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Critical Parameters for Obtaining Low Particle Densities in an HF-Last Process

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Abstract - A study was made on the relation between particle adhesion and the (remaining) degree of oxidation of a cleaned surface following different HF-treatements (HF, HF/IPA, DI-rinse). A detailed comparison between XPS (X-Ray Photoelectron Spectroscopy) and contact angle measurements shows that the latter method is sensitive to less than 1/10 of a SiO_2 monolayer on the Si (100) surface. The results obtained with XPS point out that minute amounts of suboxides (a few % of a monolayer) are the dominant cause for particle adhesion. In addition the quality of the rinsing water as well as the initial roughness (Si vs. polysilicon) play a major role.

1 - INTRODUCTION

HF-last wet processing is widely used in semiconductor manufacturing. Applications include pre-epitaxial growth, pre-silicidation, pre-metallisation and pre-gate oxidation. The advantages of HF-last processes are a lower metallic impurity concentration [1] and an oxide free surface. The lower metallic impurity concentration is especially important for pre-gate oxidation cleaning [1] and the pre-silicidation cleaning [2]. The oxide free surface is important for all the above applications, including pre-silicidation [3] and gate oxidation, where an increased thickness control can be obtained. Due to the hydrogen passivation, this surface is very stable, even after long exposure to DI-water [4]. One serious drawback, however, is that the HF-last wet processing suffers from an increased susceptibility from particle adhesion [5].

2 - XPS MEASUREMENT OF THE SURFACE STOICHIOMETRY

The surface was characterized, using XPS, as a function of dipping time in an HF(0.5 %) or HF(0.5 %)/IPA(200 ppm) solution [1] with and without a subsequent DI-water rinse whereby a detailed analysis of the photoelectron peaks allowed to identify the surface chemistry. The latter investigation was done since the surface is still undergoing significant transitions during the prolonged etching.
For only HF-dipped surfaces, dipping times less than 20 s lead to a low SiO_2 coverage with a residual Si^{4+} component corresponding to less than 4.5 at% of SiO_2. For dipping times larger than 30 s the Si^{4+} component is not detected. However due to the larger sensitivity of O 1s photoelectron peak as compared to

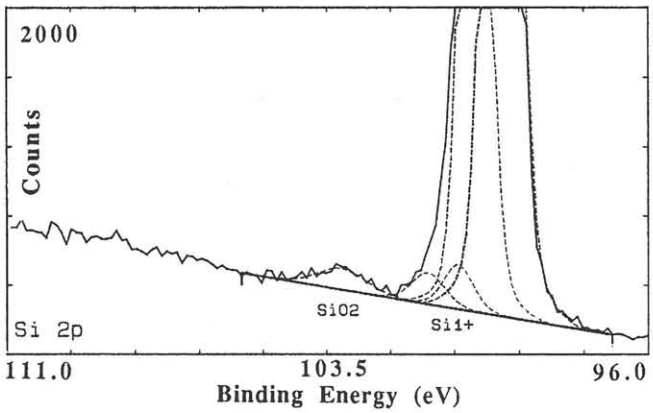

Fig. 1. XPS spectrum for the Si 2p photoelectron peak with the corresponding SiO_2 component.

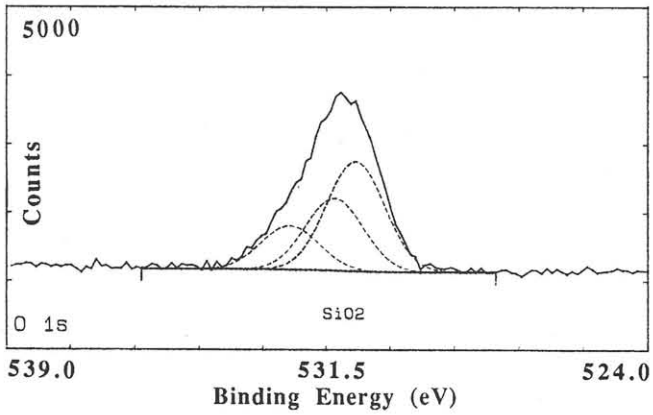

Fig. 2. XPS spectrum for the O 1s photoelectron peak with the corresponding SiO_2 component.

