Fabrication of damascene Cu wirings using solid acidic catalyst

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Abstract

The copper damascene process is one of the most promising technologies for fabricating Cu wirings for electronic devices such as LSIs. In this research, the fabrication of damascene Cu wirings was conducted using solid acidic catalyst. When a Cu-plated wafer, whose oxide is a basic oxide, is dipped into a mixture of oxidizing solution and acidic solution, surface atoms are ionized and etched off into the solution. However, because conventional nonelectrolytic etching does not have a reference surface, it is difficult to utilize for planarization. Therefore, a new nonelectrolytic machining method using a cation-exchange fabric instead of an acidic solution was developed. To be more precise, the planarization of a Cu-plated wafer was carried out by rubbing with the cation-exchange fabric in ozone water. Basically, this method exploits chemical reactions so that the physical properties of the workpiece surface are not deteriorated. Furthermore, this method uses no chemicals except for ozone water, which easily dissociates into water and oxygen molecules; thus, this method is a low-cost, environmentally friendly process. In this paper, as a preliminary experiment, the nonelectrolytic etching of a Cu sample using solutions of O3 and CO2 was carried out to inspect the dependence of the etching rate on [O3] and [H+] . The results indicate that the etching rate increased as [O3] and [H+] increased. When [H+] was high relative to [O3], a smooth etch-pit-free surface was achieved. Next, nonelectrolytic etching using a cation-exchange fabric was carried out, and properties similar to those in the case of etching using solutions were obtained. Finally, damascene Cu wirings were fabricated using ozone water and a cation-exchange catalyst.

Keywords: Damascene process; Nonelectrolytic machining; Ozone water; Catalytic reaction; Solid acidic catalyst; Ion-exchange material

1. Introduction

The copper damascene process is one of the most promising technologies for fabricating Cu wirings for electronic devices such as LSIs [1,2]. However, since chemical mechanical polishing (CMP), which conventionally involves the use of slurries that contain abrasives, is employed to fabricate Cu damascene wirings [3], it is impossible to eliminate mechanical actions completely. Much surface damage and many defects are generated not only on the Cu wirings but also on the insulating film. Electrochemical machining is one of the solutions to this problem because it does not require a processed material to be applied to any undue load; therefore, the physical properties of the workpiece surface are not deteriorated [4]. In particular, in this decade, electrochemical etching in ultrapure water has been studied as an ultraprecision ultraclean machining method [5–7]. In this method, to increase OH− ion density in ultrapure water, an ion-exchange membrane or fabric that dissociates water molecules into H+ and OH− ions is used, and therefore, its removal rate can be equivalent to that of conventional electrolytic machining. However, electrolytic machining inherently has some failings: the processability is restricted by the electrical conductivity of underlying materials, and the processing properties differ depending on the conditions of the workpiece surfaces. Recently, as a new abrasive-free planarization method, catalyst-referred etching (CARE) was developed. In CARE, processing method
in which reactive species such as radicals, generated next to the catalyst surface used as the reference plane, react with the surface atoms of the process material, and consequently, the processed surface is machined smoothly without any mechanical damage. By using a catalytic polishing pad made of platinum and hydrofluoric acid, a markedly flat damage-free processed surface of a 4H-SiC(0 0 0 1) substrate has been achieved [8,9].

In this study, we attempt to apply the concept of CARE to nonelectrolytic machining. To be more precise, a solid acidic/basic catalyst is used instead of a dissociation-assist catalyst. Most metal elements form chemical compounds with oxygen. Each of these compounds has either or both an acidic property or and a basic property, and are called an acidic oxide, a basic oxide or an amphoteric oxide, respectively. Acidic oxides react with basic substances, basic oxides react with acidic substances, and amphoteric oxides react with both basic and acidic substances. Reaction products dissolve into the processing solvent as oxide ions. The oxide of Cu, which is used as a wiring material in semiconductor devices, is a basic oxide. Thus, when it is dipped into a mixture of oxidizing solution and acidic solution, its surface atoms are ionized and etched off into the solution. As etching occurs equally over the entire workpiece surface, this method cannot be applied to planarization machining. Therefore, to localize etching reactions at the convex portion of the workpiece, a solid acidic catalyst is substituted for an acidic solution. Furthermore, no chemicals are used except for ozone water, which easily dissociates into water and oxygen molecules. Thus, this method is a low-cost, environmentally friendly process. In this study, a cation-exchange fabric and ozone water are used as the solid acidic catalyst and the oxidizing solution, respectively. The fabrication of damascene Cu wirings is carried out by this method.

