4. CONCLUSIONS

We have studied the temperature and composition dependence of interfacial smearing at Si–$Si_{1-x}Ge_x$ ($0.008 < x < 0.33$) interfaces by means of SIMS and RBS. The smearing was shown to be asymmetric; it was only observed at the surface side of the interface. The interface at the surface side was initially abrupt; below a concentration of 4×10^{20} cm^{-3} the smearing became evident and the germanium concentration decreased with 17 nm per decade. The amount of segregated germanium was proportional to the concentration in the $Si_{1-x}Ge_x$ layer and was for $x = 0.33$ approximately 4.5×10^{14} cm^{-2}. From the shape of the observed profile it is inferred that the smearing is due to the formation of a germanium ad-layer, that is incorporated during growth of the silicon capping layer. The driving force for this process is the lower energy of a germanium ad-layer on silicon relative to a silicon layer on silicon. More detailed studies are in progress.

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HYDROGEN-TERMINATED SILICON SUBSTRATES FOR LOW-TEMPERATURE MOLECULAR BEAM EPITAXY

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The preparation of hydrogen-terminated silicon surfaces for use as starting substrates for low-temperature epitaxial growth by molecular beam epitaxy is examined in detail. The procedure involves the *ex-situ* removal under nitrogen of residual oxide from a silicon substrate using a spin-clean with HF in ethanol, followed by the *in-situ* low-temperature desorption (150 °C) of physisorbed etch residues. The critical steps and the chemical basis for these steps are examined using X-ray photoelectron spectroscopy. Impurity residues at the epilayer–substrate interface following subsequent homoepitaxial growth are studied using Auger spectroscopy, secondary ion mass spectrometry, and transmission electron microscopy. Finally, scanning tunneling microscopy is used to examine the effect of cleaning methods on substrate morphology.

1. INTRODUCTION

The development of a low-temperature growth technology for silicon molecular beam epitaxy (MBE) is important not only to minimize dopant surface segregation and intermixing at heterojunction interfaces, but also to allow for epitaxial growth on substrates with preprocessed electronic devices. Of these reasons, the latter poses the most stringent requirements on growth, because the initial preparation of the substrate must also be limited to low temperature. Conventional substrate cleaning methods are not suitable since they require high temperatures in excess of ≈ 750 °C, either to anneal surface damage created by ion bombardment or to desorb a thin surface oxide[1].

In recent years, several studies based on IR spectroscopy[2–4], vibrational modes observed in electron energy-loss spectroscopy[5,6] and X-ray photoemission spectroscopy[5] have concluded that the HF-treated silicon surface is predominantly terminated by Si-H bonds. This near-perfect termination of the lattice with hydrogen is responsible for remarkably low electronic surface-recombination

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velocities[2] as well as an observed resistance against oxidation[5,7]. Such an electronically and chemically passive silicon surface is attractive for use as a starting substrate for epitaxial growth, particularly because its preparation involves only near room temperature procedures. Previously[8], we reported a substrate-cleaning procedure for epilayer growth utilizing *ex-situ* removal of a thin silicon surface oxide using HF in ethanol under nitrogen, followed by *in-situ* low-temperature (≈ 150 °C) desorption of the remaining etch residues. Silicon epilayers were grown to demonstrate that thin films grown on silicon substrates prepared by this technique were indistinguishable from those prepared by the high-temperature methods. In this paper, we examine in detail the chemistry and morphology of these HF-treated silicon surfaces and silicon epilayers grown thereon using X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), secondary-ion mass spectroscopy (SIMS), transmission electron microscopy (TEM), and scanning tunneling microscopy (STM). Impurity residues are examined as a function of etchant composition and the ambient under which the etching occurs. The passive nature of the HF/ethanol-treated silicon surface is demonstrated by examining HF-treated substrates as a function of time. The importance of substrate pretreatments, such as sacrificial oxides, is also examined.

2. EXPERIMENTAL PROCEDURE

For XPS, STM, and SIMS[9] experiments, Czochralski silicon substrates (2 in diameter, (100) ± 0.5° orientation, 0.05 Ω cm, p-type) were degreased by a 10-min immersion in 200 °C H_2SO_4. The thin oxide remaining after this step (10–15 Å, using XPS) was removed by spinning the wafer at 3600 rpm under various ambients and dispensing a total of 1500 ml of etchant in 150 ml aliquots using a polypropylene-tipped pipette. It is necessary to dispense the 150 ml of etchant in a continuous flow to ensure that the surface of the substrate near the edge is etched. Before and after etching, the substrate was rinsed using the same procedure with a total of 1500 ml of ethanol (or water, where indicated). Further rinsing had no effect on the amount of residues left on the surface. This spin-based technique will be referred to as a spin-clean treatment. Etching under nitrogen was performed in a glove box continuously flushed with nitrogen from liquid boil-off. The stainless-steel glove box was attached to the introduction port of the XPS spectrometer or MBE growth chamber. Semiconductor-grade HF, 190 proof U. S. Pharmacopia (USP) grade ethanol, and ultra-high purity deionized water were used for solutions.

For XPS measurements, wafers were loaded into a Surface Science Laboratory X-Probe photoemission system and pumped to ≈ 6×10^{-7} Pa using a combination of oil-free-backed turbomolecular, cryogenic and ion pumps. The use of ion gauges was minimized. Full silicon wafers were used because experiments with scribed and cleaved silicon pieces resulted in irreproducible results, presumably because of the presence of silicon dust on the surface.

