

Optical Characterization of Industrial Slurries[†]

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Abstract

In this work we focus on the characterization of micro- and nano-powders typically adopted for chemical mechanical polishing, extensively used whenever the global and local planarization of surfaces is required as in nanoelectronic fabs. We present an innovative method for the accurate characterization of water suspensions of nanoparticles. It relies upon the combination of a new approach to extract light-scattering information from single particles and the recently developed diagnostic tool named Single Particle Extinction and Scattering. It can be used in line. Data interpretation becomes independent of any a-priori assumptions about the samples. The results of accurate measurements performed on ceria as well as aluminium oxide slurries are reported. We show the strong advantages of this method compared with traditional ones by explicitly reporting experimental results on calibrated spheres made of different materials. We discuss possible applications for in-line characterization of ultrapure water, chemicals, slurries for abrasive processes, for example, as well as the detection of any undesired particles – which could be the key for future improvements to advanced process control systems.

Keywords: particle sizing, slurries, ceria, CMP, light scattering

1. Introduction

The worldwide nanoelectronic industrial environment is currently under pressure to achieve better goals in terms of cost reduction and manufacturing efficiency, while the rate of technological advancement must be preserved. The improvement of fab productivity through novel methods or the introduction of in-line monitoring of processes, equipment, facilities (e.g. power, gas, chemicals ...), which will make the manufacturing efficiency higher is an increasing need in this field.

1.1 Chemical mechanical polishing

One of these applications has been recognized to be monitoring the Particle Size Distribution (PSD) of the slurries used for the Chemical Mechanical Polishing (CMP) processes, required by the most advanced technology applied to the production of silicon-based technologies (Li,

2008), as well as a number of industrial processes such as, for example, compact disks, hard disks and optical surface polishing. It is generally known that CMP involves both chemical and mechanical mechanisms where the abrasive slurries are one of the main actors. Slurries are aqueous dispersions of nanoparticles where the characteristics of the abrasive material and PSD typically play an important role in determining the removal behaviour (Pate, 2011). Modern slurries are characterized by two main drawbacks that make them difficult to handle: 1) they rapidly undergo sedimentation; 2) they are affected by aggregation phenomena (Basim, 2000; Basim, 2002). Moreover, slurries are typically handled within closed-loop circuits, so that guaranteeing the stability of the suspension is a particularly demanding issue. Finally, aging effects occur during the process which affect the process performance (Cumbo, 1995; De Nardis, 2005; Remsenz, 2006).

1.2 Common slurries

The common materials available on the market are silica (SiO₂) and ceria (CeO₂) particle suspensions for the most demanding nanoelectronic applications, and aluminium, copper and other oxides for other cases (e.g. optical polishing). Ceria slurries represent the most innovative application for silicon insulation definition, and are the

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most demanding in terms of characterization due to the tight requirements and the high costs. Notwithstanding the complicated transformation method of the ceria raw material into the final slurry product and the fact that it belongs to the rare earths, with consequently increased costs and availability problems, ceria slurries are quite diffuse thanks to their improved local planarization performance with respect to silica. Moreover, they are typically used in addition to chemical additives, thus leading the high selectivity between oxides and nitrides (Merriks, 2008). Because of the natural sedimentation and aggregation behaviour of ceria particles, several studies have been performed to correlate the PSD with the features of handling and distribution systems, as well as correlation of the CMP with the material removal rate in order to guarantee the proper process control and quality level in the semiconductor manufacturing environment.

1.3 Slurry characterization

The particle size specifications in the semiconductor industry of ceria slurries are based on supplier methodology, generally based on laser diffraction. The Mastersize laser diffraction tool (Malvern TM) is a reference here.

As already mentioned, one of the most critical drawbacks of ceria slurries is the stratification and sedimentation behaviour that must be taken into account prior to and during use. This is simply caused by the high specific weight of the material. Thus, strong shaking is needed to re-disperse the solids content over the entire drum and a minimum flow speed in piping is required to avoid sedimentation. These are the main topics for the design of the Chemical Distribution System (CDS). Along the CDS, continuous shaking is still necessary to avoid sedimentation. As it appears clear from this analysis, the most important parameter to be monitored is the PSD, D_{99} percentile in particular, and NVC%. In **Figs. 1.1** and **1.2**, the effect of the NVC% and D_{99} particle class on the CMP process performance is shown in terms of the material removal rate. Since the D_{99} classification is extremely dependent on the particle size analysis technique, the monitor is typically performed indirectly on the basis of the NVC% only, since a correlation between D_{99} and NVC% has been determined. No direct measurement of the PSD is usually performed.

The state of the art for slurries in the semiconductor industry is clearly stated in the ITRS guidelines (ITRS and ITRS, 2009), which are briefly summarized and discussed below.

