Additional details of this system have been given elsewhere.[6,7]

The wafer preparation has been discussed in detail previously,[5] but will be described briefly here for the sake of completeness. The wafers used were (100) *p*-type Si substrates with resistivities between 10 and 15 Ω-cm. Before wafers are loaded into the system, they are cleaned using a wet chemical treatment consisting of an ultrasonic degrease in TCA, acetone, and methanol. A subsequent ultra-high purity water rinse is followed by a modified RCA clean[8] for removal of organic and metallic contamination. Finally a 60s 40:1 H_2O:HF dip is used to remove the oxide grown during the RCA clean. After the final HF dip, wafers are rinsed for 30 sec in ultra-high purity water, spun dry and immediately placed in a nitrogen purged glove box and loaded into the load lock chamber. During sample loading, the load lock chamber is purged with nitrogen allowing UHV conditions (10^{-9} Torr) to be achieved without a bakeout and to minimize the exposure of the wafers to air. Wafers are exposed to air for less than 10 min after the final HF dip during this procedure.

Prior to epitaxial deposition, the wafers are cleaned *in situ* using a remote hydrogen plasma clean to remove carbon and oxygen contamination. Nitrogen is rarely observed in *in situ* Auger analysis of the wafer surface before cleaning. However, if it is, the cleaning step is effective in removing nitrogen as well. The clean is performed in the deposition chamber which is shown in Fig. 1. For a typical clean, 200 sccm of hydrogen is introduced at the base of the plasma column at a pressure of 45 mTorr and inductively excited with 9 W of rf power (13.56 MHz). During the clean, which typically lasts 45 min, the substrate is heated to 250° C from the back using two quartz infrared bulbs.

DISCUSSION

HF dip

In RPCVD as well as in several other low-temperature epitaxy techniques,[2,9,10] a protective oxide is not used to prevent recontamination of the wafer surface after the *ex situ* clean. Rather, the final step in the wet chemical treatment is a dilute HF dip in order to remove as much of the oxide as possible which has formed during the cleaning process. This approach leaves the surface protected by hydrogen such that little carbon and oxygen is observed after samples are loaded into the vacuum system, and such that this contamination is removable via remote hydrogen plasma cleaning at low temperatures. Chabal *et al.*[11] have analyzed silicon wafers prepared using an RCA clean followed by an HF dip and found the resultant surface to be extremely clean (*i.e.* little carbon, oxygen, and metallic contamination) and to be hydrogen terminated. Indeed, we observe very little carbon and oxygen contamination after the *ex situ* clean using Auger analysis (Fig. 2a). The passivating effects of the HF treatment on silicon surfaces have been studied by several researchers. Takahagi *et al.*[12] found that contamination of a UV/HF treated surface increased by less than 10% after 10 min exposure to air. Fenner *et al.*[13] have studied carbon and oxygen contamination of silicon surfaces cleaned using a spin etch technique which is an alternative to an HF dip. The spin etch technique consists of spinning the samples at 3000 rpm while cleaning the surface with a few drops of alcohol and then etching with a few drops of an HF/alcohol solution. This technique eliminates a problem associated with dipping wafers in wet chemicals, where contaminants which tend to accumulate on the liquid surface adsorb onto the wafer as it is removed from the liquid. Fenner *et al.* have shown that after an HF spin etch and 1 min exposure to air, total carbon and oxygen contamination is less than 1/10 of a monolayer. We have found the surface of the wafers treated with the HF dip to be very stable under UHV conditions (~2 × 10^9 Torr). When analyzed using AES, wafers which remain in the load-lock chamber for several days after cleaning show no more carbon and oxygen on the surface than when analyzed shortly after loading. In order to determine the extent to which the HF dip passivates the silicon surface, we have analyzed carbon and oxygen contamination of wafers exposed to air for various lengths of time using AES. Figure 2 (a) shows the Auger spectra for a wafer loaded using our standard *ex situ* cleaning procedure which results in exposure to room air for ~10 min. This wafer shows an undetectable amount of carbon and very little oxygen on the surface. This small amount of