For SIMS analysis, 600 nm silicon epilayers were grown at 0.2 nm s^{-1} and at substrate temperatures of 450–650 °C. SIMS analysis was performed by Charles Evans & Associates, Redwood City, California, using cesium ion bombardment.

For STM experiments, cleaning procedures were interrupted at different stages and substrates were cleaved into ≈ 1 cm^2 pieces. These substrates were then subjected to a spin-clean procedure under nitrogen using HF in ethanol to produce an H-terminated surface. This procedure has been shown to preserve the morphology of the silicon surface[10]. The STM measurements were performed under a flowing nitrogen atmosphere using an apparatus described in detail elsewhere[11]. Tunneling voltages and currents were typically −0.5 V (sample negative) and 1.0 nA, respectively.

3. CHARACTERISTICS OF HF-TREATED SILICON SURFACES

Figure 1(a) shows typical silicon 2p spectra obtained before and after a spin-clean treatment of a degreased silicon wafer. The peak at ≈ 104 eV in the lower spectrum of Fig. 1(a) is due to photoelectrons emitted from the thin (10–20 Å) oxide (SiO_2) on the substrate surface. The peak at ≈ 100 eV is due to the underlying silicon substrate. The upper spectrum of Fig. 1(a) demonstrates that the thin SiO_2 layer is completely removed after the substrate has been spin-cleaned under nitrogen with a

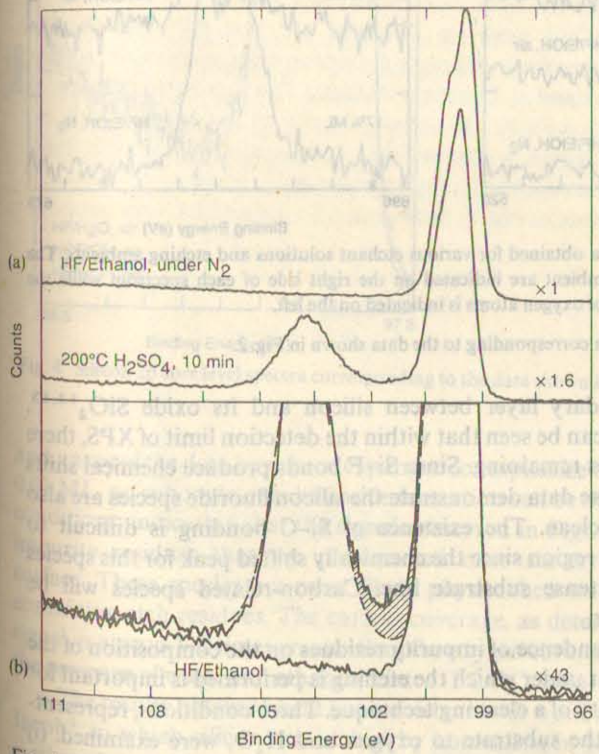
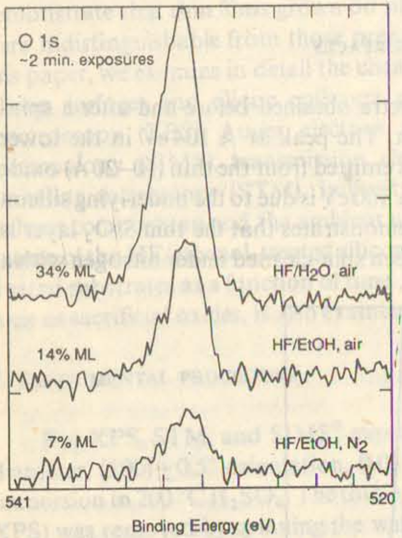


Fig. 1. (a) Typical silicon 2p core level spectra obtained before (lower spectrum) and after (upper spectrum) a spin-clean treatment in nitrogen using HF in ethanol. (b) Expansion and overlay of the data shown in (a) to emphasize the region between the silicon substrate and SiO_2 components. The dashed line represents a least-square fit to these major components. The cross-hatched region corresponds to silicon suboxide species.

1:5 HF:ethanol solution. In Fig. 1(b), the data from Fig. 1(a) are expanded and overlayed to permit closer inspection of the silicon 2p region between the silicon substrate and SiO_2 contributions. The dashed spectrum represents a least-square fit to these major components for the degreased substrate. The cross-hatched region corresponds to silicon atoms in Si^{+1}, Si^{+2}, and Si^{+3} suboxide states, which arise as part of the chemical boundary layer between silicon and its oxide SiO_2[12,13]. Following the spin-clean, it can be seen that within the detection limit of XPS, there are no silicon suboxide states remaining. Since Si–F bonds produce chemical shifts similar to Si–O bonds[14], these data demonstrate the silicon fluoride species are also not present after the spin-clean. The existence of Si–C bonding is difficult to ascertain from the silicon 2p region since the chemically shifted peak for this species overlaps with the more intense substrate line. Carbon-related species will be discussed in more detail later.



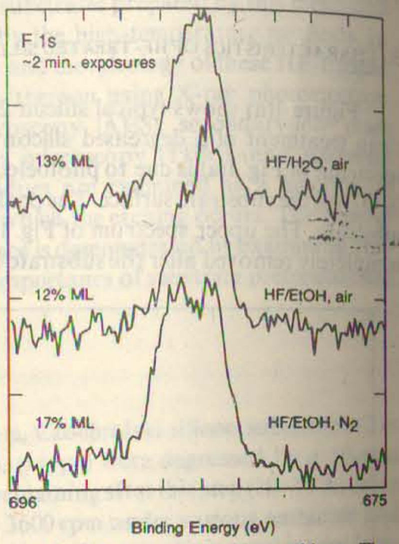


Fig. 2. Oxygen 1s core level spectra obtained for various etchant solutions and etching ambients. The compositions of the ethant and ambient are indicated on the right side of each spectrum while the percentage of monolayer coverage of oxygen atoms is indicated on the left.

