CERIUM OXIDE PARTICLES WITH CONTROLLED MICROSTRUCTURE

TECHNICAL FIELD

The invention relates to secondary cerium oxide particles with a controlled microstructure formed through agglomeration of primary particles; to the use of these secondary particles in dispersions such as polishing slurries, in particular chemical mechanical polishing (CMP) compositions; and to a preparation method thereof.

TECHNICAL BACKGROUND

The development of the electronics industry requires an increasingly considerable use of compositions for polishing various parts such as discs or dielectric compounds. In particular, the chemical mechanical polishing (CMP) process is essential for the planarization of interlayer insulating films, the formation of shallow trench isolation structures, the formation of plugs and embedded metal wiring, etc. in the manufacturing process of semiconductor devices. The compositions used for this purpose are usually commercialized in the form of dispersions and must exhibit a certain number of characteristics. In particular, they must offer a high degree of removal of material, which reflects their abrasive capacity.

In general, abrasive particles with high particle size achieve high removal rates in the CMP process. However, particles having a large particle size tend to scratch substrate that should be polished. Therefore, the particles must also have a defectuosity which is as low as possible; the term “defectuosity” is intended to mean in particular the number of scratches exhibited by the substrate once treated with the polishing composition.

In recent years, the number of layers of semiconductor elements and the increase in definition thereof have progressed dramatically, and there has been a demand for further improvement in the yield and throughput of semiconductor elements. Accordingly, in the CMP process as well, there is a growing demand for scratch-free polishing compositions.

The polishing compositions used in the CMP process usually comprises ceric oxide (CeO_2) as abrasive particles. The particles of the cerium oxide used in such compositions have various shapes and sizes. They can be obtained by various preparation methods. One of them consists in firing and pulverizing cerium compounds such as cerium carbonate. The such obtained cerium oxide particles

are called calcined ceria particles. However, in polishing methods using such abrasive grains, since the particle structure has many edges, it has been a problem to reduce scratches. For this reason, several attempts, as for example described in US2 2002/0016060, US 2003/0200702, US 2009/0113809 or JP 2023038579 A, have been made to reduce the number of scratches by reducing the particle size of the cerium oxide particles but maintaining their high abrasive capacity.

Nevertheless, there is still the need to provide abrasive particles suitable for CMP process having a high abrasive capacity while avoiding scratching. Furthermore, there is the need to provide a preparation process for such particles that can be easily carried out at industrial scale and ensures that the desired properties of the particles are obtained.

SUMMARY OF THE INVENTION

The present invention refers to secondary cerium oxide particles having a mean particle size of 100 nm or higher, determined by SEM, and wherein each secondary cerium oxide particle is an agglomerate of primary cerium oxide particles having a mean particle size of 30 to 50 nm, determined by TEM, and a crystallite size of 20 to 40 nm, determined by XRD.

In the present description, a particle will be referred to as a “primary particle” and an agglomerate of primary particles will be referred to as a “secondary particle”.

The terms “secondary cerium oxide particles” and “secondary particles” are used interchangeably herein. The same applies to the terms “primary cerium oxide particles” and “primary particles”.

Additionally, the invention refers to a dispersion comprising the secondary cerium oxide particles of the invention.

The secondary cerium oxide particles of the invention or the dispersion thereof can be used for the preparation of a polishing composition, preferably a chemical mechanical polishing composition.

Furthermore, the invention refers to a method for preparing the secondary cerium oxide particles according to the invention, wherein the method comprises the following steps:

(i) Precipitation of cerium carbonate by using cerium nitrate and ammonium bicarbonate as starting material;

(ii) calcination of the cerium carbonate particles obtained in step (i) at 350 to 450 °C for 20 to 25 hours;

(iii) calcination of the calcined cerium carbonate particles obtained in step (ii) at 700 to 1000 °C for 0.5 to 20 hours;

(iv) grinding of the cerium oxide particles obtained in step (iii).

FIGURES

Figure 1: SEM picture of the particles obtained in Comparative Example 1

Figure 2: SEM picture of the particle obtained in Example 1

Figure 3: SEM picture of the particle obtained in Comparative Example 2

Figure 4: schematic top view of a substrate after polishing showing the 12 region locations inspected for the defectuosity evaluation in the examples

DETAILED DESCRIPTION OF THE INVENTION

Before the issues of the invention are described in detail, the following should be considered:

As used herein, the singular forms "a", "an", and "the" include both singular and plural referents unless the context clearly dictates otherwise. By way of example, "a compound" means one compound or more than one compound.

The terms "comprising", "comprises" and "comprised of" as used herein are synonymous with "including", "includes" or "containing", "contains", and are inclusive or open-ended and do not exclude additional, non-recited members, elements or method steps. It will be appreciated that the terms "comprising", "comprises" and "comprised of" as used herein comprise the terms "consisting of", "consists" and "consists of".

Throughout this application, the term "about" is used to indicate that a value includes the standard deviation of error for the device or method being employed to determine the value.

As used herein, the term "average" refers to number average unless indicated otherwise.

