A Preparation method and system of cerium acetate

Chinese patent : C07C51/412 Preparation of salts of carboxylic acids by conversion of the acids, their salts, esters or anhydrides with the same carboxylic acid part

Abstract

The invention relates to a preparation method of cerium acetate, which comprises the following steps: completely dissolving cerous carbonate into a cerium nitrate solution by using nitric acid, and regulating the pH value and temperature to perform hydrolysis and impurity removal; filtering the obtained cerium nitrate solution for purification; and converting the purified cerium nitrate solution into refined cerous carbonate by using ammonium bicarbonate as a conversion agent, transforming and crystallizing by acetic acid to obtain cerium acetate, filtering, and drying to obtain the cerium acetate product. The cerium acetate product prepared by the method has high purity, and the rare-earth purity is greater than 99.99%. The non-rare-earth impurity content is low and is generally less than 10 ppm. The Cl<-> content is less than 10 ppm, and the SO4<2-> content is less than 10 ppm.

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Cerium acetate some examples of use

Cerium(III) acetate is used in combination with bromide ion, catalyzes the liquid-phase auto-oxidation of cresols. It is used in glass manufacturing, glass Polishing, optical Glass making and polishing, pigments, pharma, Speciality chemicals electronic, oaint and driers, dyes and pigments, paper industries etc.

Polishing agent: Cerium (III) Acetate is utilized as a polishing agent for glass, metals, and semiconductors. It is found in various commercial products such as lens cleaners, abrasives, and polishing compounds.

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Application of lanthanum acetate and cerium acetate and preparation method of aqueous ecological synthetic leather wet-process bass

1 Abstract

The lanthanum acetate and the cerium acetate are used as coagulants of resin slurry of the water-based ecological synthetic leather, can convert combined water molecules in resin into free water, leave a plurality of fine pore structures in a polyurethane film after being heated and volatilized, and improve the air permeability of the synthetic leather.

2 Full Text

Espacenet

https://worldwide.espacenet.com/publicationDetails/biblio?FT=D&locale=en_EP&CC=CN&NR=109680507B&KC=B

Google

https://patents.google.com/patent/CN109680507B

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Catalysis

US patent 723871 (1991)

The invention relates to concentrated water solu-ble organic salts of the lanthanides, particularly thecerium salts which are useful in the production ofexhaust emission reduction catalysts. The preferredcompositions comprise cerium acetate with gluconicacid and excess acetic acid.

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polishing powder for glass   Patent : EP0266233A1

Process for polishing organical glass with a polishing composition based on cerium

Abstract

The subject of the present invention is a cerium-based polishing composition intended for polishing organic glasses. The polishing composition of the invention is characterized in that it comprises ceric oxide and a cerous salt soluble under the polishing conditions. It is particularly well suited to the pleating of ophthalmic lenses made of organic materials.

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Cerium acetate to get special CeO2 suitable for wafer polishing (electronic industry)

Taiwan Application Serial Number 103131595, filed Sep. 12, 2014

METHOD OF MANUFACTURING CERIUM DIOXIDE POWDER AND CERIUM DIOXIDE POWDER used as a Polishing powder for electronic industry

A method of manufacturing a cerium dioxide powder is provided. The method includes mixing a cerium salt, an amine and solvent to form a mixed solution, in which the amine includes a secondary amine, a tertiary amine or a combination thereof, and the tertiary amine is selected from the group consisting of hexamethylenetetramine, triethylenediamine and a combination thereof. A solvothermal reaction of the mixed solution is performed to form the cerium dioxide powder. The cerium dioxide powder manufactured by the method is also provided herein.

BACKGROUND

In a very large scale integration (VLSI) process technique, removing unevenness of a surface of a wafer is necessary

since wafer size and an amount of metal layers are increased, and transistors and metal wires continuously toward miniaturization.

Chemical mechanical polishing is a planarization technique often used in semiconductor processes, which is to place the wafer between a carrier/head and a rotating table with a polishing pad on a surface of the rotating table. Next, a polishing agent is sprayed over the surface of the wafer, and convex portions of a deposited layer over the wafer is polished to form a planar surface through interaction of chemical etching and mechanical polishing. Currently, such technique is widely used in planarization processes of metal layers and low-k dielectric layers.