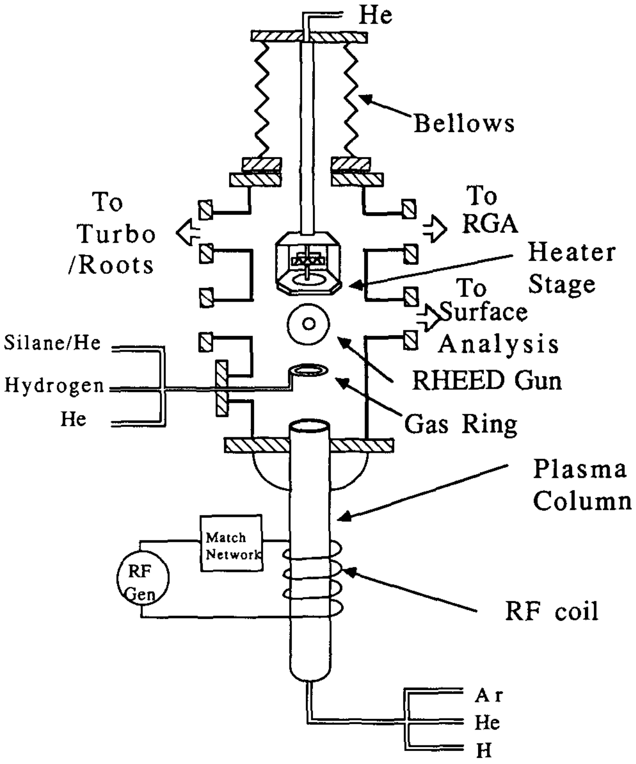


Fig. 1. — RPCVD deposition chamber schematic.

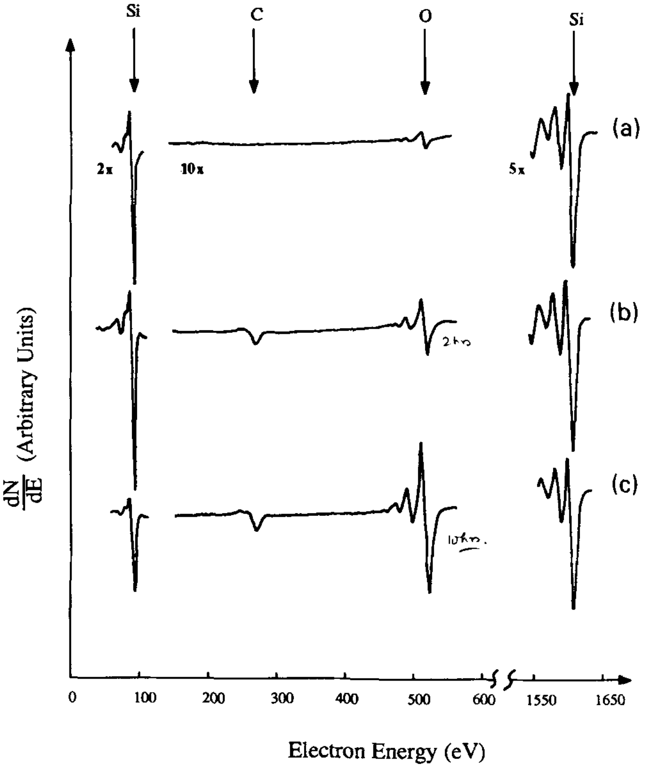


Fig. 2. — Auger spectra of Si (100) wafers after modified RCA clean with final HF dip and subsequent air exposure, a) 10 min b) 2 hr c) 10 hr.

