

HOLOGRAPHIC DETECTION AND CHARACTERIZATION OF LARGE IMPURITY PARTICLES IN PRECISION SLURRIES

BACKGROUND OF THE INVENTION

[0001] Slurries of oxide nanoparticles have widespread applications as polishing and lapping agents for photonics and for chemical mechanical planarization (CMP) of microelectronic devices. The presence of aggregates or other oversize contaminants in CMP slurries is highly undesirable because of their adverse effect on surface quality, even at part-per-billion concentrations. Efforts to prevent aggregation and eliminate contaminants are hampered by a lack of techniques for detecting and characterizing comparatively small numbers of large particles in an ocean of nanoparticles. Direct imaging, laser occultation and light-scattering techniques, for example, are ruled out by the slurries' turbidity and by the lack of contrast between the nanoparticles and the larger contaminants. Conventional particle counters are clogged and fouled by slurry particles at full concentration. Remedying these problems by dilution is impractical both because of the very large volume of fluid that then would have to be analyzed and also because the process of dilution can influence aggregation processes that might be of interest.

SUMMARY OF THE INVENTION

[0002] One embodiment relates to a method of characterizing impurities in a sample of a slurry of particles in a fluid. The method comprises flowing the sample through an observation volume of a holographic microscope, generating a first holographic image, based upon holographic video microscopy system having a laser, of the sample within the observation volume at a first time, analyzing the first holographic image for one or more regions of interest corresponding to a particle of interest, normalizing the region of interest for a contribution of a diffuse wave created by interaction of the laser with the slurry, fitting the normalized region of interest to a light scattering theory, and characterizing one or more properties of the particle of interest.

[0003] Another embodiment relates to a method of characterizing particles of interest in a slurry. The method comprises flowing the slurry through an observation volume of a holographic microscope, the slurry comprising slurry particles in a fluid and particles of interest; interacting a laser beam with a sample of the slurry and generating a first holographic image based upon holographic video microscopy of the sample within the observation volume at a first time, the holographic image capturing light from a scattered

wave generated by interaction of the laser beam with a particle of the particles of interest and a diffuse wave generated by interaction of the laser and the scattered wave with the slurry particles; analyzing the first holographic image, quantifying a contribution of the diffuse wave, applying Lorenz Mie analysis to the holographic image and characterizing the particle of the particles of interest.

[0004] The foregoing summary is illustrative only and is not intended to be in any way limiting. In addition to the illustrative aspects, embodiments, and features described above, further aspects, embodiments, and features will become apparent by reference to the following drawings and the detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0005] The foregoing and other features of the present disclosure will become more fully apparent from the following description and appended claims, taken in conjunction with the accompanying drawings. Understanding that these drawings depict only several embodiments in accordance with the disclosure and are, therefore, not to be considered limiting of its scope, the disclosure will be described with additional specificity and detail through use of the accompanying drawings.

[0006] FIG. 1 Photograph of the in-line holographic video microscope used to characterize oversize particles in CMP slurries.

[0007] FIG. 2(a) Experimentally recorded hologram of a CMP slurry containing impurity particles at part-per-billion concentration. This image displays three clear features due to light scattering by the micrometer-scale spheres. Fig. 2(b) Region of interest around the feature due to a single sphere. Fig. 2(c) Fit to predictions of the theory of holographic particle characterization. Fig. 2(d) Residual image, showing only the background due to nanometer-scale slurry particles.

[0008] FIG. 3 Radial profile of the fit to the data in Fig. 2(b). The shaded region indicates the statistical uncertainty in the estimated radial intensity profile, which is denoted by the darker curve. The lighter curve is the fit result.

[0009] FIG. 4A Joint distribution of size and refractive index for colloidal silica spheres dispersed in water. FIG. 4B Comparable result for the same sample of spheres dispersed in a slurry of silica nanoparticles.

[0010] FIG. 5 Holographically measured size distribution of contaminant particles in a thawed sample of frozen slurry. The dashed curve shows results for the same sample after 30 min of sonication.