Cerium dioxide exhibits excellent abrasive property, and thus is widely applied in modern industry field. For example, in semiconductor processes, a relatively removal rate of cerium dioxide to silicon dioxide is quite great, and thus is suitable in the planarization process of insulating layers. In an optoelectionic field, such as liquid crystal display (LCD), cerium dioxide possesses excellent abrasive effect to mother glass and thus is widely applied. However, the component and the physical property of the polishing slurry, such as particle size and dispersity, should be precisely controlled to effectively control polishing rate to obtain an ideal planar surface.

Currently, a variety of processes can be used to synthesize cerium dioxide. However, the cerium dioxide polishing powder should have an average particle size in a range of 1 nm to 200 nm and good dispersity. The powder with larger particle size can increase polishing rate, and the powder with good dispersity can avoid powder agglomeration and thus to extend available time of polishng liquid. However, the cerium dioxide powder formed using current processes cannot have all of the properties mentioned above. Therefore, there is a need of a novel method of manufacturing the cerium dioxide powder to have all of the properties mentioned above.

DETAILED DESCRIPTION

The following embodiments are disclosed with accompanying diagrams for detailed description. For illustration clarity, many details of practice are explained in the following descriptions. However, it should be understood that these details of practice do not intend to limit the present disclosure. That is, these details of practice are not necessary in parts of embodiments of the present disclosure.

Chemical mechanical polishing technique is a planarization process relied by each semiconductor plant. In the chemical mechanical polishing technique, mechanical polishing is coordinated with chemical polishing solution to oxidize protruding portions of a deposited layer over a surface of a wafer to form a soften oxide layer and then to be planarized, and thus to form a planar surface to a subsequent circuit layer. Since a cerium dioxide powder exhibits excellent abrasive property, it can be used in the planarization process of semiconductor processes. However, the cerium dioxide should have an average particle size in a range of 1 nm to 200 nm and good dispersity to effectively control polishing rate. Therefore, an aspect of the present disclosure provides a method of manufacturing a cerium dioxide powder to form the cerium dioxide powder with an average particle size in a range of 1 nm to 200 nm and good dispersity. An average particle size of the cerium dioxide powder is in a range of 2 nm to 150 nm. An average particle size of the cerium dioxide powder is in a range of 3 nm to 100 nm.

The manufacturing method includes mixing a cerium salt, an amine and solvent to form a mixed solution. The cerium

salt may be any cerium salt able to be dissolved in a solvent. The cerium salt may be cerium nitrate, cerium chloride, cerium sulfate, cerium carboxylate (e.g., cerium acetate), hydrate of above-mentioned cerium salt or a combination thereof. In some embodiments, the cerium salt includes cerium carboxylate. In some embodiments, the cerium carboxylate includes cerium acetate. The solvent includes water, alcohols, esters, ethers or a combination thereof. Other solvent, which can fully or partially dissolve the cerium salt, can also be used. A pH value of the solvent can be adjusted using acid or base. For example, the cerium salt can be firstly dissolved in water or alcohols to form a cerium ion solution, and the amine is then added into the cerium ion solution. Subsequently, a solvothermal reaction of the mixed solution is performed to form the cerium dioxide powder. The solvothermal method is used to let small nuclei grow and thus to form particles with larger particle size. Generally, small particles are easily synthesized, but larger particles with high crystallinity are difficultly synthesized. Therefore, the amine is used as a basic substance in the mixing step mentioned above in the present diclosure. When the amine is added into the cerium ion solution, a weak base environment is gradually formed, and space steric hindrance is changed due to the presence of the amine, and thus to form the cerium dioxide with larger particle size in the solvothermal reaction.

In some embodiments, the amine includes a secondary amine, a tertiary amine or a combination thereof. In some embodiments, the secondary amine is diethylamine, N-ethylpropylamine, dipropylamine, N-methylethylamine, N-propylbutylamine, imidazole or a combination thereof. In some embodiments, a molar ratio of the cerium salt to the secondary amine is in a range of 10:1 to 1:20. If the molar ratio of the cerium salt to the secondary amine is greater than 10:1, yield will be declined. If the molar ratio of the cerium salt to the secondary amine is lower than 1:20, the basic source will be wasted and cost of waste liquid treatment will be increased.

