

Nanoparticle Dispersions for Polishing Applications

Patrick G. Murray

Nanophase Technologies Corporation, Romeoville, IL, pmurray@nanophase.com

ABSTRACT

Increasingly, improvements in surface roughness and planarity are being sought in a variety of technologically advanced polishing applications related to the electronics industry. From the production of photomask blanks to the fabrication of microelectronic memory and process devices, improvements in global surface planarity and roughness, coupled with reduced incidents of defectivity, are critical to achieving the specifications of future technology nodes. Nanophase Technologies Corporation (NTC) uses a patented plasma arc synthesis technique to produce nano-sized cerium oxide (ceria) and aluminum oxide (alumina) particles in commercial quantities and quality. The small particle size, controlled particle size distribution, and unique crystal morphology of these materials are allowing new performance benchmarks to be realized in the planarization of silicon wafers and the polishing of photomask blanks, lithography optics and rigid memory substrates. However, the success or failure of a nanocrystalline material in a particular polishing application depends not only on the characteristics of the particle but also on the ability to form and maintain a stable dispersion of those particles with controlled rheology. Thus, both the attributes of the particles which provide utility in the above mentioned polishing applications as well as observations relevant to the production of stable dispersions are discussed.

Keywords: nanoparticle, ceria, alumina, polishing, CMP

1. INTRODUCTION

Nanophase Technologies Corporation produces nanocrystalline ceria and alumina in multi-ton quantities using a plasma-based vapor-phase synthesis (VPS). In the VPS process, a metal or metal oxide precursor is vaporized in a plasma arc and the evaporated precursor is allowed to combine with a reactive gas, usually oxygen. As the molecules of the newly formed metal oxide begin to associate, nanoparticles condense from the vapor phase and are then rapidly cooled so as to preclude sintering. Fortunately, the nanoparticles associate with each other through weak electrostatic forces in the dry state, which permits collection of the product as a low bulk density powder.

Many primary particle attributes which are derived from the VPS process influence the behavior and performance of these particles when they are used for demanding polishing applications typically associated with advanced electronic applications. The primary particle size, the particle morphology, the particle density and the particle surface chemistry are all set during the VPS process. These particle attributes, along with specific downstream dispersion processing operations, render these nanocrystalline materials particularly suitable for the following polishing applications: Chemical Mechanical Planarization (CMP), including Shallow Trench Isolation (STI), copper interconnect and interlayer dielectric planarization, and final polishing of extreme ultraviolet lithography (EUVL) photomask blanks, optics for lithographic processes, and rigid memory storage substrates with increased aerial density.

2. PARTICLE ATTRIBUTES

The primary particle size is set during the vapor phase synthesis. A TEM image of the VPS nanocrystalline ceria is shown in Figure 1, and a TEM image of the VPS nanocrystalline alumina is shown in Figure 2.

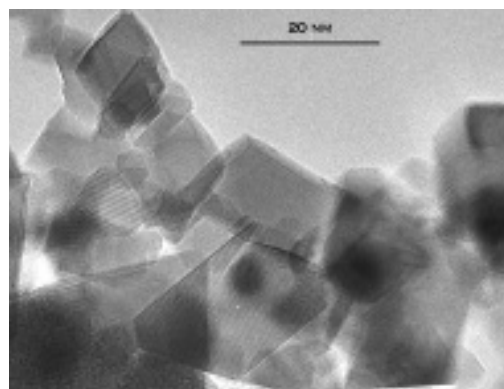


Figure 1. TEM image of VPS produced ceria

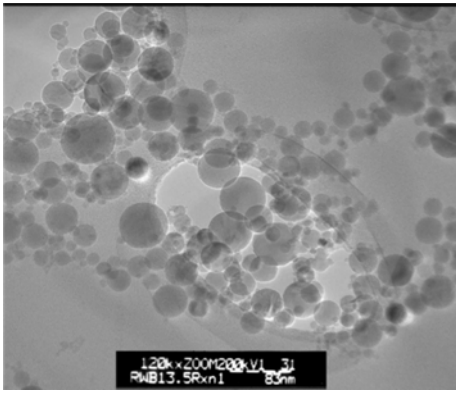


Figure 2. TEM image of VPS produced alumina

As can be observed in the TEM images, the nanocrystalline ceria and alumina are equiaxed and nanoscale in every dimension. The VPS process does not produce any high aspect ratio particles, such as needles or platelets, which may be nanoscale in one dimension, but sub-micron in another. The morphology obtained for a given nanocrystalline material is determined by thermodynamics; ceria forms sharp-edged, multi-faceted, cubic crystals while the alumina particles are spherical.