At present, the characterization of free nanoparticles in general does not meet the criteria for a wide class of applications due to lack of accuracy, high throughput, ease of operation and the actual possibility of operation for routine, in-line characterization (Zelenyuk, 2006; Ghosal,

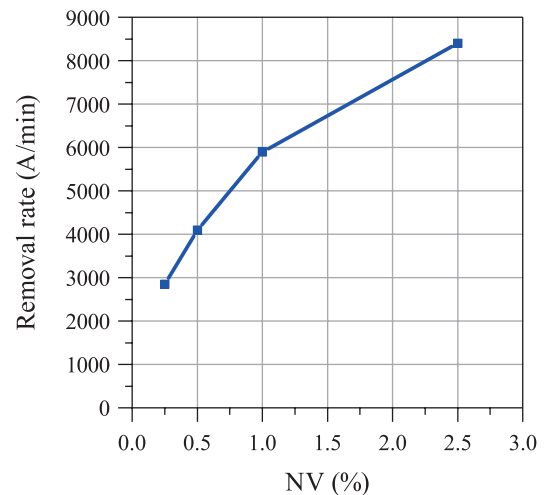


Fig. 1.1 Non-volatile content (NVC%) vs CMP removal rate.

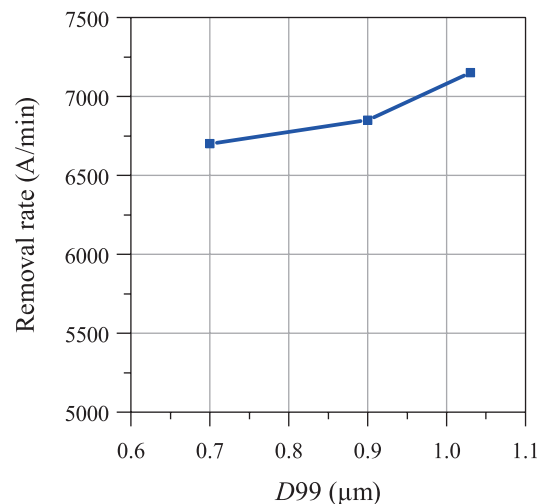


Fig. 1.2 D_{99} concentration vs CMP removal rate.

2014). Optical methods are among the most popular ones due to the non-invasiveness of the measurement, reliability, flexibility, robustness, but nevertheless they suffer from fundamental limitations which make them inapplicable for the case in point here. The main limitation is that most of these methods operate on collections of highly polydisperse particles, making it necessary to apply data analysis with inversion algorithms for extracting the PSD from the superposition of the signals given by a number of different particles. This often involves ill-posed problems like in DLS or SALS, and limits the reliability of the methods for the specific applications, especially at nano-electronic fabs. Alternatively, non-optical methods exist which can be adopted for characterizing the PSD of dense materials such as ultrasonic spectroscopy (Hipp, 1999). This method can be considered a valid alternative to optical methods, with the advantage of operation without need of any dilution.

As a matter of fact, no in-line monitoring is currently performed on the slurries at nanoelectronic fabs. Samples are picked up and sent to the producer for size characterization. This process is extremely far from what would be needed in terms of an efficient, immediate responsive tool for deciding within a short time the actions to be taken (Budge, 2009; Budge, 2013).

1.4 Future needs

A clear breakthrough here could be made by means of an in-line Particle Monitoring (PM) tool that continuously determines the PSD and generates the inputs for a Decision-Making (DM) tool capable of performing the following actions: 1) foreseeing the requisite actions to be taken during the maintenance stops, based on an effective, rational and sustainable basis; 2) adapting the CMP to maintain the required specification of the product despite the modified characteristics of the slurries that are currently present inside the machinery.

To present things in a more schematic way, the current status and the progress beyond the state of the art which would dramatically change the fab performance are compared below, referring to the main issues and needs of industry.

- 1) At present, no PM tool is available for in-line monitoring. A new sensor and the relevant tool with the specifications needed to fulfil the objective must therefore still be developed, tested and implemented in-line.
- 2) No DM protocol is available. A PM tool with the specified requirements would enable development of such a protocol.
- 3) The common way to employ sensor integration is by adapting the FDC system to match the sensor requirements in terms of physical and logical connection. It is necessary to develop a sensor interface capable of making the interfacing of the new sensors easy and intelligent.
- 4) The scattering parameters of nanoparticles can be measured with methods that estimate only the size based upon reasonable hypotheses about the composition. A possibility is to develop an extended database of both size and absorption coefficients, independent of the calibration of numerical methods.

Development of a new instrument in view of the PM tool with the requirements above is challenging simply because of the intrinsic limitations imposed by both industrial requirements and by basic physics arguments. In the following text, we report a list of the ITRS target technology issues for particle counter performance (ITRS and ITRS, 2009).

- Particle counter performance is strongly dependent on the number of particles counted per unit of time.

- The number of particles counted per unit of time determines the precision of the measurement. The precision is predictable based on particle counting statistics.
- The number of particles counted per unit of time is dependent on the sensitivity of the particle counter and the volume of the chemical measured.
- Particle measurements (with reasonable precision) at a specific particle size combined with the knowledge of particle distributions in liquid chemicals can be used in predicting particle concentrations at another size.
- PSD in continuously filtered liquid chemical systems are usually between $1/D^{2.5}$ and $1/D^{3.5}$, with $1/D^3$ being typical. While a PSD can be estimated from any sample, it is more accurate to use a large number of samples and a large number of instruments in making this determination.
- Elimination or minimization of background counts due to cosmic rays is necessary to ensure that the measured particle counts represent real particle events.

