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Large-Scale Synthesis of Water Dispersible Ceria Nanocrystals by a Simple Sol–Gel Process and Their Use as a Chemical Mechanical Planarization Slurry

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Ceria nanocrystals with a cube shape were synthesized from the hydrolytic sol–gel reaction of cerium salt in the presence of oleylamine. The overall synthetic process is very simple and readily applicable to the large-scale synthesis of tens of grams of product in a single reaction in air. These ceria nanocrystals are readily dispersible in aqueous media without the addition of any extra dispersing agent. The aqueous dispersion of the ceria nanocrystals was successfully used as a chemical mechanical polishing slurry, and it exhibited high removal selectivity between silicon oxide and silicon nitride at pH 7.

Introduction

The development of nanocrystals has been intensively pursued not only for the fundamental scientific interest of these materials but also for their many technological applications.[1] For many of these applications, the design of economical and environmentally friendly synthetic methods for the preparation of monodispersed nanocrystals is of key importance. Cerium oxide (ceria, CeO_2) nanoparticles have attracted much attention because of its broad range of applications, including oxygen-ion conductors in solid oxide fuel cells, oxygen pumps, and amperometric oxygen monitors.[2] Furthermore, cerium oxide has been commonly used as an abrasive for shallow trench isolation (STI) chemical mechanical polishing (CMP) in the fabrication of semiconductors. The STI process, which is a technique used to isolate an active area, was substituted for local oxidation of silicon, as this technique caused encroachment of the active area during the oxidation of silicon. The STI process was carried out as follows: Firstly, the trench was formed between each active area by etching, and subsequently silicon dioxide (SiO_2) was deposited. Secondly, the excess SiO_2 layer present on the active area was removed by CMP until silicon nitride (Si_3N_4) resulted, which acts as the protective layer of the active area. During STI CMP, the slurry with a low removal selectivity resulted in a decreased thickness of the field oxide through the loss of Si_3N_4. To overcome thinning of the field oxide, cerium oxide, which has a higher selectivity than silica, was used.[3] To be used, CMP slurries must satisfy various conditions, such as size uniformity, crystallinity, solvent dispersity, and particle roughness. Although ceria nanoparticles have been synthesized by using various chemical reactions in organic media, these nanoparticles are generally poorly dispersible in aqueous media.[4] Ligand-exchange reactions have been frequently used to transfer organic dispersible nanocrystals to aqueous media.[5] However, these ligand-exchange processes cannot be used for the large-scale synthesis of water-dispersible nanoparticles because of the use of expensive amphiphilic ligands and long reaction times. Herein, we report on the large-scale synthesis of uniformly sized ceria nanocrystals by a sol–gel reaction in air. All of the ceria nanocrystals were produced on an extremely large scale of over 10 g in a single reaction. Furthermore, these ceria nanocrystals are readily dispersible in aqueous media without the addition of any extra dispersing agent, and they were successfully used as a slurry for chemical mechanical polishing (CMP); the slurry exhibited high removal selectivity between silicon oxide and silicon nitride.

Results and Discussion

Cube-shaped ceria nanocrystals with an average size of 40 nm were synthesized from the reaction of cerium(III)

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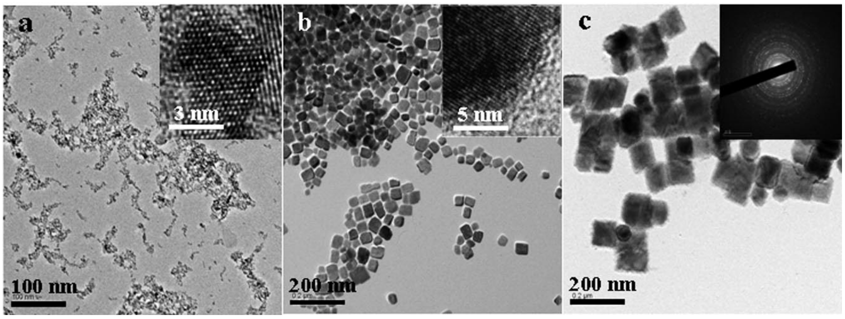

Figure 1. TEM images of (a) 3.5-nm-sized spherical ceria nanocrystals, (b) 40-nm-sized cube-shaped ceria nanocrystals, and (c) 80-nm-sized cube-shaped ceria nanocrystals. Insets are their HRTEM images and ED pattern.