Si 2p, still some indications of remaining SiO_2 bonds can be observed on the O 1s peak. This residual oxide can however not be quantified.
For HF-dipped surface with DI-water rinse a slightly larger SiO_2 coverage is found rising to 6 at% for the 10 s dipping time. With increasing dipping times (up to 30 s) again the Si^{4+} component disappears completely and only the small peak in the O 1s peak can be found.
For an HF-dip with and without DI-water rinse surfaces with a relative high percentage of Si^{1+} chemical states (up to 14 at%) are measured, which are representative of suboxides Si-O and hydrides Si-H bonds.
The HF(0.5 %)/IPA(200 ppm) dipped samples only show the Si^{4+} component for a dipping time of 10 s (fig. 1 and 2). For larger dipping times again only the O 1s peak shows the remaining presence of Si-O bonds with a concentration less than 1/10 of a SiO_2 monolayer. Irrespective of the addition of an DI-rinse the mean amount of Si^{1+} is much smaller as compared to the previous case.
Traces of fluorine are detected for all samples, and adsorbed carbon bonded to O and H is also present.

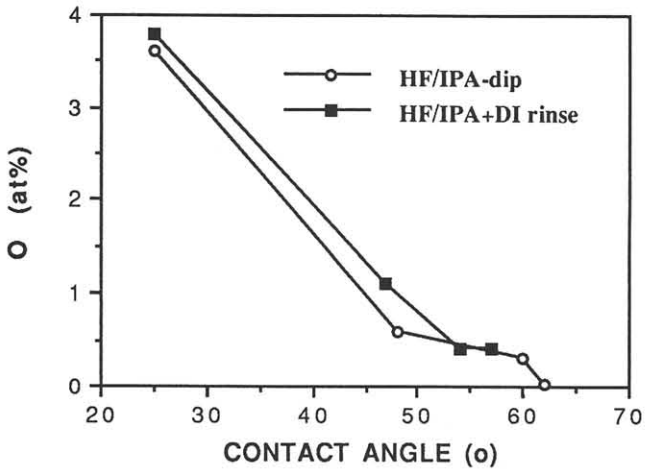

Fig. 3. Correlation between XPS and contact angle measurements for HF/IPA-dipped Si surfaces.

3 - CORRELATION BETWEEN THE XPS AND THE CONTACT ANGLE MEASUREMENTS

Although the XPS-data show the chemical changes to the surface during prolonged etching, they are very time consuming during extensive measurements of the HF-last process. Therefore a correlation has been established between changes in the surface stoichiometry, as determined by XPS (in particular the Si^{4+} component in the Si 2p peak and the intensity of the component assigned in the O 1s peak to the SiO_2 bond), and the corresponding contact angle of an H_2O droplet with the corresponding surfaces.

The contact angle varies in a similar way as the photoelectron peaks (fig. 3) and is therefore a very sensitive measure of the relative degree of oxidation of the cleaned surface. This method has however as benefit that it is more sensitive than the XPS-peaks and easier to apply during extensive measurements on particle contamination during HF-last processes.

4 - PARTICLE CONTAMINATION

Based on this correlation, we can now use the contact angle as a measure for the degree of oxidation of the surface, and focus on its variation as a function of the etching parameters. From the initial study it is clear that the dipping time is very important in obtaining an oxide free surface. Interesting enough we have found that there is a clear correlation between the degree of oxidation (as derived from XPS or contact angles) and the number of particles on this surface (fig. 4). Indeed long etch times in HF or shorter in HF/IPA both lead to an oxide free surface and a very low amount of particles. Therefore optimum conditions to obtain an oxide free surface must be pursued. As can be derived from fig. 4 long etch times in HF or the addition of IPA are appropiate cleaning conditions. However the HF-dipping time is not the only parameter. It was found that the time necessary to reach an oxide free surface (i.e. high contact angle) depends strongly on the wafer surface roughness and the water quality. Fig. 5 shows the degree of oxidation of polysilicon as a function of the dipping time in HF. Apparently much larger times are required as compared to Si to obtain large contact angles. This is probably due to the surface roughness and can be improved by using surfactants.

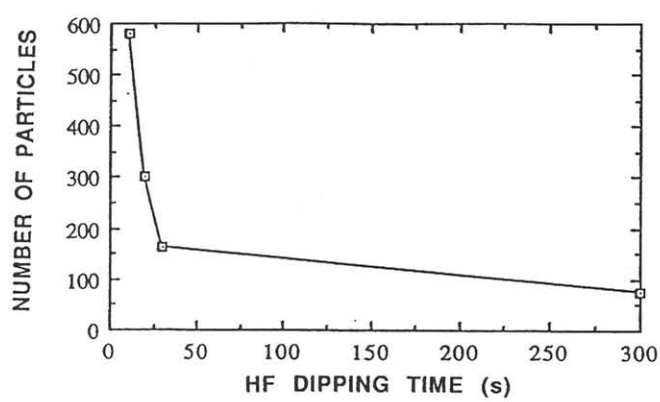

Fig. 4. Number of particles as a function of dipping time using HF (0.5%) solutions.

