

distortion. We believe that the formulation of developers that maximize contrast while minimizing swelling is desirable for attaining higher resolution in nanostructure fabrication. Hopefully, the results of this paper will permit more efficient screening of improved developer solutions through the initial observation of swelling properties.

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The Activity of HF/H₂O Treated Silicon Surfaces in Ambient Air Before and After Gate Oxidation

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ABSTRACT

A strong correlation is observed among surface charge, contact angle, and native oxide thickness in which up to 10,000 min of exposure time to ambient air, the liquid-HF/H₂O and vapor-HF/H₂O treated surfaces seem to undergo three distinct periods of evolution. The results indicate that the vapor-HF/H₂O treatment yields surfaces with greater activity in ambient air. The trends, which are explained by considering the reaction between unpassivated trivalent silicon and hydroxyl groups, are shown to be consistent with XPS data on surface carbon, fluorine, and oxygen. Following thermal oxidation, the total oxide charge, oxide thickness, and contact angle are stable over time. This is possibly due to the complete surface oxide coverage. The thermal oxide thicknesses of liquid-HF/H₂O and vapor-HF/H₂O treated surfaces are different and can be correlated to preoxidation surface XPS results. Following thermal oxidation, no differences between vapor-HF/H₂O and liquid-HF/H₂O are detected in terms of oxide charge and contact angle as a function of ambient air exposure time. However, results indicate that an increase in the waiting period prior to oxidation in ambient air results in lower oxide charge values. This is attributed to the increase in hydroxyl coverage as a function of waiting period.

Introduction and Motivation

Ultralarge scale integrated complementary metal oxide semiconductor (ULSI CMOS) technologies necessitate detailed understanding of the activity of freshly etched silicon surfaces in ambient air prior to gate insulator growth. Detailed knowledge about the effect of ambient air on cleaned surfaces is critical due to the enormous cost increases associated with closed manufacturing systems in which the activity of silicon with ambient air is indirectly suppressed by transporting the wafers in inert environments. Currently, considerable work is under way to develop capable and reliable loadlock gate insulator cluster tools. An alternative, and at times, a complementary technique to this approach is the direct method of reducing the activity of the silicon surface in ambient air by developing wafer cleaning procedures for effective passivation of surfaces.

It is well known that cleaning procedures based on a combination of SC-1 and SC-2 chemistries are very effective in removing trace metallics and particles.^{1,2} Such pro-

cedures, when performed as the final cleaning step, result in the formation of a 6 to 10 Å chemical oxide layer on top of the silicon.^{3,4} The resulting hydrophilic surface has been shown to have a high degree of activity in humid, ambient air. This has been attributed to the combined effects of Si-OH condensation and hydrolization of bridging Si-O-Si sites by water vapor, thus causing periodic film shrinkage and swelling, and in turn giving rise to surface heterogeneities.^{3,4} Moreover, as gate insulator thicknesses decrease to less than 75 Å in order to satisfy ULSI device requirements, such chemical oxides becomes increasingly harder to tolerate.

On the other hand, procedures which employ hydrous or anhydrous HF chemistries as their last step are generally regarded to be less active in ambient air. In fact, recent investigations have shown that such processes lead to the near ideal electrical passivation of silicon surfaces.^{5,6} The passivation has been mostly attributed to the presence of Si-F and Si-H groups.⁵⁻⁹ It should be noted that processes using liquid-HF/H₂O as the final cleaning step have traditionally been regarded as substantial particle adders, however recent advances in wet chemical cleaning technology

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have ensured adequate cleanliness.¹⁰ While there have been conflicting reports regarding Cu contamination following such processes,^{11,12} one benefit of note is their effectiveness in removing contaminants such as Fe, Br, and Zn which are not entirely removed by RCA cleaning.¹¹

The hydrophobicity of liquid-HF/H₂O treated silicon surfaces has also been the subject of numerous investigations. Contact angle measurements have identified the presence of hydrocarbon and fluorocarbon containing compounds following liquid-HF/H₂O treatments irrespective of DI water rinsing.^{13,14} Similar residues have been observed on wafers after vapor-HF/H₂O and DI rinse treatments.¹⁵

This study is yet another undertaking at characterizing the activity of silicon surfaces in ambient air following liquid-HF/H₂O and vapor-HF/H₂O chemistries. The work is motivated by the fact that more information is needed regarding the chemical and physical activity of silicon surfaces following HF-based sacrificial thermal oxide removal in commercially available, low pressure, continuous flow vapor-HF/H₂O systems.¹⁶ In such systems, oxide removal occurs by the action of a thin condensed layer of hydrofluoric acid and water mixture. The ability to desorb condensed matter from wafer surfaces through rapid pumpdown prior to and following oxide removal is considered unique and may play an important role in the overall activity of freshly exposed silicon surfaces. This study will compare the effectiveness of such a process to the more conventional wet bench approach. The work will also attempt to address the quality and activity of thermally oxidized silicon following such treatments.