As used herein, the terms "% by weight", "wt.-%", "weight percentage", or "percentage by weight", and the terms "% by volume", "vol.-%", "volume percentage", or "percentage by volume", are used interchangeably.

The recitation of numerical ranges by end points includes all integer numbers and, where appropriate, fractions subsumed within that range (e.g. 1 to 5 can include 1, 2, 3, 4 when referring to, for example, a number of elements, and can also include 1.5, 2, 2.75 and 3.80, when referring to, for example, measurements). The recitation of end points also includes the end point values themselves (e.g., from 1.0 to 5.0 includes both 1.0 and 5.0). Any numerical range recited herein is intended to include all sub-ranges subsumed therein.

The expression “dispersion” used herein denotes a system consisting of solid fine secondary cerium oxide particles of the invention, stably dispersed in a liquid medium, it being possible for said particles to also optionally contain residual amounts of bound or adsorbed ions such as, for example, nitrates or ammoniums.

Different parameters may be used to characterize the sizes and the distribution of sizes of the particles of the invention. The measurement methods for determining these properties are described in detail in the examples.

According to the invention, the cerium oxide (CeO_2) generally has a purity degree of at least 99.8% by weight with respect to the weight of the oxide. Cerium oxide is generally crystalline ceric oxide. Some impurities, other than cerium, may be present in the oxide. The impurities may stem from the raw materials or starting materials used in the process of preparation of the secondary cerium oxide particles. The total proportion of the impurities is generally lower than 0.2% by weight with respect to the particles of the invention. Residual nitrates are not considered as impurities in this application.

Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it may render a term unclear, the present description shall take precedence.

Unless otherwise defined, all terms used in disclosing the invention, including technical and scientific terms, have the meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. By means of further guidance, term definitions are included to better appreciate the teaching of the present invention.

In the following passages, different alternatives, embodiments and variants of the invention are defined in more detail. Each alternative and embodiment so defined may be combined with any other alternative and embodiment, and this for each variant unless clearly indicated to the contrary or clearly incompatible when the value range of a same parameter is disjoined. In particular, any feature indicated as being preferred or advantageous may be combined with any other feature or features indicated as being preferred or advantageous.

Furthermore, the particular features, structures or characteristics described in the present description may be combined in any suitable manner, as would be apparent to a person skilled in the art from this disclosure, in one or more embodiments. Furthermore, while some embodiments described herein include some but not other features included in other embodiments, combinations of features of different embodiments are meant to be within the scope of the

invention, and form different embodiments, as would be understood by those in the art.

The present invention refers to secondary cerium oxide particles having a secondary mean particle size of 100 nm or higher, determined by SEM, and wherein each secondary cerium oxide particle is an agglomerate of primary cerium oxide particles having a mean particle size of 30 to 50 nm, determined by TEM, and a crystallite size of 20 to 40 nm, determined by XRD.

The secondary cerium oxide particles of the invention can be flexibly deformed due to the pressure, which is generated by the polishing head used in the CMP process. It is believed that their cushioning properties due to the deforming of the particles result in a broaden contact between the particles and the substrate which enhances the chemical and physical effects of the CMP process contributing to higher removal rate while keeping low defectuosity.

According to the invention, due to the agglomeration of the primary particles as defined above the second cerium oxide particles are formed.

It is preferred that the primary particles have a mean particle size of 35 to 45 nm, more preferably of 38 to 42 nm, determined by TEM.

The crystallite size of the primary particles according to the invention is between 20 and 40 nm, preferably between 21 and 35, more preferably between 25 and 35 nm, determined by X-ray diffraction analysis (XRD).

The secondary cerium oxide particles formed by the primary particles of the invention have a secondary mean particle size of higher than 100 nm, more preferably of at least 120 nm, even more preferably of at least 140 nm, determined by scanning electron microscopy (SEM). Additionally, it is preferred that the secondary mean particle size is at most 300 nm, more preferably at most 200 nm, even more preferably at most 160 nm, determined by SEM.

The particular structure of the particles according to the invention results into a specific Hg porosity of the secondary cerium oxide particles; preferably the secondary cerium oxide particles of the invention have a pore volume, as measured by Hg porosity for pores between 2 and 300 nm, of 0.10 to 0.50 ml/g, more preferably of 0.15 to 0.30 ml/g, even more preferably of 0.20 to 0.28 ml/g. Without being bound by this theory, the inventors believe that such porosity enables a right compromise between the necessary hardness of the secondary particles for removing a suitable amount of material from the substrate and the limitation of the scratches on the substrate resulting from a suitable deformation of the secondary particles in the CMP process.

It is further preferred that the secondary cerium oxide particles have a nearly spherical form. In particular it is preferred that the particles have an average sphericity measured by image analysis of 0.70 or more, more preferably of 0.78 or more. The sphericity can be calculated based on the following formula:

$$4\pi*S/(L)^2,$$

where S is the projected area of the particle by SEM and L is the projected perimeter of the particle by SEM.

The sphericity can be notably determined by measuring on the pictures the values S and L on at least 80 particles, in particular at least 90 particles, more particularly on at least 100 particles.

