Settling Characteristics of Chemical Mechanical Polishing Slurries

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Extended Abstract

With decreasing feature-size, consumables have an increasingly important role in the Chemical Mechanical Polishing (CMP) processes. To achieve uniform and efficient wafer planarization, the CMP slurry abrasive particles must be uniformly suspended during handling [1]. To be able to specify the agitation requirements for the storage tank and daytank as well as the required minimum velocity for the slurry flow in the global distribution loop to keep abrasive particles suspended, the comparative settling characteristics of different slurries must be known [2]. In the present study, a number of common oxide, tungsten, copper and shallow trench isolation (STI) CMP slurries were analyzed using a commercially available liquid dispersion optical analyzer (Beckman Coulter QuickSCAN*) to measure the settling characteristics in terms of the changes in turbidity (transmission and back scattering signals) of various layers in the slurry sample [3]. The transmission and back scattering raw data were analyzed using the absolute thickness and mean value graphs to study the settling behavior of slurries. It is possible to quantify the settling rate of slurry from the absolute thickness plots. This technique allows detection of minute concentration and particle size variations in the slurry sample earlier than observation by the naked eye, making this method especially useful for the measurements of concentrated suspensions. The CMP slurries analyzed in these experiments included Cabot Semi-Sperse® SS-25, Semi-Sperse® W2000, EP-C5001 and EP-C5003; Rodel® ILD 1300, Klebosol® 30N50, MSW 1500 and Cu-S1-3116; EKC MicroPlanar™ CMP3500™, MicroPlanar™ CMP9001™ and MicroPlanar™ CMP9003™, and Hitachi Chemical HS-8005.

The above slurries (abrasive components or one component slurries) and normal blends (abrasive and additive components) of selected slurries were analyzed to determine the changes in the settling characteristics of mixtures as compared to only the abrasive component. The slurry samples were analyzed in a cylindrical glass measurement cell. The detection was composed of a pulsed near-infrared light source (\(\lambda = 850\) nm) and two synchronous detectors. The transmission detector received the light which passed through the sample (0°), while the back scattering detector received the light back scattered by the sample (135°). The detector head scanned the entire length of the sample (about 65 mm) vertically, acquiring transmission and back scattering data every 40 µm, or 1,625 acquisitions in transmission and in back scattering per scan. This technique can be used for the samples ranging from slightly turbid to concentrated and opaque (0 to 60 weight % solids) with particle size ranging from 0.1 – 1,000 µm and without prior dilution. If a slurry blend remains stable with time, the transmission and back scattering graphs do not change and different time plots superimpose on the reference line. Progressive changes in the graphs indicate mixture destabilization. An increase in transmission and/or decrease in back scattering values in the top layers (for example) of the slurry sample would illustrate the abrasive particle migration to the bottom of the sample as a result of settling. Insignificant changes in the overall transmission and back scattering values along the entire length of the graph suggest insignificant settling during the test.

This study is the first of its kind applied to CMP slurries and provides useful quantitative insight on settling characteristics of a variety of slurries. Selected results of transmission and back scattering (the profile graphs), and absolute thickness and mean value (the kinetic graphs) for different slurries are presented in Figures 1-7. In present experiments, the data acquisitions were executed once every minute in an automatic mode. The transmission and

*Quickscan is now called Turbiscan Classic and is manufactured by Formulaction, 10 impasse Borde Basse 31240 L’Union France, www.formulaction.com
back scattering profiles as a function of the sample height were measured once every minute for 200 minutes. One out of every 15 consecutive profiles was graphed for clarity. The transmission and back scattering variations as a function of time were plotted starting at time 0:00 (hour:minute; the beginning of the experiment). The slurry samples were filled up to a height of 55 mm (approx.) in the glass tube. In Figures 1-3, 4a, 4c, 5, 6a and 7a, the sample height from 0 to 7 mm (approx.) represents the bottom plug region of the glass tube. The values on the right side of above Figures indicate the time elapsed after the first measurement. The transmission and back scattering plots for the three slurries in Figures 1-3 show insignificant settling during 200-minute tests. Figures 4a, 4c, 5, 6a and 7a illustrate the sediment layer formation (a progressive increase in the back scattering values) at the sample bottoms and a clarification phenomenon (a increase in the transmission values) at the sample top layer for four different slurries. The absolute thickness profiles in Figures 4b, 6b and 7b illustrate the variations in layer thickness for three slurries as a function of time. The settling rate for specific slurry can be quantified from the slope of the curve in absolute thickness plots. These graphs also demonstrate that the settling characteristics of CMP slurries change with time. Figure 7c presents the transmission and back scattering mean value variation in the selected zone for a ceria slurry. This plot illustrates the average clarification time at a specified height in the slurry sample.