Fig. 3. Fluorine 1s core level spectra corresponding to the data shown in Fig. 2.

Understanding the dependence of impurity residues on the composition of the etchant solution and ambient under which the etching is performed is important for controlling the reproducibility of a cleaning technique. Three conditions, representing increasing exposure of the substrate to oxygen and H_2O, were examined: (i) 1:5 HF in ethanol, with the spin-clean performed under nitrogen; (ii) 1:5 HF in ethanol, with the spin-clean performed in air; and (iii) 1:5 HF in water, with the spin-clean performed in air. These conditions will be referred to as HF/ethanol/N_2, HF/ethanol/air, and HF/H_2O/air, respectively. Ambient exposure times were ≈ 2 min, which is the average time required to load the wafers into the spectrometer and begin pump-down. For each condition, silicon 2p, oxygen 1s, fluorine 1s, and carbon 1s core level data were obtained.

Figures 2 and 3 show the oxygen 1s and fluorine 1s data obtained for the three conditions. For the HF/ethanol/N_2 sample, the oxygen signal corresponds to 7% of a monolayer (where one monolayer (ML) is defined as the surface areal density of silicon atoms for the (100) surface or 6.8×10^{14} atoms cm^{-2}). The coverage of oxygen atoms increases with increasing water and air exposure to 34% of a monolayer for the HF/H_2O/air sample. The intensity of the fluorine 1s signal in Fig. 3 varies from 12% to 17% of a monolayer, with no clear trend depending on the spin-clean conditions. The silicon 2p regions for the same samples are shown in Fig. 4. The x and y axes of the data have been expanded to emphasize the suboxide region. Within 0.01 ML, no suboxide or subfluoride formation can be observed for any of the three conditions, indicating that the signals observed in Figs. 2 and 3 are due to surface impurity residues that are physisorbed onto the hydrogen-terminated silicon surface. These species are most likely physisorbed water, ethanol, and fluorine-containing etch residues. The carbon coverage, as determined from the carbon 1s signal, is always 1–2 times greater than the oxygen coverage, which is consistent with the presence of water and ethanol-related (2:1 C:O ratio) species.

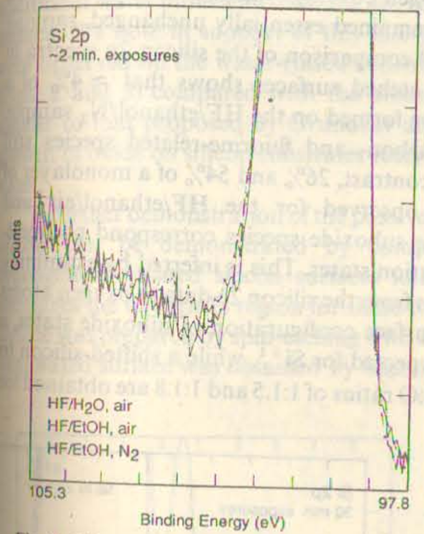


Fig. 4. Silicon 2p core level spectra corresponding to the data shown in Figs. 2 and 3.

The results obtained here are consistent with work reported by Grundner and Jacob[5], in which silicon was etched by immersion in HF in water followed by a methanol rinse. Using XPS, they observed comparable fluorine and oxygen levels, but significantly higher carbon levels. Because we have consistently observed that taking wafers in and out of liquids results in higher carbon impurity levels as compared with spin techniques, we attribute their high carbon levels to their use of an immersion technique. Immersion techniques result in higher residue levels because impurities, which tend to concentrate at the air/liquid interface, can adsorb onto the substrate as it is withdrawn from solution, analogous to the preparation of Langmuir–Blodgett films.

The passive nature of these treated surfaces can be demonstrated by examining surface impurity concentrations after prolonged exposure to the ambient in which the etching occurred. Figures 5 and 6 show the oxygen 1s and silicon 2p spectra obtained after an ambient exposure time of 30 min following the spin-clean. For the HF/ethanol/N_2 sample in Fig. 5, it can be seen that the oxygen coverage has increased only slightly from 7% to 10%. In contrast, for the air-exposed samples HF/ethanol/air and HF/H_2O/air, the oxygen coverage has increased 2.5–3 times, respectively. The fluorine concentration remained essentially unchanged, ranging from 12% to 15% of a monolayer. Careful comparison of the silicon 2p spectra in Fig. 6 with spectra obtained for freshly etched surfaces shows that ≈4% of a monolayer of silicon suboxide species have formed on the HF/ethanol/N_2 sample, indicating that most of the oxygen-, carbon- and fluorine-related species still continue to be in a physisorbed state. In contrast, 26% and 54% of a monolayer of silicon suboxide species can now be observed for the HF/ethanol/air and HF/H_2O/air samples, respectively. These suboxide species correspond predominantly to silicon in the +1 and +2 oxidation states. This is inferred by examining the ratio of *chemically shifted* silicon atoms from the silicon 2p data to oxygen atoms from the oxygen 1s data. For a simple surface configuration of suboxide states, a shifted-silicon to oxygen ratio of 1:1 is expected for Si^{+1}, while a shifted-silicon to oxygen ratio of 1:2 is expected for Si^{+2}. Si:O ratios of 1:1.5 and 1:1.8 are obtained for HF/ethanol/air and HF/H_2O/air samples, respectively. This argument is complicated by the presence of bridging Si–O–Si species.