The secondary cerium oxide particles of the invention may have an oxygen storage capacity of at least 80 µmol/g, preferably of at least 90 µmol/g determined by temperature programmed reduction. Preferably, the oxygen storage capacity is between 80 and 500 µmol/g, more preferably between 100 and 250 µmol/g.

The secondary cerium oxide particles of the invention may exhibit a specific surface area (BET) of 5 to 55 m^2/g, preferably of 10 to 50 m^2/g, more preferably of 15 to 45 m^2/g, even more preferably between 20 and 30 m^2/g, determined by using as measuring device Macsorb as described in the examples.

The secondary cerium oxide particles of the invention may exhibit a ratio of oxygen storage capacity to specific surface area (BET), named "OSC/SSA ratio", of at least 0.063 µmol/m^2, preferably of at least 5.00 µmol/m^2, more preferably of at least 6.00 µmol/m^2. The OSC/SSA ratio may notably range from 0.063 µmol/m^2 to 100 µmol/m^2, in particular from 5.00 µmol/m^2 to 25.00 µmol/m^2, more particularly from 6.00 µmol/m^2 to 10.00 µmol/m^2. The oxygen storage capacity is determined by temperature programmed reduction. The specific surface area is determined by the BET method. To this end, a device Macsorb as described in the examples can be used. The ratio OSC/SSA is representative of the surface reactivity of the cerium oxide particles. The higher this ratio is, the higher the surface reactivity will be. A high OSC/SSA then contributes in getting a high removal rate. Especially, a high OSC/SSA ratio indicates a high oxygen mobility normalized by the surface area. A higher oxygen mobility is the sign of a higher surface reactivity that will promote the interaction with the substrate and thus increase the removal rate.

Moreover, the secondary cerium oxide particles may in particular exhibit a hydrodynamic mean diameter (Dh) determined by dynamic light scattering (DLS) of 100 to 300 nm, preferably of 120 to 250 nm, more preferably of 150 to 200 nm, determined by the measurement method as described in the examples.

Laser diffraction may be used to characterize the secondary cerium oxide particles. The technique is detailed in the examples. For determining the median diameters of the secondary cerium oxide particles in powder form it is preferred to use as particle size analyser. An analyser of type Horiba, such as Horiba LA-920, can notably be used.

The secondary cerium oxide particles of the invention may thus exhibit at least one or any combinations of the following features:

- median diameter D50 of 70 to 250 nm, more preferably of 90 to 200 nm, even more preferably of 95 to 180 nm;
- diameter D10 of 50 to 150 nm, more preferably of 60 to 120 nm, even more preferably of 80 to 110 nm; and/or
- diameter D90 of 80 to 400 nm, more preferably of 90 to 300 nm, even more preferably of 100 to 250 nm.

It is additionally preferred that the secondary cerium oxide particles have a dispersion index σ/m of lower than 0.50, preferably of lower than 0.45, wherein σ/m = (D90-D10)/(2D50) and the D10, D50 and D90 are determined by laser diffraction as described in the examples.

Furthermore, it is preferred that the secondary cerium oxide particles having a surface nitrate adsorption mol ratio of 0.020 to 0.050, more preferably of 0.030 to 0.040, even more preferably of 0.035 to 0.038, determined as described in the examples.

The secondary cerium oxide particles as described above may be used in dispersion.

The dispersion according to the invention comprises in addition to the secondary cerium oxide particles of the invention a liquid medium.

The liquid medium may be water or a mixture of water and a water-miscible organic liquid. The water-miscible organic liquid should not make the secondary cerium oxide particles precipitate or agglomerate. The water-miscible organic liquid may for instance be an alcohol like isopropyl alcohol, ethanol, 1-propanol, methanol, 1-hexanol; a ketone like acetone, diacetone alcohol, methyl ethyl ketone; an ester like ethyl formate, propyl formate, ethyl acetate, methyl acetate, methyl lactate, butyl lactate, ethyl lactate. The proportion water / organic liquid may be between 80/20 to 99/1 (w/w).

The proportion of secondary cerium oxide particles in the dispersion may be comprised between 0.2 wt.-% and 40.0 wt.-%, this proportion being expressed as the weight of the secondary cerium oxide particles over the total weight of the dispersion. This proportion may be comprised between 10.0 wt.-% and 35.0 wt.-

%. According to one embodiment wherein the dispersion is a polishing composition, the proportion of secondary cerium oxide particles in the dispersion may be more particularly comprised between 0.2 wt.-% and 5.0 wt.-%, this proportion being expressed as the weight of the secondary cerium oxide particles over the total weight of the polishing composition.

The secondary cerium oxide particles of the invention or a dispersion thereof as described above may be used to prepare a polishing composition, more particularly a CMP composition. They may be used as a component of a polishing composition, more particularly a CMP composition.