[0011] FIG. 6 illustrates a computer system for use with certain implementations.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0012] In the following detailed description, reference is made to the accompanying drawings, which form a part hereof. In the drawings, similar symbols typically identify similar components, unless context dictates otherwise. The illustrative embodiments described in the detailed description, drawings, and claims are not meant to be limiting. Other embodiments may be utilized, and other changes may be made, without departing from the spirit or scope of the subject matter presented here. It will be readily understood that the aspects of the present disclosure, as generally described herein, and illustrated in the figures, can be arranged, substituted, combined, and designed in a wide variety of different configurations, all of which are explicitly contemplated and made part of this disclosure.

[0013] Described herein are systems and methods of in-line holographic video microscopy. Embodiments of the in-line holographic video microscopy systems and methods addresses the need by identifying large inclusions in commercial slurries at full concentration, and yielding accurate information on their numbers, sizes and compositions. In one embodiment, the slurry consists of silicon dioxide nanoparticles with characteristic dimensions of 70 nm dispersed in water at a volume fraction of 30.9%. Such a slurry is turbid, and so differs qualitatively from the optically transparent media that have been considered in prior art implementations of holographic particle characterization. An inclusion of interest is substantially larger than a slurry particle and has an index of refraction that differs from that of the fluid medium. In one embodiment, an inclusion particle consists of an oversized impurity particle with a characteristic dimension of one micrometer. In another embodiment, an inclusion particle consists of an aggregate formed from multiple slurry particles that have become rigidly attached to each other. The slurry is a “scattering fluid” as pertains to the application of holographic video microscopy, resulting

in a scattering signal in addition to that of any particles of interest in a sample volume that is imaged.

[0014] It is further believed that in certain embodiments, both the relative size and refractive index of the particles of interest, such as impurities, compared to the slurry (specifically, the suspended particles of the slurry) contribute to the ability to detect the particles of interest. A larger scattering by the particles of interest than the slurry particles will allow for detection of particles of interest of smaller size relative to the slurry particles. Similarly, if the background slurry particles scatter more than the particles of interest, the particles of interest will need to be larger, relative to the slurry particles, for detection.

[0015] Figure 1 illustrates one embodiment of a holographic measurement system that illuminates the sample with the collimated beam. The embodiment illustrated uses a fiber coupled diode laser operating at a vacuum wavelength of 532 nm. Light scattered by colloidal particles interferes with the remainder of the beam in the focal plane of a microscope objective lens, which relays the magnified interference pattern to a conventional video camera, in the illustrated embodiment with an effective magnification of 47 nm/pixel. The slurry flows through the laser beam in a standard microfluidic channel mounted on the microscope's stage.

[0016] The flow rate is chosen to be fast enough that a specified volume of the sample can be analyzed in a specified measurement duration, but not so fast that motion appreciably blurs the hologram during the exposure time of the video camera. The maximum usable flow rate is inversely proportional to the exposure time. The minimum usable exposure time is determined by the intensity of the illumination laser and by the sensitivity and noise characteristics of the camera. The combination of laser intensity and exposure time is chosen to ensure that the signal-to-noise ratio of recorded holograms is high enough to obtain reliable results from the holographic characterization analysis. This, in turn, determines the maximum usable flow rate for the sample, and the time required to characterize a specified volume of sample. In one embodiment, a peak flow speed of 100 micrometers per second suffices to detect and characterize the properties of 1000 oversized impurity particles dispersed in a CMP slurry at a part-per-billion concentration in a ten-minute measurement period. A series of holographic images of the sample is captured as frames in a digital video. In the illustrated embodiment, each 1280 pixel $\times$ 1024 pixel video

frame is a hologram of the particles in the $60\text{ }\mu\text{m} \times 48\text{ }\mu\text{m} \times 20\text{ }\mu\text{m}$ observation volume. Holograms obtained in comparable systems have been interpreted with predictions of the Lorenz- Mie theory of light scattering to obtain precise measurements of individual colloidal spheres' sizes and refractive indexes. Although the large concentration of nanoparticles in a typical CMP slurry contributes a random background to the recorded holograms, embodiments surprisingly find that Lorenz-Mie analysis still yields accurate and precise measurements of the properties of individual micrometer-scale contaminant particles.