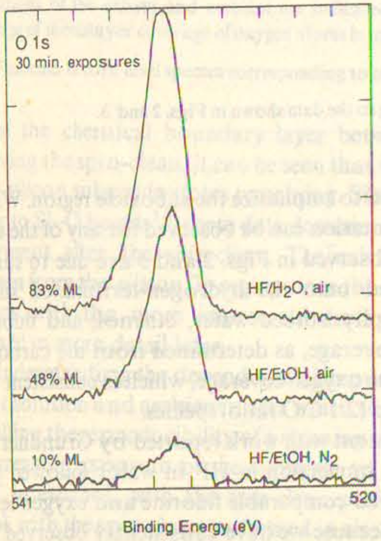


Fig. 5. Oxygen 1s core level spectra obtained for various etchant solutions and ambients, following a 30 min exposure to the ambient under which etching was performed.

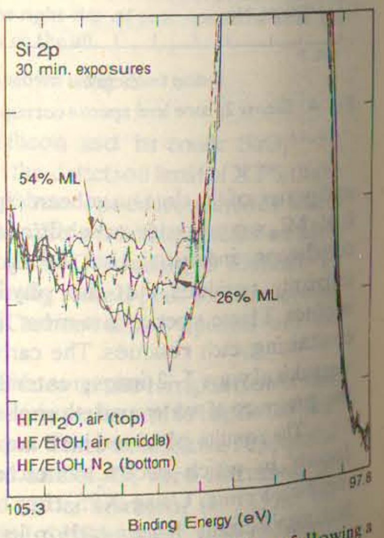


Fig. 6. Silicon 2p core level spectra corresponding to the data shown in Fig. 5.

A reduced oxidation rate is observed for the substrate subjected to a final rinse with ethanol (26% of a monolayer of suboxides) as compared with water (54% of monolayer), following equal air exposures of 30 min. The difference in chemical reactivity between the ethanol-rinsed and water-rinsed surfaces is most likely due to the increased amount of physisorbed water on the latter. Physisorbed water molecules are able to undergo dissociative chemisorption on silicon to form Si-OH and Si-H, as demonstrated by Ibach *et al.* using electron energy-loss spectroscopy[15]. Once formed, the polar Si-OH groups will act as preferential adsorption sites for additional water molecules from the air, resulting in further oxidation of the silicon surface. We note in support of this interpretation that more physisorbed species were observed on the water-rinsed substrate immediately following the spin-clean (Figs. 2 and 3) compared with the ethanol-rinsed substrate. This mechanism is similar to that proposed by Grundner and Jacob[5], who also noted the inhibited growth of oxide on silicon substrates receiving a final rinse in methanol rather than water.

A further demonstration of the passive nature of the Si-H bond on the surface of silicon can be demonstrated by comparing hydrogen-terminated and non-hydrogen-terminated silicon surfaces following exposure to room air. Figure 7 compares the oxygen 1s region for these two conditions. The hydrogen terminated surface was prepared by spin-etching with 1:5 HF in ethanol in air. A non-hydrogen-terminated surface was obtained by heating a hydrogen-terminated silicon surface

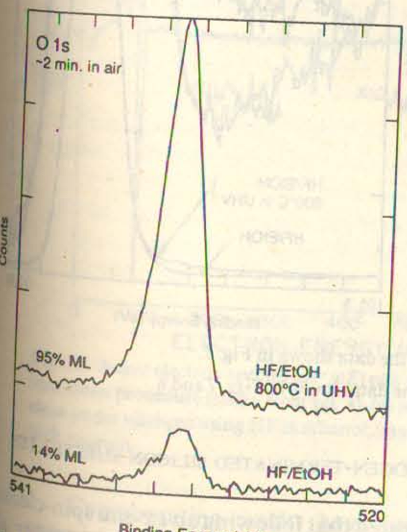
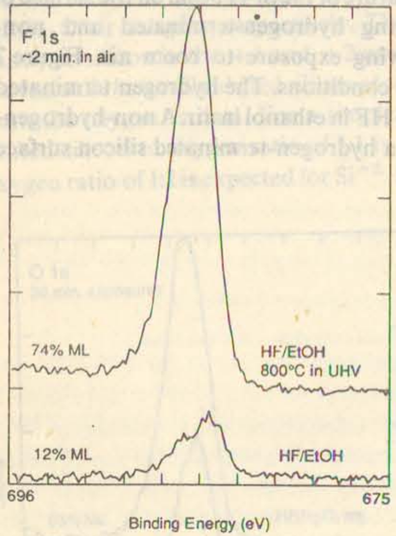


Fig. 7. Oxygen 1s core level data comparing samples exposed to air for ≈ 2 min for (i) a hydrogen terminated silicon surface prepared by a spin-clean treatment using HF in ethanol and (ii) a non-hydrogen-terminated silicon surface prepared by heating a hydrogen-terminated surface to 800 °C in ultra-high vacuum.

to 800 °C in ultra-high vacuum. Under such conditions, the hydrogen is driven from the surface, resulting in mixed 2 × 1 and 1 × 2 reconstructed domains as observed by reflection high-energy electron diffraction. Both the hydrogen-terminated and non-hydrogen-terminated silicon surfaces were exposed to room air for ≈ 2 min. As seen in Fig. 7, almost a full monolayer of oxygen atoms are present on the non-hydrogen-terminated surface, as compared with only 14% of a monolayer on the hydrogen-terminated surface. Similar results are found for fluorine levels, as shown in Fig. 8, where a six-fold increase in fluorine coverage is observed for the non-hydrogen-terminated surface. (The fluorine results from exposure to HF vapors in the glove box attached to the introduction port of the UHV system as the sample is removed to air.) Finally, the silicon 2p data in Fig. 9 demonstrate that, whereas only 4% of a monolayer of oxidized silicon has formed on the hydrogen-terminated surface, 74% of a monolayer has formed on the non-hydrogen-terminated substrate. These results are consistent with recent work by George *et al.*[16] demonstrating that the initial oxidation rate for silicon decreases as a function of increasing hydrogen coverage on the Si (111) 7 × 7 reconstructed surface.