A CMP composition (or chemical-mechanical polishing composition) is a polishing composition used for the selective removal of material from the surface of a substrate. It is used in the field of integrated circuits and other electronic devices. Indeed, in the fabrication of integrated circuits and other electronic devices, multiple layers of conducting, semiconducting, and dielectric materials are deposited onto or removed from the surface of a substrate. As layers of materials are sequentially deposited onto and removed from the substrate, the uppermost surface of the substrate may become nonplanar and require planarization. Planarizing a surface (or "polishing") the surface, is a process where material is removed from the surface of the substrate to form a generally even, planar surface. Planarization is useful in removing undesired surface topography and surface defects, such as rough surfaces, agglomerated materials, crystal lattice damage, scratches, and contaminated layers or materials. Planarization also is useful in forming features on a substrate by removing excess deposited material used to fill the features and to provide an even surface for subsequent levels of metallization and processing.

The substrate that can be polished with a polishing composition or a CMP composition may be for instance a silicon dioxide-type substrates, glass, a semi-conductor or a wafer.

The polishing composition or the CMP composition usually contains different ingredients other than the secondary cerium oxide particles according to the invention. The polishing composition may comprise one or more of the following ingredients:

- abrasive particles other than the secondary cerium oxide particles according to the invention (herein referred to as "additional abrasive particles"); and/or
- a pH regulator; and/or
- a surfactant; and/or

- a rheological control agent, including viscosity enhancing agents and coagulants; and/or

- an additive selected from an anionic copolymer of a carboxylic acid monomer, a sulfonated monomer, or a phosphonated monomer, and an acrylate, a polyvinylpyrrolidone, or a polyvinylalcohol (e.g., a copolymer of 2-hydroxyethylmethacrylic acid and methacrylic acid); a nonionic polymer, wherein the nonionic polymer is polyvinylpyrrolidone or polyethylene glycol; a silane, wherein the silane is an amino silane, an ureido silane, or a glycidyl silane; an N-oxide of a functionalized pyridine (e.g. picolinic acid N-oxide); a starch; a cyclodextrin (e.g., alpha-cyclodextrin or beta-cyclodextrin), and combinations thereof.

The pH of the polishing composition of the invention is generally comprised between 1 and 8. Typically, the polishing composition has a pH of 3.0 or greater. Also, the pH of the polishing composition typically is 7.0 or less.

The dispersions of the present invention may notably be incorporated in the polishing compositions disclosed in the following documents: WO 2013/067696; WO 2016/140968; WO 2016/141259; WO 2016/141260; WO 2016/047725; WO 2016/006553; WO 2021/081176; WO 2021/081171; WO 2021/081162; WO 2021/081148; WO 2021/081153; WO 2021/081145.

The invention also relates to a method of removing a portion of a substrate, comprising polishing the substrate with a polishing composition such as described above.

The polishing composition according to the invention preferably has a removal rate of at least 75 nm/min, preferably of at least 80 nm/min. It can be measured according to the method described in the examples.

The secondary cerium oxide particles of the invention and as described above can be obtained by a preparation method, which comprises the following steps:

(i) Precipitation of cerium carbonate by using cerium nitrate and ammonium bicarbonate as starting material;

(ii) calcination of the cerium carbonate particles obtained in step (i) at 350 to 450 °C for 20 to 25 hours;

(iii) calcination of the calcined cerium carbonate particles obtained in step (ii) at 700 to 1000 °C for 0.5 to 20 hours;

(iv) grinding of the cerium oxide particles obtained in step (iii).

It is preferred that the mixture of cerium nitrate and ammonium bicarbonate obtained in step (i) of the method of the invention is heat treated at a temperature of 100 to 150 °C for a period of 2 to 6 hours. Furthermore, according the invention after grinding the cerium oxide particles obtained in step (iii) the particles may be put in dispersion and optionally desagglomerated. This last step may notably be carried out by a milling, a double jet treatment or a ultrasonic desagglomeration.

The preparation method of the invention, notably the two successive calcination steps (ii) and (iii) of the cerium carbonate particles, in particular the specific temperature conditions and calcination times used therein, ensure that homogeneous sized secondary cerium oxide particles of the invention with controlled microstructure can be obtained after milling.

It is preferred that the first calcination step (ii) is carried out at 380 to 420 °C, more preferably at 390 to 400 °C for 20 to 25 hours, preferably for 22 hours.

Furthermore, it is preferred that the second calcination step (iii) is carried out at a temperature of 700 to 1000 °C, more preferably of 720 to 900 °C, even more preferably oft 750 °C to 850 °C, in particular preferred of 770 to 800 °C for 0.5 to 20 hours, more preferably of for 1.0 to 15 hours, even more preferably for 2.0 to 11 hours, in particular preferred for 5 to 10 hours.

According to the invention, in a first step (i) of the preparation method a cerium nitrate is mixed with an ammonium bicarbonate, preferably a cerium nitrate aqueous solution is mixed with an aqueous ammonium bicarbonate solution. Accordingly, a precipitate of cerium carbonate is obtained.

Preferably an aqueous cerium nitrate solution is prepared and the aqueous ammonium bicarbonate solution is added to the prepared cerium nitrate solution. According to an alternative, as well preferred, embodiment, the aqueous cerium nitrate solution is added to the aqueous ammonium bicarbonate solution. It is further preferred that the cerium nitrate used therein has a high purity, preferably of at least 99.9 %.