In the following section, we introduce a completely novel approach to the characterization of particles suspended in a liquid, and show experimental evidence that this is able to overcome the main issues listed above. We think this method is one of the best candidates to achieve the PM tool described above.

2. Analysis of the field scattered by single particles

In this section, we recall the fundamentals of the traditional methods for the sizing of single particles, and introduce the approach we will adopt here based upon measurement of the scattered field. As it has been recently discussed (Potenza, 2014), the knowledge of the complex field scattered by single particles, meaning either amplitude and phase, or real and imaginary parts, is hugely advantageous in assessing information about the samples. The knowledge of the whole field is the key ingredient which enables information that is otherwise not available with traditional methods to be assessed.

Traditional optical methods for measuring the size of single particles are based on the fundamentals of light scattering, typically the dependence of the scattering cross-section C_{sca} upon the particle radius a and the wavelength λ . A tightly focused light beam is usually exploited to maximize the intensity falling onto a single particle, and the scattered intensity (almost isotropic for $a \ll \lambda$) is collected over a wide solid angle (Chylek, 1976; Sachweh, 1998; Terrel, 2006; Heim, 2008). The ratio of the total scattered power and the incident intensity gives C_{sca} . In order to reduce the uncertainties introduced by the unavoidable shape effects, which can be particularly import-

ant at high scattering angles, low angle detection has been alternatively adopted. A colloidal suspension is hydrodynamically focused into a narrow stream illuminated by a perpendicular laser beam with constant intensity and an elliptical focus. The case of highly concentrated suspensions has also been addressed successfully (Mavliev, 2004). As the particles pass one by one through the laser beam spot, the scattered light is collected under a scattering angle of 5° . The signals are processed by a multichannel analyser and delivered to an electronic processing unit. The particle size is more accurately determined, also for systems subject to aggregation phenomena (Pelssers, 1990).

An alternative approach has been recently introduced based upon direct measurement of the transmitted beam intensity. By definition, this provides the extinction cross-section C_{ext} . The method was commercialized by Klotz GmbH, and has been extensively compared to the scattering-based methods in some cases of interest for basic science (Ruth, 2002).

In some cases, the two principles mentioned above have been adopted in a measurement of both the extinction and the scattering cross-sections of single particles in order to extend the accessible size range (Wells, 1996).

In any of the previous cases, the size is recovered from just one parameter, which is the measured power: the amount of light scattered or removed by the impinging light beam gives the particle size through the proper cross-section (either scattering or extinction). Any other features affecting the scattering of light remain out of control. Even if size by far determines the amount of extinguished and scattered light, other parameters are also involved, thus limiting the accuracy of the size recovery (Gebhart, 1991; Liu, 2000; Whitby, 1967). The composition, shape and internal structure of a particle also participate in determining the scattered field and intensity, and recovering the size from the measured intensity ideally requires the knowledge of this information which is usually unknown (see, for example, Bohren, 1983; Mischenko, 1999; Borghese, 2003). Moreover, especially when working at high scattering angles, the specific orientation of a given non-spherical particle represents an additional parameter that determines the scattered field and intensity, thus making the data intrinsically affected by the uncertainties introduced by the random orientations the particles have in the sensible region (Tinkea, 2008).

The new approach we adopt here (Potenza, 2014) has been shown to give strong advantages in the characterization of free particles. This approach was first used to characterize ceria slurries (Potenza, 2015) in the submicron range. Here, we report the experimental results obtained, adopting the same approach for a more general class of slurries, including CeO_2 and Al_2O_3 slurries, with the aim of proving the feasibility of easy and reliable

characterization for these kinds of suspensions.

For the basics of this approach we refer to the literature (see Potenza, 2014). Here, we just recall that for liquid suspensions of particles with a given composition, even if unknown, several drawbacks of the traditional methods have been overcome. Moreover, the presence of any polydispersity is of advantage here, since a statistical approach can be applied to the data as shown below. Therefore, the typical industrial problem of analysing samples containing particles of homogeneous composition is particularly promising to facilitate going beyond the state of the art (Potenza, 2015). Other advantages will be further discussed. The only drawback of the present approach, which is due to and in common with any other single particle detection method, is the need of highly dilute suspensions. This requires strong dilutions, and in principle could affect the physico-chemical properties of the suspension. This is the requirement also for other optical methods commonly adopted for the off-line characterization of slurries for industries, so that our results are comparable to those obtained with such methods. As discussed in the introduction, in those cases when just the properties of the concentrated sample are of interest, different approaches shall be adopted to avoid dilution (for example, the ultrasonic spectroscopy mentioned above; Hipp, 1999).

3. Single particle extinction and scattering

Simultaneous measurements of the complex scattered field have been attempted with several methods by different groups (Batchelder, 1991; Bassini, 1992; Giglio, 2004; Giglio, 2005; Potenza, 2010). Here we adopt a new method recently developed (Giglio, 2005; Potenza, 2015), which overcomes the main issues encountered by any other method. Actually, the only method which is really viable for characterizing single particles in a flux is the one described in Batchelder 1991, which was previously patented (Batchelder, 1990). Nevertheless, the method we adopt here is simpler, cheaper and more robust such that we believe it really can be adopted for in-line measurements of nanoparticles suspended in a fluid of industrial interest. For this reason, in the following text we will not compare the new method with those mentioned above to measure the complex field.