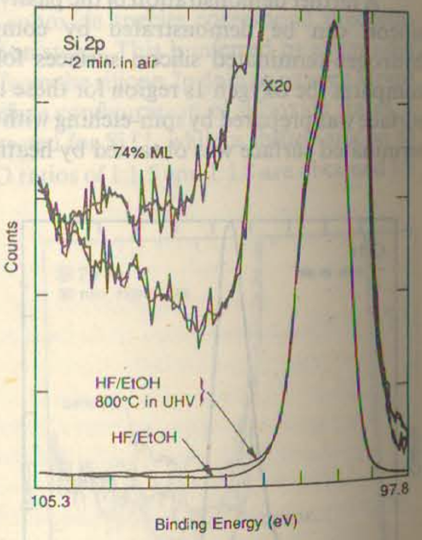


Fig. 8. Fluorine 1s core level spectra corresponding to the data shown in Fig. 7.

Fig. 9. Silicon 2p core level spectra corresponding to the data shown in Figs. 7 and 8.

4. GROWTH OF SILICON EPILAYERS ON HYDROGEN-TERMINATED SILICON SUBSTRATES

In the previous section, it was demonstrated that following an *ex-situ* spin-clean procedure, even under the best case conditions utilizing HF in ethanol under a nitrogen ambient, a significant fraction of a monolayer of physisorbed oxygen, carbon and fluorine species exist on the silicon surface. For this procedure to be useful for substrate preparation, it must be possible to desorb these species prior to the onset of epitaxial growth. These physisorbed species can be desorbed by careful heating in ultra-high vacuum at ≈ 150 °C,[8] as shown in the Auger spectra in Fig. 10. The data in Fig. 10(a), which is for a silicon substrate prior to the spin-clean procedure, shows a large oxygen peak owing to the thin SiO_2 film on the substrate and a smaller carbon peak (× 10 expansion) because of surface contamination. Immediately following the spin-clean (Fig. 10(b)), only sub-monolayer coverages of carbon and oxygen are observed, in agreement with XPS results already discussed. No fluorine signal is observed, but this is most likely due to the electron-stimulated desorption of this species. After heating the substrate to ≈ 150 °C for 10 min, all spin-clean residues, within the detection limits of Auger, have desorbed as shown in Fig. 10(c).

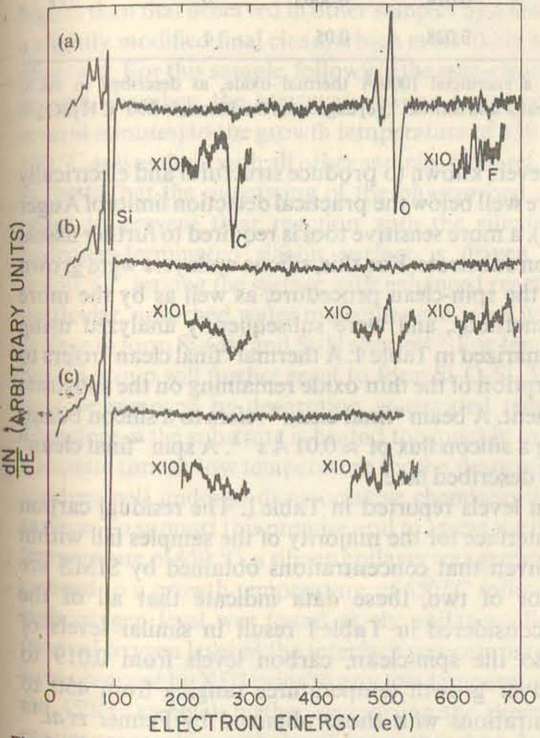


Fig. 10. Auger electron spectra (d*N*/d*E*) of a silicon surface during the various stages of cleaning by the spin-clean procedure (taken from ref. 8). (a) after the growth of a thin protective oxide; (b) after a spin-clean under nitrogen using HF in ethanol; (c) after a 10 min 150 °C desorption of etchant residues in ultra-high vacuum.

Corroborating results have recently been reported by Fenner *et al.*[17] By optimizing the sensitivity of their photoemission system, they were able to quantify the residues remaining after the low-temperature desorption step. Using a comparable spin-clean procedure, except that the duration of the 150 °C desorption step lasted for 1 h, they observed carbon, oxygen and fluorine levels as low as 0.025 monolayers, 0.005 monolayers and 0.010 monolayers, respectively.

TABLE I

SUMMARY OF SIMS RESULTS

Final clean	*Maximum temperature during clean* (°C)	*Growth temperature* (°C)	*Carbon* (ML)	*Oxygen* (ML)	*Pre treatment*	*Ref.*
Thermal	880	800	0.028	0.0004	a	8
Beam	800	800	0.027	0.0004	a	8
Spin	150	800	0.022	0.0004	a	8
Thermal	800	650	0.006	not detected	a	8
Beam	750	650	0.015	not detected	a	8
Spin	150	650	0.019	0.0008	a	8
Thermal	700	—	0.014	0.0005	b	277
Spin	ramped	450	0.028	0.05	c	

Pretreatments: (a) degreased and grew a sacrificial 1000 Å thermal oxide, as described in ref. 8; (b) precleaned using the procedure of Ishizaka and Shirak[18]; (c) degreased for 10 min in 200 °C H_2SO_4.