The concentration of the aqueous cerium nitrate solution is preferably in the range of 150 to 450 g/l, more preferably from 180 to 400 g/l, even more preferably from 200 to 350 g/l, in equivalent of cerium oxide, the concentration of the ammonium bicarbonate aqueous solution is preferably from 100 to 400 g/l, preferably from 120 to 400 g/l, in particular from 300 to 400 g/l, particularly preferably 320 to 380 g/l. Further mixing ratio of the aqueous solution of cerium nitrate and ammonium bicarbonate aqueous solution, in a weight ratio of cerium nitrate and ammonium bicarbonate contained in the aqueous solution is preferably in the range of 1.4 to 3.0. In this case cerium carbonate salts obtained are, for

example, $Ce_2(CO_3)_3$ x H_2O and the like. Then the cerium carbonate salt precipitates.

According to one particular embodiment, the medium from step (i) is further subjected to heat treatment in the temperature range of 100 to 150 °C, more preferably of 120 to 140 °C, even more preferably of 132 to 136 °C, for a period of 2 to 6 hours, preferably from 3 to 6 hours, more preferably from 3 to 5 hours, even more preferably from 3 to 4 hours. In an alternative embodiment it can be of 5 to 6 hours.

The precipitated cerium carbonate is calcined under conditions as defined above. After the two calcination steps (ii) and (iii) are conducted the obtained cerium oxide particles are grinded to obtain the secondary cerium oxide particles according to the invention. The grinding of the powder can be carried out by any method usually used in the field of the invention. Preferably, the particles obtained after step (iii) of the method of the invention are ground in a hammer mill or a blender. A high speed, like 20000 to 25000 rpm, for a short time, like 30 to 90 seconds may be used in the case of a blender.

The present invention is further illustrated by the following examples. It should be understood that the following examples are for illustration purposes only and are not used to limit the present invention thereto.

Examples

1. Measurement of the properties of the particles and compositions thereof

1.1 *Crystallite Size*

The crystallite size of the primary particles can be obtained by X-ray powder diffraction (XRD) by the Scherrer equation as usually used in the technical field of the invention:

$$B(2\theta) = \frac{K\lambda}{D\ cos\theta}$$

where

θ is the Bragg angle in radian,

β is the line broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening, in radians,

λ is the X-ray wavelength,

D is the size of the crystallites

K is a dimensionless shape factor, usually fixed to 0.9

The Scherrer equation is applied to the most intense peak located between 2θ =27 and 29°.

1.2 *Mean Particle sizes*

The mean primary particle size may be determined by pictures obtained by TEM (transmission electronic microscopy). The observation of the pictures must be made with a magnitude and an appliance which makes it possible to identify clearly the shape of the particles. It is therefore preferable to clearly distinguish the particles individually. The primary particle size is the average size of the primary particles such as measured on a high number of particles, being of at least 80, preferably at least 90, more preferably at least 100, to get a statistical analysis. The magnitude used for the observation may for instance range from 30K to 300K. The model JEM 1400 from Jeol operating at 120 kV is especially suitable.

The mean secondary particle size may be determined by pictures obtained by SEM (scanning electron microscopy). The observation of the pictures must be made with a magnitude and an appliance which makes it possible to identify clearly the shape of the particles. It is therefore preferable to clearly distinguish the particles individually. The magnitude used for the observation may for instance range from x40 000 to x500 000. A field emission-type SEM S-5500 of Hitachi High Technologies Corporation may be used.

1.3 *Mean Diameters (D10, D50 and D90)*

Laser diffraction may also be used to determine the distribution of sizes of the particles. A laser particle sizer like Horiba LA-910, 920 or 960 may be used following the guidelines of the constructor. For the measurement, a relative refractive index of 1.7 may be used. From the distribution in volume obtained by laser diffraction, various parameters usually used in statistics like D10, D50, and D90 and dispersion index may be deducted.

D10 is the diameter determined from a distribution obtained by laser diffraction for which 10% in volume of the particles have a diameter of less than D10.

D50 is the median diameter determined from a distribution obtained by laser diffraction.

D90 is the diameter determined from a distribution obtained by laser diffraction for which 90% in volume of the particles have a diameter of less than D90.

The "dispersion index" is defined by the following formula $\sigma/m = (D90-D10)/(2D50)$.

1.4 *Specific Surface Area (BET)*

The specific surface area of the particles may be determined on a powder by adsorption of nitrogen by the Brunauer-Emmett-Teller method (BET method). The method is disclosed in standard ASTM D 3663-03 (reapproved 2015). The method is also described in the periodical "The Journal of the American chemical Society, 60, 309 (1938)". The specific surface area may be determined by using the measuring device Macsorb manufactured by Mountec, the sample is placed in a glass cell, set in an apparatus, dried in a nitrogen atmosphere at 210 °C for 30 minutes immediately before measurement, and then measured for BET specific surface area.

1.5 *Hg porosity*

The Hg porosity is determined with an Autopore IV9510 analyzer.

