The Quantification of Surface Modifications in 200 and 300 mm Wafer Processing with an Automated Contact Angle System

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Abstract -- Contact angle measurement, using advanced instrumentation, is assuming an increased role in monitoring those semiconductor manufacturing processes which modify the surface characteristics of wafers. Such measurements can provide rapid, non-destructive, and spatially as well as time resolved data in an automated mode. This information can be related to processing uniformity and can in many cases provide information on the chemical state of the surface. Illustrations are provided in the wafer cleaning, lithography, and interconnect areas. New application areas illustrated include measuring the uniformity of UV photostabilization processes, measurement of contrast curves, and determination of receding and advancing contact angles of processed copper wafers.

INTRODUCTION

Contact angle measurements have been used in the semiconductor manufacturing process for many years on a limited basis. Their use has been limited principally to developing and controlling vapor phase priming for lithographic applications. There have been scattered reports of contact angle measurements for Si surface preparation. A number of factors will contribute to more extensive use of surface wetting measurements in present day and tomorrow's semiconductor manufacturing environment. Greater demands are now being placed upon controlling surface properties which are in turn related to surface film characteristics as well as surface contamination. For example, as gate oxides are reduced in thickness, it has become vital to insure that the Si surface is rendered free of nonstoichiometric oxides and other types of contaminants prior to thermal oxide growth. Hydrogen passivated surfaces are favored for thin oxide growth as well as for the growth of epitaxial silicon. As lithographic features are reduced to sub 0.25 μm, it is more difficult to insure the adhesion of the photoresist to the underlying substrate. Other enabling technologies are being developed for multi-level metallization processes such as copper damascene processing which present new challenges in process development and control. Thirdly, new instrumentation has been developed which is the subject of this paper and which permits contact angles to be measured in an automated mode both rapidly and with great accuracy at pre-defined sites of wafer surfaces that are as large as 300 mm. This instrumentation was described in an earlier paper [1]. The 300 mm capability was added within the last year.

Previously, contact angle measurements were often very subjective and lacked desired accuracy. For example, Martin reports that contact angles could only be made with an accuracy of +/- 5 degrees [2] and Chyan reports in a recent paper that his measurements have an accuracy of only +/- 2 degrees [3]. In contrast, the newly developed image analysis procedures outlined in this paper enable angles to be measured to +/- 0.1 degree. The use of multiple techniques for surface wetting measurements make it difficult to correlate results. For example, tilting angle measurements have been utilized [4]. In this technique, the wafer is tilted until the drop begins to slide off the surface. The tilt angle becomes smaller as the surface becomes more hydrophobic. This method is rather slow and leaves water tracks which prevent complete surface mapping. Other approaches such as the Wilhelmy plate technique for dynamic contact angle measurements have multiple drawbacks such as complexity and the need to restrict the size of the

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sample being studied [5]. This method is impacted by the backsurface of the wafer which does not receive the same processing as the polished side. An inverted bubble technique can also be employed [6]. Both of these techniques require considerable volumes of the test liquid to be available.

EXPERIMENTAL

All measurements were conducted with either the VCA3000 or VCA3000S Systems, which have been described earlier [1]. Typically 1 µl drops are employed to permit gravitational interactions to be ignored. Measurements were performed in a controlled environment where temperature and humidity control is maintained.

WAFER CLEANING

Wafer cleaning and surface preparation has become even more challenging with the requirement to reduce the thickness of gate oxides, improve epitaxial film quality, and to reduce overall defects which impact yield. Advances are being made in this area by the use of altered and more carefully controlled chemical processing and by the use of an arsenal of sensitive analytical techniques which provide feedback on the efficiency of the cleaning process.