Literature review has identified the most prevalent technique for analyzing native oxide growth and Si-F bonding on silicon surfaces following HF treatments to be x-ray photoelectron spectroscopy, (XPS).^{5-7,9,14} Furthermore, high resolution electron energy loss spectroscopy has shown these surfaces to be mainly comprised of Si-H groups.^{3,4} Contact angle measurements have also shed light on the hydrophobicity and hence the interaction of silicon in the presence of humid, ambient air.^{13,17,18} In an effort to improve our understanding of the complex mechanisms which account for the activity of silicon surfaces, this study hopes to determine whether the novel technique of surface charge analysis (SCA)¹⁹⁻²³ can be used to bridge the gap between XPS and contact angle data. SCA allows the immediate and nondestructive characterization of the electronic properties of the Si/SiO₂ system without requiring gate electrode formation. Since SCA can be applied to chemical and thermal SiO₂ films of any thickness, the technique is believed to be appropriate for studying the activity of HF-treated silicon surfaces in ambient air, as well as the quality and stability of thermal oxides grown on such surfaces.

Experimental

Monitor wafers were prepared by growing approximately 150 Å of sacrificial thermal oxide on 1 to 10 Ω · cm, P-100, 125 mm, CZ silicon substrates. The wafers were then implanted with boron at a dose and energy of 1E10/cm² and 110 keV, respectively. The implantation was performed to yield oxide conditions typically encountered in CMOS integrated circuit (IC) fabrication lines prior to sacrificial oxide strip and gate oxide growth. Following ion implantation, a split was made at sacrificial oxide strip where half of the monitor wafers were subjected to liquid-HF/H₂O, and the other half to vapor-HF/H₂O conditions.

The liquid-HF/H₂O treatment was considered as the control experiment and was performed in a conventional wet bench. The procedure involved submerging monitor wafers in a 10:1 water and hydrofluoric acid bath at room temperature for 40 s in order to ensure complete removal of the sacrificial oxide. The wafers were then removed from the bath and rinsed in DI water for 8 min before undergoing a 5 min nitrogen dry. The TOC of the DI water at the point of use was approximately 25 ppb. The vapor-HF/H₂O tests were performed in an Edge-2000 apparatus manufactured by Advantage Production Technology, Inc. Detailed de-

scription of various features of the system and typical cleaning procedures may be found elsewhere.¹⁶ In our case, the entire process was performed at room temperature. Following wafer insertion and initial desorption, the system was purged with argon for 4 s during which the chamber pressure was raised to approximately 1.6E-1 atm. This was followed by a 55 s oxide strip. The strip was performed by combining two streams of argon, which contained various amounts of chemicals, and directing them towards the wafer surface. The first stream was formed by flowing 1 standard liter per minute of argon through the vapor phase of an azeotropic mixture of water and hydrofluoric acid contained in a 30°C canister. The second stream, which provided supplemental water, was formed by flowing 4 standard liter per minute of argon through the vapor phase of a pure water system contained in a 60°C canister. A total pressure of 1.6E-1 atm was maintained during this interval. Upon etch completion, a secondary desorption was invoked by pumping the system, for 8 s, down to 2.6E-5 atm. The cycle ended by back filling of the etch chamber with argon, followed by wafer removal.

After the sacrificial oxide strip, the monitor wafers were further split into two groups containing equal numbers of vapor-HF/H₂O and liquid-HF/H₂O treated samples. The first group was used in Phase-1 of the study, and the second group in Phase-2. All poststrip processing and analyses were identical for both groups.

In Phase-1, most of the wafers were subjected to a series of time-dependent characterizations during which the surface charge, the water/air/solid contact angle, and the apparent native oxide thickness were measured as a function of exposure time to ambient air at an average temperature of 20.5°C, and an average relative humidity of 45%. Exposure times ranged from several minutes to several days. Some freshly etched monitor wafers were analyzed with XPS in order to determine their surface composition.