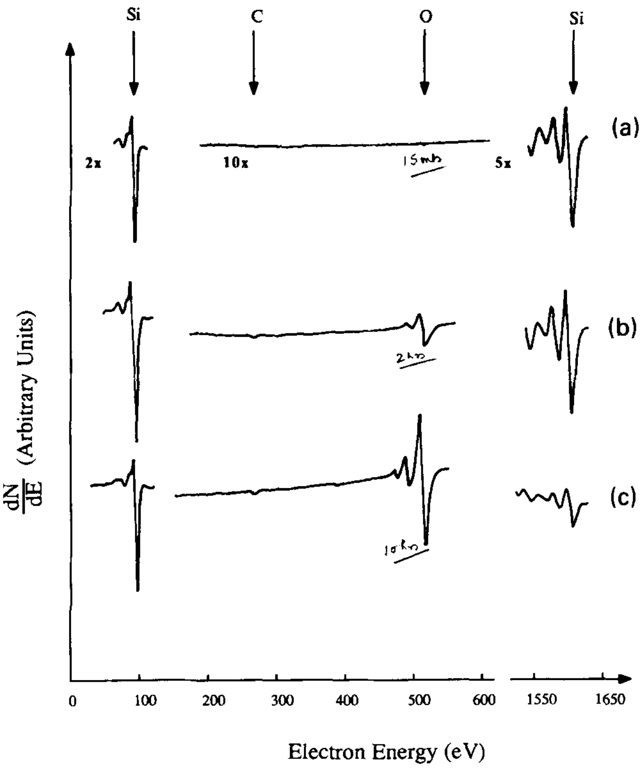


Fig. 3. — Auger spectra of Si (100) wafers after modified RCA clean with final HF dip, air exposure, and *in situ* remote hydrogen plasma clean. Air exposure time of a) 10 min b) 2 hr c) 10 hr.

oxygen is easily removed by our remote H-plasma clean (Fig. 3a). AES spectra for wafers exposed to air for 2 and 10 hr, are shown in Fig. 2 (b) and (c), respectively. It is apparent from these figures that the amount of carbon and oxygen contamination steadily increases with the duration of air exposure. This confirms the importance of loading the wafers into the vacuum system as soon as possible after completing the HF dip. After AES analysis was performed on the wafers, they were cleaned *in situ* using the remote H plasma clean to determine if the accumulated contamination could be removed. Auger spectra after the *in situ* clean are shown in Fig. 3 for exposure times of (a) 15 min (b) 2 hr and (c) 10 hr. In all cases the *in situ* clean was effective in removing carbon contamination caused by the air exposure, but only for the wafer exposed to air for 15 min was the clean effective in significantly reducing the oxygen contamination. This suggests that the oxygen bonding may be a function of the duration of the air exposure. Based on this research, we conclude that the HF dip results in a hydrogen passivated surface which can be exposed to atmosphere for short periods without significant carbon or oxygen contamination.

Remote Hydrogen Plasma Clean

The rf excitation of molecular hydrogen generates ions, electrons, neutral hydrogen atoms, vibrationally excited H_2 molecules, and electronically excited hydrogen atoms and molecules. During remote hydrogen plasma cleaning, the substrate is separated from the glow region by approximately six in. Langmuir probe measurements between the glow and the wafer show ion and electron concentrations to be below the detectable limits. This is consistent with the large collision cross section for low energy electrons in hydrogen.[14] Since electronically excited species are short lived and the concentration of charged species is low, we conclude that the wafer cleaning due to the remote hydrogen plasma treatment is due to neutral species, either atomic H or vibrationally excited H_2, and we therefore consider the wafer to be remote from the plasma.

RHEED analysis of wafers cleaned using the remote hydrogen plasma clean at 250° C shows 1/3-order streaks (Fig. 4a) indicative of a (3 × 1) reconstruction pattern. This (3 × 1) pattern is consistent with the observations of Chabal[15] for a silicon (100) surface exposed to atomic H. We therefore conclude that atomic H is responsible for passivating the wafer surface. The (3 × 1) reconstruction pattern has been found to be due to alternating monohydride and dihydride units[15] as shown in Fig. 5a. The (3 × 1) reconstruction pattern can be transformed to a (2 × 1) reconstruction pattern by heating the wafers to or above 305° C (Fig. 4b). This results in desorption of some of the hydrogen, which we believe produces a surface characterized by only monohydride coverage (Fig. 5b). The (2 × 1) reconstruction pattern shown in Fig. 5b is the same reconstruction pattern expected for a hydrogen free surface, in which case,

