



Effect of bath additives on copper electrodeposited directly on diffusion barrier for integrated silicon devices



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ABSTRACT

Polyethylene glycol (PEG) and Janus Green B (JGB) have been widely used as suppressor and leveler, respectively, for copper electrodeposition to fill damascene structures of highly integrated silicon devices. In this study, we investigated fundamental nucleation behavior of copper electrochemically deposited on tungsten diffusion barrier without using a copper seed layer in a citrate-based, neutral electrolyte. Concentrations of PEG and JGB were varied to optimize the nucleation and growth of a thin and uniform copper film on tungsten, ultimately considering the application of this copper electrodeposition method to copper fill of sub-45 nm damascene structures. Important fundamental properties of copper nucleation directly on tungsten such as the nuclei density, size distribution, 3D nucleation mode, and surface roughness were investigated when forming a uniform copper film thinner than 30 nm on tungsten by manipulating additive composition in electrolyte. In consequence, a thin and smooth copper film was electrodeposited resulting from instantaneous nucleation and high area density of copper clusters in the electrolyte including 10 μM PEG and 10 μM JGB.

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1. Introduction

Recently, electronic devices such as cellular phone, personal computer, and electronic camera become smaller for their portability, but they also require very high and multifunctional performance. In order to reduce their size even with improved performance, more transistors and capacitors with decreased node width should be manufactured within an ultra-large-scale-integrated (ULSI) silicon chip. Transistors, capacitors, and other components of the ULSI silicon chip are interconnected with copper circuit [1]. Trenches and vias, which are main components of copper interconnect, are also scaled down to the width of tens of nanometers for more device integration. Problems for copper interconnect include the difficulty of filling narrow trenches and vias of high aspect-ratio with copper by electrodeposition method. Thus, we have suggested a method of copper electrodeposition directly on metallic and non-metallic diffusion barriers without using a copper seed layer to have more inner space for copper fill [2,3]. Recently transition metals such as W, Ta, Ti, Ru, Cr, Ni, Co, Pt, Pd, Nb, Mo, Ir, and Os have been promisingly considered as diffusion barrier material due to their excellent resistance to copper diffusion as well as high electrical conductivity compared to non-metallic diffusion barriers [4–6].

However, it has been evident that it is not easy to superfill nanometer-scale trenches and vias of which dimension decreases continuously according to the reduction of device node width with

copper [7]. There have been many efforts to achieve void-free copper fill by controlling bath chemistry including additive compounds [8–12]. Leveler and suppressor molecules prohibit abnormally concentrated copper electrodeposition near the entrance region of damascene structures by being absorbed preferentially at their top-corners. Accelerator molecules as a super catalyst expedite copper reduction process at the bottom of damascene structures, which consequently lead to a bottom-up copper fill. It was reported that the presence of suppressor molecules in an electrolyte suppresses an increase in deposition current density significantly even though the rotation of working electrode mounted with wafer specimen increases it generally [8].

In this research, fundamental nucleation study of very thin copper layers directly electrodeposited on tungsten diffusion barrier is conducted according to the composition of additives in a citrate-based electrolyte. Additives such as polyethylene glycol (PEG) and Janus Green B (JGB) were added to the electrolyte as suppressor and leveler, respectively. Accelerator such as bis-(3-sulfopropyl) disulfide was not included in the electrolyte for direct copper growth on tungsten because ultimately we aim to develop a fundamental electrodeposition process for copper fill of damascene structures narrower than 45 nm and less than 200 nm in depth. Void-free copper fill of relatively wide damascene structures using an electrolyte including both PEG and JGB were previously investigated by several researchers in the aspect of theory building and experimental performance [13,14]. However, the effect of additive composition on the nucleation and growth of copper directly reduced on transition metal diffusion barrier was rarely investigated at the basic level. Consequently, we studied the nucleation and growth behavior of very thin copper layers on tungsten diffusion barrier

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fundamentally with changing additive composition in the electrolyte including PEG and JGB.

2. Experimental details

A 100-nm thick tungsten diffusion barrier layer was sputter-deposited on thermally grown silicon oxide of 4 in. silicon wafer. The tungsten-deposited silicon wafer was cleaned with ethanol and rinsed with deionized water before copper electrodeposition. The silicon wafer was cut into rectangular specimens with a dimension of 1.5×2 cm, and then the wafer specimen was mounted on the Teflon housing, as shown in Fig. 1. It was fixed by Teflon working electrode. An area of tungsten surface exposed to the electrolyte was approximately 1 cm^2 .

The base electrolyte contains $0.05 \text{ M CuSO}_4 \cdot 5(\text{H}_2\text{O})$ and $0.05 \text{ M } (\text{NH}_4)_2\text{HC}_6\text{H}_5\text{O}_7$ in common. pH of the electrolyte was 7, which was controlled using NH_4OH solution. PEG and JGB were used as suppressor and leveler, respectively. The concentration of PEG in the electrolyte was varied from 0 to $1000 \mu\text{M}$, whereas that of JGB was $10 \mu\text{M}$ if it was added. Experiments were carried out in a three-electrode cell using a potentiostat (Gamry Inc.). A saturated calomel electrode (SCE) was used as a reference electrode, and a pure copper plate with a dimension of $5 \times 5 \times 0.6 \text{ cm}$ was used as a counter electrode. Copper deposition was performed by applying a constant cathodic potential of -1.0 V to the specimen-mounted working electrode for 10 s. Cyclic voltammetry (CV) was performed to characterize cathodic and anodic polarization behavior in the range of 2.0 to -2.0 V at a scan rate of 5 mV/s . The morphology of deposits was examined using a field emission scanning electron microscopy (FESEM, Quanta 200, FEI) with an operating voltage of 15.0 kV . SEM images were employed to identify the nucleation mode, which could be confirmed by comparing experimental current transient curves with three-dimensional (3D) nucleation models developed by Scharifker and Hills [15–17] and by using a statistical consideration of size distribution of copper clusters. Atomic force microscope (AFM, XE-100, Park Systems) was used to measure the surface roughness of copper deposits. It was operated in non-contact mode using a non-contact cantilever tip (PPP-NCHR 10 M).