In some embodiments, the tertiary amine includes bicyclic tertiary amine, polycyclic tertiary amine (e.g., tricyclic tertiary amine) or a combination thereof. In some embodiments, the tertiary amine includes bicyclic tertiary alkyl amine, polycyclic tertiary alkyl amine (e.g., tricyclic tertiary alkyl amine) or a combination thereof. In some embodiments, the tertiary amine is selected from the group consisting of hexamethylenetetramine, triethylenediamine and a combination thereof. In some embodiments, a molar ratio of the cerium salt to the tertiary amine is less than 1. In some embodiments, a molar ratio of the cerium salt to the tertiary amine is in a range of 1:2 to 1:8. In some embodiments, a molar ratio of the cerium salt to the tertiary amine is in a range of 1:3 to 1:7. In some embodiments, a molar ratio of the cerium salt to the tertiary amine is in a range of 1:4 to 1:6. In some embodiments, a concentration of the tertiary amine is in a range of 0.03 mol/L to 0.20 mol/L. In some embodiments, a concentration of the tertiary amine is in a range of 0.05 mol/L to 0.15 mol/L. In some embodiments, a concentration of the tertiary amine is in a range of 0.07 mol/L to 0.13 mol/L. In some embodiments, a concentration of the cerium salt is in a range of 0.01 mol/L to 0.03 mol/L.

Temperature, pressure and reaction time of the solvothermal reaction are also related to synthesis of the cerium dioxide. In some embodiments, performing the solvothermal reaction of the mixed solution is at a temperature in a range of 50° C. to 300° C. In some embodiments, performing the solvothermal reaction of the mixed solution is at a pressure in a range of 0.1 atm to 100 atm. In the aforementioned ranges of temperature and pressure, nucleation and

reaction of the cerium dioxide will occur. In some embodiments, the reaction may be in a range of 15 minutes to 12 hours. The solvothermal reaction may be performed in a closed or open system.

The present disclosure also provides a cerium dioxide powder for polishing, which is manufactured by the method mentioned above. In one specific embodiment, the cerium dioxide powder has an average particle size in a range of 1 nm to 200 nm. In some embodiments, the cerium dioxide powder has an average particle size in a range of 3 nm to 12 nm. In some embodiments, the cerium dioxide powder has an average particle size in a range of 5 nm to 10 nm. Such cerium dioxide powder is very suitable as the polishing powder in the chemical mechanical polishing process in semiconductor field since it possesses larger particle size and good dispersity.

Example 1

A cerium salt was dissolved in deionized water to form ion solution. Next, diethylamine (secondary amine) was added into the ion solution and stirred at ambient temperature. A molar ratio of the cerium salt to diethylamine was 5:2. After homogeneous mixing, the solution was placed and sealed in a solvothermal bottle made of Teflon, and solvothermal reaction was then performed at 110° C. and 2.7 atm with 25 minutes. After completion of the reaction, a compound sample was obtained. For X-ray diffraction pattern analysis, as shown in FIG. 1, the compound had five main diffraction peaks of (111), (220), (311), (200) and (222), which is consistent with ICDD No. 43-1002 and thus recognized as cerium dioxide with cubic fluorite structure. According to Scherrer Equation and measured half-height width of the (111) peak, the grain size was 10.2 nm. In addition, as shown in FIG. 2, the particle size of the cerium dioxide powder was in a range of about 8 nm to about 12 nm using a transmission electron microscope.

Comparative Example 1

A cerium salt was dissolved in deionized water to form ion solution. Next, butylamine (primary amine), which has the same molecular weight as diethylamine, was added into the ion solution and stirred at ambient temperature. A molar ratio of the cerium salt to butylamine was 5:2. After homogeneous mixing, the solution was placed and sealed in a solvothermal bottle made of Teflon, and solvothermal reaction was then performed at 110° C. and 2.7 atm with 25 minutes. After completion of the reaction, a compound sample was obtained. For X-ray diffraction pattern analysis, as shown in FIG. 3, the compound was recognized as cerium dioxide with cubic fluorite structure. According to Scherrer Equation and measured half-height width of the (111) peak, the grain size was 5.6 nm. As shown in FIG. 4, the particle size of the cerium dioxide powder was in a range of about 4 nm to about 7 nm using a transmission electron microscope. Compared to Example 1 using organic amine with the same molecular weight as the basic source, the synthesized cerium dioxide using secondary amine has larger particle size than that using primary amine.