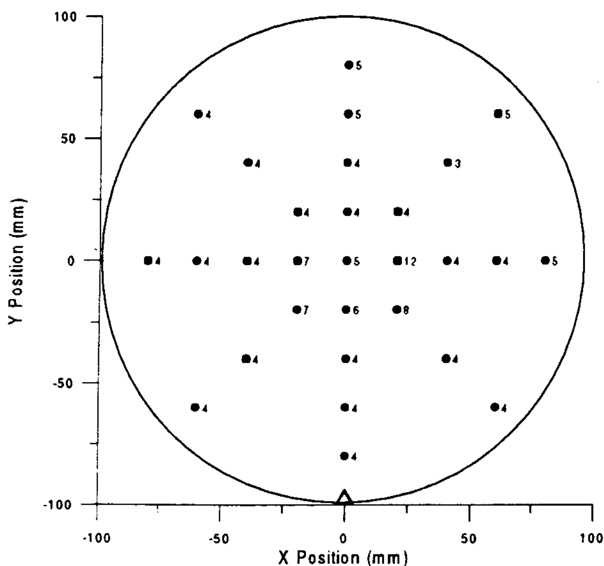

Figure 1: Contact Angles on a Cleaned Wafer

Contact angle measurements, using DI water, can be employed to provide a map on the uniformity and reproducibility of the process. This is illustrated in Figure 1 for a cleaning process which leaves the wafer in a hydrophilic state with some spatial non-uniformity. It should be noted that small contact angles for hydrophilic surfaces are normally difficult to measure using alternate techniques [6]. To perform these measurements a special algorithm which utilizes the symmetry of the reflected image of the water drop on the wafer surface is employed.

Relating the contact angle measurements to the microstructural chemical bonding on the surface is an area which warrants further study. The contact angle is a measure of the free energy of interaction between the test liquid and the surface. Thus, by monitoring this interaction especially with liquids of different polarities, it should be possible to make inferences about the chemical nature of the surface. Martin et al.[2] showed that there was no relationship between the contact angle and the amount of hydrogen passivation for vapor phased cleaned wafers. More recently Chyan et. al.[3] reported that contact angle measurements with water show preferential hydrogen-bond interactions between water and the silicon surface oxide and thus are not a direct measure of the degree of hydrogen termination. Work on wafer preparation prior to epitaxial silicon growth indicate that only the use of multiple analytical techniques will provide a complete picture of the chemical species existing at the surface. Besides $Si\text{-}H_x$ bonds F, O, and C bonds and contaminants are of interest [7,8]. Thus, at this stage it appears that the main diagnostic role for contact angle measurements in silicon wafer surface preparation is to provide a reliable measure of the processing consistency.

LITHOGRAPHY

The most widespread use of contact angle measurements in lithography today is for controlling the vapor phase silylation process with such primers as hexamethyldisilazane which modifies the high-energy hydrophilic surfaces and improves resist adhesion as well as reduces penetration of the developer or rinse liquid between the resist features and the modified surface. This topic has been covered many times in the literature. However, there are still misunderstandings which deserve comment. It should be stressed that the optimum contact angle after vapor priming will be dependent upon the particular lithographic process; ie., the type of resist, the thermal

processing applied as well as the development and rinsing process. This angle can range between 55 and 70 degrees, but the optimum angle must be established by experimental study. It is especially beneficial to perform studies with a critical dimension (CD) matrix to determine where line lifting does occur. In addition, the contact angles of the surface can be measured with several different liquids having different polarity and the surface tension of the modified surface can be calculated [9].

The degree of surface coverage, f, by the trimethylsilyl (TMS)groups can be estimated from the equation

$$\cos \Theta = -0.949 f + 0.994$$

where Θ is the measured contact angle.It was found by Trefonas et al. [10] that resist features adhere when the fraction of surface.coverage by TMS groups is about 0.43.

