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Effect of cerium modification on the formation of colloidal silica

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ABSTRACT

Colloidal silica was modified by cerium ion to improve its polishing performance. The active silicic acid was mixed with cerium ion and was then titrated into the seed solution for surface modification via surface growth process. According to the experimental results, we found that the additional cerium ion can improve the surface growing ability on the seed (colloidal silica) surface. The particles size of cerium modified colloidal silica is larger than that without cerium modification. The mean particle size of the modified colloidal silica is decreased by increasing the seed concentration. The removal rate of SiO_2 of the modified colloidal silica is higher than that of without cerium modification colloidal silica.

1. Introduction

Cerium oxide was used to polish glass for many years. [1] Recently, cerium oxide became an important polishing abrasive in modern industries, such as mother-glass polishing for the LCD and dielectric layer [2,3] and polishing for the shallow trenches isolation process in the IC industry. There were several works to investigate the fine cerium oxide powder. [4–6]. However, cerium oxide powder was easily sediment due to the aggregation of cerium oxide. When using the cerium oxide slurry to polish, it needed to be continuously stirred to prevent the unstable polishing rate from the sedimentation of cerium oxide (since the removal rate is varied with the solid content of slurry). In addition, the large agglomerate of cerium oxide would induce the scratch on the surface of the wafer. Colloidal silica was known as stable and well suspension slurry. [7–14] Cerium modified colloidal silica was a designed material which is well suspended like colloidal silica and has a high polishing rate like cerium oxide. In our previous reports, [12,13] the colloidal silica was modified with aluminum ion and cerium ion, respectively. However, the effect of cerium on the formation of the colloidal silica has not been studied. In this study, we investigated the formation of cerium modified colloidal silica. Furthermore, we used an inexpensive process to estimate the polishing performance of the modified slurry by using a general polishing tool.

2. Experimental procedure

2.1. Preparation of modified colloidal silica

The active silicic acid was prepared from the commercial sodium silica (30 wt% SiO_2, 13 wt% Na_2O) via the ion-exchange process. The process to prepare the active silicic acid and the seed (small size colloidal silica) were described in other report. [12] A solution of 1.25 g KOH with the desired concentration of seed was diluted with de-ionic water (DIW) to 260 ml and was then maintained at 100 °C. On the other hand, the 500 ml 3.24 wt% active silicic acid solution mixed with the desired concentration of ammonium cerium nitrate was titrated into the above heated solution. The titrating rate was controlled at 2.6 ml min^{-1}. Since the active silicic acid was acidic, the additional 2.5 g KOH was added in the heated solution to maintain the pH of the heated solution in 10–11. The cerium modified colloidal silica was characterized by the mean particle size (dynamic light scattering, DLS), and the morphology by transmission electron microscopy (TEM). The calculating equations of particle number and particle size of colloidal silica were based on the assumption of mass conservation and complete surface growth (particle number kept constant) during titration, which was listed in Eqs. (1) and (2). The detailed descriptions were reported in our previous paper [14].

$$n_s = n_f = \frac{W_s}{\rho_s 4/3\pi(d_s/2)^3} = \frac{W_s + W_a}{\rho_f 4/3\pi(d_f/2)^3} \quad (1)$$

$$\frac{d_f}{d_s} = \left(\frac{W_s + W_a}{W_s}\right)^{1/3} \quad (2)$$

Where, n_s, the initial particle number; n_f, the final particle number, W_s, the mass of silica in seed; W_a, the mass of silica in the active silicic acid; $\rho_a = \rho_s$, the density of silica particle (2.2 g cm^{-3}); d_s, the initial particle diameter of colloidal silica (the particle size of seed); d_f, the final particle diameter of modified colloidal silica. If W_a, W_s and d_s were known, d_f and n_f could be calculated.

2.2. Polishing test

A small wafer (2 cm × 2 cm) was cut from a 6 in. wafer and was then mounted on the stainless steel cylinder with a thermal plastic adhesive. The mounted wafer was polished by the polishing tool (Josheph, SS-2000). The polishing parameters were the following: down force = 1407–4222 Pa, carrier speed = 10–40 rpm, slurry flow rate ~20 ml min^{-1}, polished time = 5 min, polishing pad: IC 1400 (Rodel), and the polished film: SiO_2 film from LPCVD (low pressure chemical vapor deposition) process. The original thicknesses of these films were about 2000 Å measured by Ellipsometer (Mary-102, Fivelab Co.). The removal rate of SiO_2 was calculated from the difference of the film thickness of silica before and after polishing.

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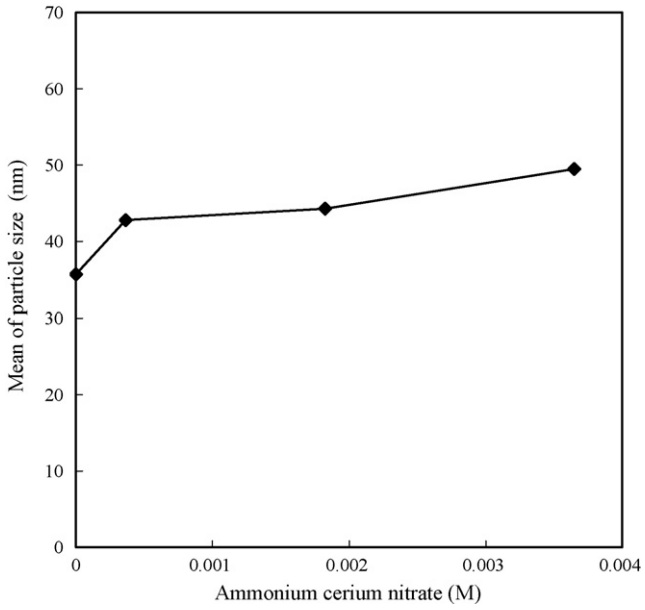

Fig. 1. The effect of cerium concentration on the mean particle size of modified colloidal silica at 1.24 wt% of seed.