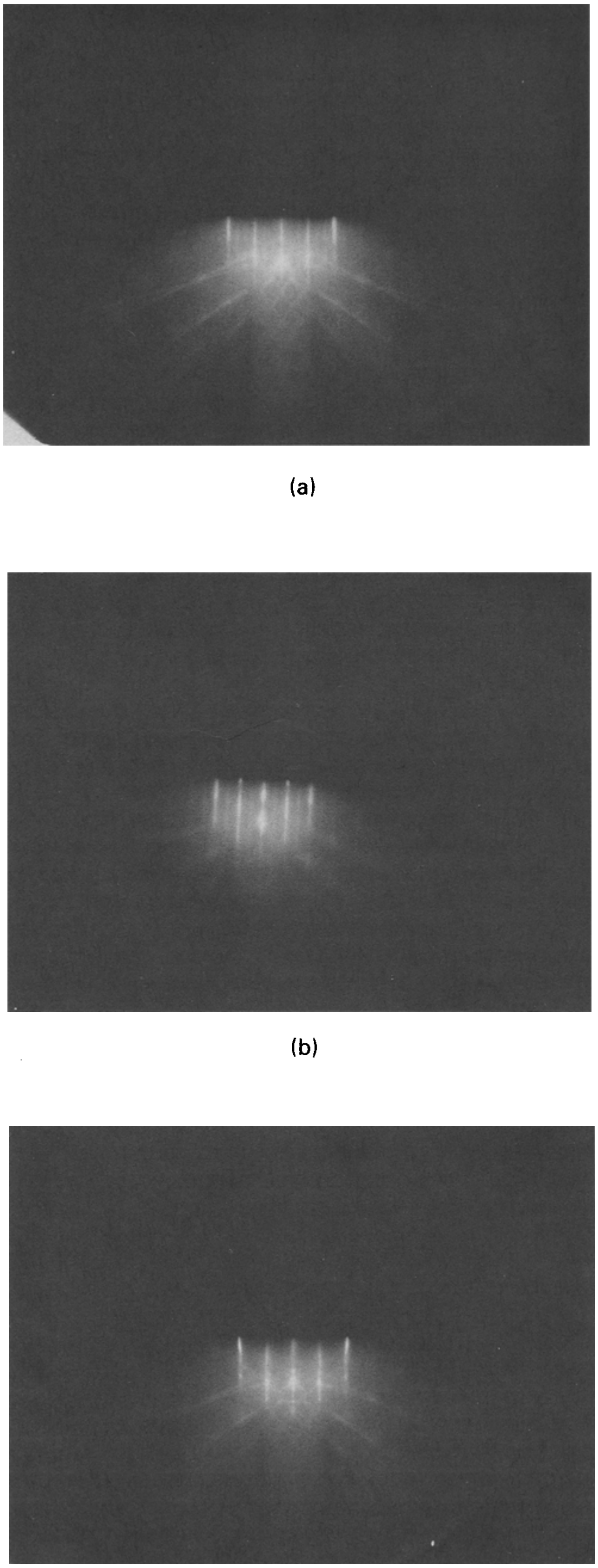


Fig. 4. — RHEED diffraction pattern of silicon (100) substrate in the ⟨110⟩ direction. a) after 45 min remote H plasma clean at 250° C, b) after 45 min remote H plasma clean at 250° C plus 5 min 305° C bake c) after *ex situ* clean.

