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Preparation of Ce-doped colloidal SiO_2 composite abrasives and their chemical mechanical polishing behavior on sapphire substrates

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HIGHLIGHTS

- Novel Ce-doped colloidal SiO_2 composite abrasives were prepared.
- The chemical mechanical polishing (CMP) performances of the composite abrasives on sapphire substrate were investigated.
- Novel composite abrasives show excellent polishing characteristics comparison with pure colloidal SiO_2 abrasive.
- We explore and report the acting mechanism of composite abrasives to sapphire CMP.

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ABSTRACT

Chemical mechanical polishing (CMP) has become a widely accepted global planarization technology. Abrasive is one of key elements during CMP process. In order to enhance removal rate and improve surface quality of sapphire substrate, a series of novel Ce-doped colloidal SiO_2 composite abrasives were prepared by chemical co-precipitation method. The CMP performances of the Ce-doped colloidal SiO_2 composite abrasives on sapphire substrate were investigated by using UNIPOL-1502 polishing equipment. The analyses on the surface of polished sapphire substrate indicate that slurries containing the Ce-doped colloidal SiO_2 composite abrasives exhibit lower surface roughness, higher material removal rate than that of pure colloidal SiO_2 abrasive under the same testing conditions. Furthermore, the acting mechanism of the Ce-doped colloidal silica in sapphire CMP was investigated. X-ray photoelectron spectroscopy analysis shows that solid-state chemical reactions between Ce-doped silica abrasives and sapphire surface occur during CMP process, which can promote the chemical effect in CMP and lead to the improvement of material removing rate.

1. Introduction

Sapphire, single crystal form of a-alumina, is widely used in a variety of modern high-technology applications because of its excellent optical, chemical and mechanical properties such as high hardness, great thermal stability, chemical inertness, especially used as a substrate material in the photoelectronic, microelectronic and semiconductor industries, ranging from optical windows, read/write laser sources to GaN-based light emitting diodes (LEDs), etc [1–6]. In all of these applications, the surface flatness of sapphire substrate is a key factor that influences its performances. Undoubtedly, its planarization machining is very important [7]. However, the intrinsic nature of sapphire (great hardness and chemical inertness) poses great challenges to such machining. In order to achieve the above mentioned surface quality of sapphire, several polishing technologies are put forward by researchers [8]. At present, chemical mechanical polishing (CMP) is the only widely used global planarization technology in the manufacturing of semiconductor and sapphire substrates [9–12].

In CMP, abrasives are one of key influencing factors on the polished surface quality. The sizes and distribution, dispersibility, hardness and species of abrasive are crucial for a desired CMP performance [13]. In order to improve surface planarization and material removing rate (MRR) of sapphire, several polishing abrasives have been studied. Zhu et al. [14] have studied the effect of abrasive hardness on the CMP of (0001) plane sapphire. They found that, hard abrasives (such as monocrystalline and polycrystalline

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diamond, α- Al_2O_3 and γ-Al_2O_3) can improve MRR of sapphire, but surface arithmetic average surface roughness (Ra) which is measured at various points on the actual contour of the absolute value of the distance to the baseline of the arithmetic mean within a sampling length is higher. Nevertheless, using silica sol as polishing abrasives for sapphire can get lower Ra, but MRR of sapphire is lower. Hu. et al. [15] have researched the CMP of sapphire wafers with boron carbide and colloidal silica abrasives. They found that, B_4C abrasive eliminated the uniformity in thickness within sapphire wafer, but the colloidal silica can achieve a nanoscale flatness of sapphire surface. Xiong et al. [16] adopted silicon carbide, alumina and silica sol as polishing abrasives for CMP of sapphire. The results show that, under the same condition, Ra of sapphire polished with silica sol abrasive is lower than that with silicon carbide and alumina abrasives. In general, silica sol is widely regarded as ideal polishing abrasive for sapphire CMP since it can get better surface quality [17,18]. However, MRR of sapphire with colloidal silica as polishing abrasive is still lower and needs to be improved.

Currently, silica-based composite particles as CMP abrasives capture increasing attention, and chemical modifying of silica abrasive has been proved to be an effective way to improving its polishing performances in CMP. Zhao [19] synthesized SiO_2/CeO_2 abrasive for CMP of oxide wafer and Lei [20] developed porous Fe_2O_3/SiO_2 abrasive for CMP of hard disk substrate. Zhang et al. [21] prepared silica composite abrasive by coating with a layer of polystyrene. The silica-based composite abrasives resulted in both high planarization efficiency and good planarization quality. Up to date, preparation of silica-based composite abrasive for sapphire CMP has seldom been reported. In this paper, Ce-doped colloidal SiO_2 composite abrasives were prepared and their CMP performances on sapphire substrates were investigated.

