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Chemical mechanical glass polishing with cerium oxide: Effect of selected physico-chemical characteristics on polishing efficiency

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ABSTRACT

Cerium oxide with an excellent glass polishing efficiency was prepared by annealing carbonate or oxalate precursors. The temperature of calcination was identified as a critical parameter that governs the key properties, including the polishing efficiency, of the polishing powders; conversely, the time of calcination appears to be less important. Only the cerium oxides prepared at temperatures above 700 °C exhibited good glass polishing capabilities in terms of both the material removal rate and the quality of the polished surface; the maximum polishing efficiency was produced by the samples annealed at 1050 °C. Polishing powders were characterized using X-ray diffraction (XRD), advanced microscopic techniques (SEM, TEM), Brunauer–Emmett–Teller (BET) surface area, X-ray photoelectron spectroscopy (XPS) and other techniques. Detailed XRD and microscopic investigations revealed a strong correlation between the crystallinity of cerium oxide and its polishing efficiency, which is consistent with the mechanical effect of the polishing mechanism. However, XPS measurements suggest that the chemical characteristics, namely the presence of the Ce^{3+} ions, also play an important role in glass polishing and planarization. Both mechanical and chemical contributions to the polishing process are influenced by the calcination temperature.

1. Introduction

The process of glass polishing and planarization is of fundamental importance in many industries, including jewelry, precise optics, laser techniques and electronics [1–4]. Cerium oxide is one of the most effective glass polishing agents, providing high-quality polished surfaces [2,5,6]. The high polishing efficiency of cerium oxide stems from its chemical properties because the polishing of glass and certain other surfaces is not only a purely mechanical process, but it also involves a complex set of chemical interactions between the polishing agent, the polished surface and the polishing medium [7]. Although mechanical factors, such as pressure or relative motion of the polishing tool with respect to the polished surface, dominate in the material removal process, chemical interactions cause surface smoothing and planarization. This process is commonly described as chemical mechanical polishing (or planarization) (CMP) [1,4,8–10], and the factors affecting its efficiency have been increasingly investigated recently in relation to the growing demand for high-quality surfaces in the production of modern electronic devices.

Ceria-based polishing powders are typically prepared via the thermal decomposition of suitable precursors, which are typically cerium oxalates, hydroxides, acetates, or carbonates [5,11–14]. The contents of cerium oxide in the polishing powders vary over a relatively broad range from ca. 50 to 100% [15], and the presence of other rare earth metals in the polishing powders is not considered a critical factor because cerium oxide forms solid solutions with the oxides of other lanthanide elements [16] and incorporates them into its crystal lattice without changing its crystalline structure. However, the content of cerium oxide in high-grade, commercially available polishing powders typically approaches 100% [15]. Based on the theory of CMP, the polishing agent should have suitable mechanical characteristics, such as mechanical resistance, particle size distribution and crystallinity [13,14,17–20]; concurrently, it should retain sufficient chemical reactivity to interact with the polished surface under given conditions [21–23]. In some branches, such as in shallow trench isolation CMP, the

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polishing selectivity is required, i.e. an ability to remove silicon dioxide and not silicon nitride [24].

It is generally accepted that the properties of cerium oxide are governed primarily by the conditions that it experiences during thermal treatment (annealing), primarily by the calcination temperature [25]. It was found for the polishing agents prepared from carbonate precursors that the polishing efficiency (expressed in terms of the removal rate) increases with the calcination temperature [24,26,27], with the most dramatic changes occurring in the temperature range of ca. 300–700 °C. According to Praveen et al. [24], the efficiency of polishing agents did not increase with further increasing the calcination temperature up to 1000 °C, whereas we observed in our earlier works a certain increase for the polishing agents annealed at temperatures slightly above 1000 °C [26,27]. In the temperature range of ca. 300–700 °C, not only the main physical characteristics of cerium oxide change dramatically, but also its sorption ability and reactivity [28]. It is therefore unclear, which characteristics may be related to the polishing efficiency. Controversies exist, for example, around an effect of the particle size and morphology of the polishing agents, or concentration of the polishing slurry [29]. Great advances were achieved in recent time in understanding the chemical aspects of the polishing process, especially in the shallow trench isolation CMP (as reviewed by Srinivasan et al. [30]), where pH control as well as chemical and other additives are frequently used to enhance the polishing selectivity [24,31]. Experiments with oxidizing agents, such as hydrogen peroxide, emphasized the role of the cerium speciation (the Ce(III)/Ce(IV) ratio) in CMP [32,33]. As the polishing efficiency decreased in the presence of hydrogen peroxide, it was deduced that Ce^{3+} rather than Ce^{4+} is effective in the polishing of silicate substrates. This conclusion seems to be correct despite the fact that hydrogen peroxide may exhibit a dual (both oxidizing and reducing) effect on cerium ions [34], as the presence of the Ce^{3+} ions in the polishing slurry (filtrate) was confirmed by UV–vis spectroscopy [24].