The surface charge was measured using the surface charge analyzer (SCA), which had a proven precision of 1E10/cm². The technique which was based on photoelectrical measurements^{19,20} used low intensity light chopped at high frequencies. The resulting surface photovoltage signal was then used to characterize the electrical properties of the Si/SiO₂ system. The surface charge values were determined from the total charge of the Si/SiO₂ system with the silicon surface biased to align the Fermi level with the intrinsic level. Under such conditions, the contribution of interface traps to the charge could be neglected. As no additional processing was required, our measurements directly reflected variations in the HF/H₂O treated surfaces.

The contact angle was measured using a conventional optical goniometer. The technique, which had a precision of ±2°, involved visual measurement of the contact angle via a microscope equipped with a built-in protractor. A five microliter droplet of DI water was first introduced onto the substrate, and was allowed a certain amount of time to spread on the surface before contact angle measurements were made on both sides of the droplet. The average value of the left side and right side contact angles was reported for greater accuracy. The droplet age was kept constant at 3 min. Precise control of the droplet age was very important due its pronounced effect on contact angle.

The apparent native oxide thickness was measured with a precision of ±1 Å using ellipsometry at a wavelength of 6328 Å, beam angle of 70° and a fixed refractive index of 1.460. The results were then correlated to XPS data on actual native oxide thicknesses obtained from the literature.

In Phase 2, the monitor wafers were first divided into five groups containing equal numbers of wafers treated with liquid-HF/H₂O and vapor-HF/H₂O and were then subjected to a waiting period in ambient air. The purpose for these tests was to determine whether any correlations existed between thermal oxide characteristics and the exposure of HF/H₂O treated silicon surfaces to ambient air prior to thermal oxidation. Five waiting periods of 25, 55, 125, 1440, and 1560 min were used. Wafers from all five groups

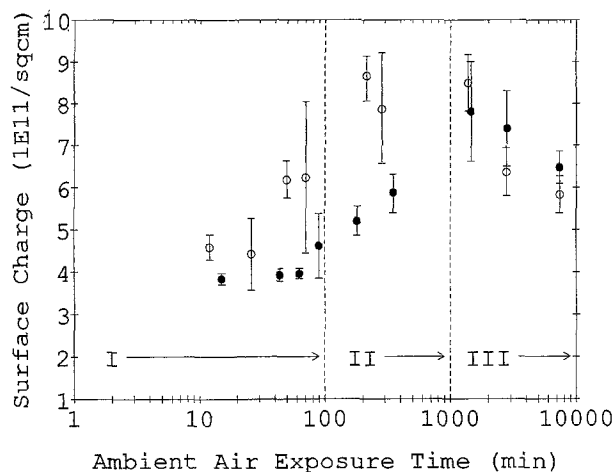


Fig. 1. Surface charge vs. ambient air exposure time for freshly etched surfaces; (○) vapor-HF/H₂O; (●) liquid-HF/H₂O.

were then combined and processed through a 150 Å thermal gate oxidation cycle at 950°C. The initial temperature ramp-up and stabilization intervals were done in a diluted oxygen mixture, while the main oxidation was performed using oxygen containing 3% chlorine. The procedure included a 30 min postoxidation nitrogen anneal. Following gate oxidation, the wafers were subjected to a series of time-dependent characterizations during which the total oxide charge, the contact angle, and the thermal oxide thickness were measured as a function of exposure time to ambient air.

Results and Discussion

Phase 1; silicon surface characterization following HF treatments.—Figure 1 shows the variation of surface charge with ambient air exposure time for both liquid-HF/H₂O and vapor-HF/H₂O treated surfaces. The error bars represent one standard deviation. The vapor-HF/H₂O treated wafers experience greater change and can be characterized as the more active of the two types. This can also be deduced from the larger standard deviation associated with this treatment. Upon exposure to ambient air, liquid-HF/H₂O and vapor-HF/H₂O treated surfaces undergo three distinct evolutionary periods.

The initial evolutionary period persists up to approximately 100 min of air exposure time, during which, the wafers exhibit very low levels of activity. This is believed to be mainly due to hydrogen passivation of the silicon surfaces.

