Microelectronic Engineering 87 (2010) 1751–1755

Contents lists available at ScienceDirect

Microelectronic Engineering

journal homepage: www.elsevier.com/locate/mee

Investigation on the controllable growth of monodisperse silica colloid abrasives for the chemical mechanical polishing application

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ARTICLE INFO

Article history:
Received 21 January 2009
Received in revised form 13 August 2009
Accepted 2 October 2009
Available online 9 October 2009

Keywords:
Silica
Colloidal abrasives
CMP
Growth
Integrated circuit

ABSTRACT

With the rapid development of chemical mechanical polishing technique as well as its increasing application in IC foundry, the abrasives of slurry are required to have different specifications in terms of size and size's distribution, which play a vital role in the material removal and defect control. In this study, we monitor in detail the growth process of colloidal silica abrasives changing from the tiny nuclei to large nanoparticles by means of the electron microscopy images. Using the procedure we develop, we are capable of producing monodisperse colloidal silica nanoparticles ranging from 60 to 130 nm in diameter, which are mostly often applied as abrasives in chemical mechanical planarization/polishing (CMP) process of integrated circuit (IC) manufacturing. The physicochemical properties of the silica synthesized by our procedure are also characterized by the X-ray diffraction (XRD) patterns and thermal analysis. The polishing test adopting the colloidal silica as abrasives is performed on silicon wafer to evaluate the CMP properties.

1. Introduction

With the continuing decrease of feature sizes of integrated circuit (IC) chips, the introduction of copper Dual Damascene structure and the high/low K dielectric materials pose greater challenges to the planarization precision of IC manufacturing [1,2]. The chemical mechanical planarization (CMP) is the only and best up to now global planarization technique that can remove the overburden deposition layers, leaving planarized surface with Cu interconnects embedded into the dielectric layer [3,4]. The CMP processes are also applied in planarizing tungsten plugs and poly-silicon/silicide gates as well as fabricating shallow trench isolation (STI) structure [5–9]. The CMP processes in an IC manufacturing flow have been used so frequently as to exceed 10 times at the 65 nm technology node [1]. Besides, the CMP techniques are widely adopted for polishing silicon blanket wafers and other substrates [10].

In a CMP process, the polished wafer is held by a carrier and contacted to the pad upon a down pressure. Both the wafer and pad rotate to each other at a relative speed, and at the same time the slurry flows onto the pad and spreads out owing to centrifugalization [11]. With the help of slurry, the wafers are polished owing to different material removal rates (MRR) in concave and convex regions of the surface. With the increasing application of CMP the slurries are consumed in large volumes. The abrasives are the solid components of slurry that provide mechanical friction to the polished material surface, and the soluble chemicals that are present in the slurry are responsible for the corrosive activity and other purposes. The CMP process integrates the chemical and mechanical synergic interactions for realizing the fast global planarization for wafers. It is believed that large and spherical nanoabrasives with narrow size distributions not only produce a high material removal rate but avoid surface scratches. As compared to other abrasives such as alumina and ceria that are usually irregular in size and shape, spherical silica nanoparticles are more frequently employed in CMP process of semiconductor manufacture.

Unlike the calcined silica powders from silicon tetrachloride that are agglomerated and hard to redisperse, colloidal silica abrasives in CMP application are well known for their stability, suspension property and low viscosity [12]. The colloidal silica monodisperse in size is often synthesized by the Stöber process through hydrolysis and condensation of TEOS precursors in an alcohol media that is catalyzed by ammonia or acid [13–15]. The diameter of as-synthesized silica strongly depends on the ratios of reactants including those of water to TEOS and alcohol to TEOS, etc. However, with respect to the large-scale production of silica colloidal abrasives used in CMP process, the organic-precursor based route may not be acceptable for the sake of cost and some other reasons. Therefore, in this study, we fabricate the colloidal

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doi:10.1016/j.mee.2009.10.005

silica in an alternative way with inorganic silicic acid as precursor. Although the tiny silica sols are traditionally fabricated in similar ways, the large-size silica nanoparticles are seldom prepared successfully [16–23]. The silica nanoparticles are formed by aggregation reactions among silicic acid molecules.

2. Experimental

All the reagents are of chemical purity grade, and purchased from Shanghai Chemicals Corp. without further treatment before use.

2.1. The preparation of silicic acid

About 568 g (2 mol) of sodium silicate ($Na_2SiO_3{\cdot}9H_2O$, molecular weight 284.2) was dissolved in 5000 mL of deionized water. Then, 2000 mL of wet cation exchange resins (around 1 mm in size of each resin particle, polystyrene/divinylbenzene support with sulfonic acid groups) were added to the sodium silicate solution under mechanical agitation, leaving the sodium ions to be adsorbed onto the sulfonic groups and the protons released into solution. After about 30 min, the silicic acid solution was decanted into a container and conserved as a stock solution at 5 °C.