The chemical purity of the particles produced by the VPS process is extremely high, since high purity raw materials can be sourced, nothing else is added except high purity oxygen, and no by-products or waste streams are generated. This situation may be contrasted with particles produced by fumed or precipitated processes, wherein the products are often contaminated with various rogue ions such as chlorides or sulfates.

The density of the nanocrystalline particles obtained from the VPS process is near theoretical. For polishing applications, this lack of porosity results in non-friable particles which do not change size or shape during a polishing operation, resulting in consistency and reproducibility in removal rates and other performance figures of merit.

The VPS process allows for a great degree of control over the chemistry at the particle surface. For example, as will be discussed subsequently, the particle surface chemistry can be “tuned” with the plasma process so that a high positive zeta potential (+45 mV is typical) results when the particles are dispersed in water. This high positive zeta potential allows concentrated, stable dispersion to be prepared which can be used directly for polishing or subjected to further chemical or physical treatments.

Perhaps most importantly, the particles which form under the VPS synthesis conditions are discrete, individual nanocrystals which, once properly dispersed, do not form secondary aggregate or agglomerate structures as is common with silica and milled ceria. This property translates directly into consistent removal rates and reduced defectivity and sub-

surface substrate damage during polishing. For example, dispersions of the VPS nanocrystalline ceria at 20 weight percent which are over two years old show no evidence of particle size growth.

3. DISPERSION ATTRIBUTES

The success or failure of a nanocrystalline material in a particular polishing application is highly dependent upon the ability to prepare and maintain a stable dispersion. This enables improvements in surface roughness to be achieved along with a corresponding reduction in surface defects and residual particles, both of which are necessary whether the application is microelectronic wafer planarization or lithographic optics polishing.

In moving toward this objective, it is necessary to tailor the zeta potential of the particles to accommodate a wide range of pH environments to ensure that the particles provide sufficient removal rate while being strongly resistant to flocculation during polishing.

Nanocrystalline ceria and alumina made by the VPS process can be dispersed in water such that the particles carry a very high positive zeta potential because of the unique surface chemistry imparted to the particles during VPS synthesis. In these cases, the natural pH of the dispersions is acidic and well below the isoelectric pH of the materials. These dispersions are most widely used in CMP applications and other metal polishing applications. Because of the high positive zeta potential, stable dispersions at concentrations of 20 to 25 weight percent are readily prepared. Even dispersions as concentrated as 50 weight percent have been prepared for specific applications.

Once the nanocrystalline alumina or ceria has been dispersed down to individual, fully solvated primarily particles, a variety of further complimentary physical and chemical processing can be accessed. For example, oftentimes in sensitive polishing applications it is desirable to remove a small fraction of the larger particles which can contribute to scratches or defects on the substrate. This truncation operation, virtually impossible to perform in the dry state, is straightforward and controllable with the dispersion given the proper equipment. From a polishing perspective, this means that the particle size distribution can be controlled to a performance specification. Normally, since only a fraction of the whole lognormal particle size distribution is removed in such an operation, the mean particle size does not change, but instead only the standard deviation about the mean particle size is reduced. In polishing, this means that the removal rate is unaltered, but typically the defectivity is reduced and the surface roughness which can be achieved is improved.

An additional benefit of a stable dispersion is that a variety of performance additives such as buffers, chelants, dispersants, and lubricants can be added. Depending on the

polishing application, such additives are often necessary to convert a dispersion of abrasive particles to a ready-to-use polishing slurry.

As an example, a typical particle size distribution for an aqueous dispersion of NTC's VPS produced ceria is shown in Figure 3 at pH 4.0. As shown, the particle size distribution is narrow and centered around 100 nm (volume-weighted average).

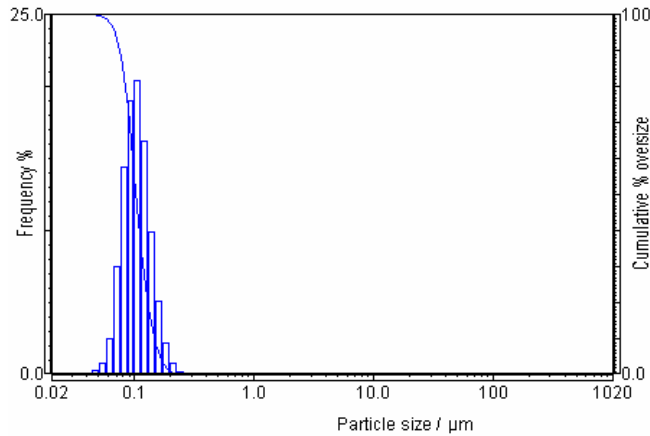


Figure 3. Mean volume weighted particle size histogram for post-processed VPS ceria in water at pH 4.0.