The intermediate evolutionary period ranges from approximately 100 to 1000 min. During its preliminary stages, the wafers experience the rapid annihilation of the hydrogen passivation layer, and the subsequent formation of positively charged trivalent silicon centers at the surface. The rapid formation of such positively charged centers, is readily detected by the surface charge analyzer. During the secondary stage of this period, the rate of change of surface charge with ambient air exposure time begins to decrease and eventually diminishes. This is believed to be due to the gradual reaction of the available trivalent silicon centers with airborne hydroxyl groups thus resulting in the formation of electronegative Si-OH sites. The fact that there seems to be a delay time associated with this charge compensation process may be attributed to the presence of an incubation period prior to native oxide formation.^{14,24}

The final evolutionary period ranges from approximately 1,000 to 10,000 min (and possibly beyond). It is initially characterized by steady, yet moderate, decreases in surface charge. This phenomenon is essentially a continuation of the secondary stage of the intermediate period in which hydroxyl groups continue to replace trivalent silicon centers, thus rendering the surfaces less and less positive. Towards the end of the third evolutionary period, the rate of

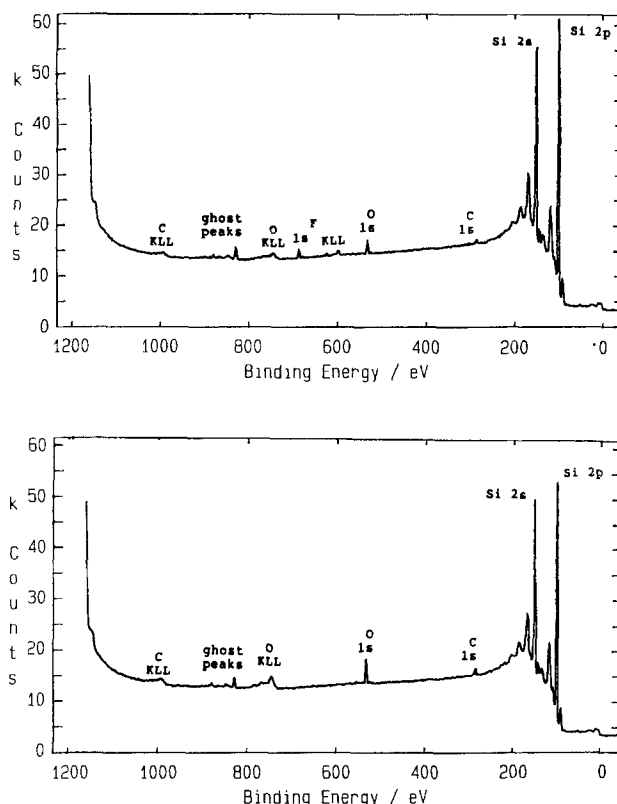


Fig. 2. XPS spectra of freshly etched surfaces: (a, top) vapor-HF/H₂O; (b, bottom) liquid-HF/H₂O.

change of surface charge with ambient air exposure time slows down. This indicates that a balance is beginning to be reached between the combined effects of Si-OH condensation and hydrolization of the Si-O-Si backbones by water vapor, and the reaction of neighboring Si-OH groups to form bridging Si-O-Si bonds.^{3,4}

In the initial and intermediate evolutionary periods, surfaces treated with liquid-HF/H₂O exhibit a net lower charge. The phenomenon can be explained by considering the nature of the chemical impurities left on the freshly etched silicon surfaces. XPS analysis of several monitor wafers immediately following HF/H₂O treatments is shown in Fig. 2. The results indicate the liquid-HF/H₂O treated samples to have approximately 2.2 times more oxygen on their surface compared to the vapor-HF/H₂O treated wafers. The oxygen, which is most probably bonded or chemically adsorbed to silicon, can be traced to the DI water rinsing step of the liquid-HF/H₂O process. In spite of the short duration of the rinse step, the high dissolved oxygen content of the DI water (possibly 1 ppm) can react with a small fraction of the Si-H groups to form highly negative Si-O centers, thus resulting in a less positive overall surface charge during the first 1,000 min of exposure time to ambient air. The fact that no significant differences are observed between the two treatments in the final evolutionary period is most probably due to complete oxidation of the silicon surfaces.