Because the contamination levels known to produce structural and electrically active defects in epitaxial layers are well below the practical detection limits of Auger and XPS (of the order of 0.01 ML), a more sensitive tool is required to further assess the atomic cleanliness of the silicon substrate. For this, silicon epilayers were grown on silicon substrates cleaned by the spin-clean procedure, as well as by the more conventional high-temperature methods, and were subsequently analyzed using SIMS. The SIMS results are summarized in Table I. A thermal "final clean" refers to a high-temperature thermal desorption of the thin oxide remaining on the substrate following the indicated pretreatment. A beam "final clean" refers to a silicon beam-assisted thermal desorption using a silicon flux of ≈ 0.01 Å s^{-1}. A spin "final clean" refers to the spin-clean procedure described here.

We consider first the carbon levels reported in Table I. The residual carbon levels at the epilayer–substrate interface for the majority of the samples fall within the range of 0.014–0.028 ML. Given that concentrations obtained by SIMS are accurate to only within a factor of two, these data indicate that all of the pretreatments and final cleans considered in Table I result in similar levels of residual carbon. With respect to the spin-clean, carbon levels from 0.019 to 0.028 ML are observed for epilayer growth temperatures ranging from 450 to 800 °C. Comparing these concentrations with those obtained by Fenner *et al.*[17] immediately following the 150 °C etch-residue desorption step, but prior to further heating to the epilayer growth temperature (0.052–0.025 ML of carbon), one may conclude that a 10 min desorption step at 150 °C in ultra-high vacuum is sufficient to remove most of the carbon-related residues. No further significant reduction in carbon residues occurs as the substrate is heated to the growth temperature (800 °C is the highest growth temperature examined here).

The various wafer pretreatments listed in Table I also address the issue of whether it is necessary to remove the as-received surface of the substrate for reduced carbon residues[18]. Table I compares samples in which (i) surface material was removed by repeated solution oxidation and stripping using the procedure of Ishizaka and Shiraki;[18] (ii) surface material was removed by a sacrificial 1000 Å thermal oxide;[8] and (iii) the as-received wafer received only a degrease. Within the error limits of SIMS, the carbon data show no dependence on these treatments, indicating that carbon contamination is confined to the wafer surface only and not located subsurface. Extensive pretreatments designed to remove surface material will thus have no effect on final carbon residues.

We consider next the oxygen residues summarized in Table I. Except for the spin-clean sample grown at 450 °C, oxygen residues at the epilayer-silicon interface ranged from 0.0004 ML to below the detection limit of SIMS. No dependence on either the wafer pretreatment or final clean is observed.

The residual oxygen level for the spin-clean sample grown at 450 °C in Table I is higher than that observed in other samples by a factor of ≈ 100. This sample received a slightly modified final clean, which most likely accounts for the high oxygen level observed. For this sample, following the spin-clean procedure and insertion into the growth chamber, the temperature was continuously and quickly ramped (over several minutes) to the growth temperature of 450 °C, without pausing for 10 min at 150 °C as was done with all other samples from ref. 8[19]. The surface science literature suggests that the outgassing of the physisorbed species must be done carefully in order to prevent their reaction with the silicon surface. The hydrogen on the hydrogen-terminated silicon surface is driven off at temperatures as low as ≈ 430 °C[8], leaving the surface with enhanced reactivity towards impurity species. In particular, adsorbed water molecules can react with the non-hydrogen-terminated surface to form Si-OH and Si-H species[15]. For temperatures greater than 250 °C, the Si-OH group will further react to form Si-O-Si. These initial oxidation species can only be removed by desorption at elevated temperatures in excess of ≈ 750 °C. Therefore, if the substrate is heated too quickly to the growth temperature, without adequate time at low temperature for the desorption of physisorbed residues, these residues will undergo disassociative chemisorption and remain on the substrate surface. To support this premise and to assess the importance of the very low growth temperature of 450 °C, a silicon epilayer was grown on a substrate which was quickly ramped to a growth temperature of 650 °C following the spin-clean. Again, a very high oxygen level was found at the epilayer-silicon interface. In both cases, the residual oxygen level at the interface was comparable with the physisorbed oxygen level observed by XPS prior to any low-temperature desorption step (≈ 0.07 ML for the 450 °C sample), further supporting the premise that the physisorbed oxygen species are reacting with the silicon rather than desorbing.

Cross-sectional TEM analysis was performed on the thermal-, beam-, and spin-cleaned samples grown at 800 °C and 650 °C reported in Table I. A typical micrograph is shown in Fig. 11. In all cases, impurity residues, seen as the dark inclusions in Fig. 11, are observed at the epilayer–substrate interface. These residues are not laterally uniform, but rather segregate into small patches along the interface. The TEM micrographs do not show any structural defects in the Si (111) epilayers associated with these impurity clusters. It is not known at this time whether the impurity clusters in Fig. 11 are due to oxygen or carbon.