The porosity was obtained with an autopore IV 9510 Automatic Mercury Porosimeter following the guidelines of the constructor and after a pretreatment at 210°C for 30 min. The sample size was around 0.2 grams, the mercury contact angle was 130°, the mercury surface tension was 485 dyn/cm. From the obtained data, the data in connection with a pore size range of 2 to 300 nm was selected to calculate the corresponding pore volume.

1.6 *Hydrodynamic Mean Diameter (Dh)*

The hydrodynamic mean diameter can be determined by dynamic light scattering (DLS). This technique allows measurement of the hydrodynamic mean diameter Dh of the solid objects, the value of which is affected by the presence of aggregates of particles. Therefore, the measurement is usually performed on a dispersion of the particles in water. Dh is determined with the appliance Zetasizer Nano-ZS of Malvern following the guidelines of the constructor. The sample usually needs to be diluted in deionized water. A dilution factor of x30 000 may be applied.

1.7 *Sphericity*

Sphericity is calculated based on the following formula:

$$4\pi*S/(L)^2,$$

where S is the projected area of the particle by SEM and L is the projected perimeter of the particle by SEM.

The sphericity is determined by measuring on the pictures the values S and L on 100 particles.

1.8 *Oxygen Storage Capacity*

The oxygen storage capacity of the particles can be measured by temperature programmed reduction (TPR).

The oxygen storage capacity (OSC) is an index by which capacity of oxygen released from the particles surface and bulk can be quantified. The OSC is obtained with a temperature programmed reduction analyzer, BELCATII, manufactured by MicrotracBEL Corp. with a carrier gas containing by volume 90% argon and 10% hydrogen, at a gas flow rate of 30 ml/min. The heating rate of the sample (0.5 g) is 10 °C / min.

1.9 *Surface nitrate adsorption*

The surface nitrate adsorption amount can be measured by following method:

- Preparing 55g of a 3 wt.% diluted slurry in 100 ml beaker by dispersing the original powder or diluting the original slurry in deionized water and agitate it for 1 min;
- Adjusting the slurry at pH 5 with 0.01M NaOH;
- Adjusting the slurry from pH 5 to 9 w/ 0.01M NaOH; and
- Calculating the surface nitrate amount from the titration amount adjusted from pH 5 to 9.

1.10 *pH-value*

The pH value of the polishing composition at 25°C is a value measured using a pH meter (manufactured by Toa Denpa Kogyo Co., Ltd., "HM-30G"). It is the value after 1 minute from immersing the electrode of the pH meter in the polishing liquid composition.

1.11 *Nature of the particles obtained*

For each example and comparative example a X-ray diffractogram of the powder is prepared to confirm the signature of the crystalline CeO_2 (sheet ASTM 34-394).

2. Preparation of the particles

2.1 *Comparative Example 1*

A high-purity cerium nitrate salt (99.9 % pure) was dissolved with water to prepare 1l of an aqueous cerium nitrate solution having a concentration of 50 g/l in terms of cerium oxide. This solution was added into 1 l of an aqueous solution of ammonium bicarbonate having a concentration of 150 g/l and mixed therewith to obtain 2300 g of a slurry of a cerium carbonate precipitate. The precipitate was subjected to a treatment at 135 °C for 1 hour. The resulting mixture was calcined at 300 °C for 4 hours to give 50 g of cerium oxide powder having a specific surface of 100.9 m^2/g. A second calcination was performed at 800°C for 0.25 hours to obtain cerium oxide powder exhibiting a specific surface area of 32.9 m^2/g.

2.2 *Comparative Example 2*

A dilute of cerium nitrate is prepared by adding 567g of 2.917 M trivalent cerium nitrate solution, 204.0 mg of a 35.5 wt.-% H_2O_2 solution and 1321.1g of deionized water. This solution, which has an H_2O_2/Ce molar ratio of 1/450, is loaded into a semi-closed reservoir and then degassed with vigorous agitation and with nitrogen bubbling for 2 hours. A dilute solution of aqueous ammonia is prepared by adding 1249.0 g of deionized water and a solution of 360.1 g of 27.1% aqueous ammonia. This solution is loaded into a semi-closed 3l jacketed reactor and then subjected to agitation (stirrer with three swept blades at 300 rpm) and nitrogen bubbling for 2 hours. The temperature of the reaction mixture is then increased to 80° C. in approximately ¾ hour and then maintained at this temperature for 4 h under nitrogen sweeping and agitation (the agitation speed was increased from 300 rpm to 450 rpm after 25 min due to gelation). At the end of this heat treatment, the reaction mixture is left to cool and is then acidified to pH 2 by adding 68% nitric acid. The nitrogen sweeping is stopped, and the suspension is finally washed by Nutsche filtration, elimination of the filtration water and resuspension of the cake in deionized water. Several cycles of washing by filtration with deionized water are carried out until a conductivity of less 0.5 mS/cm is obtained. The suspension finally obtained is adjusted to 9 wt.-% with respect to CeO_2. The suspension is observed by SEM (see Figure 3). The particles are in the form of separated and independent primary cerium oxide particles. This is consistent with the fact the mean size of the secondary cerium oxide particles and the mean size of the primary cerium oxide particles that were measured are very close (see table 1).