[0017] Particles of interest (often contaminants) typically are larger than the particles that constitute the slurry. The largest such contaminant particle that can be characterized by this technique depends on the configuration of the holographic recording instrument. In one embodiment, the accessible range of sizes runs from 200 nanometers to 20 micrometers. Because this is a particle-resolved measurement technique, moreover, holographic characterization can detect and count rare particles.

[0018] To demonstrate this technique and verify its efficacy, a well-characterized commercial CMP slurry (Dow Ultrasol 2EX) consisting of silica nanoparticles with a nominal diameter of 70 nm was seeded with colloidal silica spheres (Bangs Laboratories, Catalog Number SS04N, Lot Number 5303). The 1.5 micrometer-diameter silica spheres contribute clearly visible bulls-eye features to the hologram in Fig. 2(a). These features were detected using an image-analysis filter that emphasizes centers of rotational symmetry and then select the surrounding region for analysis. One embodiment utilizes the analysis technique described in PCT/US2015/015666, incorporated herein by reference. Specifically, the orientation-alignment transform is used to detect features of interest. It is possible to perform the actual fitting using the standard technique, essentially ignoring the presence of the slurry. Surprisingly, the values obtained in this way are reasonably close to the independently verified properties of the particles.

[0019] However, in another embodiment the analysis considers the slurry and accounts for it. Equations (2b) and (4b) below are novel approaches to accomplish this, and yield values for particle characteristics that experimentally have been confirmed to be accurate. Figure 2(b) shows a typical feature detected in this way.

[0020] An ideal hologram for holographic particle characterization results from the superposition of a coherent collimated beam with the light scattered out of the beam by an illuminated particle. When the particle is embedded in a nanoparticle slurry, both the illumination and the scattered wave are attenuated by multi-particle light scattering, and the resulting diffuse wave contributes time-dependent speckle to the recorded hologram. This random-scattering contribution has not been considered in previous applications of holographic particle characterization, including those for which random scattering might conceivably have played a role. These additional effects can be accounted for provided that the coherent interference pattern contributes measurably to the overall intensity distribution.

[0021] The incident field is first modeled as a monochromatic plane wave propagating along $\hat{z}$ and linearly polarized along $\hat{x}$,

$$\mathbf{E}_0(\mathbf{r}) = u_0(\mathbf{r}) e^{-\kappa(D-z)} e^{ikz\hat{z}}, \quad (1)$$

[0022] where $u_0(\mathbf{r})$ is the transverse amplitude profile and $k = 2\pi n_m/\lambda$ is the wavenumber of light with vacuum wave-length λ propagating through a medium of refractive index n_m . Scattering by the slurry attenuates this beam with an effective penetration depth κ^{-1} that depends on the concentration of slurry particles and on their light-scattering characteristics. If the channel thickness, D , is much greater than the attenuation depth, then the recorded hologram will be dominated by diffuse scattering and no information will be retained about the properties of the particle. In this formulation, the imaging plane is located at $z = 0$ and light enters the slurry at the top of the channel, which is located at $z = D$.

[0023] The same scattering process that attenuates the incident light also creates a diffuse light field, $\mathbf{E}_d(\mathbf{r}, t)$, some of which propagates toward the imaging plane. The diffuse field gives rise to the speckle pattern in dynamic light scattering and diffusing wave spectroscopy. It evolves with depth into the slurry both because more light from the incident wave is scattered into the random field and also because the random field itself is scattered. It evolves in time as the particles rearrange themselves in the slurry. In one embodiment, the time-dependent part of the signal is analyzed to obtain information about the slurry itself. This could include information about the particle-size distribution and the concentration of slurry particles. As described above, the time dependent information can

be used to calibrate the diffuse background intensity that is used to analyze the large-particle hologram. Polarization and phase randomization in the diffuse beam tend to suppress interference with the unscattered beam. In the absence of particles, therefore, the intensity in the focal plane is approximately

$$I_0(\mathbf{r}, t) = |\mathbf{E}_0(\mathbf{r}) + \mathbf{E}_d(\mathbf{r}, t)|^2 \quad (2a)$$

$$\approx u_0^2(\mathbf{r}) e^{-2\kappa D} + |\mathbf{E}_d(\mathbf{r}, t)|^2, \quad (2b)$$

[0024] Further assuming the speckle pattern to have Gaussian statistics, Eq. (2) can be used to obtain independent estimates for the unscattered amplitude $u_0(\mathbf{r}) \exp(-\kappa D)$ and the diffuse field's time-averaged amplitude, $u_d = \langle |\mathbf{E}_d(\mathbf{r}, t)| \rangle_t$, from video sequences, $I_0(\mathbf{r}, t)$, of the flowing slurry.