Example 2

A cerium salt was dissolved in deionized water to form ion solution. Next, N-ethylpropylamine (secondary amine) was added into the ion solution and stirred at ambient temperature. A molar ratio of the cerium salt to N-ethylpropylamine was 5:2. After homogeneous mixing, the solution was placed and sealed in a solvothermal bottle made of Teflon, and solvothermal reaction was then performed at 105° C. and 2.5 atm with 20 minutes. After completion of the reaction, a compound sample was obtained. The compound was recognized as cerium dioxide with

cubic fluorite structure using X-ray diffraction pattern analysis. According to Scherrer Equation and measured half-height width of the (111) peak, the grain size was 12.8 nm. The particle size of the cerium dioxide powder was in a range of about 10 nm to about 13 nm using a transmission electron microscope.

Comparative Example 2

A cerium salt was dissolved in deionized water to form ion solution. Next, pentylamine (primary amine), which has the same molecular weight as N-ethylpropylamine, was added into the ion solution and stirred at ambient temperature. A molar ratio of the cerium salt to pentylamine was 5:2. After homogeneous mixing, the solution was placed and sealed in a solvothermal bottle made of Teflon, and solvothermal reaction was then performed at 105° C. and 2.5 atm with 20 minutes. After completion of the reaction, a compound sample was obtained. The compound was recognized as cerium dioxide with cubic fluorite structure using X-ray diffraction pattern analysis. According to Scherrer Equation and measured half-height width of the (111) peak, the grain size was 7.5 nm. The particle size of the cerium dioxide powder was in a range of about 4 nm to about 8 nm using a transmission electron microscope. Compared to Example 2 using organic amine with the same molecular weight as the basic source, the synthesized cerium dioxide using secondary amine has larger particle size than that using primary amine.

Example 3

A cerium salt was dissolved in deionized water to form ion solution. Next, dipropylamine (secondary amine) was added into the ion solution and stirred at ambient temperature. A molar ratio of the cerium salt to dipropylamine was 5:2. After homogeneous mixing, the solution was placed and sealed in a solvothermal bottle made of Teflon, and solvothermal reaction was then performed at 110° C. and 2.7 atm with 25 minutes. After completion of the reaction, a compound sample was obtained. The compound was recognized as cerium dioxide with cubic fluorite structure using X-ray diffraction pattern analysis. According to Scherrer Equation and measured half-height width of the (111) peak, the grain size was 7.2 nm. The particle size of the cerium dioxide powder was in a range of about 6 nm to about 10 nm using a transmission electron microscope.

Comparative Example 3

A cerium salt was dissolved in deionized water to form ion solution. Next, hexylamine (primary amine), which has the same molecular weight as dipropylamine, was added into the ion solution and stirred at ambient temperature. A molar ratio of the cerium salt to hexylamine was 5:2. After homogeneous mixing, the solution was placed and sealed in a solvothermal bottle made of Teflon, and solvothermal reaction was then performed at 110° C. and 2.7 atm with 25 minutes. After completion of the reaction, a compound sample was obtained. The compound was recognized as cerium dioxide with cubic fluorite structure using X-ray diffraction pattern analysis. According to Scherrer Equation and measured half-height width of the (111) peak, the grain size was 4.8 nm. The particle size of the cerium dioxide powder was in a range of about 2 nm to about 5 nm using a transmission electron microscope. Compared to Example 3 using organic amine with the same molecular weight as the basic source, the synthesized cerium dioxide using secondary amine has larger particle size than that using primary amine.

