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Colloidal nano-abrasives and slurry for chemical-mechanical polishing of semi-conductor materials

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Chemical-mechanical polishing or planarization (CMP) is one of the key fabrication processes in the semiconductor industry. Colloidal nano-abrasives with different particle sizes are required for slurries in different CMP processes of semiconductor. So the controlled-growth of particle sizes, particle size distribution and their application become more and more important. In this paper, based on additional experiments and analysis, colloidal nano-abrasives with different particle sizes were prepared by ion-exchange and hydrothermal processes, and their size and stability were characterized by transmission electron microscope (TEM) and a Zeta potential instrument. Results show that colloidal nano-abrasives with diameters of 10-20 nm, 50-70 nm, 80-90 nm were obtained, and the zeta potential (less than −45 mV) also illustrates that the colloidal nano-abrasives was of high stability. One kind of colloidal nano-abrasives with average diameter of 80-90 nm was used to prepare one polishing slurry for silicon wafers. The polishing rate was more than 600 nm/minute and the root mean square (RMS) of surface roughness for polished silicon wafers was less than 0.4 nm, which shows that this type of slurry with the self-made colloidal abrasives not only gives higher polishing rate, but also provides less surface roughness.

Key words: chemical mechanical polishing, slurry, colloidal silica, nano-abrasive, silicon wafer.

Introduction

With the continuously shrinking of device dimensions (feature size: 90 nm or less) and the increase in the device density for integrated circuit (IC) technologies, a higher resolution of photolithography has to adapt the lithographic tools with high numerical aperture (NA) lenses and shorter wavelength light ($R=K_1(\lambda/NA)$). However, the depth of focus (DOF) of the lithographic system decreases with the increase in numerical aperture ($DOF=K_2(\lambda/(NA)^2)$). And so the reduced depth of focus imposes a stringent requirement for flat and planar surfaces, and planarization has become essential for successful manufacturing of multilevel metallization designs, particularly for those with line dimensions below 0.25 μm [1]. Chemical mechanical polishing or planarization (CMP) is one of the best global planarization methods in semiconductor processing [2-5]. Colloidal silica as a nano-abrasive is the most important one for CMP slurries now. What is more, particle size and the distribution of colloidal silica have an important effect on polishing rate and polished surface roughness. However the particle size of colloidal silica nano-abrasives is usually small and their particle size distribution is very wide, which are unfavorable factors to polishing properties [6]. So the controlled-growth of particle size, particle size distribution and their application become more and more important. In this study, the preparation and characterization of controlled size colloidal silica nano-abrasives were performed, and the polishing properties of these nano-abrasives including polishing rate and surface were also studied by a polisher (CP-4) and atomic force microscope (AFM).

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Experimental

Based on the methods of particle growth by ion exchange and hydrothermal synthesis, the colloidal silica nano-abrasive with large particles was prepared [7]. The main experimental steps include the following: (1) active silicic acid is synthesized by water glass through ion exchange; (2) a seed is prepared (colloidal nuclear); (3) the particle is step-grown; (4) colloidal particles are matured and purified etc.

The microstructure of colloidal silica particles was investigated with transmission electron microscope (TEM) (Philips TECNAI 200, Netherlands), and the colloidal silica sample was diluted and deposited on a copper grid and dried. The stability of colloidal silica particles was studied through a Zeta potential Analyzer (Zetasizer HS3000, Malvern Instruments, England). All CMP tests were performed with a CP-4 CMP polisher (CP4, Center For Tribology, Inc, USA). Atomic force microscopy (AFM, Q-Scope250, Quesant Instrument Corporation, USA) was used to characterize the surface morphology of the sample.

Results and Discussion

Microstructure and particle size of the colloidal silica

The particle size and microstructure of the abrasive in a CMP slurry have an important effect on the polishing properties such as polishing rate and polished surface roughness. Colloidal silica abrasives with different particle sizes were prepared by a step-polymerization process, and are seen in Fig. 1-3. These figures show that the particle sizes of the colloidal silica are about 10-20 nm, 50-70 nm, 80-90 nm. What is more, most of particles are spherical, and the distribution of particle size is very narrow. In order to explain the mechanism of particle growth, high resolution TEM was performed on colloidal silica with a large particle size (seen in Fig. 4). The particle size by self-polymerization of silicic acid is typically 2-5 nm, if the large particle size silica is agglomerate of small particles, we would see the small particles on its surface. As seen in Fig. 4, no small particles can be seen on the particle surface, which shows that the colloidal silica abrasives with large particle size are not agglomerates of small particle, but arise from step-growth of small particles by the formation of Si-O-Si bonds.