2. Experimental procedure

First, nonelectrolytic etching of a Cu sample using only liquid solutions was carried out. Fig. 1 shows a schematic of the experimental setup, which consists mainly of a PFA (perfluoroalkoxy polymer resin) bottle, an etching vessel and a solution-sending pump. In the PFA bottle, a mixed solution of O₃ and CO₂ is prepared by bubbling CO₂ gas into ozone water. CO₂ is used to make the solution acidic. The hydrogen-ion concentration of the solution can be controlled by varying the CO₂ bubbling rate. Hereafter, the O₃ concentration and the hydrogen-ion concentration of the solution are represented as [O₃] and [H⁺], respectively. The solution was sent to the etching vessel by a pump. In the etching vessel, we placed a Cu sample onto which the solution was sprayed using a polytetrafluoroethylene (PTFE) nozzle. As the Cu sample, a 1-μm-thick Cu film plated onto a Si wafer was used. After etching, the surface morphology was observed using a Michelson-type phase-shifting interferometer (Zygo, NewView 200CHR). Next, the nonelectrolytic etching of the Cu sample using a solid acidic catalyst was conducted. In this work, a sulfonated graft-polymerized polyethylene fabric was used as the solid acidic catalyst. Fig. 2 shows the structural diagram of the sulfonated graft-polymerized polyethylene fabric. We call this catalyst the cation-exchange fabric. Fig. 3 shows a schematic of the experimental setup, which consists of a vessel filled with ozone water, a cylindrical rotator around which the cation-exchange fabric is fixed, and a sample holder into which the Cu sample is placed. The Cu sample was set in contact with the cation-exchange fabric. The Cu-plated wafer described above was used as the Cu sample. Ozone water was continuously supplied to the vessel to remove reaction products. The surface morphology after etching was observed using a Michelson-type phase-shifting interferometer and an optical interferometer. Finally, the Cu damascene wiring was fabricated using a solid acidic catalyst. The same experimental setup as shown in Fig. 3 was used. As the Cu sample, a commercial
Cu film plated onto a patterned Si wafer was used. The formed damascene Cu wiring was observed by scanning electron microscopy.

3. Results and discussion

Fig. 4 shows the surface morphology of the Cu sample after etching using a mixed solution of O₃ and CO₂. The experimental conditions were as follows: [O₃] 2.3 ppm; [H⁺] 2.5 x 10⁻⁵ mol/L; flow rate of solution from the nozzle 70 mL/min; etching time 30 min. Only the portion onto which the solution was sprayed was etched like a hole. Although the results are not shown here, two experiments were conducted to compare the results: one in which only ozone water was used and the other in which CO₂-dissolved deionized water was used as the solution. In both cases, no etched hole was observed. These results mean that the Cu sample is etched only when both O₃ and CO₂ are present in the solution. In addition, the etching rates and surface morphologies after etching with various [O₃] and [H⁺] were compared. Fig. 5 shows the dependence of the etching rate on [O₃] and [H⁺]. The lines indicate the cases in which [H⁺] is 7.9 x 10⁻⁵, 3.3 x 10⁻⁵, and 2.1 x 10⁻⁵ mol/L in descending order. The etching rate increased as [O₃] and [H⁺] increased. If either of them was low, the etching rate was restricted to the asymptotic value. In the graph, ◯ represents the case in which the processed surface was smooth and no etch pit was observed; conversely, × represents the case in which many stains and etch pits were observed on the processed surface. This means that [H⁺] must be high relative to [O₃] in order to obtain a smooth etch-pit-free surface. This is probably a result of the reaction mechanism whereby Cu is initially oxidized, and then the oxidized Cu is etched by H⁺ ions.

When [O₃] is relatively high, the oxidation rate is so high that an oxidized film is formed on the surface. As a result, the localized etching of the oxidized film, "pit corrosion", occurred. On the contrary, when [H⁺] is sufficiently high, an oxidized film is not formed, hence etch pits are not generated. Fig. 6(a) shows the surface morphologies of the Cu sample after etching using a cation-exchange fabric instead of an acidic solution. The experimental conditions were as follows: [O₃] 8.2 x 10⁻⁵ mol/L; rotation speed of the rotator 60 rpm; etching time 10 min. An etched trench was observed along the rotating direction of the rotator. The etched depth was about 100 µm. Compared with the case in which only liquid solutions were used, a large area was evenly etched. This is because all the portions in contact with the solid acidic catalyst were evenly etched.
Thus, this method is more suitable to the planarization of a large area. As in the case of etching using only solutions, two experiments were conducted. Figs. 6(b) and (c) show the surface etched using deionized water instead of ozone water, and the surface etched using an anion-exchange fabric instead of a cation-exchange fabric, respectively. In each case, no etched trench was generated. These results indicate that in the case of etching using a solid catalyst, oxidation and acidic properties are also important factors. Fig. 7 shows an optical interferometer image of the trenched portion in Fig. 6(a). Stains and pits are not observed. This is because the hydrogen-ion concentration measured at the surface of the cation-exchange fabric was about $1.0 \times 10^{-3}$ mol/L, which is in the region where the processed surface becomes smooth and etch-pit-free, as shown in Fig. 5. Finally, damascene Cu wirings were fabricated using the cation-exchange fabric and ozone water. The rotation speed and $[O_3]$ were the same as in the previous experiments and the machining time was 60 min. Fig. 8 shows a SEM image of the fabricated damascene wirings. Cu wiring was fabricated without etch pits or any remaining residue on the insulating film. Although there was some surface roughness and dishing, they could be reduced by optimizing the experimental conditions and by replacing the base material of the solid catalyst with a rigid material.

4. Conclusion

In this study, experiments on nonelectrolytic etching using a solid acidic catalyst were carried out. As a preliminary experiment, nonelectrolytic etching of a Cu sample using solutions of $O_3$ and $CO_2$ was conducted, and the dependence of the etching rate on $[O_3]$ and $[H^+]$ was measured. The etching rate increased as $[O_3]$ and $[H^+]$ increased. When $[H^+]$ was high relative to $[O_3]$, a smooth etch-pit-free surface was achieved. In the case of nonelectrolytic etching using a cation-exchange fabric instead of $CO_2$, similar results were obtained. Finally, damascene Cu wirings were fabricated using ozone water and a cation-exchange catalyst. On the processed surface, neither etch pits nor residues were observed.

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