Chemical additives may exhibit a multiple effect on the polishing process, as they affect not only the interactions on the polished surface, but also complex interactions of the polishing agents with other components of the polishing slurry and with the polishing pad [35], which make difficult to discriminate between the polishing agent–related effects and other (side) effects. There is still relatively few studies which demonstrate clear relationships between the preparation conditions, the measurable and/or controllable characteristics of the polishing powder and its polishing efficiency [12,14,36,37]. To establish the relations between the preparation route of the ceria-based polishing agent, its physico-chemical characteristics and polishing efficiency, we prepared a series of cerium oxides by calcination of the cerium carbonate precursor at different temperatures ranging from 200 to 1200 °C. The glass polishing efficiency was measured in a simple arrangement without a further treatment (e.g. milling) of the polishing agents and without a chemical modification of the polishing slurry. A set of well-established methods together with some more advanced ones, such as electron microscopy (SEM, TEM/HRTEM) or X-ray photoelectron spectroscopy (XPS), were used for a detailed characterization of the polishing agents. It was proven that the calcination temperature affects both mechanical processes during CMP (mainly by governing the crystallinity of cerium oxide) as well as chemical interactions (mainly by governing the Ce(III)/Ce(IV) ratio).

2. Material and methods

2.1. Preparation of polishing powders

If not stated otherwise, cerous nitrate ($Ce(NO_3)_3 \cdot 6H_2O$) of reagent-grade purity (99.9%, trace metal basis) and ammonium bicarbonate (99.5%) were used to prepare the ceria-based polishing powders used in this study using a carbonate precursor, and oxalic acid dihydrate ($>99\%$) was used to prepare the polishing powders using an oxalate precursor. The chemicals were obtained from Sigma-Aldrich (Steinheim, Germany). The carbonate precursor was prepared via the precipitation of an aqueous solution of cerous nitrate (0.2 mol/L) with an excess of ammonium bicarbonate (0.5 mol/L) during stirring; the completeness of the precipitation was checked via reaction with oxalic acid. After adding the final amount of ammonium bicarbonate, agitation continued for one additional hour, and the precipitate was left until the following day. Next, the precipitate was separated by filtration, washed with water and then dried overnight at 110 °C. Certain polishing powders were prepared from the rare earths concentrate originating from Kola apatite [38]; this concentrate was dissolved in nitric acid and further treated in a similar way to the cerium nitrate solution. Cerium oxalate was prepared from the cerium nitrate solution via precipitation with saturated oxalic in a similar way as cerium carbonate. Polishing powders were prepared from these precursors via calcination at pre-determined temperatures between 200 and 1200 °C for two hours with an exception of the experiments, in which an effect calcination time was examined.

2.2. Methods of characterization

A FEI Nova NanoSEM 450 scanning electron microscope (SEM) was used to examine the polishing powders in two modes: secondary electrons (SE) and back scattered electrons (BSE). Typically, a powdered sample was dispersed in ethanol and treated in an ultrasonic bath for 10 min before deposition onto a silicon wafer chip.

High-resolution transmission electron microscope (HRTEM) analysis was performed with an FEI Talos F200X. A regular, 300-mesh copper grid coated with silicon dioxide (SiO_2)/monoxide (SiO) was used during sample preparation.

X-ray diffraction (XRD) measurements were performed using an MPD 1880 diffractometer (Philips). The crystallite sizes were calculated from the diffraction line broadening using the Scherrer formula [39]:

$$a = \frac{K\lambda}{\beta \cos\theta} \tag{1}$$

where K is the shape factor, λ is the wavelength of the applied radiation, β is the broadening of the diffraction line, and θ is the diffraction angle. The Scherrer calculator from the X-Pert HighScore Plus SW package was used for these calculations.

The specific surface area of the sorbents was measured using the BET method (N_2 adsorption) with a Sorptomatic 1900 Carlo Erba instrument.

XPS measurements were performed with a PHI VersaProbe II XPS system (by Physical Electronics) with a monochromatic Al-Kα source (15 kV, 50 W) and a photon energy of 1486.7 eV. All spectra were measured in a vacuum of 1.3×10^{-8} Pa at room temperature (i.e., 20 °C). The powder samples of cerium oxide were mounted with double-sided tape in a sealed glove box to minimize possible redox reactions. The analyzed area on each sample was 200 μm in diameter, and the survey scan spectra were measured with a pass energy of 187.850 eV, a binding energy range of 0–1300 eV and an electron volt step of 0.8 eV. For the high-resolution spectra, a pass energy of 23.500 eV and an electron volt step of 0.2 eV were used. Dual-beam compensation was used for all measurements. The obtained spectra were evaluated with MultiPak software (version 9.4.0.7.; Ulvac – PHI, Inc.), and all binding energies were referenced to the carbon peak C 1 s at 284.80 eV.

The particle size distribution was measured using the photosedimentation method using a centrifugal particle-size analyzer