Colloidal Dynamics
leaders in colloid measurement

The CMP Slurry Monitor - Background

Abstract

The CMP slurry monitor uses electroacoustic and ultrasonic attenuation measurements to determine the size and zeta potential of slurry particles. The article describes these measurement techniques, and gives some background information on zeta potential.

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1 The Zeta Potential

The CMP Slurry Monitor uses electroacoustic and ultrasonic attenuation measurements to determine the size and zeta potential of slurry particles. In this article we describe these measurement techniques and give some background information on the **zeta potential**.

CMP (Chemical Mechanical Polishing) slurry particles are electrically charged. This charge may arise from the dissociation of surface groups or the preferential desorption or adsorption of ions at the surface. In nearly every case, the electric charge lies on the particle surface, rather than in the interior of the particle.

The surface charge density can be controlled by altering the concentration of **potential determining ions** in the suspending electrolyte. In those slurries where the particles have acid or base groups on the surface, the hydrogen ion is potential determining, and the charge can be controlled by adjusting the pH.

The charge on the particles is balanced by an equal and opposite charge on the ions in the liquid. These mobile charges are drawn to the particle surface, but they are also jiggling around under Brownian motion, and instead of forming a compact layer of countercharge on the particle surface, they form a **diffuse cloud** around the particle, as illustrated in Figure 1.

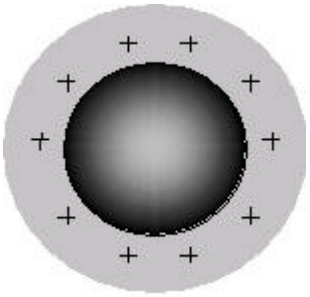

Figure 1: The Electrical Double Layer

This diffuse layer and the layer of charge at the particle surface are known as the **electrical double layer**.

It can be shown (Hunter 1987, p 332) that the charge density in the diffuse layer decreases exponentially with distance from the particle surface. The exponential decay length is denoted by the symbol κ^{-1}, and is called the Debye length, or simply the double-layer thickness.

In a symmetric two-species electrolyte (ibid.):

$$k^{-1} = 3.2888\sqrt{c}(nm)$$

where c is the ionic strength in mol L^{-1}. Thus for a .001M electrolyte the double layer is about 10 nm thick, and for 0.1M it is 1 nm.

The voltage drop between the particle surface and the region beyond the double layer is called the **zeta potential**, denoted by the symbol ζ. This voltage depends on the particle charge density and on the double layer thickness. As more salt is added, the double layer shrinks and this tends to reduce ζ in the same way as the voltage across a capacitor drops as the capacitor plates are moved closer together.

2 The Importance of Zeta Potential

Particles of the same material will have the same sign of charge, and so they will repel each other if their double layers overlap. The zeta potential is important because it provides a measure of the strength of this repulsive force. If the zeta potential is too small (typically less than 25mV in magnitude), the maximum electrical repulsion will not be strong enough to overcome the Van der Waals attraction between the particles, and as a result they will flocculate. This can cause a concentrated CMP slurry to form a gel in the drum, and it can impact on the polishing performance when flocculation occurs in the blend tank that feeds the polishers.

On the other hand, if the slurry particles are to be filtered out as part of a CMP waste treatment or recycling process, then flocculation may be desirable. In that case the pH could be adjusted to give a low zeta potential. Zeta control can also be used to prevent slurry particles from depositing on the wafer.

The standard techniques for measuring particle size and zeta are limited to very dilute suspensions, for these techniques involve light passing through the suspension. Thus they cannot be applied to CMP slurries, which are opaque, without a very substantial dilution.

This dilution is inconvenient, but more importantly it will change the zeta potential (and the size too if the change in zeta causes flocculation or de-flocculation) unless the dilutent has exactly the same chemical properties as the background electrolyte in the CMP slurry. The diluted sample used in these conventional instruments is also much more prone to contamination by surface active molecules, since there is so much less particle surface area for the contaminant to adsorb to.

