Application of In-situ Observation Technologies in CMP Process for Upgrading the Process Integrity

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Abstract
In developing a basic understanding of what is happening during the chemical mechanical polishing process, evaluation techniques based on in-situ (in-liquid) observation are useful. Compared with in-air measurement, in-liquid measurement is often very difficult. Chemical mechanical polishing is a wet process, which absolutely requires evaluation based on in-liquid measurement. In this study, we tried three different evaluation techniques based on in-liquid measurement that uses light and a probe in order to analyze the surface reactions and behavior of abrasive particles during the polishing process. As a result, we determined that these techniques can be used as useful evaluation methods. In this paper, we describe the observation results with the hope that we can popularize these in-situ (in-liquid) evaluation techniques.

Keywords: Chemical mechanical polishing, In-situ, Ellipsometry, Fluorescent microscopy, Kelvin probe, Surface reaction, Abrasive particle, Fluorescent particle, Benzotriazole, Wet process

1. Introduction
The chemical mechanical polishing (CMP) technique is, as its name suggests, a polishing technique that combines chemical reactions and mechanical polishing. Generally speaking, polishing intricately involves a mix of many different elements. At present, the CMP technique for the manufacturing of LSIs (large-scale integrated circuits) is required to address severe challenges, such as subnanometer-level planarization, improved polishing selectivity, and decreased defects.

Satisfying these requirements calls for detailed analysis and deep understanding of the characteristics of polishing and cleaning, which absolutely require a technique that enables accurate observation and evaluation of these characteristics.

The best way to accurately understand the nature of something is to observe and evaluate the nature of the thing in situ; in fact, many in-situ observation and evaluation techniques have been developed.

In research and development activities for basic evaluation of the CMP mechanism, many in-situ observation techniques have been also used to evaluate the mechanism. Up to now, however, these techniques have had difficulty in identifying the essence of the CMP mechanism. The reason is that the polishing process involves a pad with a complicated surface profile, micro abrasive particles with diameters of several tens to several hundreds of nm, and slurry or a similar substance that contains many chemical substances such as a surfactant, oxidizer, and chelator, all of which make it difficult to accurately understand what is happening on the surface of the material being polished.

An observation and evaluation technique for the CMP process must satisfy the following three essential measurement requirements: first, the CMP process must be able to be evaluated in a solution; second, a nanometer-level resolution must be available; third, it must be possible to make measurements within a short time. In reality, however, no observation/evaluation technique is available that satisfies all these requirements at the same time. This paper deals with applications to CMP...
process evaluation of some evaluation techniques focusing on in-liquid (in-situ) observation.

2. In-situ (in-liquid) observation techniques useful for CMP process development

As in-situ (in-liquid) observation techniques, we applied three different approaches to the evaluation of the CMP process. Two of them were based on light and the remaining one on a probe. All of them allowed for easy in-air measurement without any particular problems, but, in contrast, presented difficulties in in-liquid observation. This paper discusses not only the evaluation results, but also technical problems associated with the techniques with the hope that the discussion will help develop evaluation techniques in the future.

2.1 Optical evaluation technique 1: ellipsometry

Ellipsometry\(^1\)\(^2\) has been traditionally used in LSI manufacturing to evaluate the thicknesses of thermally oxidized films formed on Si substrates. Changes in the polarization state of light reflected by a substrate (obtained by measuring the phase difference \(\Delta\) between the elliptic polarizations \(p\) and \(s\) and the amplitude reflectance ratio \(\tan \Psi\)) depend on the optical characteristics of the substrate. Based on this principle, ellipsometry is used to make non-destructive measurements of film thicknesses at the angstrom level and evaluate the refractive index and other film characteristics.

In this experiment, we used UVISEL, a spectroscopic ellipsometer (from Horiba, Ltd.) to evaluate the passivation characteristics of a BTA (benzotriazole) inhibitor film developed on a Cu film. Inhibitors are added to Cu slurry for the purpose of retarding corrosion of Cu wiring by forming a complex protective film on the Cu surface during CMP.

**Figure 1** (a) shows the sample measurement section of the experimental device. A cell containing a Cu substrate soaked in a solution is placed in the center. Light is applied to the Cu substrate surface from the right to analyze the characteristics of the light reflected on the substrate surface. Fig. 1 (b) is an enlarged image of the cell, which contains a Si substrate with a Cu film formed on it. The cell is made of a material called PEEK and has quartz-glass windows on the right and left sides that allow incident and reflected light to pass through them. It should be noted that the cell is so designed that light is applied and reflected at an angle of 70 degrees against the substrate, with the quartz windows inclined 70 degrees to allow light to enter and go out of the windows at a right angle for the purpose of preventing light from being refracted at the interface between the windows and solution.