The method we use here has been developed by the optics group at the University of Milan. It is named Single Particle Extinction and Scattering (SPES) because of its ability to access simultaneous measurements of the extinction cross-section and the amplitude of the forward scattered field for each particle. These parameters are ultimately related to the real and imaginary parts of it. The SPES method is described elsewhere (Potenza, 2015). It

relies upon a self-reference interferometric scheme in which particles are driven through the focal region of a light beam, and the transmitted light is collected on a sensor placed in the far field. Particles are delivered into the beam through a flow cell (Hellma 137 series), the dilution being properly chosen so that just one particle is present in the beam at a time. The superposition of the intense transmitted beam and the faint scattered wave gives time-dependent interference patterns which deliver the information of both the extinction (power reduction of the main beam) and scattering (intensity modulations due to interference). Collecting data at high speed with a time base much smaller than the particle transit time through the beam and adopting a segmented sensor allow recovery of the information on both. The advantages with respect to current methods for measuring single particles are: high size resolution; simultaneous measurement of size and refractive index of single particles; calibration-free; very simple optical layout; minimum fake events. More specifically, working with slurries, one can rely on 1) the knowledge of the composition, and 2) the almost isometric shape of the grains (Potenza, 2015). The former is of paramount importance since the refractive index of compact grains is well known, which allows recognition of spurious grains and aggregates of grains. The latter is important since data are not affected by any uncertainty coming from the shape and orientation of the grains in the scattering volume (see, the simulations in Potenza, 2014). As a result, a precise measurement of the single particle sizes is possible that is free from any contribution of spurious events. A precise PSD can then be obtained and followed with time, which is one of the basic requirements for a routine, in-line process control.

The almost complete absence of fake events warrants a specific discussion here. It is mainly due to 1) the continuous measurement of the transmitted beam, so that the system does not produce any signal at the detection limit when measuring very small particles, and 2) the fast signal detection, which makes an accurate pulse shape analysis of the signals possible. In both cases fake events such as cosmic rays, electronic noise, as well as double transits through the beam can be accurately rejected. Moreover, air bubbles can be easily recognized from the pulse shape analysis, thanks to the unique, known relative refractive index of air with respect to the liquid.

In order to show the specific properties of the SPES method and the way we show data in the following sections, we report some experimental results obtained with calibrated polystyrene (PS) spheres suspended in water. In **Fig. 3.1** we report the raw data in the complex field (abscissas and ordinates represent the real and imaginary parts, respectively). Data are represented in the complex field by a two-dimensional histogram where the number of events detected within a given two-dimensional bin

is represented in grey tones (white corresponds to zero particles, black to the maximum number in the plot). Disturbances in the signals give rise to the spread in the complex plane around the centroid of the distribution, which is more extended towards the lower real and imaginary parts. Bin size was chosen in such a way to be close to the ultimate sensibility of the method in the intermediate region of the accessible range. Spheres of 290, 430 and 600 nm in diameter, refractive index (in air) $n = 1.59$ for the laser source adopted here were measured. The data show a trend identified by the black continuous line, the size increasing for larger complex amplitudes. For the sake of clarity we report the expected complex values for ceria, $n = 2.1$ (dotted line). Moreover, we stress here that for non-spherical particles, the population is expected to be characterized by a spread in the vertical direction which is larger for higher aspect ratios (Potenza, 2014). By contrast, isometric particles show a distribution that is much narrower close to the expected lines in the figure.

In **Fig. 3.2** we report the PSD as obtained by the same data in **Fig. 3.1**. The size has been recovered by simply associating the measured field of each particle to the corresponding size, on the basis of the exact Mie theory. Notice that no true inversion is needed here, thanks to the single particle measurement. The histogram represents the distribution, expressed as the fractional abundance (%) of particles within each bin. Each bin was chosen to be close to the sensibility of the method in the intermediate size range (where noise affects the data at minimum). The red line is the cumulant distribution, while the blue triangles show the expected sizes on the basis of the calibration of the samples.

In order to show the specific ability of the SPES method to give two independent parameters, we show in **Fig. 3.3** the results obtained from measurement of a suspension

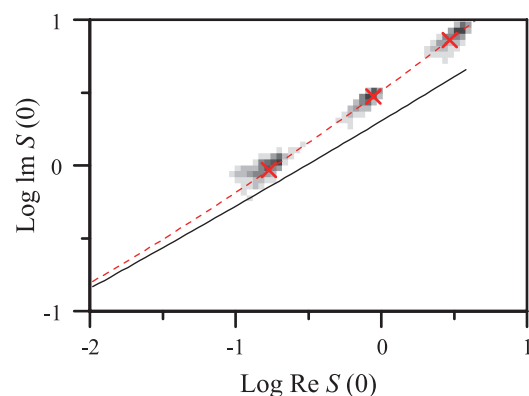


Fig. 3.1 An example of the complex field data obtained with calibrated PS spheres. The 2D histogram represents the number of particles detected within each 2D bin. The continuous line represents the expected complex fields for PS spheres. The dotted line represents the expected fields for $n = 2.1$, respectively.