3 The ESA Effect

The CMP Slurry Monitor measures zeta and size in concentrated suspensions, so there is no need to dilute, and the technique can be applied in-line, in real time.

The CMP Slurry Monitor can measure in concentrated suspensions because it measures *sound* rather than light, so there is no need to see through the slurry. The sound waves are generated by the slurry particles. To generate these sound waves we apply a high frequency electric field to the colloid. This field causes the particles to move, since they are charged, and this backwards and forwards motion generates the sound waves.

The sound has the same frequency as the applied field, which is usually in the MHz range. This effect of sound wave generation in a colloid by an applied electric field was discovered by Cannon et al. (1984), who christened it the *electrokinetic sonic amplitude*, or **ESA** effect.

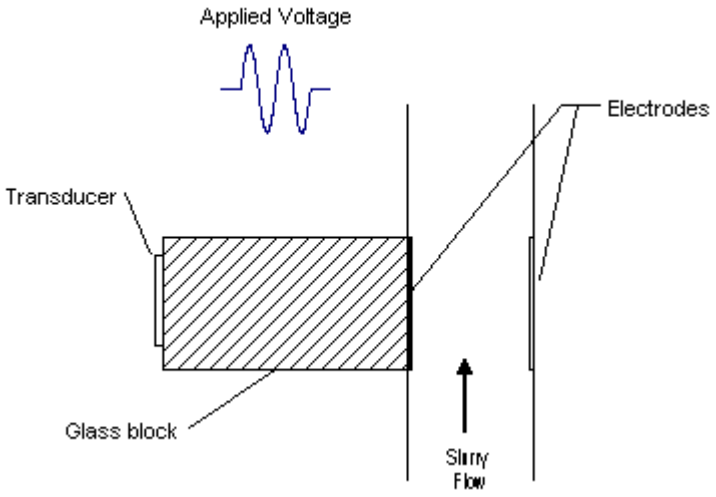

Figure 2: Components of the ESA Sensor

In Figure 2 above we show the main components of the ESA sensor in the CMP Slurry Monitor. The measurement is made by applying a pulse of voltage across the colloid. This generates a sound wave pulse that travels down the glass block on the left-hand side of the figure. When the wave reaches the transducer at the end of the block it generates a voltage pulse. The pulse from the transducer in the figure passes into signal processing electronics that determine the amplitude and phase of this signal. Thus for each applied pulse two numbers are recorded, that is a magnitude and a phase.

Measurements are made over a range of frequencies between 1 and 20 MHz and in this way an ESA magnitude and phase angle spectrum is determined.

The purpose of the glass block is to introduce a delay between the applied voltage and the measured ESA signal. By the time the sound waves reach the transducer the applied voltage is turned off, and in this way we avoid the problem of interference between the applied voltage, which is typically 200 volts, and the small ESA voltage, which is of order a few mV.

4 The Dynamic Mobility

The ESA signal represents the sum of the millions of sound waves from the individual particles in the cell. The amplitude of the pressure wave from a single particle is proportional to where r is distance from the particle and θ is the angle between the direction of the particle velocity and the position vector $\boldsymbol{r}$. $\Delta\rho$ is the particle density minus that of the solvent and U is the particle velocity.

$$\Delta r U \frac{\cos q}{r^2} \qquad (1)$$

From this formula it can be seen that there is no signal from neutrally buoyant particles. This may seem surprising, for these particles move in the electric field, so you would expect them to generate sound waves. In fact they do generate sound, but the sound wave from the particle in this case is cancelled at large distances by the sound wave from the diffuse part of the double layer. The above formula refers to the "far-field" sound wave, and at this distance there is no signal from a buoyant particle. It is this far-field signal that determines the ESA, and so buoyant particles do not produce an ESA signal.