2. Experimental

2.1. Chemicals

Chemicals used in the synthesis were ceric ammonium nitrate ($(NH_4)_2Ce(NO_3)_6$), ammonia($NH_3 \cdot H_2O$), carbamide($CO(NH_2)_2$), colloidal SiO_2, sodium hexametaphosphate and deionized(DI) water.

2.2. Preparation of material

2.2.1. Preparation of Ce-doped colloidal SiO_2 composite abrasives

Synthesis of Ce-doped colloidal SiO_2 abrasives with different CeO_2 contents: 10 wt. % crystal silica seed solution were heated to 100 °C in a four-neck flask. A certain amount of 2.5 wt.% active silicic acid solution, 0.4wt.% $(NH_4)_2Ce(NO_3)_6$ solution, 0.05 wt.% $CO(NH_2)_2$ solution and 1.5 wt. % ammonia were simultaneously added in drops into the crystal silica seed solution in the four-neck flask under continuously stirring. The liquid volume in the four-neck flask was kept constant by controlling evaporating speed of water and feeding speed of the solutions. The reaction liquid was keeping at PH of 9.0–11.0 by controlling the dropping velocity of ammonia. The solid concentration of 10 wt. % colloidal SiO_2 composite abrasive solution was obtained after the end of reaction.

In above synthesis process of composite abrasives, the cerium was doped into colloidal SiO_2 abrasives in the form of cerium oxide since the reaction liquid is alkali (At pH = 9–11, $Ce^{4+} + 4OH^- \rightarrow CeO_2 + 2H_2O$). By adding different amounts of 0.4wt. % $(NH_4)_2Ce(NO_3)_6$ solution versus crystal silica seed solution, Ce-doped colloidal SiO_2 composite abrasives containing 0.5 wt %, 1.0 wt % and 1.5 wt % CeO_2 (mass ratios CeO_2 of vs SiO_2) were obtained.

The pure colloidal SiO_2 abrasive was prepared by the same method mentioned above except adding $(NH_4)_2Ce(NO_3)_6$ solution.

2.2.2. Preparation of polishing slurries

Preparation of polishing slurries: Before polishing, 10 wt. % prepared colloidal solutions were diluted to solid concentration of 6 wt. %, then 3.0 wt. % sodium hexametaphosphate as dispersant were added into the solution. Finally, the above-mentioned mixtures were filtrated with a 10 μm pore filter to obtain polishing slurries. The pH of prepared polishing slurries is about 10.5.

2.3. Characterization of Ce-doped colloidal SiO_2 composite abrasives

The composite abrasives were characterized by means of Mastersizer 2000 instrument, scanning electron microscope (SEM), Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS) and X-ray photoelectron spectroscopy (XPS).

Elementary analysis of the sample was measured by Model 2100 Trift II time-of-flight secondary ion mass spectroscopy (TOF-SIMS).

SEM analyses were accomplished using a JEOL JSM-6700F field emission scanning electron microscope with voltage of 10 kV.

The filtrate of Ce-doped colloidal silicon dioxide after polishing was characterized by the inductively coupled plasma-atomic emission spectrometry (ICP-AES, PERKINE 7300DV).

XPS spectrum was obtained by ESCALAB 250Xi electron spectrometer using a focused monochromatized Al Kα radiation (hυ = 1486.6 eV). The binding energy of C 1s (283.35ev) was used as reference.

2.4. Polishing test

Polishing tests were conducted by using a UNIPOL-1502 polishing equipment (Shenyang Kejing instrument, Co. LTD, China). The polishing pad was a Rodel porous polyurethane pad. The slurries supplying rate is 180 ml/min. The parameters of polishing were down force of 6 kg, plate rotating speed of 60 rpm and conditioning time of 2 h. Work pieces were φ50.8 mm × 0.45 mm α-Al_2O_3 sapphire substrates with c (0001) orientation. The average roughness (Ra) and of the sapphire substrates are about 2.535 nm. After polishing, the Sapphire substrates were washed with ultrasonic in a cleaning solution containing 0.5 wt.% surfactant in deionized(DI) water. Finally, they were dried by a multifunctional drying system.

Ra was measured by an Ambios XI-100 surface profiler (Ambios Technology Corp., U.S.A) with the resolution of 0.1 Å and the measuring area of 500 μm × 500 μm. The depth of focus is 3.0 μm, the working distance is 7.4 mm, and the numerical aperture is 0.30. The mass of the sapphire substrate was measured by a AL104 analytical balance with accuracy of 0.1 mg (METTLER TOLEDO, Switzerland). The material removal rate was calculated by formula. (1).

$$MRR = \frac{\Delta m \times 10^6}{\rho \pi R^2 \tau} \quad (1)$$

where:

MRR-material removal rate, μm/h
Δm-mass of material removed of substrates before and after polishing, g
R-radius of sapphire substrate, mm
τ-polishing time, h (in the test, τ = 2 h)
ρ-density, g/cm³ (density of sapphire substrate, ρ = 3.98 g/cm³).