[0025] Both the attenuated illumination and the diffuse scattered field are incident on a sphere at height z_p above the imaging plane. As before, it is assumed that light coherently scattered from the illumination contributes more to the recorded hologram than light scattered out of the diffuse field. This condition can be ensured by appropriately reducing the channel depth, D , to the greatest extent consistent with maintaining the desired flow characteristics and measurement duration. The scattered field at point $\mathbf{r}$ in the imaging plane therefore is approximately given by

$$\mathbf{E}_s(\mathbf{r}) \approx u_0(\mathbf{r}_p) e^{-\kappa D} \mathbf{f}_s(k(\mathbf{r} - \mathbf{r}_p)) \quad (3)$$

[0026] where $\mathbf{f}_s(k\mathbf{r})$ is the Lorenz-Mie scattering function that describes how an $x^\wedge$ -polarized plane wave is scattered by a sphere of radius a_p and refractive index n_p . Equation (3) accounts for the illumination's attenuation before reaching the particle, and the further attenuation of the scattered wave as it propagates to the focal plane. For simplicity, we model this latter effect as a single exponential factor, which neglects the optical path length's dependence on scattering angle.

[0027] The hologram in Fig. 2(c) is obtained from the intensity of the field in the imaging plane,

$$I(\mathbf{r}) = |\mathbf{E}_0(\mathbf{r}) + \mathbf{E}_s(\mathbf{r}) + \mathbf{E}_d(\mathbf{r}, t)|^2 \quad (4a)$$

$$\approx u_0^2(\mathbf{r}) e^{-2\kappa D} \left| \hat{x} + e^{ikz_p} \mathbf{f}_s(k(\mathbf{r} - \mathbf{r}_p)) \right|^2 + |\mathbf{E}_d(\mathbf{r}, t)|^2. \quad (4b)$$

[0028] This result omits terms that describe interference between coherent and diffuse waves, whose time average should vanish. In this model, the overall effect of the slurry is to reduce the contrast of the target particle's hologram, and to contribute Gaussian additive noise, both of which reduce the hologram's effective signal to noise ratio but do not otherwise affect its symmetries.

[0029] The diffuse wave's contribution to the measured hologram can be quantified through analysis of video sequences that do not contain holograms of particles. The first term in Eq. (4b) suggests that the quality of information that can be retrieved from the hologram is controlled by the channel thickness D . Indeed, if D is much larger than the slurry's attenuation length, the scattering particle's hologram will be entirely obscured by diffuse scattering, and other methods would be required even to detect the sphere's presence. It should be appreciated that sample cell may be selected based on the desired channel thickness.

[0030] The image in Fig. 2(d) results from the nonlinear least-squares fit of Eq. (4) to the data in Fig. 2(c). The difference between the measured and fit holograms is plotted in Fig. 2(d). The particle's radius obtained from this fit, $a_p = 0.749 \pm 0.006 \mu\text{m}$, is consistent with the manufacturer's specification, and the refractive index, $n_p = 1.439 \pm 0.002$, is consistent with values obtained for the same sample of silica spheres under ideal imaging conditions. The quality of the fit may be judged from the radial profile, plotted in Fig. 3, which tracks the experimental data to within random contributions due to the slurry particles, which are indicated by the shaded region.