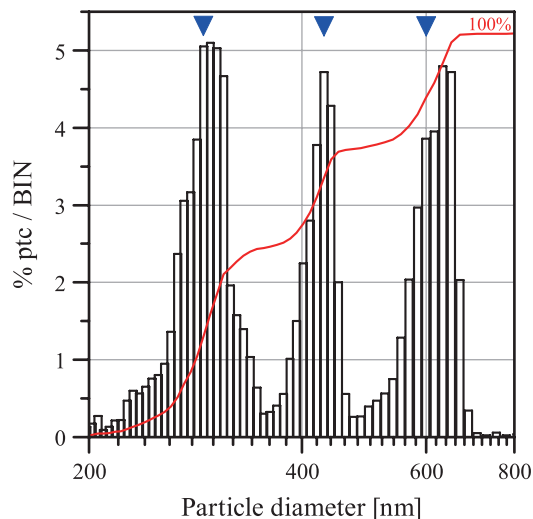


Fig. 3.2 PSD obtained from the data reported in Fig. 1.1. The histogram reports the experimental data, the red line the cumulant curve, the blue triangles are the expected median values.

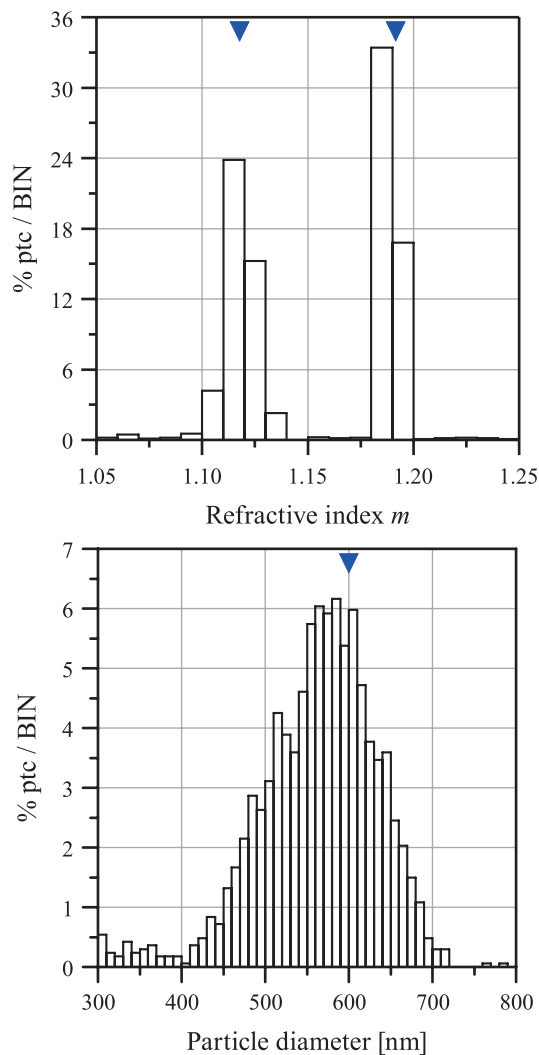


Fig. 3.3 Results obtained with PMMA and PS spheres 600 nm in diameter. a) The index distribution is as expected (see text for details). b) The size distribution is not influenced by different scattering properties due to the different materials. For comparison, see Fig. 3.2.

containing spheres of 600 nm in diameter, made of PS and PMMA. The two materials present different refractive indexes so that we can distinguish them in the complex field and recover the corresponding refractive index distribution. Moreover, when inverting data to recover the size, we still obtain a single distribution centered at 600 nm. Both results cannot be obtained with any traditional single particle method. The refractive index can be accurately measured by capitalizing on the statistical parameters of the bimodal distribution, turning out with relative refractive indexes (in water) $m = 1.12$ and $m = 1.19$. The expected values for the wavelength $\lambda = 635$ nm are $m = 1.118$ for PMMA (Szczurowski, 2014) and $m = 1.192$ for PS (Sultanova, 2009).

In the following sections we report results obtained with ceria slurries under different conditions of interest for industries, and we also show an analysis of Al_2O_3 slurries to extend the analysis to perhaps the most diffuse abrasive materials in the industry worldwide.

4. Ceria slurries

We first consider the case of ceria slurries. We have considered a sample of slurry commonly adopted for a CMP process for global planarization of metal or dielectric layer of semiconductor production. Samples of ceria have been carefully analysed through the SPES method, operating in the size range from some 100 nm to approximately 1 micron.

In the first series of measurements, the samples were prepared by accurately shaking the high-concentration slurries (carefully preventing the sample from forming air bubbles), and a small amount of slurry was strongly diluted in ultrapure water. A series of samples was prepared by passing the dilute suspensions through an ultrasonic bath for different time intervals. The aim was to check whether any differences arise in the size distribution of samples treated for different times due to some kind of aggregation process occurring in the original slurry, which would be broken by sonication. Notice that after dilution, the characteristic time for aggregation is large enough to allow measuring for hours without suffering any aggregation process. Data collected at different times after the sample preparation confirm this assumption. Moreover, data from samples sonicated for different times (including no sonication) did not bring any appreciable difference.