From equation (1) it can be seen that the ESA signal is proportional to the particle velocity. Thus we can use the ESA measurement to determine the amplitude and phase of the particle velocity relative to the applied voltage. For the field strengths that we apply in the ESA measurement, we have found (O'Brien et al 1995) that the velocity amplitude is proportional to the field strength and that the phase lag is independent of field strength. Thus the velocity amplitude divided by the field and the phase lag are properties of the particle. Together, these two properties define the **dynamic mobility** of the particle. The determination of this mobility is the first step in the calculation of zeta and size from the ESA.

Although we are mainly interested here in the dynamic mobility as a stepping stone in the determination of size and zeta, the dynamic mobility is an important quantity in its own right, so we will pause to give it a more precise definition.

When a particle is subjected to an alternating electric field, it moves with a sinusoidal velocity. If the frequency of the field is sufficiently high, inertia forces will cause the particle motion to lag the applied field. This is illustrated in Figure 3, where the broken line represents the applied field strength and the unbroken curve is the particle velocity. V is the amplitude of the particle velocity. As mentioned above, V is proportional to the amplitude of the field strength E.

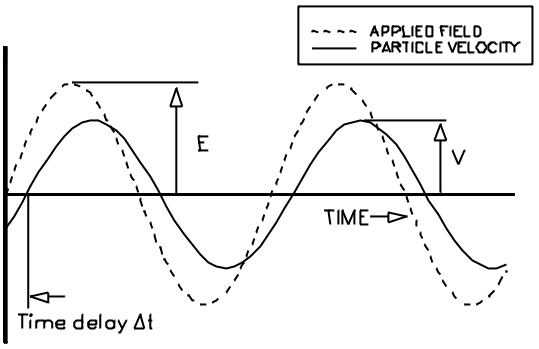

Figure 3: Particle Motion Lagging Applied Field

The dynamic mobility is denoted by the symbol μ_D. It is defined to be a complex quantity with a magnitude given by V/E and an argument equal to $2\pi f(\Delta t)$, where f is the applied frequency in MHz and Δt is the time delay between the applied field and the particle velocity, measured in seconds. The CMP Slurry Monitor reports the dynamic mobility measurements along with particle size and zeta potential.

4.1 Double layer distortion in small particle systems

As mentioned above, the dynamic mobility is influenced by the particle inertia, but it is also affected by double layer distortion. This distortion comes about because the diffuse layer carries an opposite charge to the particle and so the applied electric field tends to move the diffuse layer ions in the opposite direction to the particle. With an alternating electric field this leads to an alternating distortion of the double layer.

The distortion causes the center of the diffuse layer charge to lag that of the particle and as a result the diffuse layer exerts an electrical retarding force which slows the particle down. The double layer takes a time of order ε/K to distort when the field is applied, where ε is the permittivity of the solvent and K is the solvent conductivity. Thus when the frequency of the applied field w rises to the point where the ratio $w\varepsilon/K$ is O(1), there will be insufficient time for the double layer to reach full distortion, since the period of the applied field will then be comparable to the relaxation time for the double layer.

For an electrolyte of conductivity 0.1 S/m, this occurs at frequencies of around 20 MHz, which is the maximum measurement frequency in the ESA sensor. Since double layer distortion slows the particle down, the effect of this reduced distortion is to increase the magnitude of the dynamic mobility with frequency. And since the retarding force *lags* the applied field, the net electric driving force *leads* the applied field at these frequencies. As a result the dynamic mobility for the CMP particles often has a phase lead.

5 Getting Size and Zeta from Dynamic Mobility

The measured dynamic mobility represents an average over all particles, and hence we can write

$$< m(w) >= \int m(w, a)\, p(a)\, da$$

where <μ(ω)>is the measured mobility at frequency ω and μ(ω,a) is the average dynamic mobility o particles of radius *a* at that frequency. *p(a)da* is the mass fraction of particles with radii in the range *a "da*/2.

To determine the size and zeta from the measured dynamic mobility spectrum we need a theory that tells us how μ(ω,a) depends on these quantities. For particles which are more than 100 nm in diameter we use O'Brien's (1988) formula for μ which is valid for spheroidal particles with thin double layers. For the smaller particles that are usually encountered in CMP slurries we use a formula which is valid for thick double layers and which takes double layer distortion into account.