Cu samples were soaked in pure water solutions (with a concentration of 10 mmol/L) of two different inhibitors, BTA and m-BTA (methyl BTA), for three minutes to allow a protective film to form on the surface of each Cu sample. After these samples were soaked in the pure water solution contained in the cell for a long time, changes in the Cu surface conditions were observed, i.e., the durability of the protective films was tested. **Figure 2** shows the results of the durability test, indicating the temporal changes in the
conditions of the protective films of the inhibitors formed on the Cu surfaces.

These results indicate that when approximately 300 minutes had passed, the protective film on the Cu formed by the BTA inhibitor started to gradually increase in thickness, while that formed by the m-BTA inhibitor remained almost unchanged. Although the possibility exists that Cu-BTA caused some changes, the results alone cannot determine the durability of the protective film.

Using an estimated optical-structure model of the Cu surface, ellipsometry estimates the actual surface structure by fitting the spectral characteristics estimated from the structure model with the measurement data. It is assumed that on the Cu substrate, a Cu oxidized film forms, on which a Cu-BTA complex layer develops into a protective film. The thicknesses of the protective layers shown in Fig. 2 are also derived from this optical model. Then, we focused attention on the changes in the thicknesses of the Cu oxidized films located at the interfaces between Cu and BTA and between Cu and m-BTA.

**Figure 3** shows a comparison of the changes between BTA and m-BTA. It indicates that BTA, which caused changes in film thickness, also allowed the Cu oxidized film at the interface to increase in thickness. On the other hand, for m-BTA, the Cu oxidized layer at the interface remains unchanged in thickness as the m-BTA protective layer does. For BTA, it is estimated that water passed through the surface protective layer and diffused to the Cu surface to oxidize the Cu surface, which resulted in the increase in the film thickness of the Cu oxidized layer on the interface. This means that the integrity of the Cu-BTA protective layer is doubtful.

As stated earlier, ellipsometry allows for the measurement of the refractive index and other optical characteristics, as well as the thicknesses of thin films. Based on this, we determined the refractive indices of the Cu-BTA and Cu-mBTA protective films from the measurement results using the aforementioned optical structural model. **Figure 4** shows the results. For Cu-mBTA, the protective layer did not undergo significant changes in the refractive index even after the pure-water immersion test of 600 minutes. For Cu-BTA, on the other hand, the refractive index started to gradually decrease in the early stage of the immersion and abruptly decreased to nearly 1.0, when nearly 400 minutes had elapsed. This decrease in refractive index indicates, in regard to its physical properties, that the Cu-BTA film decreased in density. In other words, the decrease in the density of the protective film means that the film is likely to develop a defect, which allows water to more easily pass through the film, resulting in degraded protection performance. It is thought that the decrease in refractive index until the elapsed time reaches 400 minutes demonstrates the fact that water enters the Cu-BTA layer until the refractive index finally decreases to nearly 1.3 and that the final decrease to nearly 1.0
suggests that the Cu-BTA layer has collapsed. The temporal changes in the refractive index of the Cu-BTA layer agree with the temporal changes in the growth of the Cu oxidized film at the interface (Fig. 3) and in the thickness of the Cu-BTA layer (Fig. 2).

The results of the in-situ (in-liquid) ellipsometry measurements reveal that as an inhibitor, m-BTA exhibits better properties than BTA.

The in-liquid ellipsometry measurements shown in Figs. 2 through 4 require several minutes per measurement because the wavelength is changed during measurement. A technique is also available for evaluating changes in a short time. Specifically, it evaluates optical characteristics without changing the wavelength. Since this technique makes measurements without changing the wavelength, the evaluation duration is less than one second, enabling evaluation of short-time surface reactions.

Specifically, the technique estimates changes on the surface layer by applying incident light of a certain wavelength to a sample to detect the phase difference of reflected light. When the change in film thickness is less than approximately 100 nm, the relationship between the phase difference and film thickness changes is linear. Figure 5 shows the measured growth of the Cu oxidized film right after the film is soaked in pure water and the measured growth of the Cu-BTA protective layer when a BTA solution is dropped, both measured with the evaluation technique mentioned above.

Immediately after the Cu film is soaked in pure water, the measured \( \Delta \) values start to decrease. The decreases in \( \Delta \) value mean that an oxidized film is growing on the Cu film surface; we clearly observed that the Cu surface immediately started to oxidize from the oxygen dissolved in the pure water. At a certain point in time, a high-concentration BTA solution with 0.1 mol/L of BTA was dropped. When this solution completely mixed with the pure water contained in the cell, the BTA solution showed the same concentration used in the previous evaluations, i.e., a concentration of 10 mmol/L. Immediately after the BTA solution was dropped, the \( \Delta \) value decreased abruptly and then gradually. An analysis of the growth of the BTA layer on the Cu surface during this process has been reported through joint research with University of Yamanashi based on EOI (Ebara Open Innovation); specifically, the research provided a detailed analysis stating that, first, a BTA molecular layer is absorbed, which is followed by the growth of a Cu oxidized film at the interface between Cu and BTA. The results shown in Fig. 5 probably indicate that the abrupt decrease in \( \Delta \) value reflects the BTA adsorption and the subsequent slow decreases reflect the growth of a Cu oxidized film at the interface.