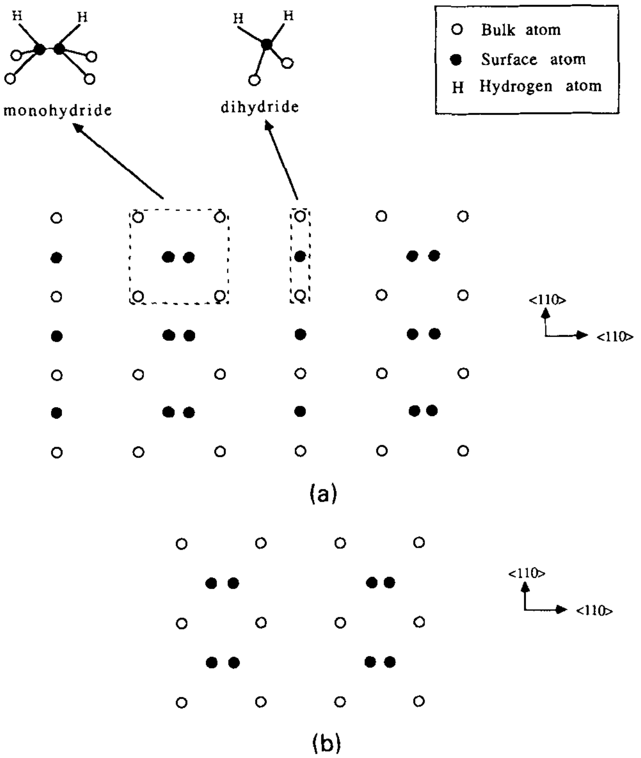


Fig. 5. — Schematic of H coverage for various reconstruction reconstruction patterns of silicon (100) surface. a) (3 × 1) reconstruction pattern b) (2 × 1) reconstruction pattern.

the surface dimer atoms share two bonds. The (2 × 1) reconstruction pattern also results if the remote H plasma clean is performed in the temperature range of 305–400° C. In this case, the stable hydrogen termination of the surface is again the (2 × 1) reconstruction pattern (monohydride coverage). We have found the (3 × 1) and (2 × 1) reconstructed surfaces resulting from the remote H plasma clean to be stable under UHV conditions. RHEED analysis shows that the (3 × 1) and (2 × 1) patterns are maintained when the samples cool to room temperature, and wafers that are allowed to remain in vacuum for 24 hr after cleaning show no increase in carbon or oxygen based on AES analysis. A (1 × 1) diffraction pattern is observed for wafers analyzed using RHEED after the *ex situ* treatment (Fig. 4c) and for wafers subjected to the remote H plasma clean at temperatures less than 190° C regardless of the surface reconstruction before cleaning. This (1 × 1) hydrogen terminated surface is attributed by Chabal[15] to disordered dihydride and monohydride termination (*i.e.* disordered (3 × 1) cells). Chabal found the (1 × 1) surface to have roughly the same amount of hydrogen on the surface as the (3 × 1) reconstruction pattern using Nuclear MicroAnalysis (NMA), as well as similar ratios of dihydride and monohydride bonding using Electron Energy Loss Spectroscopy (EELS). As was the case for the (3 × 1) reconstruction pattern, if a (1 × 1) reconstructed sample is heated to >305° C, the surface reconstruction is transformed to the (2 × 1) reconstruction pattern. However, heating the (1 × 1) reconstruction pattern to 250° C does not generate the (3 × 1) reconstruction pattern. The (3 × 1) reconstruction pattern is only observed after the remote H plasma clean at ~250° C.

By passivating the silicon surface with hydrogen, the remote H plasma clean eliminates the need to begin deposition immediately after cleaning. In fact, in our typical deposition process, the wafer is transferred to the surface analysis chamber for AES analysis after the *in situ* clean is completed, after which it is then transferred back to the deposition chamber for epitaxial growth. Thus, for a typical wafer, there is at least a 30 min delay between the end of the clean and the beginning of the deposition.