On substituting the theoretical formula for μ(ω,a) in the above equation we obtain an integral equation in which the unknowns are the size distribution p(a) and the zeta potential. The computer program in the Slurry Monitor adjusts these quantities to give the best fit between the theoretical and dynamic mobility spectra.

6 Attenuation Measurements

The ESA measurements cannot be used to determine particle size for particles less than 70nm diameter. The reason is that the inertia forces on such particles are too small to cause a measurable phase lag in the dynamic mobility. We still use the ESA to determine the zeta potential for such small particles, but to get the size in this case we use attenuation measurements.

Instead of applying a voltage across the colloid as in the ESA measurement, the voltage for the attenuation measurement is applied across the ESA transducer, as shown in Figure 4.

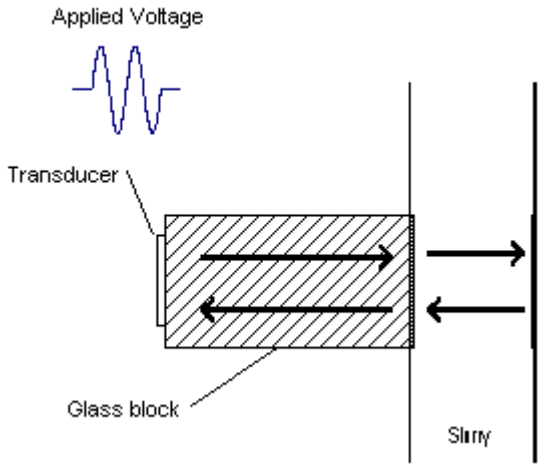

Figure 4: Voltage Applied across the ESA Transducer

This causes the transducer to expand and contract at the frequency of the applied voltage, thereby launching an ultrasound beam down the glass delay line. When that beam strikes the end of the glass block, a portion of the incident sound wave is reflected, and some is transmitted into the colloid. The transmitted beam crosses the colloid where it bounces off the electrode on the other side and crosses the colloid again.

During its passage back and forth through the colloid, the sound wave is attenuated. A portion of that attenuated wave then passes back into the glass block. When it reaches the transducer, it generates a voltage pulse with an amplitude that is proportional to the sound wave intensity. This quantity is recorded for each of the thirteen frequencies.

The attenuation depends on particle size. In fact there is a unique attenuation spectrum for each size of particle. The theoretical formulae for this attenuation spectrum are given in the paper by Allegra and Hawley (1971). By using these formulae (with a correction for particle concentration), we adjust the particle size distribution to fit the measured attenuation spectrum. With this technique we are able to measure down to a median particle diameter of 20 nm.

Earlier in this article, we said that the zeta potential can often be controlled by varying the pH. This is true for the Alumina and Silica particles that are commonly used in CMP slurries. As an illustration of this point, we show below (Figure 5) a graph of measured zeta potentials for an alumina slurry as a function of pH. These measurements were made on a laboratory version of the CMP Slurry Monitor.