We subsequently evaluated the etching behavior of the BTA complex layer using the same technique. Figure 6 shows the results of the evaluation. Specifically, we evaluated the etching behavior of the Cu-BTA layer by
soaking in pure water a Cu film with a Cu-BTA layer developed on it, and then dropping a solution of TMAH (tetramethylammonium hydroxide) onto it. At first, the $\Delta$ value stayed constant because the film was soaked in pure water. Then, we dropped a TMAH solution with a high concentration of 5% to evaluate changes in $\Delta$ value. Right after the TMAH solution was dropped, the $\Delta$ value started to increase, meaning that the BTA complex layer on the surface was etched. The $\Delta$ value peaked and then started to decrease gradually. The TMAH was diluted and resulted in a 0.5% concentration, which was still strongly alkaline; it is thought that a protective film of, for example, Cu(OH)$_x$ grew on the Cu surface once cleaned, which caused the changes.

These findings indicate that the use of different ellipsometry techniques allows for the evaluation of short-time surface reactions as well as angstrom-level surface reactions that occur slowly over a long-time.

2.2 Optical evaluation technique 2: fluorescent microscopy

In the CMP process, particularly in the polishing process, the abrasive particles in slurry play an important role. It is thought that these particles, existing between the polishing pad and the substrate to be polished, mechanically contact and scrape off the reaction layer formed by a chemical reaction between the chemical in the slurry and the substrate being polished. This means that in improving the polishing speed, planarity, and cleaning performance after polishing as part of polishing process development, it is imperative to properly understand how abrasive particles behave during the polishing process. However, these abrasive particles are as small as 100 nm or less in diameter, making it difficult to observe the behavior of these microparticles.

It is reported that as a technique for observing how abrasive grains behave during the polishing process, an attempt was made to make measurements using total reflection microscopy based on evanescent light.

Observation based on evanescent light, however, can be applied only to the top surface of 100 nm or so. In reality, abrasive particles move around not only on the top surface, but also deep inside the porous pad. It is also necessary to understand how abrasive particles behave in such deep regions. This understanding is required particularly, for example, in evaluating the residual abrasive particles, cleaning performance, and pad conditioning.

As a technique for observing the behavior of abrasive particles, we tried particle observation based on fluorescent silica particles and a fluorescent microscope. The observation results are shown below.

We used red and green fluorescent silica particles that had a large diameter of 1.0 µm and a diameter of 50 nm, which was close to those of abrasive particles. In a preparatory experiment, green fluorescent silica particles were used and, as a result, both of the IC-1000 pad and the PAV roll brush for cleaning glowed green, demonstrating that abrasive particles could not be separately detected. On the other hand, when the red fluorescent silica particles were used, both the pad and brush only glowed weakly, revealing that only the red fluorescent silica particles selectively glowed, allowing the behavior of the abrasive particles to be observed.

The actual evaluation experiment used the method shown in Figure 7. Specifically, we placed a pure-water solution containing fluorescent silica particles on a cover glass and then soaked a PVA (poly alcohol) roll brush and IC-1000 pad in the solution to observe the fluorescent silica particles, likened to abrasive particles, using an inverted laser confocal microscope.

This observation technique is characterized by its ability to allow for observation not only of silica particles at the interfaces between the cover glass and brush and between the glass and pad but also, by changing the focus, of particles inside the brush and pad. Figure 8 shows the observation results. Specifically, it shows the light emissions from the red fluorescent particles.
silica particles with a 1.0 µm diameter at the interface between the PVA roll brush and cover glass and inside the brush (at points 20 µm and 40 µm from the surface). The brush is porous, with holes connected with each other. It was observed that on the surface, silica particles are not uniformly distributed and were making Brownian movement without adhering to the brush surface. This clearly indicates that the silica particles pushed out from the flat section of the PVA surface entered the inside of the roll even to a depth of 40 µm.