In addition to adhesion, one must be concerned with the wetting of the polymer solution and the substrate during coating as well as the resist and underlying substrate with the developer and rinse liquid during the development step [11]. The most conventional approach is to measure the contact angle on the surface of interest using liquids of different polarity and then to calculate the surface tension (energy) of the surface. In general, a liquid will wet the surface if its surface tension is lower than that of the solid surface. Nagata and Kawai have demonstrated that there is a correlation between polar part of the surface energy and adhesion [12]. The surface tension of the liquid can be measured by pendant drop image analysis [13]. It is also possible to measure the wetting of polymer solutions directly by filling the instrument syringe with the resist or antireflecting layer solution and applying it directly to the surface of interest. A low contact angle will indicate spreading or wetting of the surface by the liquid. Here the dynamic imaging capability is of particular value, as it can be employed to observe the wetting process over time, in intervals as small as 1/60 of a second.

Recently, Carpio et al. [14] have shown that the contact angle measurements can be used to monitor UV photostabilization processes of both photoresist and antireflective films. It is important to note that contact angle measurements are sensitive to surface modifications, occurring at a depth of 20 to 30 angstroms, and that the changes in the bulk of the film may differ. Contact angle measurements can be used to compare two photostabilization units which are supposed to be matched, since they are operating with the same type of Fusion H mod bulb. However, Figures 2 and 3 show that one has a greater intensity than the other which is reflected by a lower contact angle for DI water. There is a greater intensity near the center. Both systems have non-uniformities across the 200 mm wafer surface.

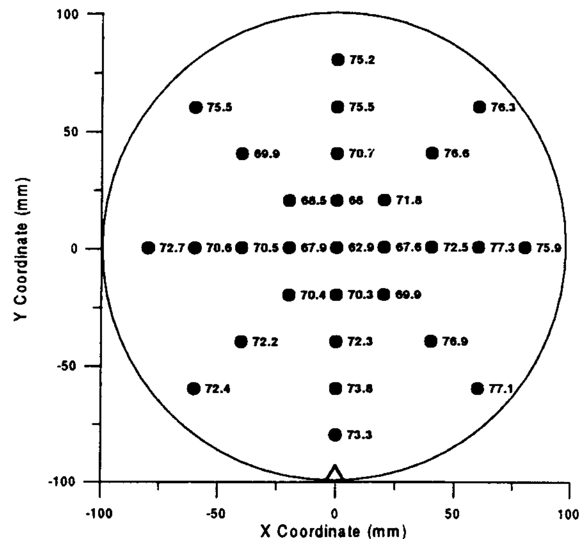

Figure 2: Photostabilization Unit #1

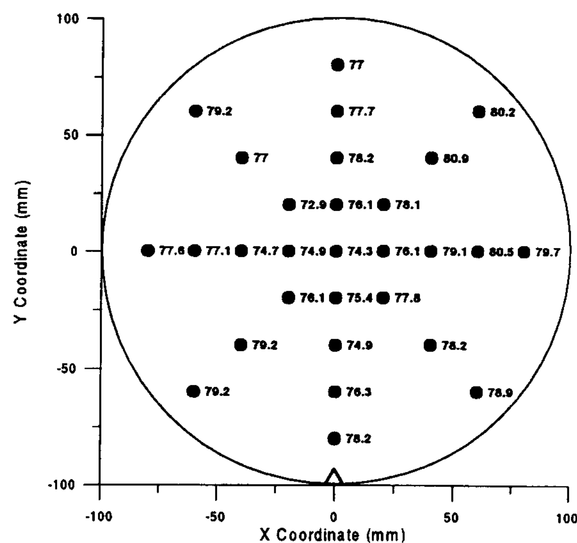

Figure 3: Photostabilization Unit #2

The relationship between contact angle and the development time is of particular interest, and also highlights the advanced capabilities of the image

capture and automated data analysis software. The ability to follow the change in shape of a drop of the developer over time appears to be a fruitful area for research. This capability was discussed in Carpio et al [1]. In this paper, measurements were performed with TOK NMD-3 0.26 N tetramethylammonium hydroxide based developer and the JSR KRFM20G 248 nm chemically amplified photoresist which had received different exposure doses using a 7X7 exposure matrix on the same wafer. It is interesting to note in Figure 4 that the slope of the contact angle vs. time curve varies with the exposure dose. The "noisy" appearance of this data probably can be attributed to the presence of standing waves, which were confirmed by cross sectional SEM pictures of lithographic features produced in this resist. In addition, there is also the possibility that there is a change in the surface energy of the TMAH developer (probably a decrease) due to an increase in the dissolution concentration of the photoresist [15]. If the slopes are plotted vs. dose, a contrast curve can be plotted in Figure 5.