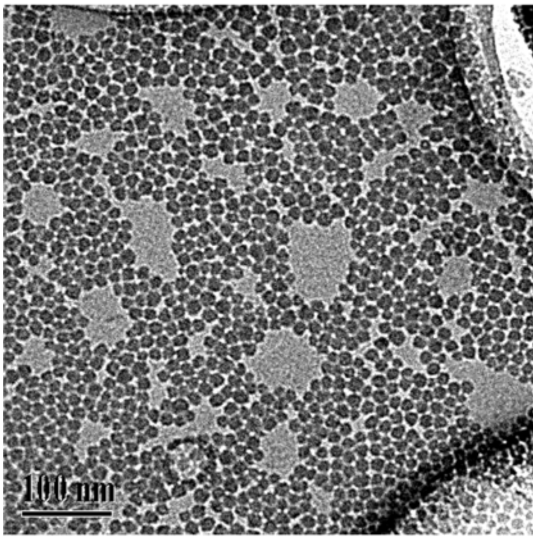

Fig. 1. Colloidal silica abrasives of 10-20 nm.

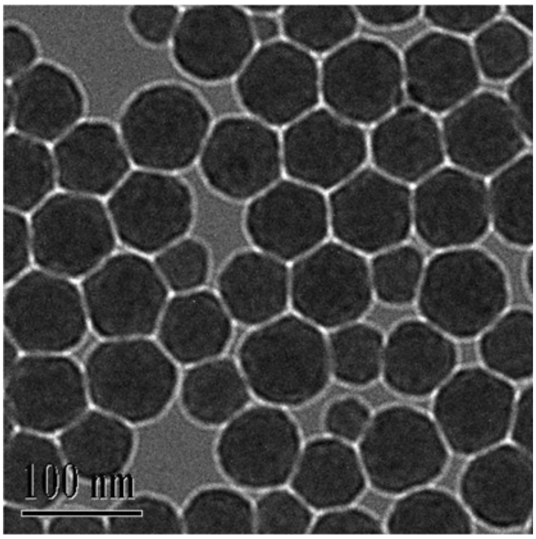

Fig. 2. Colloidal silica abrasives of 50-70 nm.

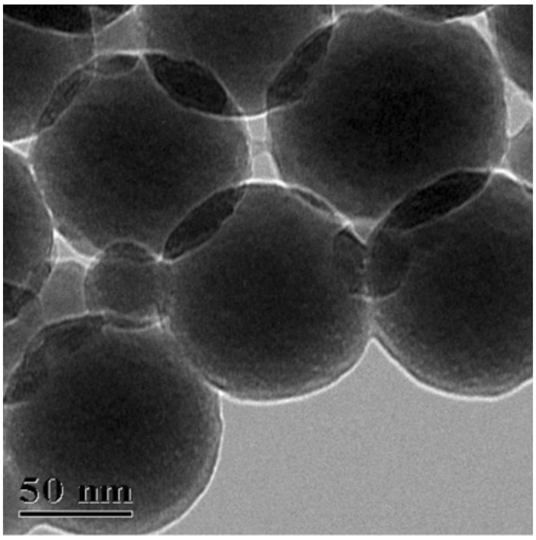

Fig. 3. Colloidal silica abrasives of 80-90 nm.

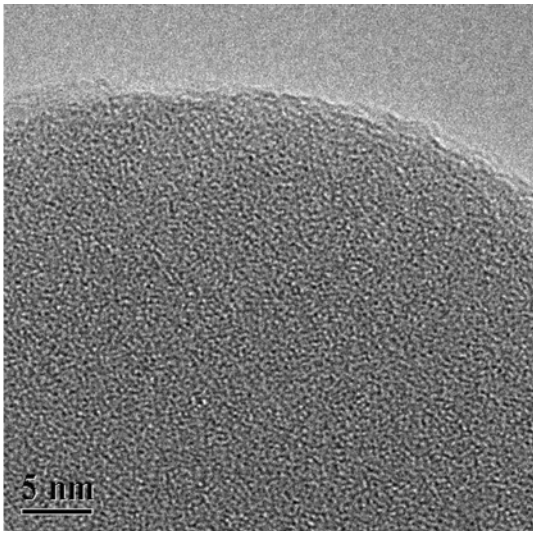

Fig. 4. HRTEM of colloidal silica abrasive.

Stability of colloidal silica nano-abrasive

The stability of the colloidal silica abrasive was characterized by the Zeta potential of sols, the results of which are seen in Fig. 5. As we know, the unstable region of colloidal abrasives is commonly considered to be from −30 mV to 30 mV. The results of the Zeta potential measurement for three types of colloidal silica abrasives are shown in Fig. 5 and the average Zeta

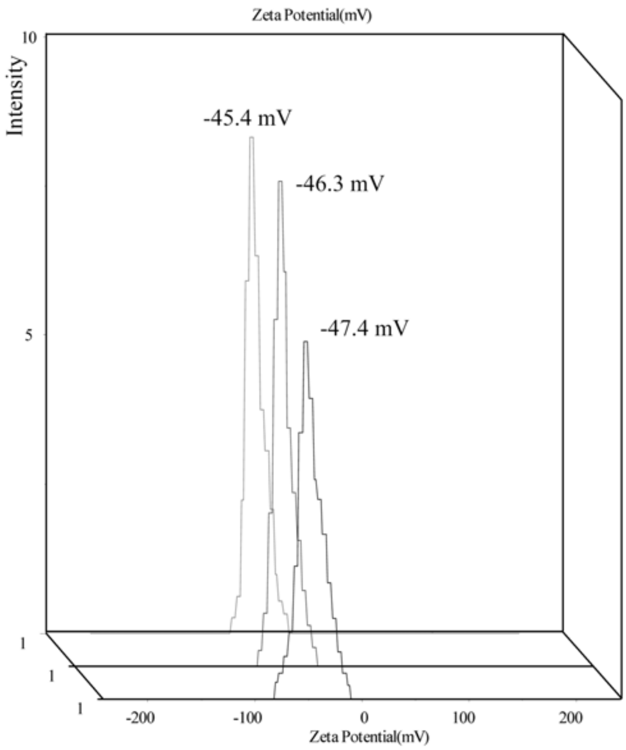

Fig. 5. Zeta potential of colloidal silica abrasives.