**Figure 9** shows the distribution of the fluorescent silica particles in the vertical direction, obtained from much data about two-dimensional distributions of silica particles at different depths as shown in Fig. 8. In this way, the technique also allows for the observation of the distribution in the depth direction inside the PVA roll brush. The distribution shown in Fig. 9, that of particles of 1.0 µm diameter and the distribution of fluorescent silica particles of 50 nm diameter, which are almost the same as the diameters of abrasive particles, was also observed through a similar experiment; the use of this technique allows for the observation of the behavior of the actual abrasive particles. Although there is some concern that the fluorescent silica particles have physical properties different from those of abrasive particles, we think that fluorescent silica particles are almost the same as normal silica particles in adhesiveness, suggesting that fluorescent silica particles can be safely likened to abrasive particles.

### 2.3 Probe technique: Kelvin probe

For Kelvin-probe evaluation, we conducted an experiment using a tungsten probe with a diameter of 20 µm, based on a scanning electrochemical microscope system from Princeton Applied Research.

For more information, see evaluation results reported in ICPT2014 of the watermark based on the technique that scans droplets. Kelvin probes are also used in studies of electrochemical etching and even for evaluations in wet atmospheres. The CMP process is a wet process. Therefore, speculating whether a Kelvin probe may be used to evaluate, for example, occurrences of corrosion defects caused by slurry, we made the stage shown in **Figure 10** to try to evaluate changes in Volta potential in a wet atmosphere. With a thin layer of a solution arranged on the sample to be evaluated, we scanned the surface with the probe, not soaking it in the solution, to measure the changes in surface potential.

First, we measured the changes in potential when the oxidized film on the Cu surface was etched. **Figure 11** shows the changes in potential on the surface of Cu film on which an oxidized film had naturally grown after the Cu film was soaked in pure water and then citric acid was dripped on it. Citric acid is a selective etching solution for Cu oxidized films. The results indicate that the dropped citric acid etched the Cu oxidized film on the surface, which accordingly caused rapid decreases
in potential. Subsequently, the potential decreased at a lower rate and minimized, which then gradually increased. The experiment mentioned earlier\(^5\) demonstrated that the fact that the potential is low indicates an electrochemically active state. It is thought that the naturally oxidized film on Cu was etched to make the clean Cu surface exposed, resulting in decreases in potential. The subsequent gradual decreases probably resulted from complexation between Cu and citric acid because citric acid is an organic acid that forms a Cu complex. The increases in potential that followed were probably caused by reoxidation, which must be considered in detail in light of the results obtained with ellipsometry and other evaluation techniques.

We then also made similar measurements of the formation of a BTA protective film. Figure 12 shows the changes in Volta potential during the Cu-BTA complex layer formation caused by a BTA solution dropped into the pure water solution in which Cu was soaked. The first few drops of the BTA solution abruptly decreased the potential, which immediately started to increase, but stayed at low levels without returning to the original level. After that, we dropped the BTA solution again. The potential also decreased but did not exhibit the same level of recovery as in the first droppings. This phenomenon is in line with the abrupt increase in film thickness followed by the subsequent slow increases observed through the ellipsometry-based evaluation (Fig. 5). The first abrupt decrease in potential and the subsequent increase represent the adsorption of the BTA and the formation of Cu-BTA complex protective film, respectively. The second droppings of BTA also caused a decrease in potential. This fact can be explained if it is assumed that, although BTA is adsorbed, the Cu oxidized film does not grow large because a complex layer already exists. In the first place, we assumed that the BTA protective layer would act as a barrier layer and the Cu potential would increase from the potential in the original state where no BTA layer exists; however, the experiment results revealed that the potential decreases. We measured the potential values in air for the regions with and without BTA layers to find out that the potential in the region with a BTA layer formed was higher than that in the surrounding regions, causing a barrier layer. It is thought, however, that the BTA layer does not provide a complete barrier layer (as demonstrated by the results of the ellipsometry experiment in Fig. 4) and consequently the reaction on the Cu surface continues, resulting in low surface potential values.

This Kelvin probe technique, which uses a probe with a large diameter of a few tens of µm, does not provide a sufficient spatial resolution for evaluation of LSI wiring. Similar techniques for evaluating surface potential include the Kelvin force microscopy (KFM), a method based on an atomic force microscope (AFM) having an nm-level resolution, which cannot be used for in-liquid measurement evaluation. As a technique that enables in-liquid potential measurement, open-loop electric potential microscopy (OL-EPM)\(^6\) has been developed. We are currently trying to apply the in-liquid potential evaluation to the CMP process as the EOI.
3. Conclusion

In this paper, we have presented the results of some experiments conducted based on in-situ (in-liquid) evaluation techniques with the objective of understanding the CMP process and cleaning mechanism. It is true that not many attempts have been made to apply in-liquid evaluation techniques to the research and development of CMP processes. The reason is probably that after all, in-liquid measurement is more difficult than in-air and in-vacuum measurements. We will make efforts to further develop some of the in-liquid evaluation techniques discussed in this paper toward a more sophisticated CMP process.

References

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