Carbon analysis of all samples indicate significant amounts of physisorbed surface hydrocarbons (Fig. 2). In the case of the liquid-HF/H₂O process, this may be attributed to organic leachate from the walls of the wet bench and the acid bottles, as well as ion exchange resins used in DI water production.^{13,14} Organic residues following vapor-HF/H₂O treatment may originate from the interaction of the azeotropic mixture with the walls of the canister or from reactor itself. The liquid-HF/H₂O treated wafers seem to have roughly 1.5 times as much hydrocarbons compared to their vapor-HF/H₂O counterparts. While this is most probably due to the fact that vapor-HF/H₂O treatment does not include a rinse step (DI water, having a TOC of 25 ppb, will act as an additional source of organics), the effective-

ness of the postoxide strip desorption interval of the vapor-HF/H₂O process cannot be ruled out. The fluorine content of the liquid-HF/H₂O treated wafers is within the detection limit of the instrument, however surfaces treated with vapor-HF/H₂O contain measurable amounts of Si-F groups. Due to the hydrous nature of the vapor-HF/H₂O treatment of this study, we suspect an Si-F coverage of only a few hundredths of a monolayer. It should be noted that Morita and coworkers⁹ who have studied the effect of anhydrous HF treatment, report the presence of a completely fluorine-terminated silicon surface.

Before proceeding with the planned contact angle *vs.* ambient air exposure time experiments, the variation of the contact angle as a function of droplet age was studied. A strong dependence of contact angle is observed with droplet age, thus characterizing the air/water/solid system as dynamic, in which water continuously alters the solid surface through oxidation and roughening, thus rendering the surface more hydrophilic. The measurements indicate that, up to a droplet age of 6 min, the contact angle decreases by $3.7 \pm 0.2^\circ$ per minute. Statistically, no slope differences were observed between liquid-HF/H₂O and vapor-HF/H₂O treated samples. For purposes of comparing our results to those obtained by Gould and Irene who adopted an inverted bubble technique for measuring the contact angle and did not observe such a phenomenon,¹³ a useful transformation of our data was made. Since for each experiment, the equation of the straight line relating contact angle with droplet age was known, the extrapolated y intercept was perceived as the initial contact angle had it been measured immediately following droplet introduction.

Alternatively, the droplet age for each measurement was fixed at 3 min, thus allowing sufficient time for focusing and angle measurement using the microscope/protractor assembly, without resulting in droplet breakdown due to evaporation. Figure 3 shows the variation of the contact angle with exposure time to ambient air for both liquid-HF/H₂O and vapor-HF/H₂O treated surfaces. It is interesting to note that, over time, the contact angle is more sensitive to changes on the vapor-HF/H₂O treated surface. Furthermore, despite the contact angle differences between the two processes, both curves experience three distinct periods of evolution which correlate well with previously observed trends in surface charge (Fig. 1).

During the initial period, which again persists for approximately 100 min, the liquid-HF/H₂O treated wafers show greater hydrophilicity. This is consistent with XPS data taken immediately following HF treatments showing oxide densities to be 2.2 times greater on the liquid-HF/H₂O treated wafers (Fig. 2). In spite of the fact that these wafers had more organic residues, which in the absence of other effects should render them more hydrophobic, the

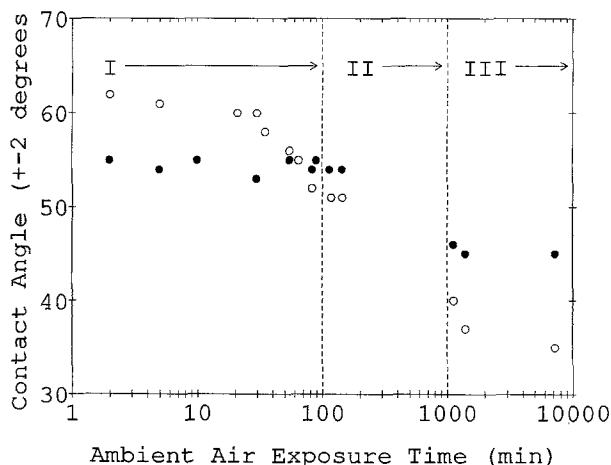


Fig. 3. Contact angle *vs.* ambient air exposure time for freshly etched surfaces: (○) vapor-HF/H₂O; (●) liquid-HF/H₂O.