The passivating effect of exposure of a Si (100) surface to atomic H was studied previously by Hirayama and Tatsumi.[16] It was found that H exposure at temperatures less than 200° C resulted in significantly less adsorbed oxygen than for wafers without this treatment when the wafers were exposed to air for 12 hr. We have studied the passivating effect of the remote H plasma clean at 250° C by exposing cleaned wafers to room air and observing the change in carbon and oxygen contamination using AES analysis. Auger spectra taken immediately after the H plasma clean showed no detectable carbon or oxygen. Secondary Ion Mass Spectroscopy (SIMS) analysis of films deposited after the H plasma clean shows carbon and oxygen concentrations to be ~1 × 10^{12} and 5 × 10^{12} cm^{-2}, respectively. Figure 6 shows Auger spectra for wafers subjected to the remote H plasma clean and subsequently exposed to air for (a) 15 min (b) 2 hr and (c) 10 hr. Again, the carbon and oxygen contamination are seen to increase steadily with the duration of exposure to air, and the best results are obtained when exposure time is limited to a few minutes. RHEED analysis after air exposure showed the 1/3 order streaks were maintained for the samples exposed for 15 min and 2 hr, but only integral order streaks were apparent for the sample exposed to air for 10 hr. By contrast, the HF dipped samples show a (1 × 1) RHEED pattern after 15 min, 2 hr, and 10 hr air exposure. While the (1 × 1) pattern is composed of disordered (3 × 1) unit cells, it must be pointed out that the arrangement of the Si-H bonds on the (1 × 1) surfaces is different with a different amount of strain compared to the Si-H bond configuration for a silicon surface exposed to atomic H,[15] which gives a pure (3 × 1) pattern. The disorder associated with the (1 × 1) pattern for an HF treated surface may make the Si surface more susceptible to adsorption of oxygen and carbon than for a well-ordered (3 × 1) reconstructed surface as for the remote hydrogen plasma clean case. Comparison of AES spectra for wafers exposed to air after the remote H plasma clean and after the HF dip is complicated by the fact that the silicon peaks for the wafers analyzed after the *in situ* clean/air exposure are smaller than for the wafers analyzed after the HF dip/air exposure wafers. However, taking the relative peak heights into account, the remote H plasma clean appears to be slightly more effective than the HF dip in passivating the surface.

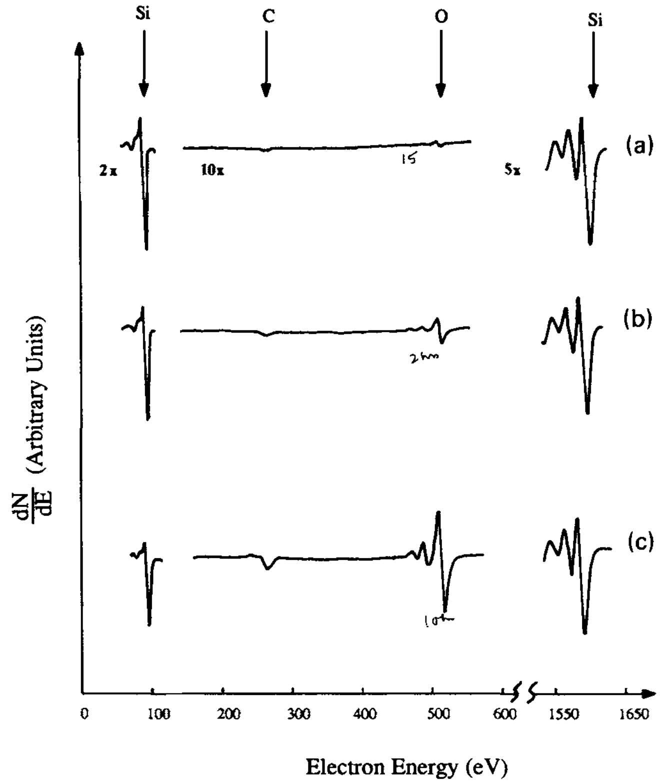
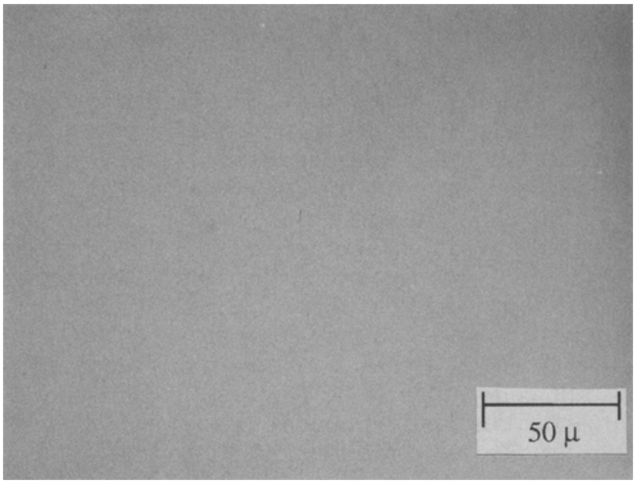


Fig. 6. — Auger spectra of Si surface after remote H plasma clean and subsequent exposure to air. a) 15 min in air b) 2 hr in air c) 10 hr in air.