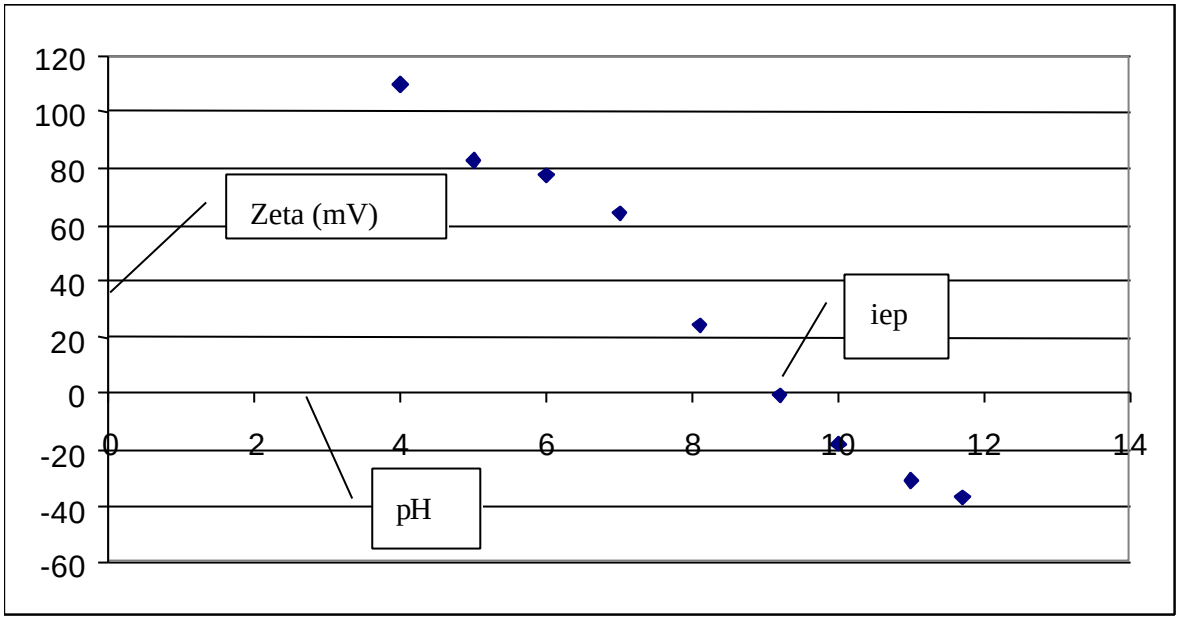

Figure 5: Measured Zeta Potentials for an Alumina Slurry as a Function of pH

From Figure 5 it can be seen that the zeta potential decreases with increasing pH until, at a certain pH, it drops to zero. That pH is called the **isoelectric point** (iep), and it is a characteristic of the particles. For the alumina particles used in this study, the iep is about 9.3. For pH values above the iep, the zeta potential is negative. Silica has an iep below 2, and so in nearly every case the zeta potential for silica particles is negative. Thus an alumina particle will stick to a silica surface unless the pH is greater than 9.3.

7 Applications

In the neighborhood of the iep, the zeta potential is so low that the suspension is unstable, and so the particles begin to flocculate. In the next figure (Figure 6) we show the CMP Monitor measurements of particle size that were made concurrently with the above zeta measurements.

The quantity d50 is the median particle diameter, while d85 and d15 provide a measure of the spread in particle sizes; 15% of the particle mass lies below d15 and 85% lies below d85.