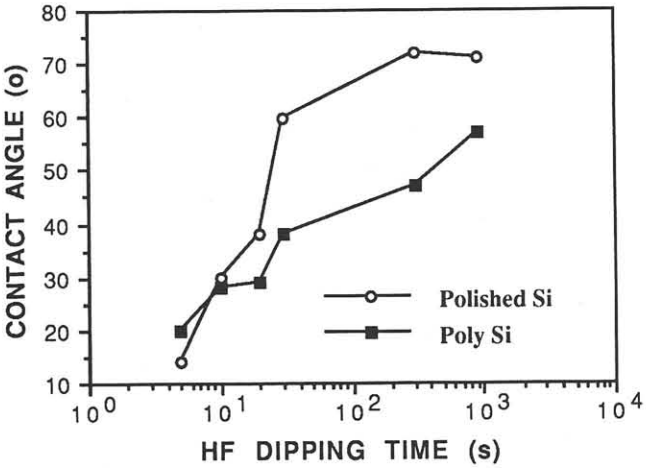

Fig. 5. Contact angle as a function of dipping time for HF (0.5%)-dipped cristalline and poly Si surfaces.

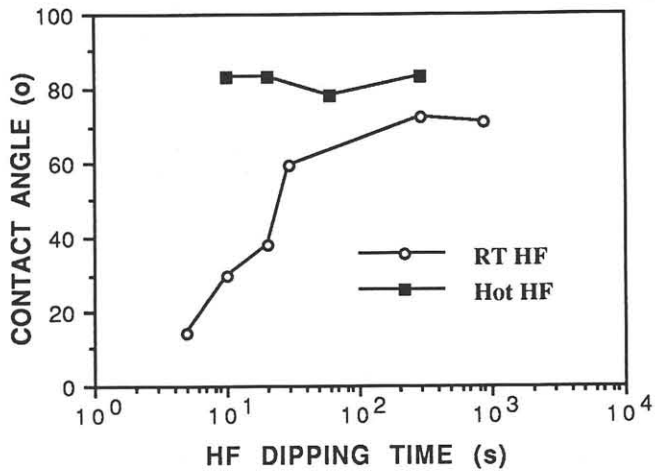

Fig. 7. Contact angle as a function of dipping time for HF (0.5%)-dippped Si using room temperature (RT HF) and 70°C (Hot HF) for the temperature of the bath.

Fig. 6 shows the influence of the water quality on the contact angle (degree of oxidation) as a function of the dipping time. The temperature of the HF bath is another important variable. In fig. 7, the contact angle variation is shown as a function of the dipping time in a bath of 0.5% HF at room temperature and for the same bath at 70°C. Si treated by HF solutions at 70°C have an oxidation degree which is significantly lower than wafers which have been exposed to room temperature HF even for long periods of time. At room temperature the contact angle saturates at values of slightly above 70° whereas for HF at 70°C, the contact angle shows values already after 10 s of over 80°. This shows that the high temperature can be effectively used to get the surface completely oxide-free. A possible mechanism could be that the high temperature prevents surfactant organic layers to adhere to the surface and by this, higher hydrophobicity is obtained.

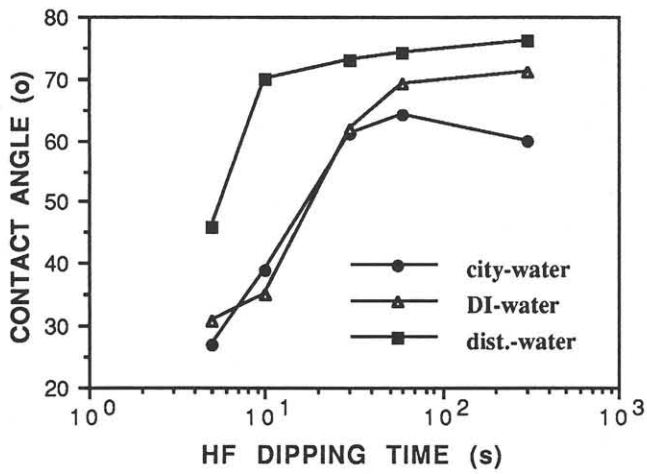

Fig. 6. Contact angle as a function of dipping time when various types of water are used in the treatment.

5 - CONCLUSION

The reduction in particles on a cleaned surface is closely related with the degree of (residual) oxidation of that surface. The latter can be determined by XPS (using the Si 2p peak and the O 1s) and with a higher sensitivity using contact angles. The latter has shown to correlate nicely with XPS-data. The exact condition of the cleaning (etching time, IPA addition, surface roughness, water quality and temperature of the bath) plays a major role.

6 - REFERENCES

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