A number of measurements were performed in such a way to test the reliability of the method, both experimentally and from the point of view of data analysis. We show here typical examples of the measurements, focusing on assessing the PSD. Finally, in order to focus on one of the main issues which is the stability of suspensions and the

presence of unwanted large grains, we show results obtained with slurries which suffered aggregation processes due to instabilities induced by chemical additives.

The results are shown in the complex plane in **Fig. 4.1**. One population is evident here, polydispersity determining the extension over the complex plane. The complex fields scattered by a polydisperse suspension of spheres with the typical refractive index of ceria is drawn as the dashed line. Notice that the spread around the line is compatible with the presence of grains of homogeneous composition and almost isometric shape, which is in accordance with the expected case for ceria. The red continuous line was obtained as the line joining the median values of the distributions obtained as the vertical sections of the raw data results. In **Fig. 4.2** we show the PSD obtained as described above from the same data shown in **Fig. 4.1**. Abscissas are expressed in nm, ordinates represent the fraction of the whole population contained in each bin. A total amount of several 10^4 events is represented in the figure which allows channelling the diameters in narrow bins with an appreciable number of counts each. This makes the Poisson's errors associated to the number of counts for each bin reasonably small, as indicated by the error bars (which indicate one standard deviation error).

Here we present results obtained with the same slurry as above, mixed with a chemical (MBIT) adopted for HSS applications. The same preparation procedure was adopted to ensure full consistency with the previous measurements. **Fig. 4.3** represents the results for this sample. Although the amount of detected particles is much less compared to **Fig. 4.1**, the relative population shows important contributions for the largest sizes (upper right region of the plot). These can be attributed to the presence of aggregates composed of several particles. In **Fig. 4.4**

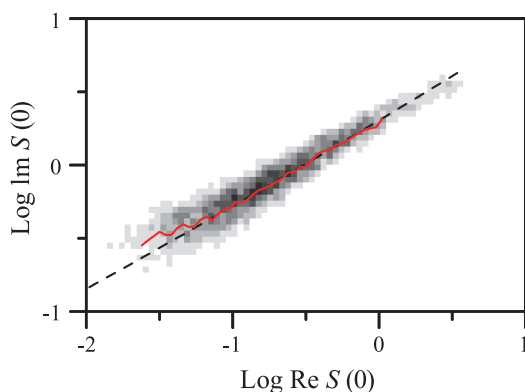


Fig. 4.1 Raw data obtained with ceria slurry, expressed as the histogram in the complex plane. The dashed line is the expected field distribution for spheres with the refractive index of ceria. The red continuous line describes the median of the distribution obtained by selecting bins along the vertical direction.

we present the results of measurements performed on the same sample of **Fig. 4.3** after passing through strong sonication. The population in this case shows 1) an evident depression of the upper size population, and 2) a population which is compatible with the results shown in **Fig. 4.1**. In this case, the presence of aggregates is evidenced solely by the PSD. More generally, aggregates can be better recognized if they grew in size to acquire the typical fractal structure. In such a case, the response of the SPES measurements permit a clear assessment of the fractal nature of the objects (Potenza, 2014).

Notice that the identification of aggregates is one of the key issues for the exploitation of slurries for high-quality applications, as for example in semiconductor fabs. We then consider this series of measurements as the bench-

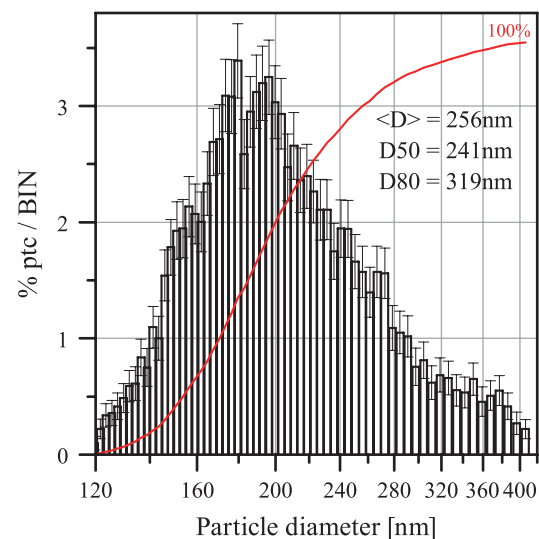


Fig. 4.2 The PSD as obtained from the raw data in **Fig. 4.1**, as described in the text. Error bars represent the Poisson's standard deviations for the number of particles within each bin.

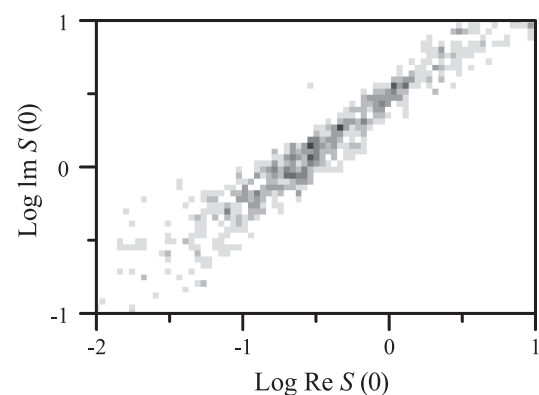


Fig. 4.3 Experimental results obtained with ceria slurry mixed with chemicals (see text). The measurement was performed just after the sample preparation. The difference to **Fig. 4.1** is evident in the upper part of the diagram, corresponding to the larger particles.