chloride heptahydrate in oleylamine at 265 °C. A low-magnification transmission electron microscopic (TEM) image revealed the cube-shaped nanocrystals with an averages edge dimension of 39 nm (Figure 1b). A high-resolution transmission electron microscopic (HRTEM) image of the ceria nanocrystals showed that they exhibited a cross-lattice pattern, which demonstrates the highly crystalline nature of the nanocrystals (Figure 1b). The powder X-ray diffraction (XRD) pattern (Figure 2) of the nanocrystals showed that they possessed a cubic fluorite structure (F_{m3m}, a = 5.41134 Å, JCPDS Card No. 34-0394). The crystal size of the ceria nanocrystals calculated by using the Scherrer formula was 37 nm, which matched well with the TEM data. By controlling the reaction temperature, while keeping the other experimental conditions unchanged, we were able to control the size of the ceria nanocrystals. For example, 3.5-nm-sized ceria nanocrystals were obtained by lowering the reaction temperature to 200 °C (Figure 1a), and larger 80-nm-sized ceria nanocrystals were synthesized by performing the reaction at an increased temperature of 280 °C (Figure 1c). Under optimized synthetic conditions, we were able to synthesize these ceria nanocrystals on an extremely large scale of over 10 g in a single reaction by using 200 mL of solvent (see Supporting Information).

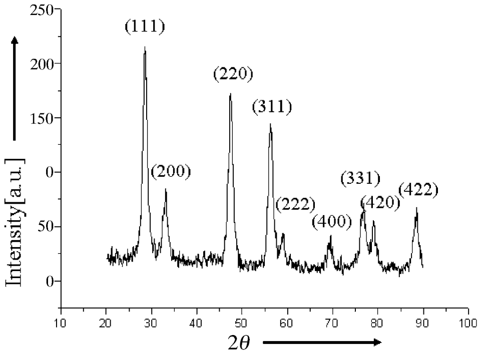

Figure 2. XRD pattern of the 40-nm-sized cube-shaped ceria nanocrystals.

To obtain water-dispersed ceria nanocrystals, the nanocrystals were washed several times with ethanol to remove the excess amount of oleylamine. After centrifugation, water was added until the concentration of the solution reached 1 g of ceria nanocrystals per 100 mL of water, which resulted in a white muddy dispersion after vigorous shaking. Figure 3 shows the photographs of the water-dispersed ceria nanocrystals that were kept for more than one week. Dynamic light scattering (DLS) measurements for ceria nanocrystals with core dimensions of 40 and 80 nm revealed that the average particle sizes in aqueous dispersions were 108 and 144 nm, respectively (see Supporting Information), which demonstrates that aggregation occurred in the aqueous dispersion. The FTIR spectrum of the water-dispersed ceria nanocrystals showed a strong and broad band at 3300 cm^{-1}, which is a result of the Ce–OH that was located on the surface of the ceria nanocrystals. These surface Ce–OH groups seem to allow these nanocrystals to be water dispersible.

Figure 3. Photographs of aqueous solutions containing ceria nanocrystals with particle sizes of 3.5, 40, and 80 nm.

We tested the performance of 40 and 80-nm-sized ceria nanocrystals for STI CMP processing, and the results are shown in Figure 4. The larger 80-nm-sized nanocrystals exhibited a higher removal rate for the plasma enhanced tetraethyl orthosilicate (PETEOS) film relative to that of the 40-nm-sized nanocrystals (351.8 Å min^{-1} vs. 22.9 Å min^{-1}).[6] In contrast, the removal rate for a chemical vapor deposition (CVD) grown Si_3N_4 film did not show that much size dependency (4.1 Å min^{-1} by using 80-nm-sized nanocrystals and 2.8 Å min^{-1} by using 40-nm-sized nanocrystals). The removal rate of the material increased as the contact area between the wafer and the abrasive increased. It was reported that the contact area is related to the size of the abrasive,[7] and the removal rate of SiO_2 increased when a ceria slurry with a large size at STI CMP was used.[8] In this study, the 80-nm-sized ceria nanoparticle slurry exhibited a higher removal rate of SiO_2 than that of the 40-nm-sized nanoparticle slurry. In contrast, there was no significant size-dependent removal rate for Si_3N_4. Consequently, the selectivity between silicon oxide and silicon nitride increases by increasing the particle size. We also performed polishing experiments at various pressures to verify the Preston equation [Equation (1); k_p: Preston coefficient],[9] which is a well-known removal model for the wafer-scale materials. According to this equation, the removal rate (RR) is proportional to the product of the polishing pressure (P) and velocity (V).