Example 4

Cerium nitrate was dissolved in deionized water to form ion solution with a concentration of 0.02 mol/L. Next, hexamethylenetetramine (tertiary amine) was added into the ion solution with a concentration of 0.10 mole/L (based on the deionized water) and stirred at ambient temperature. A molar ratio of the cerium nitrate to hexamethylenetetramine was 1:5. After homogeneous mixing, the solution was placed and sealed in a solvothermal bottle made of Teflon, and solvothermal reaction was then performed at 180° C. with 60 minutes. After completion of the reaction, a compound sample was obtained. The compound was recognized as cerium dioxide with cubic fluorite structure using X-ray diffraction pattern analysis. The cerium dioxide powder was hexagonal-shaped and had a particle size in a range of about 30 nm to about 60 nm using a transmission electron microscope.

Example 5

Cerium acetate was dissolved in deionized water to form ion solution with a concentration of 0.02 mol/L. Next, hexamethylenetetramine (tertiary amine) was added into the ion solution with a concentration of 0.10 mole/L (based on the deionized water) and stirred at ambient temperature. A molar ratio of the cerium acetate to hexamethylenetetramine was 1:5. After homogeneous mixing, the solution was placed and sealed in a solvothermal bottle made of Teflon, and solvothermal reaction was then performed at 120° C. with 60 minutes. After completion of the reaction, a compound sample was obtained.

The compound was recognized as cerium dioxide with cubic fluorite structure using X-ray diffraction pattern analysis. The cerium dioxide powder was spherical and had a particle size in a range of about 5 nm to about 10 nm using a transmission electron microscope.

The obtained compound samples including cerium dioxide and deionized water of Examples 4-5 were placed to observe sedimentation. FIG. 5 are photos of the compound samples synthesized from different cerium salts ((1) cerium nitrate (i.e., Example 4); (2) cerium ammonium nitrate; (3) cerium acetate (i.e., Example 5); (4) cerium sulfate) at different times (T=0 min (after shaking), 1 min, 5 mins, 10 mins, 30 mins, 60 mins, 120 mins and 250 mins). As shown in FIG. 5, the compound sample of (3) was always turbid compared to those of (1), (2) and (4). In other words, the compound sample of (3) was self-stabilized, and thus there was no sedimentation occurred.

FIG. 6 is a light transmittance diagram of the compound samples synthesized from different cerium salts ((1) cerium nitrate (i.e., Example 4); (2) cerium ammonium nitrate; (3) cerium acetate (i.e., Example 5); (4) cerium sulfate) at different times measured by a UV-VIS spectrometer. As shown in FIG. 6, compared to those of (1), (2) and (4), the compound sample of (3) had very low light transmittance continuously, and the light transmittance was decreased

with time, which means that the compound sample of (3) was self-stabilized.

Given the above, the present disclosure indeed provides the cerium dioxide powder with larger particle size and good dispersity, and thus the cerium dioxide powder can be acted as the polishing powder in the chemical mechanical polishing process in semiconductor field.

According to some embodiments, a method of manufacturing a cerium dioxide powder includes mixing a cerium salt, an amine and solvent to form a mixed solution, in which the amine includes a secondary amine, a tertiary amine or a combination thereof, and the tertiary amine is selected from the group consisting of hexamethylenetetramine, triethylenediamine and a combination thereof; and performing a solvothermal reaction of the mixed solution to form the cerium dioxide powder.

According to some embodiments, a method of manufacturing a cerium dioxide powder includes mixing a cerium salt, an amine and solvent to form a mixed solution, in which the cerium salt includes cerium carboxylate, and the amine includes a secondary amine, a tertiary amine or a combination thereof; and performing a solvothermal reaction of the mixed solution to form the cerium dioxide powder.

According to some embodiments, a cerium dioxide powder manufactured by the method mentioned above.

The foregoing outlines features of several embodiments so that those skilled in the art may better understand the aspects of the present disclosure. Those skilled in the art should appreciate that they may readily use the present disclosure as a basis for designing or modifying other processes and structures for carrying out the same purposes and/or achieving the same advantages of the embodiments introduced herein. Those skilled in the art should also realize that such equivalent constructions do not depart from the spirit and scope of the present disclosure, and that they may make various changes, substitutions, and alterations herein without departing from the spirit and scope of the present disclosure.

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