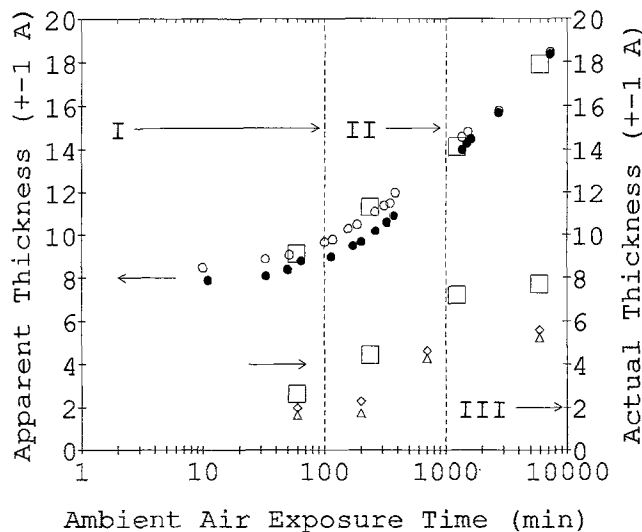


Fig. 4. Apparent and actual native oxide thicknesses *vs.* ambient air exposure time for freshly etched surfaces: (○) vapor-HF/H₂O, this study; (●) liquid-HF/H₂O, this study; (□) liquid-HF/H₂O⁷; (◇) liquid-HF/H₂O without DI rinse⁷; (Δ) vapor-HF/H₂O.⁹

greater oxide coverage seems to be the dominating factor in their relative hydrophilicity.

Figure 3 shows that after exposing the vapor-HF/H₂O treated samples to ambient air for 2 min, a contact angle of $62 \pm 2^\circ$ is observed. This corresponds to a transformed, initial contact angle of $73 \pm 2^\circ$ (*i.e.*, at zero droplet age) which is close to Gould and Irene's,¹³ as well as Ohmi and Shibata's¹⁹ reported values of $78 \pm 3^\circ$ for unrinsed liquid-HF/H₂O treated substrates. The difference is most likely due to the fact that our vapor-HF/H₂O process is not exactly the same as their unrinsed liquid-HF/H₂O treatment.

During the intermediate period (again ranging from approximately 100 to 1000 min), rapid decreases in contact angle are observed thus indicating an increase in the surface polarity due to the emergence of charged trivalent silicon centers and their gradual reaction with hydroxyl groups. It is interesting to note that in the case of both liquid and vapor-treated samples, the times corresponding to the sudden decrease in contact angle (Fig. 3) are well synchronized with the emergence of positively charged trivalent silicon centers (Fig. 1).

In the third evolutionary period, the contact angles for both types of surfaces begin to approach their respective final values. This is due to the gradual replacement of trivalent silicon centers with Si-OH groups, and the emergence of the previously stated steady-state condition. In the case of the vapor-HF/H₂O treated surface, the contact angle reaches a final value of $35 \pm 2^\circ$ which corresponds to a transformed, initial contact angle of $41 \pm 2^\circ$. This is in close agreement with Gould and Irene's¹³ reported value of $39 \pm 3^\circ$ for thermally oxidized silicon. It is interesting to note that in the third evolutionary period, despite the presence of equivalent monolayers of oxide, the vapor-HF/H₂O treated surfaces show greater hydrophilicity. Under such conditions, the only discrepancy between the two surfaces must be the lower concentration of physisorbed organics present on the vapor-HF/H₂O treated surfaces, thus rendering them more hydrophilic.

The apparent native oxide thicknesses as a function of exposure time to ambient air following liquid-HF/H₂O and vapor-HF/H₂O treatments was also studied. The results are shown in Fig. 4. During these measurements, the refractive index was fixed at 1.460. The slight differences between the two curves may be due to actual refractive index differences caused by various amounts of surface organics. Since we did not perform time-dependent XPS analysis, in order to determine the actual native oxide thickness, our data is correlated to actual native oxide results available from the literature. Figure 4 shows our results to be in agreement with the ellipsometric findings of Raider and coworkers⁷

