

## Role of UV/Chlorine Exposure During Dry Surface Conditioning Before Integrated Epi Deposition Process

J. Ruzyllo, E. Röhr, M. Caymax, M. Baeyens, T. Conard, P. Mertens, and M. Heyns

IMEC, Kapeldreef 75, 3001 Leuven, Belgium  
\* On sabbatical leave from Penn State University  
Department of Electrical Engineering  
University Park, PA 16802

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### Abstract

Native/chemical oxide etching using the anhydrous HF (AHF)/methanol process before epitaxial deposition was investigated in a cluster incorporating surface processing module and epi deposition reactor. The results of this research indicate that the AHF/methanol process alone leaves the Si surface in a state which does not allow growth of the haze-free epitaxial layer at 800 °C. If the surface is exposed to chlorine ambient following oxide etch, however, haze is eliminated and a high quality epi layer is grown. This effect is attributed primarily to the reduction of fluorine remaining on the surface following AHF/methanol oxide etch by chlorine. The proposed pre-epi surface preparation procedure, which does not involve any elevated temperature step, shows excellent promise for low-temperature fully integrated epitaxial processes.

### Introduction

In order to accomplish a defect-free epi layer, a defect and contaminant free surface of the substrate is required at the onset of the epitaxial deposition. The chance to achieve this goal is best when the surface following cleaning is transferred to the epi reactor in a fully controlled, ultra-clean environment. Such an environment can only be assured when the surface preparation module is integrated with an epitaxial reactor. In turn, such integration is most effectively accomplished when the surface preparation steps are carried out in the gas-phase. This reasoning implies the need to develop effective methods of gas-phase conditioning of silicon surfaces meeting the stringent requirements of the epitaxial processes. The trend toward lower temperature epi processes brings about new challenges regarding surface preparation procedures. This is because the decrease of the temperature of epi deposition to 800 °C and below renders thermal reduction of native/chemical oxide in hydrogen, ineffective.

The goal of this experiment was to develop methods of gas-phase surface conditioning which can be integrated with low temperature epitaxial deposition. The gas-phase chemistries employed were demonstrated previously to allow relatively broad control over the surface condition. In this study they are used specifically prior to epitaxial deposition in a cluster integrating surface preparation and epi deposition steps.

### Experimental

The cluster used in this experiment incorporated the commercial *Primaxx* dry cleaning module and the ASM single wafer epi deposition reactor. Wafers were transferred between these two modules by a wafer handler in controlled N<sub>2</sub> ambient. 150 mm, p-type, (100) Si wafers were used. As a reference an *ex situ* native oxide etch consisting of 2% HF, 30 seconds dip followed by rinse-dry cycle was used. Gas-phase processes carried out in the cluster included (i) AHF/methanol oxide etch at 300 torr and 20 °C - 40 °C preceded by 30s. exposure to UV/O<sub>2</sub> at 100 torr and (ii) UV/Cl<sub>2</sub> exposure

at 10 torr and varied time and temperature. The epi deposition process was carried out using dichlorosilane at 800 °C and 40 torr. No pre bake was applied in the epi reactor and thickness of epi layers was about 300 nm. Haze before and after epitaxy was measured using Censor ANS system and then the difference ("delta haze") was used as a primary indicator of the process performance. In addition, XPS was used on the wafers before epi deposition while SIMS profiling was used to determine chemical composition of the epi layer/substrate interface after deposition. Also, VPD-TXRF and AFM were used as additional measures of surface quality.

## Results and Discussion

Early experiments carried out in this study demonstrated that the AHF/methanol process, although effective in chemical oxide etching, does not result in Si surface chemistry favorable from the point of view of subsequent moderate temperature epi deposition. This is exemplified by higher "delta haze" in the epi layers grown on the (AHF)/methanol treated surfaces as compared to dilute HF treated surfaces. In addition, the haze resulting from this process was consistently displaying a non-uniform distribution. The observed pattern could have been related to the gas flow dynamics in the process chamber indicating dependence of the etching process on the transport of species in the gas-phase.

This deleterious effect was tentatively linked to the excess fluorine remaining on the surface following AHF/methanol etch observed using XPS both in this study as well as in previous investigations (e.g. [1,2]). Past experiences did show that the UV/Cl<sub>2</sub> exposure applied subsequently to AHF/methanol etch is very effective in decreasing surface concentration of fluorine [3]. Under the process conditions in this experiment this reduction was typically from about 3.0 % to about 0.5 %. Hence, the UV/Cl<sub>2</sub> exposure was introduced to the surface conditioning sequence as a step immediately following AHF/methanol oxide etch. As seen in Table 1 this additional treatment did eliminate the haze in the epi layers resulting from the AHF/methanol etch. Moreover, the UV/Cl<sub>2</sub> exposure alleviates entirely the haze non-uniformity observed after the (AHF)/methanol process. As seen in Table 1 no connection between haze and surface roughness was found. Also, TXRF measurements did not show any correlation between metallic contaminants on the surface and haze. Both these observations seem to validate an early assumption that the excess fluorine was responsible for the haze formation during the epitaxial growth.

Table 1 Haze Difference Before and After Epi Deposition and Surface Roughness for Different Pre-Deposition Surface Treatments.

PROCESS	DELTA HAZE (ppm)	Rms (nm)
dHF+rinse	0.013	0.08
AHF/meth.	0.235	0.09
AHF/meth.+UV/Cl <sub>2</sub> , IR 40%, 30 s	0.005	0.08
AHF/meth.+UV/Cl <sub>2</sub> , IR 40%, 120 s	0.085	

The effectiveness of haze control was found to be dependent on the parameters of the UV/Cl<sub>2</sub> process. Figure 1 shows variations of "delta haze" as a function of time of UV/Cl<sub>2</sub> exposure. The shape of the curve in Fig.1 suggest two different effects controlling the haze in this case. For exposures up to 30 seconds a gradual decrease of haze is observed while prolonged exposures lead to an increase of haze. The former is likely due to the improved chemical purity of the surface resulting for the UV/Cl<sub>2</sub> exposure. The latter may be related to possible roughening of the surface during longer exposures to UV/Cl<sub>2</sub> following AHF/methanol exposure.