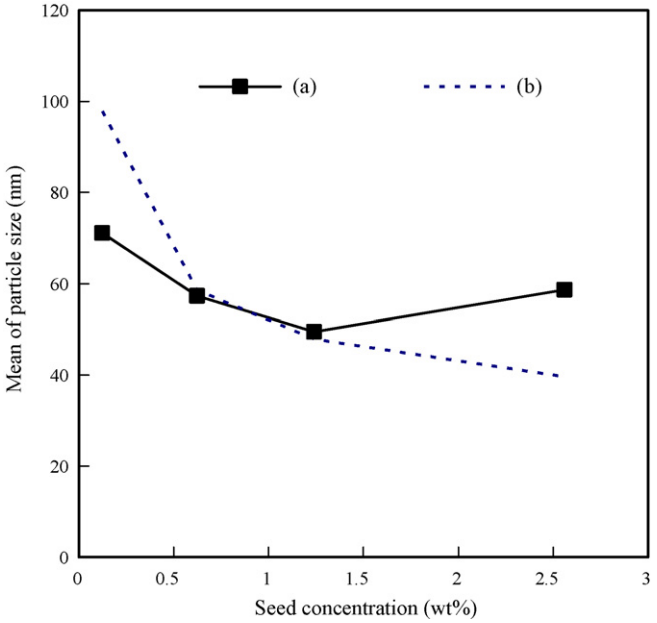

Fig. 3. The effect of seed concentration on the mean particle size of (a) the colloidal silica modified with 0.00364 M ammonium cerium nitrate and (b) the calculated particle size.

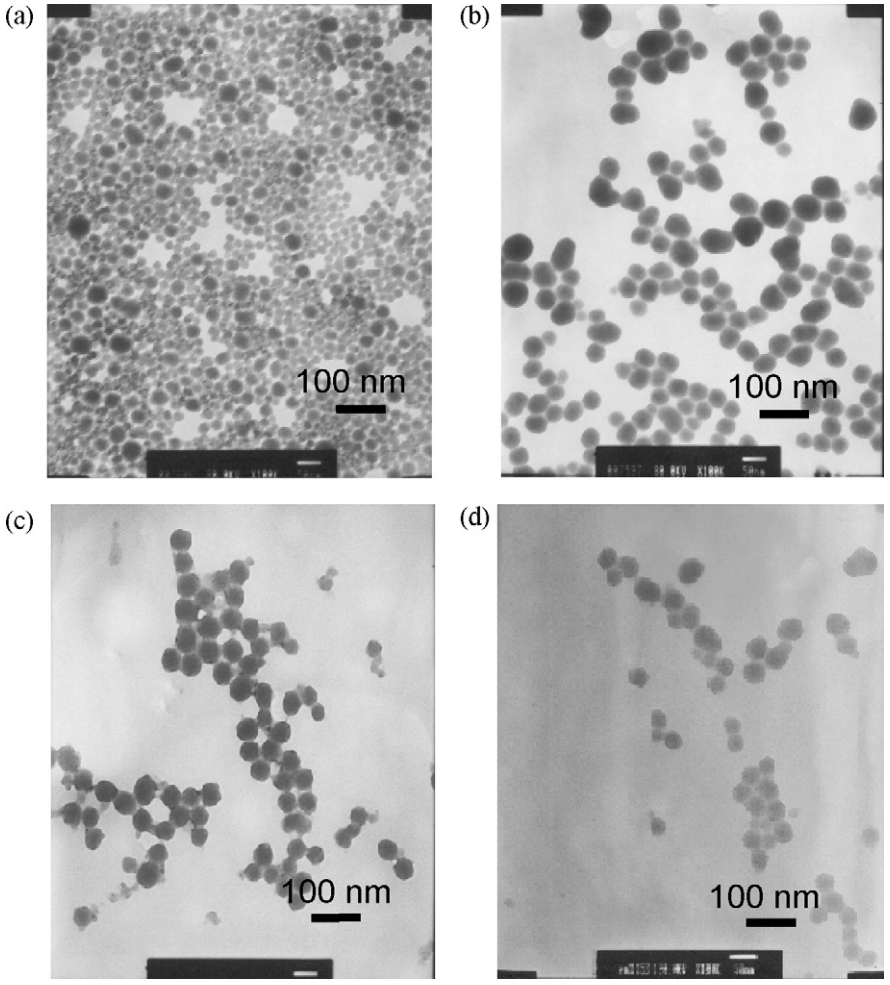

Fig. 2. The particles' morphology of (a) without cerium modification colloidal silica and modified colloidal silica with cerium ion [Ce^{4+}] = (b) 0.000364 M; (c) 0.00182 M and (d) 0.00364 M at 1.24 wt% of seed.