Even though a stable dispersion can be formed at pH values below the isoelectric points without any additional chemical dispersant, formulating with a dispersant under these conditions can extend the life of the slurry in the polishing application by making the dispersion less sensitive to silicates, metal ions, and other species which will increase in concentration during polishing. Moreover, the presence of a dispersant, particularly a polymeric dispersant, can aid in post-polishing cleaning and reduce the amount of residual slurry particles which may remain behind on the substrate.

Most glass polishing, on the other hand, is conducted at an elevated pH, generally with ceria, since glass is softened at higher pH. Examples of this would include the preparation of photomask blanks and the finish polishing of lithography optics and rigid memory storage media discs. However, as the pH of the dispersion is raised, and the isoelectric point of the particle is approached, flocculation of the dispersion is most likely. This is to be avoided at all costs, since poor surface finish and high levels of defects will be observed on the substrate. An example of this is shown in Figure 4, where the larger, agglomerated particles evident in the distribution could be expected to negatively impact all important process metrics.

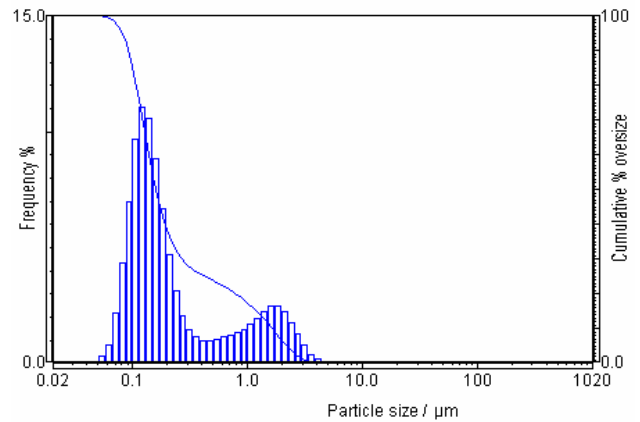


Figure 4. VPS ceria dispersion after crossing the isoelectric pH without the appropriate particle surface treatment

Fortunately, when the appropriate particle surface treatment is employed, a stable dispersion on the other side of the isoelectric point (at pH 8.0) is achieved, as shown in Figure 5. Under these circumstances, the particles will have a highly negative zeta potential (-45 mV is typical) and the dispersion will be stable based on the electrostatic repulsion of the particles.

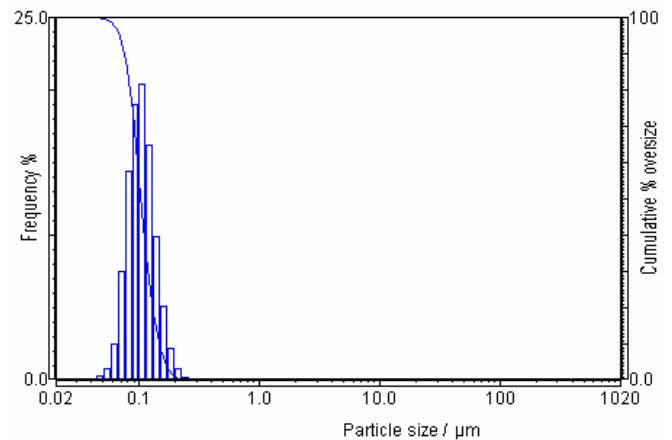


Figure 5. VPS ceria dispersion in water, pH 8.0, surface treated particle

4. CONCLUSIONS

Nanocrystalline ceria and alumina produced using Nanophase Technologies Corporation's VPS process have unique attributes which render them especially suitable for use in polishing applications. As examples, the morphology, density and primary particle size of these materials have been instrumental in achieving angstrom level surface roughness with no subsurface damage in the polishing of photomask blanks [1] and in setting new industry benchmarks for selectivity and reduced defectivity the fabrication of microelectronic devices [2].

However, the successful application of these nanocrystalline materials in high performance polishing applications requires an understanding of those factors which influence dispersion stability in the environment in which the particles are to be used. The ability to control zeta potential, both at particle inception and in dispersion, has proven to be a key enabling capability in this regard.

5. REFERENCES

- [1] Murray, P. G., *et. al.*, "Nanocrystalline Ceria Dispersions for Ultrafine Polishing and Defect Reduction in EUVL Photomask Blank Manufacture," Optifab 2003, May 19-23, 2003, Rochester, NY.
- [2] "Rodel Solidifies Position in Direct STI Market," Press Release, Rodel, Inc., December 3, 2003.