2.2. The preparation of silica nuclei

About 50 mL of silicic acid solution was admixed with 10 mL of 1 M NaOH solution and then transferred into a Teflon-liner stainless steel autoclave. After sealing the autoclave, the solution was heated to 160 °C and hydrothermally reacted for 12 h. After natural cooling, the 60 mL of as-prepared silica nuclei was taken out and used for the next steps.

2.3. The controllable growth of silica nanoparticles

Under the temperature of 70–90 °C, the silicic acid was added into the 60 mL of nuclei solution with a proper rate of about 1.0–5.0 mL/min by a peristaltic pump. The pH of growth solution is controlled at 7–8 using NaOH solution. Once the solution fills the 1000 mL of flask, keep the solution unchanged in volume by balancing the titrating rate and evaporation rate. The total growth process lasts about two days. At several different designated times, some volume of colloidal silica was taken out as samples for measurement and the residual parts continue to grow, in this way the growth process of silica is monitored.

2.4. Characterization

The silica colloid samples were imaged by transmission electron microscopy (Hitach-800 TEM) and scanning electron microscopy (Hitachi-S4700 SEM). The dried silica products were studied with thermal gravimetric analysis (Netzsch STA-429C TGA) and differential thermal analysis (DTA). The phase change of dried silica with heating treatment was characterized by X-ray diffraction (Rigaku D/max-2200VPC XRD).

2.5. Polishing test

Three inch polished silicon wafers (P type and (1 1 1) orientation) are subjected to CMP testing on a CETR CP-4 machine (CETR, Inc., Campbell, CA) using the slurry consisting of colloidal silica prepared by us. The pad is IC1000 type with grooves from Rohm & Haas Co. The material removal rate (MRR) was determined on the basis of weight loss before and after polishing, and the surface quality is evaluated by means of the atomic force microscopy (Q-ScopeTM250 AFM) and scanning electron microscopy.

3. Results and discussion

3.1. The preparation of silica nuclei

The silica nuclei or seeds play an important role in the subsequent growth of silica. Fig. 1 is the TEM images of seeds obtained under hydrothermal condition. The spherical seeds are of 10–20 nm and not very uniform in size. The seeds we prepared seem to be larger than those reported previously, which are beneficial to their later growth for enhancing efficiency [18]. Probably due to the high specific surface energy, the silica nuclei tend to coalesce to each other during drying on copper grid in TEM preparation. In the hydrothermal environment, the silicic acid ($Si(OH)_4$) molecules in solution condense altogether to form separate thousands of nuclei in burst, and then the silicic acid is depleted completely. Therefore, prolonging reaction could not grow the silica particles.

3.2. The growth of silica nanoparticles

For the purpose of silica growth, the precursor has to be supplemented into the nuclei solution. The titrating rate of precursor solution should be as slow as possible to ensure the sequential deposition of silicic acid molecules on silica nuclei, avoiding nucleating spontaneously. Fig. 2 depicts the SEM images of silica nanoparticles sampled at T_1, T_2, and T_3 time ($T_3 > T_2 > T_1$). All the silica nanoparticles display monodisperse feature in size, and they have

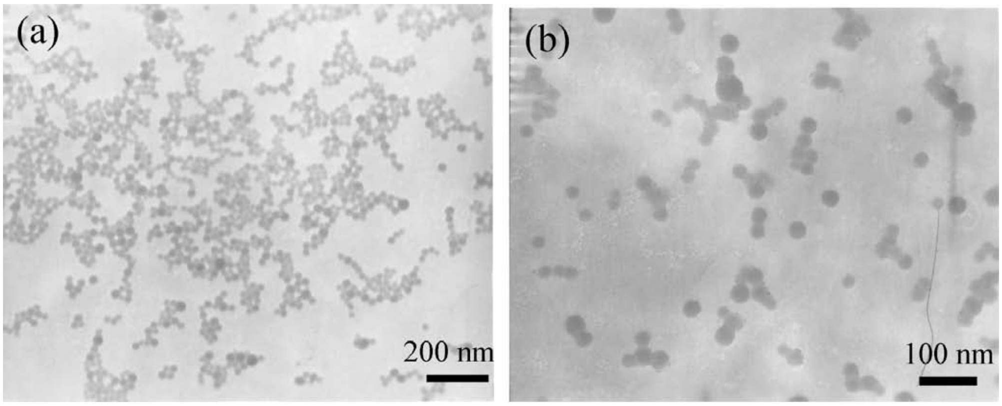

Fig. 1. (a, b) The TEM images of silica seeds prepared at 160 °C in a hydrothermal way.