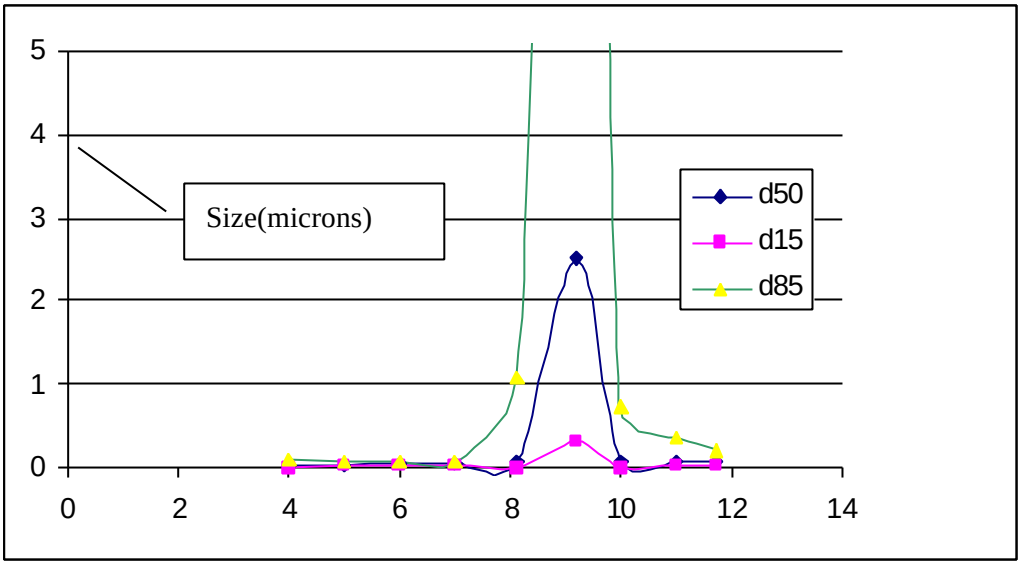

Figure 6: CMP Monitor Measurements of Particle Size

From Figure 6 it can be seen that the particle size grows in the neighborhood of the iep as the particles flocculate. The size of the flocs is limited in this case by the shear rate, for flocs that are too large are torn apart by the flow.

As a final example we show the results of a study to determine the sensitivity of the Slurry Monitor to the presence of a few large particles. In this experiment, some 500 nm diameter silica particles were added to a suspension of silica particles with a median size of 30nm. The results are shown in Figure 7 below.

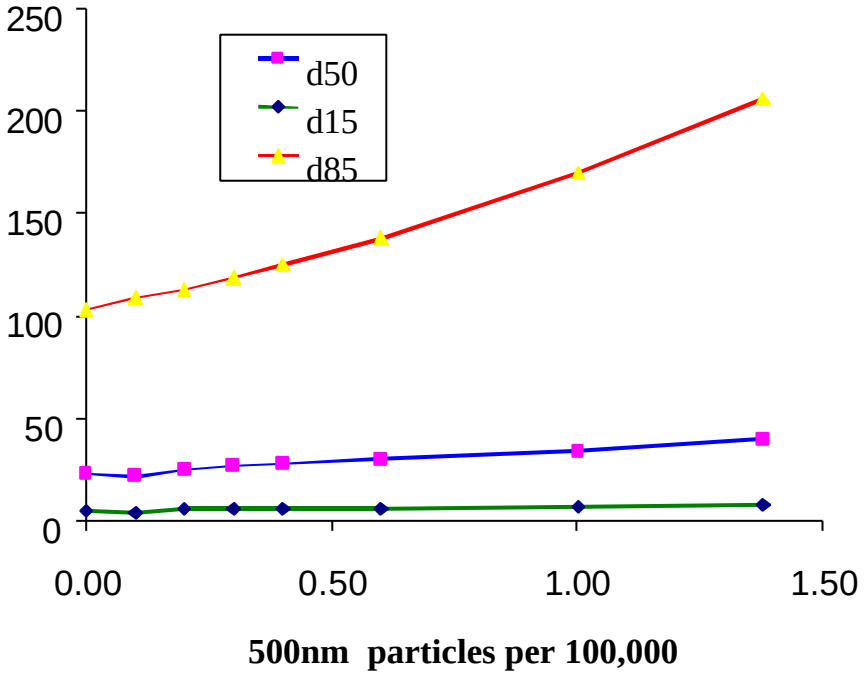

Figure 7: Sensitivity of the Slurry Monitor to the Presence of Large Particles

The vertical axis in this case is particle size in nm. From Figure 7 it can be seen that the d85 is quite sensitive to the presence of the large particles, for by the time we have 1 large particle per 100,000 small particles, d85 has increased from 100 to 170 nm. From Figure 7 it can be seen that there is very little noise in the data, so it would be possible to detect the presence of one 500 nm particle per 500,000 primary 30 nm particles with this technique.

Of course the polisher performance may depend on other factors in addition to particle size and zeta potential, and for this reason the Slurry Monitor is designed to measures particle concentration, pH, temperature, conductivity and pressure in addition to size and zeta potential. By monitoring these quantities, and ensuring that the slurry stays within specified limits, the user can provide more rigorous control of the polishing process.

8 References

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