Part of the suspension is dried in an incubator at 200° C to get a CeO_2 powder for XRD analysis.

2.3 *Example 1* (inventive)

161.2 mL of a trivalent cerium nitrate solution containing 48.4 g in terms of CeO_2 was prepared in a 500 ml beaker. 638.8 ml of NH_4HCO_3 aqueous solution containing 82.4 g in terms of NH_4HCO_3 was prepared in a 1 l semi-closed reactor. The above-described cerium nitrate solution was mixed with the NH_4HCO_3 aqueous solution in approximately 1 h under agitation. The reaction mixture thus obtained was diluted with deionized water to leach the volume of 1 l, and then introduced into the autoclave. The reaction mixture was heated up to 135°C in approximately 2 hours and maintained for approximately 3.5 hours under agitation. The reaction mixture was cooled and filtered by nutsche filtration to obtain filtered cake. The filtered cake was calcined at 400°C for 22 hours, followed by 775°C for 8 hours, and ground using a blender at 22500 rpm for 1 minute, to obtain CeO_2 powder.

Dispersion preparation:

For the DLS measurement, a slurry of the CeO_2 particles was prepared by adding 285 ml of an aqueous solution of nitric acid at pH 4 to 15 g of the CeO_2 powder prepared in Example 1. This slurry was wet milled with φ5mm zirconia beads and passed through 25 μm sieves.

Dried powder after dispersion:

For the second BET measurement, the dispersion was dried in an oven at a temperature of 200°C for a duration of 15 hours so as to obtain a dried powder of the CeO_2 particles.

The physical properties of the particles obtained in Comparative Example 1 and in Example 1 are indicated in the attached table. “SSA” stands for “specific surface area”, as measured by the BET method; OSC stands for Oxygen Storage Capacity; OSC/SSA is the ratio of the two.

		Property		Comp. Example 1	Comp. Example 2	Example 1
Primary particle		crystallite size (XRD)	[nm]	20	30.0	29.0
		Primary mean size (TEM)	[nm]	19	30.0	41
Secondary particle	Powder	secondary mean size (SEM)	[nm]	515.6	31.0	146.5
		D10 (laser diffraction LA-920)	[µm]	0.34	0.09	0.10
		D50 (laser diffraction LA-920)	[µm]	0.93	0.14	0.15
		D90 (laser diffraction LA-920)	[µm]	2.64	8.00	0.22
		σ/m	[-]	1.23	28.04	0.40
		Sphericity	[-]	0.67	0.91	0.80
		SSA (BET)	[m^2/g]	32.9	35.2	21.8
		Hg porosity between 2 and 300 nm pores	[ml/g]	0.06	0.15	0.26
		Oxygen Storage Capacity	[µmol/g]	140.26	147.87	136.22
		OSC/SSA	[µmol/m^2]	4.26	4.20	6.25
		Surface nitrate adsorption	[mol ratio]	0.068	0.106	0.035
	Dispersion	Dh (DLS)	[nm]	552	96	153
	Dried powder after dispersion	SSA (BET)	[m^2/g]	47.6	35.2	29.5

Table 1

3. Polishing Test

Preparation of the slurries: the slurry of the CeO_2 particles was prepared by adding 285 ml of an aqueous solution of nitric acid at pH 4 to 15 g of the CeO_2 powder prepared in Example 1. This slurry was wet milled with φ5mm zirconia beads and passed through 25 µm sieves.

A slurry of the particle of Comparative Example 1 was prepared in a similar manner. The slurry of the particles of Comparative Example 2 was used as it is.

For the polishing tests, the concentration was adjusted to 1 wt.-% and the pH was set at 6 by addition of aqueous ammonia. The polishing machine used was a Struers Tegramin-25. The surface to be polished was made of amorphous silica. The pad was cleaned with deionized water before polishing. The suspension was introduced on the surface to be polished under a controlled flow-rate.

- pressure applied on the head: 40N
- rotation speed: 150 rpm
- pad: neoprene (MD-Chem) - new pad for every dispersion tested
- flow-rate of the dispersion: 6/20 (Internal scale of the polisher)
- dispersion: amount of cerium oxide particles of 1 wt.-%
- pH of the dispersion: 6 (obtained by addition of diluted NH_4OH)
- density of the substrate: 2.2 g/cm^3
- radius of the substrate: 2 cm
- polishing time: 20 minutes

The loss of weight of the substrate was recorded. The first polishing run is considered as preparation of the pad, and only the second and the third runs are used for the calculations. The final weight loss value being the mean value of the second and third polishing runs. The removal rate (RR) expressed in nm/min was then calculated as:

$$RR = \frac{\Delta m \cdot 10^4}{\pi . R^2 . \rho . \Delta t}$$

wherein:

- Δm is the weight loss of the substrate;
- R radius of the substrate;
- ρ density of the substrate;
- Δt polishing time.