In addition to carbon and oxygen, another impurity often observed at the epilayer–silicon interface is that of boron. Unintentional p+boron-doped layers

Fig. 11. Low-resolution cross-section transmission electron micrographs typical for all epilayer—substrate interfaces studied here.

have been reported by many laboratories following cleaning procedures using a high-temperature thermal desorption of a thin oxide layer[20,21,8]. It has been shown that the mechanism for boron incorporation involves the presence of an oxide layer on the substrate surface[21] and one would thus anticipate that the use of the spin-clean procedure to remove the oxide prior to introduction into the growth chamber would significantly reduce unintentional boron levels. In our previous work, we demonstrated that the spin-clean procedure can reduce boron levels by a factor of ≈100 as compared with standard thermal-clean methods[8].

5. SURFACE MORPHOLOGY

Past studies of substrate cleaning technologies were generally concerned with atomic cleanliness, with little attention given to the issue of resulting substrate morphology. With the development of scanning tunneling microscopy methods, it is now possible to examine in high resolution the topography and electronic structure of semiconductor surfaces following surface preparation. For example, STM has been used to characterize surface reconstructions on cleaved silicon surfaces[22,23] as well as on flash-annealed surfaces[24]. Here, we apply STM topographic imaging to directly observe the effects of various surface cleaning procedures on the substrate morphology.

An STM topograph of a Si(100) surface prepared by the method of Ishisaki and Shiraki[18], but prior to a thermal desorption in the growth chamber, is shown in Fig. 12. The STM image is obtained after removing the thin oxide present following the Ishisaki and Shiraki clean using an HF ethanol spin-clean under nitrogen.

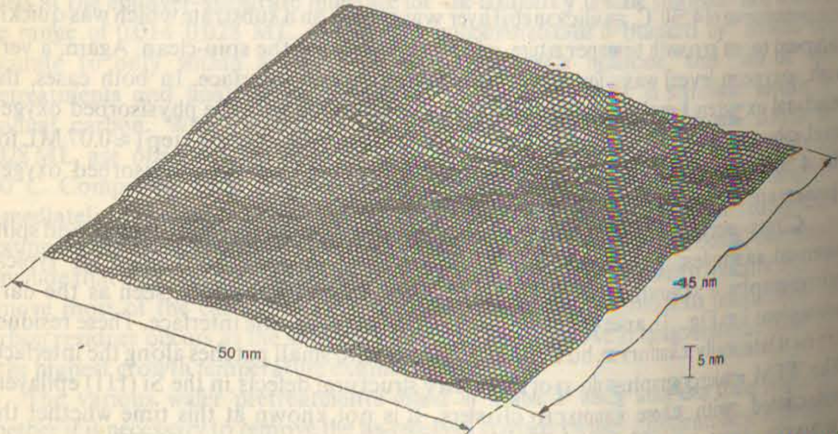


Fig. 12. STM topograph of a substrate precleaned using the method of Ishizaki and Shiraki[18], but prior to thermal desorption of the thin oxide layer. The image size is 45 × 50 nm.

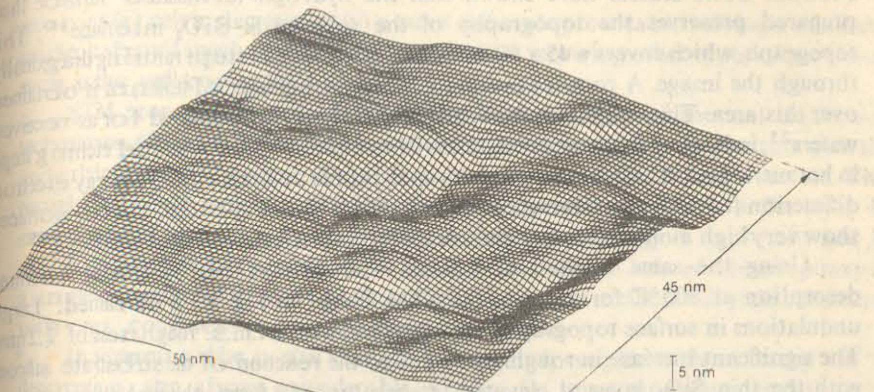


Fig. 13. STM topograph of a substrate precleaned using the method of Ishizak and Shiraki[18], following a thermal desorption at 800 °C of the thin oxide layer under ultra-high vacuum conditions.

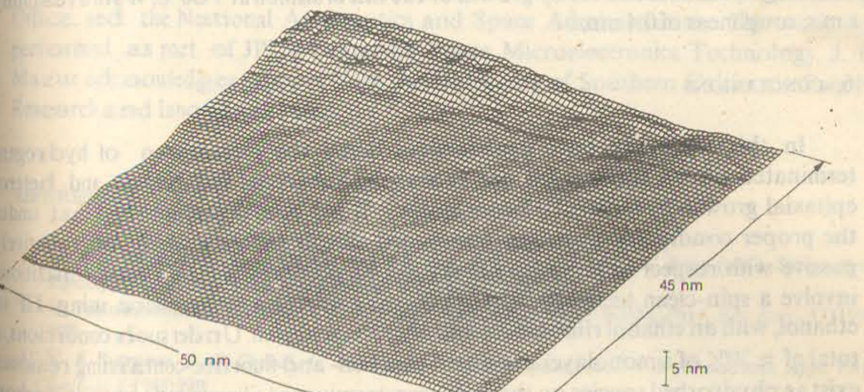


Fig. 14. STM topograph of a substrate precleaned using the method of Ishizaki and Shiraki[18], following the thermal desorption at 800 °C of the thin oxide layer under ultra-high vacuum conditions and the subsequent growth of a 100 nm silicon buffer layer at 700 °C and 0.2 nm s^{-1}.