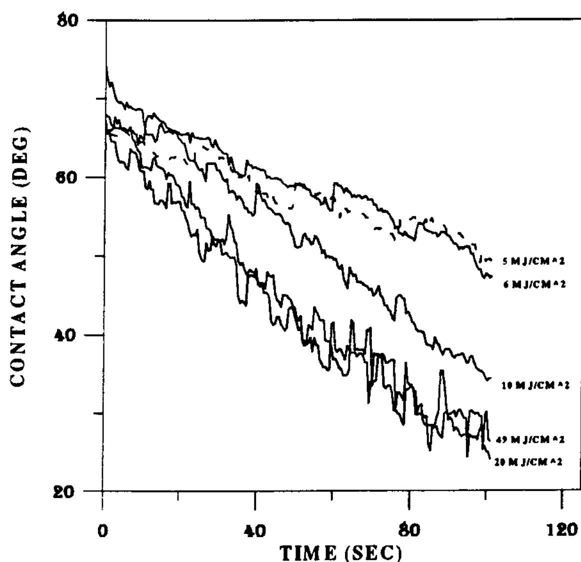

Figure 4: Dynamic Wetting Analysis of Developer on Resist

INTERCONNECT

Many low k dielectric films currently being considered for advanced copper damascene processing are organic films that are spun on. It is reasonable to assume that the curing process of these films, which could include undesirable oxidation, can be monitored in a manner similar to that which has been discussed for lithographic polymer films.

A promising area for the use of contact angles is monitoring the metallization processing steps. Both electroless and electrolytic copper deposition processes are among the processes receiving attention in the industry. Contact angle measurements conducted with DI water for both types of deposited films reveal spatial variation and a hydrophobic character of the surface. It is well known that organic levelers and brighteners, for example, are added to plating baths to improve the characteristics of the deposited films. These additives are usually proprietary and are subject to concentration changes over the bath lifetime [16]. Thus, it is reasonable to assume that contact angle measurements are related in some manner to the nature and concentration of these additives.

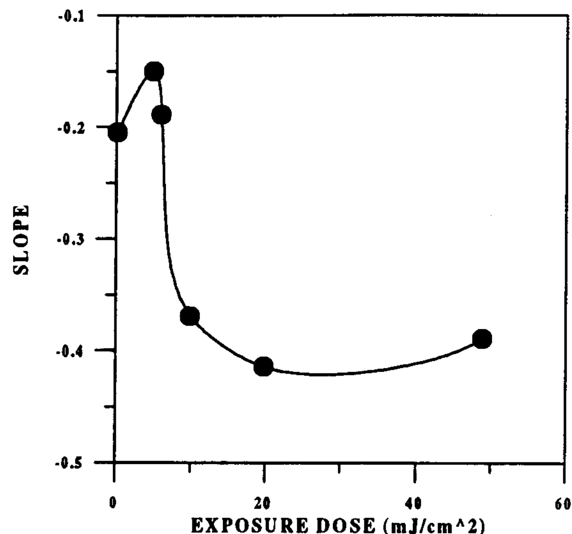

Figure 5: Developer/Resist Wetting Rate vs. Exposure Dose

The corrosion properties of copper is an area which has previously received attention and which no doubt will be receiving added attention. Thomas et al. [17] showed that the corrosion characteristics of benzotriazole-treated copper were related to the receding contact angle. They found no dependence of the contact angle upon copper oxide thickness. This contrasts with Si where the contact angle was shown to vary smoothly from nearly 90° on bare Si to 0° for silicon dioxide thicknesses greater than about 30 angstroms [18]. A series of papers from a research group from the Keio University of Japan have utilized contact angle measurements in studying copper corrosion inhibitors. These authors made use of the liquid drop method to measure the advancing contact