The settling behavior of EP-C5003 slurry was very similar to EP-C5001 slurry. ILD 1300, Klebosol® 30N50 and MicroPlanar® CMP9003™ slurries showed insignificant settling during 200-minute test. MSW 1500 slurry showed quick settling characteristics. Alumina- and silica-based slurries display different settling characteristics of mixture as compared to only the abrasive component. In most alumina-based slurries, normal blends settled more quickly as compared to the abrasive component, whereas silica-based slurries settling behavior was nearly the same for the abrasive component and their normal blend. However, in some alumina-based slurries, where chemical reactions take place between the abrasive component and the additive, the slurry blend settled more quickly and at a more uniform rate as compared to only the abrasive component. The settling rate of the abrasive components of CMP slurries seems to strongly depend on their weight % solids. The alumina slurries with higher weight % solids settled slowly as compared to other alumina slurries with lower weight % solids. Test results for all the slurries and their normal blends are not included in this paper for brevity. Results of slurry handling studies in our laboratory have demonstrated that in spite of the quick settling nature of some of the above CMP slurries, these slurries can be successfully handled by the slurry blending and distribution systems based on vacuum-pressure-dispense and pressure (pump)-pressure-dispense technologies if appropriate flow velocities are maintained in the slurry delivery system and the global distribution loop. Further, these slurry abrasives could be kept suspended when proper agitation was provided in the daytank and storage tanks.

Conclusions
The CMP slurries show significantly different settling characteristics based on their formulation. The majority of silica-based slurries demonstrate slow settling behavior, whereas alumina- and ceria-based slurries usually have quick settling characteristics. However, these slurries can be successfully handled and kept dispersed if appropriate flow velocities are maintained in the slurry delivery system and the global distribution loop, and proper agitation is provided in the storage tanks. This study illustrates the applicability of a quick, robust, highly repeatable and economical solution for the quantitative dispersion analysis of CMP slurries. This study also shows the possibility of using comparative settling information for different slurries to specify the mixing/stirring requirements for the storage tank and daytank as well as the required minimum velocity for the slurry flow in the global distribution loop.

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References

Figure 1. Transmission and Back Scattering Plots for Cabot Semi-Sperse® SS-25 Oxide Slurry (Silica Particles).
Figure 2. Transmission and Back Scattering Plots for EKC MicroPlanar™ CMP3500™ Tungsten Slurry (Silica + Alumina Particles).

Figure 3. Transmission and Back Scattering Plots for Cabot Semi-Sperse® W2000 Tungsten Slurry (Silica Particles).
Figure 4a. Transmission and Back Scattering Plots for Cabot EP-C5001 Copper Slurry (Alumina Particles).

Figure 4b. Absolute Thickness Plots for Cabot EP-C5001 Copper Slurry (Alumina Particles).
Figure 4c. Transmission and Back Scattering Plots for Cabot EP-C5001 Copper Slurry (Alumina Particles) and H₂O₂ Blend.

Figure 5. Transmission and Back Scattering Plots for EKC MicroPlanar™ CMP9001™ Copper Slurry (Alumina Particles).
Figure 6a. Transmission and Back Scattering Plots for Rodel® Cu-S1-3116 Copper Slurry (Alumina Particles).

Figure 6b. Absolute Thickness Plots for Rodel® Cu-S1-3116 Copper Slurry (Alumina Particles).
Figure 7a. Transmission and Back Scattering Plots for Hitachi Chemical HS-8005 STI Slurry (Ceria Particles).

Figure 7b. Absolute Thickness Plots for Hitachi Chemical HS-8005 STI Slurry (Ceria Particles).
Figure 7c. Transmission and Back Scattering Mean Value Plots for Hitachi Chemical HS-8005 STI Slurry (Ceria Particles).