Figure 2 demonstrates that the wafer temperature also has an effect on the haze formation, although, for temperatures below approximately 60-70 °C (about 25% IR power) this effect is negligible. It is interesting to note that chlorine exposure without UV enhancement is accomplishing the same effect in terms of haze control as UV/Cl<sub>2</sub> exposure providing, however, wafer temperature is

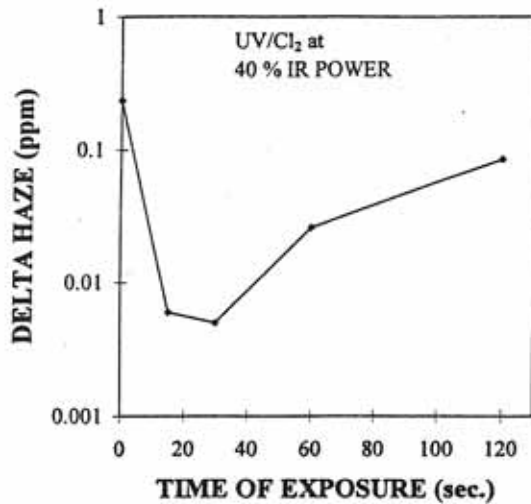


Fig. 1 Haze difference before and after epi deposition vs. time of exposure to UV/Cl<sub>2</sub> ambient at 40% IR Power corresponding to wafer temperature of about 140°C.

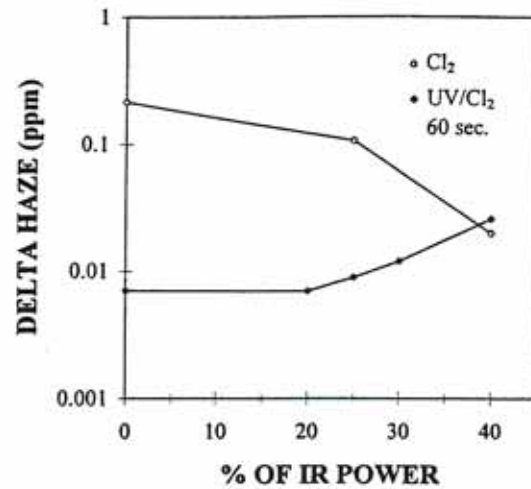


Fig. 2 Haze difference before and after epi deposition vs. % of IR power determining wafer temperature (40% ~ 140°C) during exposure to UV/Cl<sub>2</sub> and Cl<sub>2</sub> only.

is sufficiently high (Fig. 2). On the other hand, the same results can be obtained at room temperature in the case the UV stimulation is applied (zero IR power in Fig. 2). These results suggest that Cl<sub>2</sub> dissociation is at least partially surface catalyzed and can take place without UV stimulation providing wafer temperature is sufficiently high. It is speculated that following dissociation of chlorine the Si-F complex may be dislodged by Cl attacking the Si back bond. As a result of this reaction with Si, chlorine is also leaving the surface and the Si surface is slightly etched in the process. Consequently, an *in situ* sequence including (AHF)/methanol and UV/Cl<sub>2</sub> exposures applied before epitaxial deposition results in chemically pure epi/substrate interfaces.

As revealed by SIMS depth profiling this sequence provides, in terms of chemical purity, interfaces superior to the dilute HF dip followed by a D.I. water rinse (Table 2). Worth noting is the ability of chlorine not only to reduce surface fluorine, but also to have a dramatic effect on the oxygen surface concentration. The relatively high oxygen concentration in the case of dHF+rinse treatment is probably due to the fact that this process uses water rinse and in addition is performed *ex situ* while all others in Table 2 are integrated with epi deposition. It should be also pointed out that very little chlorine remains on the surface as a result of UV/Cl<sub>2</sub> exposure which is an indication that slight etching of Si is taking place and chlorine leaves the surface in the form of silicon tetrachloride. The resulting purity of the epiSi/Si interfaces has a very beneficial effect on the electrical characteristics of these interfaces as revealed by the leakage current measurements [4].

Table 2 Concentration of Selected Elements at Epi/Substrate Interface as Determined by SIMS Depth Profiling ( $\times 10^{12} \text{ cm}^{-2}$ ).

PROCESS	C	O	F	Cl
dHF+rinse	1.1	250	0.03	11
AHF/meth.	1.4	80	0.054	1.7
AHF/meth.+UV/Cl <sub>2</sub> , IR 40%, 30 s	1.3	0.95	0.0017	0.024
AHF/meth.+UV/Cl <sub>2</sub> , IR 40%, 120 s	0.34	0.55	0.002	0.0041

## Summary

The results of this experiment demonstrate that the process proposed for the gas-phase Si surface conditioning before integrated epitaxial deposition produces surfaces allowing growth of the haze-free epitaxial layers at 800 °C. Process requires sequential application of AHF/methanol oxide etch step followed by the UV/Cl<sub>2</sub> treatment. In this sequence chlorine is responsible for the reduction of fluorine and oxygen resulting in the F and O concentration at the epiSi/Si interface below levels accomplished using conventional dHF oxide etch. The process is entirely chemical and features very low thermal budget as the highest temperature during the entire surface conditioning sequence does not exceed 150 °C. The proposed method uses fully clusterable commercial surface processing module, and hence, is immediately available for low-temperature epi deposition processes including selective epitaxy.

## References

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