angle [19,20,21,22]. Our measurements reveal that after chemical-mechanical polishing (CMP) processes with different commercially available slurry formulations that the copper surface can shown a range of contact angles. These contact angles are modified by post-CMP cleaning processing. A forthcoming publication will address the corrosion characteristics of copper processed films as well as the contact angle measurements of these surfaces [23].

In addition to sessile drop measurements, receding and advancing contact angle measurements on surfaces can be made by recording a moving picture of the drop as it is decreased or increased in volume by means of a motorized syringe, respectively. Figure 6 shows that the time dependence of the receding angle for different sites on a copper wafer which has been subjected to a CMP process. Figure 7 reveals that the receding contact angle is directly proportional to the volume of the drop, but the advancing contact angle shows no dependence upon drop size. The receding angle is a good measure of the high-energy wetting phase on the surface. The corresponding sessile drop measurements averaged 70.4 degrees.

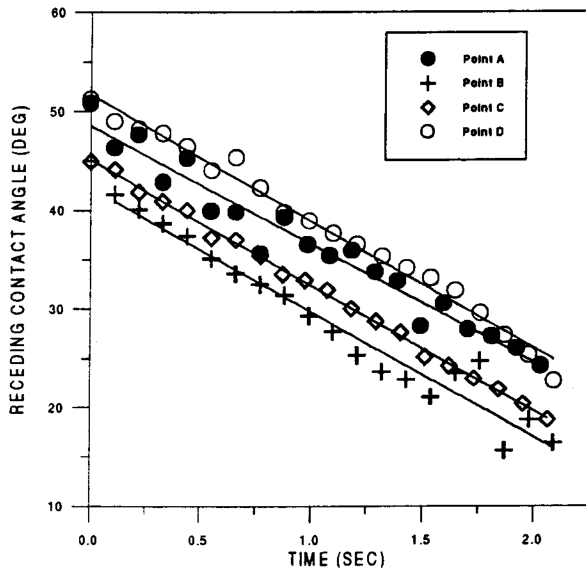

Figure 6: Dynamic Analysis of Receding Contact Angles on a Copper Surface After CMP

CONCLUSION

The advent of new advanced image-based instruments with improved accuracy, repeatability and data display and storage options have increased the utility of the contact angle technique. We have demonstrated several new areas for analysis and expect that many others may be identified in the future.

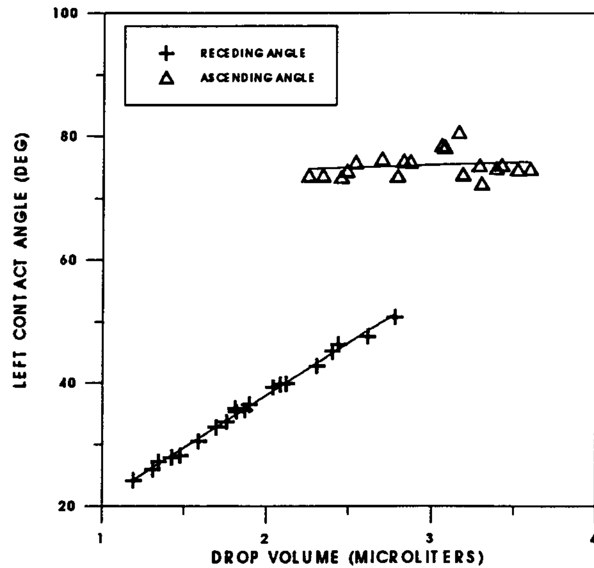

Figure 7: Advancing and Receding Contact Angle Dependence on Drop Volume

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