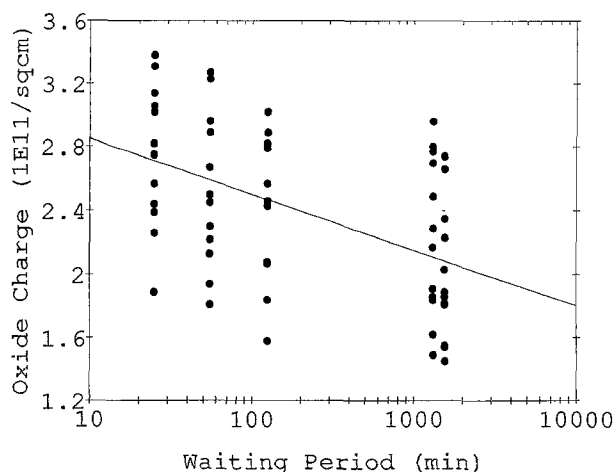


Fig. 5. Total thermal oxide charge vs. waiting period prior to thermal oxidation. Due to statistical insignificance, the various types of HF treatments and ambient air exposure times have not been distinguished in this figure.

who additionally, performed time-dependent XPS for native oxide thickness measurement (also show in Fig. 4). The fact that their XPS results agree semi-quantitatively with the recent results of Morita and coworkers,⁹ emphasizes the validity of their approach. Moreover, the fact that our ellipsometric results are in close agreement with those of Raider and coworkers, leads us to deduce that, in our investigation, both liquid-HF/H₂O and vapor-HF/H₂O treated surfaces undergo three distinct periods of evolution which correlate very well with previously stated surface charge and contact angle trends.

Phase 2; characteristics of thermal oxides grown after HF treatments.—Multiple regression analysis of the data indicates the waiting period to be the only significant factor affecting total oxide charge. An increase in the waiting period prior to oxidation in ambient air results in a gradual decrease in oxide charge values (Fig. 5). This may be due to the increase in hydroxyl coverage as a function of waiting period however, the results are not well synchronized with those in Fig. 1. HF treatment and ambient air exposure time after thermal oxidation do not affect total oxide charge since the interaction of thermally oxidized surfaces with ambient air are governed by the same reaction mechanisms described in the final evolutionary period of Fig. 1. Upon thermal oxidation, the total charge attains an average value of $2.4 \text{E}11/\text{cm}^2$ which, when compared to the final surface charge results of Fig. 1, seems to be two to three times lower. This is to be expected since thermal oxidation essentially accelerates the charge compensation process described in the final evolutionary period of Fig. 1.

As for contact angle measurements of thermally oxidized wafers, multiple regression analysis indicates that none of the factors investigated here are significant. Regardless of sample history, an average contact angle of $33 \pm 2^\circ$ is obtained which is consistent with the above-mentioned total oxide charge results in indicating a high degree of inactivity for thermally oxidized silicon surfaces in ambient air.

Contact angle measurements as a function of droplet age of up to 6 min, indicate that regardless of the HF treatment, the contact angle of thermally oxidized wafers decreases at a slower rate compared to freshly etched surfaces (2.6 ± 0.2 as opposed to $3.7 \pm 0.2^\circ$ per minute). In the case of thermally oxidized wafers, surface oxidation due to the water droplet should no longer play a role in decreasing the contact angle. Instead the contact angle decrease may be attributed to increased surface roughness upon exposure to water.⁹ At a droplet age of 3 min, the observed average contact angle of $33 \pm 2^\circ$, corresponds to a transformed contact angle of $40 \pm 2^\circ$ (i.e., at zero droplet age). This agrees well with Gould and Irene's reported value of $39 \pm 3^\circ$ for thermally oxidized silicon wafers.¹³ It should be noted that the observed inac-

tivity of thermal oxide in the presence of ambient air is at odds with the findings of Ohmi and coworkers who report an 11° drop in contact angle upon exposing thermally oxidized and annealed wafers to ambient air for 100 min.¹⁹

In comparing the above results with those of Fig. 3, it is noticed that thermal silicon oxidation does not significantly reduce the contact angle beyond that of what has been accomplished by several monolayers of a chemical oxide. This is to be expected since contact angle is a function of the top several monolayers of a material and gives no information about its bulk properties. Furthermore, as indicated earlier, the observed differences in hydrophobicity between vapor-HF/H₂O and liquid-HF/H₂O treated surfaces in the final evolutionary period of Fig. 3 were attributed to the presence of organic residues. After thermal oxidation (which should volatilize all organics) the fact that no differences in hydrophobicity are observed, reinforces our claim.