Previous STM studies have shown that the hydrogen-terminated surface thus prepared preserves the topography of the original Si—SiO_2 interface[10]. This topograph, which covers a 45 × 50 nm area, shows several steps running diagonally through the image. A root-mean-square (r.m.s.) roughness of 0.059 nm is obtained over this area. This roughness is slightly larger than that observed for as-received wafers[25], indicating that some roughness if introduced by the repeated etching steps in hot nitric acid. This is consistent with spot-profile analysis of low-energy electron diffraction (LEED) measurements which indicate that acid-etched Si(111) surfaces show very high atomic step densities compared with alkaline-etched surfaces[25].

Using the same method of Ishizaki and Shiraki, but following thermal desorption at 800 °C for 10 min, the STM image in Fig. 13 is obtained. Large undulations in surface topography are apparent, with a r.m.s. roughness of 1.2 nm. The significant increase in roughness is due to the reaction of the substrate silicon with the thin SiO_2 layer at elevated temperatures to form the volatile reaction product SiO. This reaction in thicker SiO_2 films (> 5 nm) on silicon has been shown to result in voids in the oxide and pitting of the substrate surface[26]. Most of this oxide desorption-induced roughness can be smoothed by the growth of a silicon buffer layer. As shown in the STM topography in Fig. 14, the large undulations have been largely smoothed over by growth of 100 nm of silicon at 700 °C, with a resulting r.m.s. roughness of 0.4 nm.

6. CONCLUSIONS

In this study, we have examined in detail the preparation of hydrogen-terminated silicon surfaces for use as starting substrates for homo- and hetero-epitaxial growth by molecular beam epitaxy. It has been demonstrated that under the proper conditions, hydrogen terminated silicon surfaces which are relatively passive with respect to impurity uptake can be prepared. The optimal conditions involve a spin-clean technique under a flowing nitrogen atmosphere using HF in ethanol, with an ethanol rinse before and after the acid etch. Under such conditions, a total of ≈30% of a monolayer of oxygen-, carbon- and fluorine-containing residues exist as physisorbed species on the hydrogen-terminated silicon surface. The carbon residues are desorbed in the growth chamber under ultra-high vacuum conditions to leave ≈0.02 ML of carbon-related species at the epilayer–substrate interface in films grown as low as 450 °C (the lowest temperature examined in this work). To remove the oxygen residues, it is necessary to carefully outgas the hydrogen-terminated silicon surface at low temperature (150 °C) in order to prevent reaction of the physisorbed oxygen with the silicon surface. With careful low-temperature outgassing, the oxygen residue at the epilayer–substrate interface is ≈0.0005 ML. The use of elaborate substrate pretreatments designed to remove some of the initial substrate surface has no effect on the amount of residual carbon or oxygen at the epilayer–substrate interface. The impurity levels obtained by this spin-clean technique, coupled with careful outgassing at 150 °C in the growth chamber, are comparable with levels that remain at the epilayer–substrate interface using standard high-temperature (800 °C) thermal desorption cleaning methods. It should be noted that, whereas in this study the spin-clean was applied to substrates receiving (i) only a degrease or (ii) a more elaborate pre-clean involving a sacrificial oxide, it should apply equally well to substrates receiving other types of pre-cleans such as the well-known RCA clean.

STM topographs demonstrated that high-temperature thermal desorption techniques that involve the decomposition of a thin oxide layer via reaction with the underlying substrate result in significant roughening of the substrate surface. This roughness can be smoothed by the subsequent growth of a silicon buffer layer. In experimental situations where starting surface morphology is important and in which silicon buffer layers cannot be grown (for example, GaAs on silicon epitaxy in a single-chamber MBE system), the use of a spin-clean method will yield substrates with r.m.s. roughness equal to the as-received wafers.

In summary, the *ex-situ* spin-clean procedure, coupled with an *in-situ* 150 °C desorption step, shows considerable promise for low-temperature growth technology for molecular beam epitaxy. The critical steps in this cleaning method and the chemical basis behind these steps have been identified and characterized.

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THE INITIAL STAGES OF GROWTH OF SILICON ON Si(111) BY SLOW POSITRON ANNIHILATION LOW-ENERGY ELECTRON DIFFRACTION

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Low-energy electron diffraction (LEED) is used to investigate the initial stages of growth of silicon on Si (111) between 556 and 900 K. The partial coverages θ_h of the growing film are derived from the intensity variation during evaporation of the 00 and 7 × 7 spot. A preferred growth is observed in the second layer long before the first layer is completed. Surface defects caused by superstructure disorder on the grown islands act as nucleation centers for the diffusing adatoms, so at 633 K substrate temperature the grown islands show no ordered superstructure, although the film is epitaxial. The 7 × 7 spots show all the features of diffraction of a substrate with a non-scattering overlayer for coverages below two monolayers. The grown films show below 650 K an unordered superstructure, in an intermediate temperature range a mixture of 5 × 5 and 7 × 7 domains, and finally, above 870 K, perfect 7 × 7 superstructure. The average size of islands increases from 30 to 40 000 atoms.

1. INTRODUCTION

Low-temperature epitaxial growth of silicon on silicon is of interest from both the technological and scientific point of view. Not only the final film but also especially the growth process itself is of strong interest. Although many reflection high-energy electron diffraction (RHEED) measurements exist, quantitative data are lacking. Unfortunately RHEED intensity is largely determined by dynamic effects which result from the grazing incidence and the high number of diffracted beams. Time-resolved low-energy electron diffraction (LEED) is a better suited method for observing growth, as kinematic diffraction theory is sufficient for the evaluation[1]; thus, parameters such as the coverage θ_h in the different layers, the average island size, the island size distribution and the superstructure behaviour during growth are available quantitatively without the need for dynamic calculations.

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