[0031] Figure 4A shows a compilation of 875 single-particle measurements of the radii and refractive indexes of silica spheres from the same monodisperse sample. Each data point in the plot reflects the measured properties of a single sphere and is colored by the relative probability $\rho(a_p, n_p)$ of measurements in the (a_p, n_p) plane. The mean radius, $a_p = 0.79 \pm 0.01 \mu\text{m}$, agrees with the manufacturer's specification. The mean refractive index, $n_p = 1.45 \pm 0.01$, is slightly smaller than the value 1.485 for bulk silica at the imaging wavelength, and is consistent with the spheres' having a 2 % porosity, as has been discussed elsewhere. The data for this plot was acquired in 10 min.

[0032] Figure 4B shows comparable results for the same batch of silica spheres dispersed in the silica slurry. Values for the radius, refractive index and porosity are consistent with those obtained under ideal imaging conditions. This result demonstrates that holographic particle characterization can yield accurate and precise results for the properties of micrometer-scale colloidal particles dispersed in nanoparticle slurries at full concentration.

[0033] Applying this technique to the stock solution of silica slurry yielded no detectable features after 30 min. More than 2×10^9 silica nanoparticles would have passed through the observation in that time, demonstrating that the slurry is free from detectable contaminants at the part-per-billion level. The lower limit on the detectable concentration of oversize impurity particles is set by the flow rate and the duration of the measurement. Longer measurements at higher flow rates permit detection of smaller concentrations of impurity particles. For additional analysis, aggregation was deliberately induced by freezing it and then thawing the slurry sample for analysis. The destabilized slurry now features a large number of micrometer-scale objects, which the system and methods described herein detected as nanoparticle aggregates. These aggregates are drawn from a very broad size distribution, with a sizable percentage of particles with dimensions exceeding $5 \mu\text{m}$.

[0034] However, it should be considered that the type of aggregate or contaminant may further matter. For example, transient aggregates may not have deleterious effects under the strong shear forces encountered during polishing that a solid contaminant of like-size would have. To investigate the nature of the observed aggregates, the thawed slurry was subjected to 30 min of sonication. The dashed curve in Fig. 5 shows the resulting holographically-measured size distribution. Whereas sonication appears to have disrupted the largest aggregates, smaller aggregates with radii ranging up to $1 \mu\text{m}$ remain intact. These aggregates are small enough that they are not evident under visual inspection, and do not appear in bright-field images. Because they are robust enough to survive sonication, they likely would render the slurry unacceptable for use in polishing. Additional insights into the individual particles' mechanical characteristics may be inferred from their holographically-measured refractive indexes. Porous particles tend to have refractive indexes that are lower than the bulk value by an amount that depends on the particles' porosity. High-index particles in a low-index fluid medium tend to display lower

refractive indexes as their porosity increases. Estimates for the porosity, in turn, can be used to assess whether the detected particles are likely to be deleterious to the intended application. Non-deleterious particles, such as dispersed gas bubbles, similarly can be distinguished from damaging solid particles on the basis of their refractive index.

[0035] These results demonstrate that holographic characterization can be used to detect and measure the proper- ties of individual contaminant particles in CMP slurries without requiring dilution. The particle-resolve measurements yield estimates for the distribution of contaminant sizes without invoking *a priori* models for the distribution.

[0036] As shown in Figure 6, e.g., a computer-accessible medium 120 (e.g., as described herein, a storage device such as a hard disk, floppy disk, memory stick, CD-ROM, RAM, ROM, etc., or a collection thereof) can be provided (e.g., in communication with the processing arrangement 110). The computer-accessible medium 120 may be a non-transitory computer-accessible medium. The computer-accessible medium 120 can contain executable instructions 130 thereon. In addition or alternatively, a storage arrangement 140 can be provided separately from the computer-accessible medium 120, which can provide the instructions to the processing arrangement 110 so as to configure the processing arrangement to execute certain exemplary procedures, processes and methods, as described herein, for example. The instructions may include a plurality of sets of instructions. For example, in some implementations, the instructions may include instructions for applying radio frequency energy in a plurality of sequence blocks to a volume, where each of the sequence blocks includes at least a first stage. The instructions may further include instructions for repeating the first stage successively until magnetization at a beginning of each of the sequence blocks is stable, instructions for concatenating a plurality of imaging segments, which correspond to the plurality of sequence blocks, into a single continuous imaging segment, and instructions for encoding at least one relaxation parameter into the single continuous imaging segment.