$$RR = k_p PV \tag{1}$$

Pressure was varied from 0.6 to 2 psi, whereas the carrier speed was set at the constant value of 75 rpm. The polishing removal rate was increased by increasing pressure, which demonstrates the good agreement with the Preston equation (see Supporting Information).

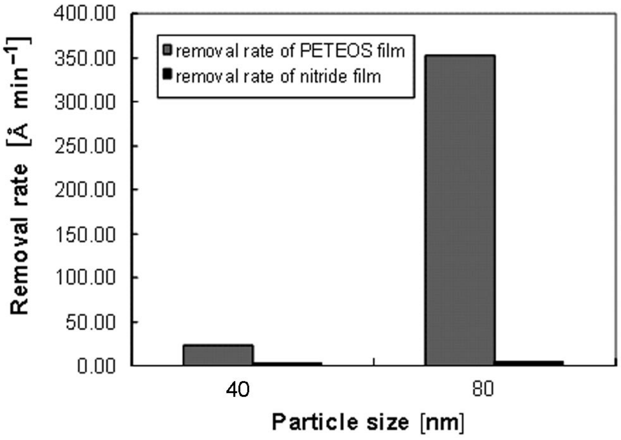

Figure 4. Results of CMP field evaluation test.

Conclusion

Cube-shaped ceria nanocrystals were synthesized from the hydrolytic sol–gel reaction of cerium salt in the presence of oleylamine. We were able to control the size of the nanocrystals by varying the reaction temperature. The overall synthetic process is very simple and readily applicable to the large-scale synthesis of tens of grams in a single reaction step in air. Furthermore, the ceria nanocrystals are readily dispersible in aqueous media without the addition of any dispersing agent, and a very stable aqueous dispersion results. The aqueous dispersion of the ceria nanocrystals was successfully used as a CMP slurry, and it exhibited high removal selectivity between silicon oxide and silicon nitride at pH 7. The polishing removal rate was increased by increasing the size of the nanocrystals and the pressure of the system, which agreed very well with the Preston equation.

Experimental Section

Synthesis of Cube-Shaped Ceria Nanocrystals: Cerium(III) chloride heptahydrate (1.56 g, 4 mmol) was added to oleylamine (20 mL, 60 mmol, 16.3 g, technical grade). The resulting solution was heated to 90 °C, which resulted in the formation of a homogeneous and clear dark-brown solution. The mixture was heated to 265 °C and aged at that temperature for 2 h, which resulted in a black colloidal solution. After cooling to room temperature, ethanol (100 mL) was added to cause the precipitation of the CeO_2 nanocrystals. The precipitate was retrieved by centrifugation to produce white-brown colored CeO_2 nanocrystals. This ethanol washing procedure was repeated three times, and the resulting nanocrystals were readily dispersible in water. For large-scale synthesis, we used a 10-fold amount of all reagents.

Chemical Mechanical Planarization Process: Wafers with a structure of SiO_2 (5000 Å, thermal oxidation)/Si (100) were used in the study. The polishing slurry containing 1 wt.-% ceria nanocrystals was prepared, and the pH of the slurries was fixed to 7. A R&D CMP Machine POLI-380 (G&P Technology) was used to determine the polishing rate, and the rotating speed of the plate and the carrier were 80 and 75 rpm, respectively. To investigate the dependency of the removal rate on the pressure, the pressure between the plate and the carrier was varied from 0.6 to 3 psi, and the flow rate of the slurry was set at 200 mL min^{-1}. The removal rates of the SiO_2 wafers were measured at 15 points by using ellipsometry.

Supporting Information (see footnote on the first page of this article): FTIR spectrum of dried ceria nanocrystals before and after the addition to water, photograph of the water dispersion of ceria nanocrystals, results of the CMP field evaluation: pressure vs. removal rate, and DLS results of ceria nanocrystals in aqueous dispersion.

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