Regardless of the HF treatment and the waiting period, even up to several days of post oxidation air exposure time, no statistically significant variations in the thermal oxide thicknesses were observed. However, the thermal oxide thickness differences between the liquid-HF/H₂O treated wafers and the vapor-HF/H₂O treated wafers are statistically significant. The thickness of the thermal oxide layer on the liquid-HF/H₂O treated wafers ranges from 147 to 151 Å, while that of the vapor-HF/H₂O treated wafers ranges from 150 to 156 Å. This may be due to the presence of more organics on the liquid-HF/H₂O treated wafers. Given the fact that temperature ramp-up in the oxidation furnace was performed in a nitrogen-diluted oxygen environment, it is unlikely that the lower growth rate in the case of liquid-HF/H₂O treated samples is due to the formation of silicon carbide islands as reported by Meuris and coworkers.²⁵ Instead, we believe the growth-rate difference may be due to the fact that, for a fixed oxidation time, in the case of the liquid-HF/H₂O treated wafers, a larger fraction of the oxidation time is spent in volatilizing the surface organics. Given the relatively short oxidation times necessary to grow 150 Å at 950°C , the so called "incubation time," which is longer for the liquid-HF/H₂O treated samples, can be rate retarding. Such organic residues have been known to hinder native oxide growth in ambient air,^{7,14} and it is believed that our observations are an extension of this phenomenon.

Conclusions

A strong correlation was observed among surface charge, contact angle, and native oxide thickness in which, up to 10,000 min of exposure time to ambient air, the liquid-HF/H₂O and vapor-HF/H₂O treated surfaces underwent three distinct periods of evolution. Results indicated that the vapor-HF/H₂O treatment yielded surfaces with greater activity in ambient air. The trends, which were explained by considering the reaction between unpassivated trivalent silicon and hydroxyl groups, were shown to be consistent with XPS data on surface carbon, fluorine, and oxygen. Following thermal oxidation, the total oxide charge, oxide thickness, and contact angle were stable over time. This was believed to be due to the complete surface oxide coverage. The thermal oxide thicknesses of liquid-HF/H₂O and vapor-HF/H₂O treated surfaces were different and could be correlated to preoxidation surface XPS results. Following thermal oxidation, no differences between vapor-HF/H₂O and liquid-HF/H₂O were detected in terms of oxide charge and contact angle as a function of ambient air exposure time. However, results indicated that an increase in the waiting period prior to oxidation in ambient air resulted in lower oxide charge values. This was attributed to the increase in hydroxyl coverage as a function of waiting period.

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The Use of Ultraviolet Radiation at the Congruent Sublimation Temperature of Indium Phosphide to Produce Enhanced InP "Schottky" Barriers

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ABSTRACT

This paper describes an ultraviolet radiation-assisted process, optimized around the congruent sublimation temperature of InP, which fabricates a very thin insulating layer on InP. In developing this process, we demonstrate, among other effects, that the increase in the barrier height is not caused by the oxidation of the surface enhanced by the presence of ozone, but enhanced by a photoinduced electron transfer (PET) process. In the past, some researchers have considered similar devices to be enhanced metal-semiconductor Schottky diodes. Although we achieved a barrier height of 0.7 V, we present measurements of series resistance and ideality factors which question the Schottky character of these devices. Furthermore, the dramatic increase in series resistance, as the barrier increases, suggests that the gate speed for microwave devices fabricated with this technology may be less than expected because of a larger than expected resistance capacitance time constant. The instability of these devices, when exposed to air, suggest that among the oxides which make up the enhanced layer, P_2O_5 is the primary material responsible for enhancement.

A comparison of the basic transport properties of GaAs and InP yields an advantage to InP in peak and saturation velocities,¹ breakdown field, and thermal conductivity.² These benefits have led to encouraging device results in higher power,³ faster speed,⁴ lower noise,⁵ and increased radiation hardness.⁶ However, the low Schottky barrier, formed for metal-semiconductor (MES) interfaces, generates large leakage currents that eventually degrade the speed, power, and gain of MES devices. To eliminate this problem, researchers typically use a metal-insulator-semiconductor (MIS) structure using SiO_2 as the insulator. But

others have demonstrated the instabilities of the SiO_2 /InP interface under dc operating conditions.⁷ This paper describes an ultraviolet (UV) radiation-assisted process, optimized around the congruent sublimation temperature of InP, which produces Schottky barriers up to 0.7 V. Based on series resistance and ideality factor measurements, this paper also concludes that these devices exhibit behavior more like MIS structures with a very thin insulating layer rather than Schottky diodes. In addition, the increase in series resistance, as the barrier height increases, suggests that the gate speed at microwave devices fabricated with