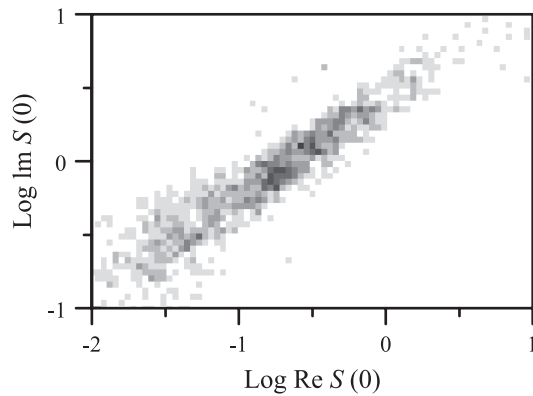


Fig. 4.4 Experimental results obtained with the same sample as in **Fig. 4.3** put in an ultrasonic bath. The additional population evidenced in **Fig. 4.3** is drastically depressed, indicating the aggregate nature of the objects which are broken into their original components.

mark to validate the present approach as a candidate for the most demanding characterization of slurries.

5. Aluminium oxide slurries

In this section we present an example of the results obtained with exhaust AlO_3 slurries for polishing plastic ophthalmic lenses. The expected sizes are appreciably larger than for ceria slurries, so that the accessible range of fields with the instrument exploited for ceria is not suitable for these particles. We then adopted a different realization of the SPES method, an instrument capable of measuring real and imaginary parts more than 10 times larger. Measurements performed with the SPES instrument adopted for ceria confirmed this choice. In **Fig. 5.1** we show the raw data in the complex plane. Notice that the real and imaginary parts are 10 times larger than in the previous figures. The fields of about 20,000 particles are represented, accurately selected on the basis of stringent validation procedures mentioned above. The continuous blue line is the expected field distribution for spheres with the expected refractive index ($n = 1.75$ in vacuum), obtained through a simplified model (Van de Hulst, 1957). No free parameters are present in this plot. The data are in good accordance with the expected values for spheres in the small size range (left-hand bottom part of the plot; we stress that the plot is represented on a logarithmic scale), while the larger sizes present an evident discrepancy. Here we give evidence that this is in accordance with what was expected in the case that fractal aggregates are present in the suspension. The black, dashed line is the field distribution obtained on the basis of the model describing the scattered fields from fractal aggregates, obtained following a simplified model (Van de Hulst, 1957) for the Rayleigh-Gans approximation of the Mie theory

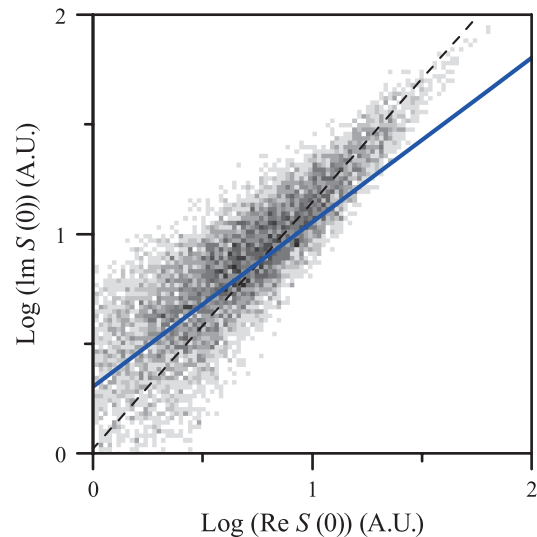


Fig. 5.1 Experimental results obtained with more than 20,000 particles detected by the SPES instrument. The histogram represents the raw data in the complex plane. The blue, thick, continuous line is the expected distribution of fields scattered by spherical particles with the expected refractive index ($n = 1.75$ in vacuum), based upon a simplified Van-de-Hulst model calculated for a fractal dimension $d = 1.8$. The black, dashed line represents the expected values for aggregates (see text for details).

adapted to the case of fractal aggregates (Potenza, 2014). It considers the effect of the reduced amount of matter within an aggregate with a given fractal dimension which determines an increase of the imaginary parts with respect to the values for compact particles. Here the smallest particles have been considered to form aggregates with a fractal dimension $d = 1.8$, a typical value for aggregates formed by instabilities due to electric activity between small grains. This is the case for small mineral grains like those studied here. Notice that a precise value of the fractal dimension does not overly affect the behaviour of the field distribution. Irrespective of the specific values for the parameters in this model (monomer size, fractal dimension), we stress that in the complex plane, a behaviour like that is only compatible with the presence of aggregates. In fact, imaginary parts larger than those for spheres of a given index solely indicate particles with a smaller index, which can only be obtained for non-compact objects.

