Control Effect of Nanometer SiO₂ Hydrosol on Alloy Impurity in CMP Process of ULSI

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This article analyzed and studied the concentration mechanism of metal impurities of ULSI multilayered wiring CMP in the special-purpose nanometer SiO₂ grinding compound in the substrate chip surface and the process of purification with chelating agent; we also obtained the remarkable effect and the effective application in the microelectron component preparation.

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1. INTRODUCTION

With the development of microelectronic technology, the characteristic size entered the 65 nm and wiring layer already achieved above ten, in the really large-scale integrated circuit (ULSI). Each layer has to carry on globe planarization for photoetching effect and product rate. The only best method of planarization is chemical mechanic planarization (CMP) [1–4], whose mechanical effects depend on some fixed factors such as polishing pad, rotary speed, and polishing pressure. The key is the abrasive in polishing process; SiO₂ colloid is the best abrasive among existing abrasives because of its high purification and broad appliance. The increasing sensitivity of devices is affected by the metal impurities that would cause big leakage electric current, low penetration, soft penetration, reliability deterioration, and undesirable influence. It has suppressed the development of microelectronic technology and the widespread application. Therefore, to obtain the high performance devices, the superficial impurity must fall below the harmful value. Substrate surface metal reduces a magnitude every ten years, along with the microelectron development. The ULSI substrate surface metal relies intensely on the metal impurities density in the solution environment. At present, the metal impurities degree must be cut down behind ppt level ($m/Si = 10^{-12}$). This research has analyzed the gathering process of copper contaminations. Meanwhile, the control of adsorption states using chelant has also been studied deeply.

2. EXPERIMENT

2.1. Experiment of metal impurity adsorption on ULSI substrate

In new processing surface of the ULSI substrate chip and the multilayered wiring CMP, there are a lot of hanging bonds that cause strong superficial field. Metal impurities have a very strong adsorption function on surface. Copper that has harmful effect on device is an example.

2.1.1. Experiment and result

Respectively, we use the polishing slurry to carry on CMP on the substrate chip under the condition that copper content is 60 ppb and 23 ppb, particle size is 30–40 nm, the density is 20 wt%, PH value is 10.3. After the DI water cleans polishing the chip, it is examined with the graphite stove atom absorption spectrum (GFAAS). And the results are in Table 1.

Seen from Table 1, Cu content of the new processing ULSI surface with CMP is dozens of times more than the metallic ion of the SiO₂ colloid. From that it can be seen that the new processed surface has strong function of enrichment function to metallic ions.

2.2. The adsorption experiment of control copper after joining the chelating agent to the ULSI special-purpose SiO₂ polishing slurry

Experiments have indicated that the content of copper on wafer surface has been improved greatly after CMP using

TABLE 1

Sort	Number			
	250902	250904	250803	250807
Cu (ppb) SiO ₂ colloid	23	61	23	62
Cu (ppb) in ULSI substrate surface	1800	2060	1780	2070

TABLE 2

The chelating agent	PPA	AMPS	DTPMP	DTMPA
Cu (ppb) after CMP	15.35	9.67	1.44	8.39

purified SiO₂ as abrasive. Only reduction of metal content in slurry is far from satisfactory if metal impurity must be removed from wafer surface, because it cannot realize purification of metal impurities in polishing slurry through present technology and the vanishment of the micrometal impurities absolutely. Moreover, the processing procedure and the environment can cause contamination. We will adopt a kind of chelant to transform the metal impurities to stable complexants. So easily cleaning can be kept because chemisorption cannot form on new surface [4–10].

2.2.1. Experiment and result

- (1) Silicon wafer (100) N-type, electronic resistivity 8–14 Ω · cm.
- (2) SiO₂ polishing slurry: particle size 30–40 nm, the density 20 wt%, and PH = 10.3 Cu content 100 ppb.
- (3) In the above polishing fluid joining 0.1 wt% chelating agent, respectively: polyacrylic acid (PPA), acrylic amides sulfonate copolymer (AMPS), divinyl three amines five methylenes phosphoric acid (DTPMP), and second grade two-alkene three amines four methylenes phosphoric acid (DTMPA).

The silicon wafer was carried on CMP for 20 min; the result was examined by graphite stove atom absorption spectrum (GFAAS) to determine. The results are in Table 2.

Results show that metal impurities are reduced remarkably by adding polishing fluid with the chelating agent after CMP.

2.2.2. Experimental result and analysis

In the ULSI preparation, controlling of metal impurities on substrate and ULSI multilayered wiring CMP wafer is the essential microelectronic technology that needs further resolve. A large number of coppers enriched because there are a lot of hanging bonds on new processing surface. Moreover, the copper is behind the silicon in chemistry activity sequence chart; thus the copper in the silicon substrate surface can get up the redox reaction:

copper atoms resulting from chemical reaction absorbed on silicon substrate. Density balance is destroyed because of the reduction of copper ions on solid surface, which causes the copper diffusion from liquid to surface. The diffusion causes the superficial cupric ion to respond with the silicon; after response, the ion reduces again in the surface, and the liquid diffuses to the surface, goes round and round; the copper density on new surface is more than that in the polishing slurry; in this environment, the copper ion gathers on the silicon substrate surface. If joining the chelant, after the copper ion and the chelant form the extremely stable chelate, the redox reaction is hard to carry on. The chelant ion is very big after complex. There is only the very weak vander waal strength to physisorption in the silicon substrate surface; the cupric ion is cleaned easily from the surface. Therefore, in order to meet with the electronic technology rapid development, chelant can be used to reduce metal contamination besides purifying of polishing slurry. In the substrate and in the multilayered wiring CMP processing process, besides effectively purifying the density of the CMP polishing fluid, at the same time, joining the chelating agent to the polishing fluid is a extremely effective method of reducing the surface metal impurities in the ULSI preparation process.

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