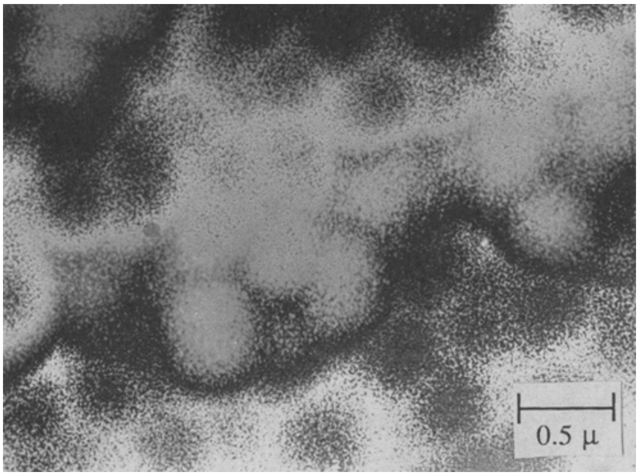
The mechanism for carbon and oxygen removal is believed to be atomic hydrogen combining with adsorbed species to form volatile molecules which in turn desorb into the gas phase. It is not expected that this method will create significant surface damage since we expect ion bombardment to be minimal, and since we do not observe a significant silicon etch rate. We have measured the thickness of a polysilicon layer before and after a typical 45 min clean and found no detectable thickness change using a "Nanospec" spectrophotometer.[17] Since our Nanospec measurements have been found to be repeatable to within +/− 15Å, the H plasma clean has an etch rate of less than 0.7Å/min. A low silicon etch rate suggests that the clean is not very effective in breaking silicon-silicon bonds which is necessary to create damage. Indeed, wafers cleaned at 250° C and 12 W rf power show no observable defects under Nomarski microscopic examination after a dilute Schimmel etch (Fig. 7a) or using plan view Transmission Electron Microscopy (TEM) (Fig. 7b). However, on some occasions crystalline defects such as dislocation loops are observed using TEM, but their cause has not yet been determined.

CONCLUSIONS

We have discussed a technique for cleaning and passivating a silicon surface at very low tempera-



(a)



(b)

Fig. 7. — a) Nomarski micrograph of Si (100) surface after 70 min remote H plasma clean at 250° C and defect etch (400x) b) plan view TEM of Si (100) surface after 70 min H plasma clean at 250° C.

tures (250° C), which is highly important for low temperature epitaxial growth. This technique consists of an initial *ex situ* wet chemical treatment with a final dilute HF dip which removes most of the oxygen from the surface and hydrogen passivates the surface. After the wet chemical treatment, wafers are transferred to the vacuum system where they are subjected to an *in situ* remote H plasma clean which supplies atomic hydrogen to volatilize and remove carbon, nitrogen, and oxygen from the surface leaving behind different hydrogen terminated surfaces at different substrate clean temperatures. We observe a (1 × 1) RHEED pattern at clean temperatures below 190° C which we believe corresponds to silicon monohydride and dihydride termination, a (3 × 1) pattern between 200° C and 280° C, corresponding to ordered monohydride and dihydride coverage, transitioning to a (2 × 1) pattern with exclusively monohydride termination around 300° C. These results are consistent with the observations of Chabal *et al.*[15] for exposure of Si to atomic H in a UHV chamber. Wafers prepared in this manner are found to have very little carbon, nitrogen, and oxygen contamination and are adequately clean to support epitaxial growth of silicon films at temperatures between 150 and 480° C. We have compared the surface conditions and passivating effect of an *ex situ* dilute HF treatment and the remote plasma hydrogen clean described in this paper. Both methods provide good passivation for short periods of time (~15 min), and the remote hydrogen plasma clean appears to provide slightly better passivation. In addition, the remote hydrogen plasma clean provides excellent passivation in a UHV environment over very long periods of time so that it is not necessary to initiate epitaxial growth immediately after the *in situ* clean.

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17. "Nanospec" is a trademark of the Nanometrics Corporation.