By exploiting again the simplified model for the forward scattered field (Van de Hulst, 1957), expanding at the second order the real and imaginary parts, and by inverting the outcoming relations in terms of the reduced particle radii, we can give an estimate of the PSD of the particles represented in **Fig. 5.1**. In **Fig. 5.2** the diameter distribution is represented for the same 20,000 particles as above. We stress that this approach to the inversion, al-

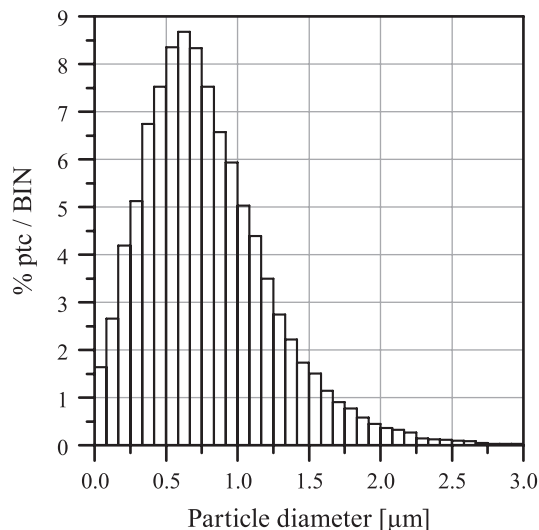


Fig. 5.2 PSD obtained from the raw data in **Fig. 5.1**. The particles in the upper part of the distribution are mainly composed of aggregates, while the smallest ones are compact objects.

though roughly describing the particles as spheres, takes advantage of the complete independence of the result on the knowledge of the particle refractive index. It is therefore particularly suitable for analysing heterogeneous data as the one of interest here, which contains both compact particles and aggregates. Within the simplified model adopted here, each particle is associated to its diameter without any free parameter.

From the statistical analysis of this distribution we obtain an average size of 780 nm and a median of 711 nm. The 10th, 25th, 75th, 90th percentiles are 250 nm, 547 nm, 1021 nm, 1363 nm, respectively.

6. Discussion and conclusions

The data presented so far clearly show the superior ability of the complex field approach to give insights into the details of real, polydisperse suspensions of small particles like those in slurries. In connection with the SPES technology, several advantages are introduced, and their effectiveness makes this approach capable of overcoming the present status and the most important ITRS target technology issues for particle counters listed above. We can sum up the progress beyond the state of the art which is achievable through the SPES method by discussing each item mentioned above, taken from the ITRS target technology issues.

- Capable of operating in-line, and integrated into a DM tool as described above
- Suitable for specific applications in nanoelectronic fabs
- The scattering parameters give access to precise sizing and classifies the composition

- The scattering parameters give access to information about the presence of aggregates
- Performance is not dependent on the number of particles counted per unit of time
- The results and the quality of the results are not obtained on the basis of any statistical approach
- Background counts due to cosmic rays and electronic noise do not affect the measurements
- Air bubbles are rigorously got rid of on the basis of a deterministic algorithm

We stress that thanks to the given composition and very simple structures of the single grains, the ceria slurries are well described solely on the basis of the PSD. This is strongly supported by the 2D histograms, which show the correctness of the choice of one refractive index to recover the PSD. Differences like that shown above can then be fully understood in terms of the PSD and properly determined thanks to our approach. Nevertheless, in the case of Al_2O_3 , the presence of aggregates can be clearly recognized in the complex plane.

An additional advantage of the complex field approach is to recognize events clearly attributable to spurious particles such as water impurities (Potenza, 2015). This is typically not the case of very dense slurries such as those measured here, where proper handling protects them from the presence of impurities, but could be of importance in connection with stringent requirements in process control such as the presence of unwanted grains suspended in the slurry.

Moreover, the opportunity to monitor slurries easily and in-line will enable industries to better decide about the use of these materials. Increasing interest is given to the possibility of reusing exhaust slurries, which is currently difficult simply due to the impossibility of adequately characterizing these materials. The slurry market for applications less demanding than nanoelectronic fabs could be fruitfully integrated by introducing reused slurries, once properly characterized (Seo, 2007; Testa, 2011; Testa, 2014).

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Nomenclature

2D	Two-dimensional
CMP	Chemical Mechanical Polishing
CDS	Chemical Distribution System
DM	Decision Making
HSS	High Selective Slurry
FDC	Fault Detection System
IC	Integrated Circuit
ITRS	International Technology Roadmap for Semiconductors
NVC%	Non-Volatile Content
PM	Particle Monitoring
PMMA	Polymethylmetacrylate
PS	Polystyrene
PSD	Particle Size Distribution
SPES	Single Particle Extinction and Scattering
STI	Shallow Trench Isolation
ULSI	Ultra-Large-Scale Integration
a	Particle radius
C_{ext}	Extinction cross-section
C_{sca}	Scattering cross-section
d	Fractal dimension
D	Particle diameter
m	Relative refractive index (with respect to the surrounding medium)
n	Refractive index (with respect to the vacuum)
$S(0)$	Complex amplitude of the forward scattered field
λ	Light wavelength

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Author's short biography



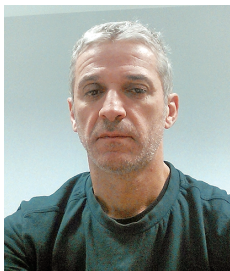
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