[0037] System 100 may also include a display or output device, an input device such as a key-board, mouse, touch screen or other input device, and may be connected to additional systems via a logical network. Many of the embodiments described herein may be practiced in a networked environment using logical connections to one or more remote computers having processors. Logical connections may include a local area network (LAN) and a wide area network (WAN) that are presented here by way of example

and not limitation. Such networking environments are commonplace in office-wide or enterprise-wide computer networks, intranets and the Internet and may use a wide variety of different communication protocols. Those skilled in the art can appreciate that such network computing environments can typically encompass many types of computer system configurations, including personal computers, hand-held devices, multi-processor systems, microprocessor-based or programmable consumer electronics, network PCs, minicomputers, mainframe computers, and the like. Embodiments of the invention may also be practiced in distributed computing environments where tasks are performed by local and remote processing devices that are linked (either by hardwired links, wireless links, or by a combination of hardwired or wireless links) through a communications network. In a distributed computing environment, program modules may be located in both local and remote memory storage devices.

[0038] Various embodiments are described in the general context of method steps, which may be implemented in one embodiment by a program product including computer-executable instructions, such as program code, executed by computers in networked environments. Generally, program modules include routines, programs, objects, components, data structures, etc. that perform particular tasks or implement particular abstract data types. Computer-executable instructions, associated data structures, and program modules represent examples of program code for executing steps of the methods disclosed herein. The particular sequence of such executable instructions or associated data structures represents examples of corresponding acts for implementing the functions described in such steps.

[0039] Software and web implementations of the present invention could be accomplished with standard programming techniques with rule based logic and other logic to accomplish the various database searching steps, correlation steps, comparison steps and decision steps. It should also be noted that the words “component” and “module,” as used herein and in the claims, are intended to encompass implementations using one or more lines of software code, and/or hardware implementations, and/or equipment for receiving manual inputs.

[0040] With respect to the use of substantially any plural and/or singular terms herein, those having skill in the art can translate from the plural to the singular and/or from the singular to the plural as is appropriate to the context and/or application. The

various singular/plural permutations may be expressly set forth herein for the sake of clarity.

[0041] The foregoing description of illustrative embodiments has been presented for purposes of illustration and of description. It is not intended to be exhaustive or limiting with respect to the precise form disclosed, and modifications and variations are possible in light of the above teachings or may be acquired from practice of the disclosed embodiments. Therefore, the above embodiments should not be taken as limiting the scope of the invention.

WHAT IS CLAIMED:

1. A method of characterizing impurities in a sample of a slurry of particles in a fluid, comprising:
flowing the sample through an observation volume of a holographic microscope;
generating a first holographic image, based upon holographic video microscopy system having a laser, of the sample within the observation volume at a first time;
analyzing the first holographic image for one or more regions of interest corresponding to a particle of interest;
normalizing the region of interest for a contribution of a diffuse wave created by interaction of the laser with the slurry;
fitting the normalized region of interest to a light scattering theory; and
characterizing one or more properties of particle of interest.
2. The method of claim 1, wherein the sample is a slurry.
3. The method of claim 1, wherein the slurry comprises particles of 200nm or less size.
4. The method of claim 3, wherein the particle of interest has a size of about 200 nanometers to about 20 micrometers.
5. The method of claim 1, wherein the peak flow is about 100 micrometers per second.
6. The method of claim 1, further comprising selecting a sample cell of depth *D*.
7. The method of claim 1, wherein characterizing the particle of interest comprises determining radius and refractive index.

8. A method of characterizing particles of interest in a slurry, comprising:
flowing the slurry through an observation volume of a holographic microscope, the slurry comprising slurry particles in a fluid and particles of interest;
interacting a laser beam with a sample of the slurry and generating a first holographic image based upon holographic video microscopy of the sample within the observation volume at a first time, the holographic image capturing light from a scattered wave generated by interaction of the laser beam with a particle of the particles of interest and a diffuse wave generated by interaction of the laser and the scattered wave with the slurry particles;
analyzing the first holographic image;
quantifying a contribution of the diffuse wave;
applying Lorenz Mie analysis to the holographic image;
characterizing the particle of the particles of interest.