The calculated removal rate of the secondary cerium oxide particles according to the invention and from the comparative examples 1 and 2 is given in the table below:

	Example 1	Comp. Example 1	Comp. Example 2
Removal rate [nm/min]	84	48	3

Table 2

4. Defectuosity

At the end of the polishing test, the defectuosity is evaluated by counting the number of scratches observed on the surface of each polished substrate.

The polished surface is examined using Scanning Electron Microscopy (SEM) equipped with a Field Emission Gun (FEG) source. The instrument used is an Ultra55 from Zeiss. Images with a resolution of 1024x768 pixels and a pixel size of 19.53 nm are captured using an in-lens secondary electron detector, operating at an acceleration voltage of 0.5 V and a working distance in the range of 2 - 3 mm. For each sample, 12 regions are imaged, distributed evenly according to the layout shown in Figure 4.

The number of scratches per imaged region is counted. The total number of scratches per sample is determined as the sum of scratches across the 12 imaged regions.

	Example 1	Comp. Example 1	Comp. Example 2
Total number of scratches	28	135	33

Table 3

CLAIMS

1. Secondary cerium oxide particles having a secondary mean particle size of 100 nm or higher, determined by SEM, and wherein each secondary cerium oxide particle is an agglomerate of primary cerium oxide particles having a mean particle size of 30 to 50 nm, determined by TEM, and a crystallite size of 20 to 40 nm, determined by XRD.

2. The secondary cerium oxide particles according to claim 1, wherein the secondary cerium oxide particles have a pore volume, as measured by Hg porosity for pores between 2 and 300 nm, of 0.10 to 0.50 ml/g.

3. The secondary cerium oxide particles according to claim 1 or 2, wherein the secondary cerium oxide particles have a specific surface area (BET) of 5 to 55 m^2/g.

4. The secondary cerium oxide particles according to any one of the preceding claims, wherein the secondary cerium oxide particles have a ratio of oxygen storage capacity to specific surface area (BET) of at least 5.00 $\mu mol/m^2$, wherein the oxygen storage capacity is determined by temperature programmed reduction.

5. The secondary cerium oxide particles according to any one the preceding claims, wherein the secondary cerium oxide particles have hydrodynamic mean diameter Dh of 100 to 300 nm, determined in dispersion by dynamic light scattering.

6. The secondary cerium oxide particles according to any one of the preceding claims, wherein the secondary cerium oxide particles have an average sphericity of 0.70 or more, determined by image analysis.

7. The secondary cerium oxide particles according to any one of the preceding claims, wherein the secondary cerium oxide particles have a median diameter D50 of 70 to 250 nm, determined by laser diffraction.

8. The secondary cerium oxide particles according to any one of the preceding claims, wherein the secondary cerium oxide particles have a diameter D10 of 50 to 150 nm, determined by laser diffraction.

9. The secondary cerium oxide particles according to any one of the preceding claims, wherein the secondary cerium oxide particles have a diameter D90 of 80 to 400 nm, determined by laser diffraction.

10. The secondary cerium oxide particles according to any one of the preceding claims, wherein the secondary cerium oxide particles have a dispersion index σ/m of lower than 0.50, preferably of lower than 0.45.

11. The secondary cerium oxide particle according to any one of the preceding claims, wherein the secondary cerium oxide particles having a surface nitrate adsorption mol ratio of 0.020 to 0.050.

12. Dispersion of the secondary cerium oxide particles according to any one of claims 1 to 11.

13. Use of the secondary cerium oxide particles according to claims 1 to 11 or the dispersion according to claim 12 for the preparation of a polishing composition, preferably a chemical mechanical polishing composition.

14. Polishing composition comprising the secondary cerium oxide particles according to claims 1 to 11 or the dispersion according to claim 12.

15. Polishing composition according to claim 14, further comprising one or more of the following ingredients: abrasive particles other than the secondary cerium oxide particles according to any one of claims 1 to 11; and/or a pH regulator; and/or a surfactant; and/or a rheological control agent, including viscosity enhancing agents and coagulants; and/or an additive selected from an additive selected from an anionic copolymer of a carboxylic acid monomer, a sulfonated monomer, or a phosphonated monomer, and an acrylate, a polyvinylpyrrolidone, or a polyvinylalcohol; a nonionic polymer, wherein the nonionic polymer is polyvinylpyrrolidone or polyethylene glycol; a silane, wherein the silane is an amino silane, an ureido silane, or a

glycidyl silane; an N-oxide of a functionalized pyridine; a starch; a cyclodextrin, and combinations thereof.

16. Method for preparing the secondary cerium oxide particles according to any one of claims 1 to 11, wherein the method comprises the following steps:

(i) Precipitation of cerium carbonate by using cerium nitrate and ammonium bicarbonate as starting material;
(ii) calcination of the cerium carbonate particles obtained in step (i) at 350 to 450 °C for 20 to 25 hours;
(iii) calcination of the calcined cerium carbonate particles obtained in step (ii) at 700 to 1000 °C for 0.5 to 20 hours;
(iv) grinding of the cerium oxide particles obtained in step (iii).