potentials are respectively −45.4 mV (10-20 nm), −46.3 mV (50-70 nm), −47.4 mV (80-90 nm). They are all less than –45 mV, which illustrates that the colloidal silica nano-abrasives are very stable. Furthermore, the absolute value of the zeta potential increased slightly with an increase in particle size. The number of particles decreased with the increase in size for the same concentration of silica, which will reduce the colliding probability of the colloidal particles and increase the stability of colloidal abrasives.

Polishing properties of colloidal silica nano-abrasives

In order to examine the polishing properties of

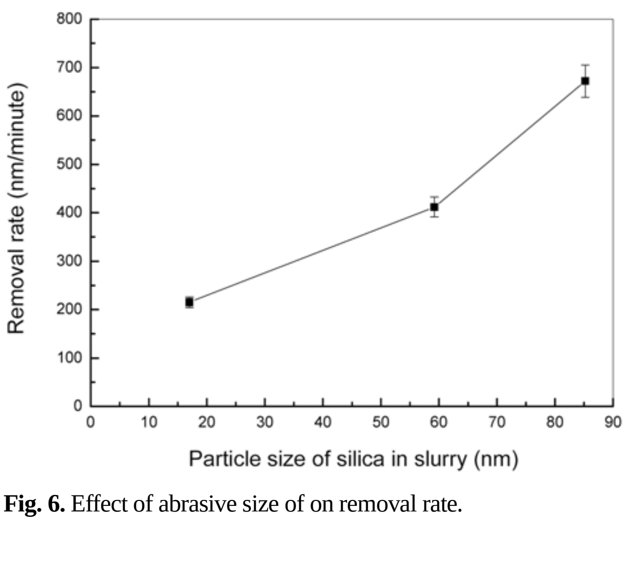

Fig. 6. Effect of abrasive size of on removal rate.

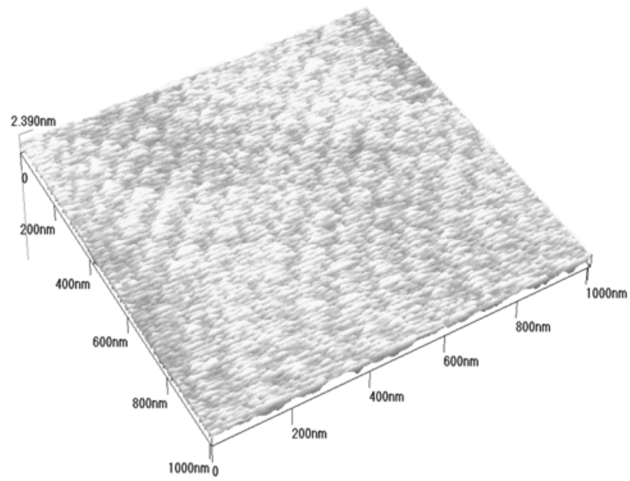

Fig. 7. AFM of Si wafer after CMP.

colloidal silica abrasives made in this study, some CMP experiments with silicon wafers were performed. The other ingredients and polishing conditions were the same, and the effect of particle size on the polishing rate was investigated. As seen in Fig. 6, the removal rate of the CMP process increases with an increase in the particle size of abrasives. When the average particle size of abrasive is about 85.2 nm, the removal rate can be increased to 672 nm/minute.

In order to consider the effect of particle size on the polished surface roughness, the surface of a polished wafer was examined by AFM. As seen in Fig. 7, the surface is very flat, and its roughness is 0.3851 nm. That is to say, the surface roughness did not increase with an increase in particle size, which shows that the colloidal nano-abrasive with large particles not only provides high polishing rate, also achieves a very small roughness.

Conclusions

In this study, the preparation and properties of colloidal silica nano-abrasive were discussed. Some conclusions are summarized as follows:

(1) Colloidal silica nano-abrasives with controlled particle sizes were prepared by a simple process, and their particle sizes were 10-20 nm, 50-70 nm, 80-90 nm.

(2) A colloidal silica nano-abrasive with a large particle size is not aggregates of small particles, but forms by step-growth of small particles and by the formation of Si-O-Si bonds.

(3) The Zeta potentials are less than −45 mV, which shows that these colloidal abrasives are very stable.

(4) Polishing results show that their polishing properties achieved high polishing rate and low surface roughness simultaneously.

Acknowledgements

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