3. Results and discussion

CVs in three different baths were conducted for tungsten diffusion barrier, as shown in Fig. 2. The base electrolyte does not contain any additive except copper sulfate and citrate complexing agent, which were effective in electrodepositing thin copper films on non-metallic diffusion barriers [2,3]. The other baths contain only PEG or JGB individually as additive in the base electrolyte. It was previously suggested that JGB of high molecule weight replaces other compounds like PEG existing in a seed surface [18]. Supposing that the suggestion regarding JGB in a multi-additive containing electrolyte is plausible, it is necessary to investigate the role of PEG or JGB independently in order to avoid missing the effect of PEG in the citrate-based electrolyte including both additives. CV curves are shifted to lower current density in cathodic

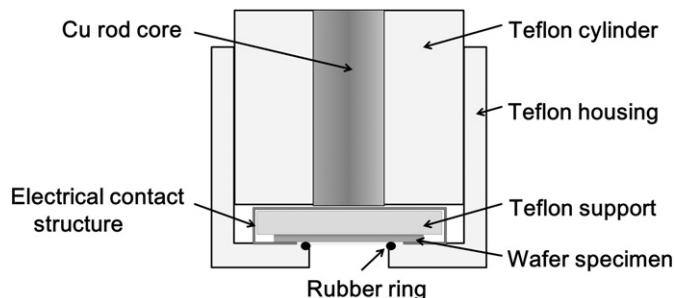


Fig. 1. Schematic diagram of the cross-sectional structure of working electrode including a wafer specimen.

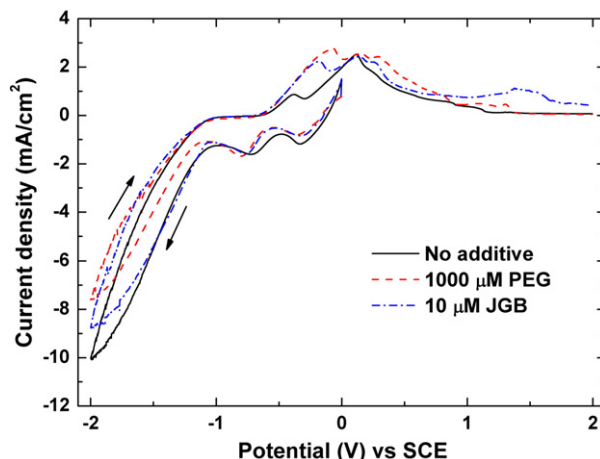


Fig. 2. Cyclic voltammetry obtained from three electrolytes of pH 7. Its scan rate is 5 mV/s .

potential region when PEG or JGB is added. It implies that larger cathodic polarization occurs by adding $10 \mu\text{M}$ JGB or $1000 \mu\text{M}$ PEG to the base electrolyte because the adsorption of JGB or PEG molecules on tungsten hinders copper reduction partly. From our previous report, we found that applying deposition potential near -1.0 V in the citrate-based electrolyte without additives is proper to produce a thin and uniform copper film resulted from a high nuclei density of copper [4]. Potentials more positive than -1.0 V have led to relatively coarse copper deposit, whereas more negative potentials have resulted in rough copper deposit accompanied by hydrogen evolution. Thus, copper depositions in this study were carried out at a constant potential of -1.0 V .

Current transient curves obtained from potentiostatic depositions were compared with Scharifker and Hills' theoretical model to determine 3D nucleation mode during copper deposition [15–17]. The theoretical model includes instantaneous and progressive nucleation. Instantaneous nucleation is preferred to form a thin and uniform copper film. However, any experimental result cannot correspond with exactly instantaneous nucleation, which indicates that no more nuclei should form after initial nuclei are created at the beginning of electrodeposition. The 3D instantaneous nucleation is expressed as follows.

$$\left(\frac{i}{i_m}\right)^2 = 1.9542 \left(\frac{t_m}{t}\right) \left\{ 1 - \exp \left[-1.2564 \left(\frac{t}{t_m}\right) \right] \right\}^2 \quad (1)$$

The 3D progressive nucleation can be identified by the following expression as

$$\left(\frac{i}{i_m}\right)^2 = 1.2254 \left(\frac{t_m}{t}\right) \left\{ 1 - \exp \left[-2.3367 \left(\frac{t}{t_m}\right)^2 \right] \right\}^2 \quad (2)$$

where i_m is a maximum current density and t_m is a time at i_m . Fig. 3 shows the normalized curves of current transient curves in three baths according to Scharifker and Hills' model. When PEG or JGB is added to the base electrolyte, the curves are shifted from progressive nucleation to instantaneous nucleation because of the inhibition effect of PEG and JGB. The curve of the electrolyte containing $1000 \mu\text{M}$ PEG was closer to that of instantaneous nucleation. PEG as suppressor works effectively in suppressing further copper nucleus nucleation once copper nuclei are formed initially.

Fig. 4 shows SEM images of copper deposits on tungsten diffusion barrier according to additive condition in the electrolyte. We are concerned on the area density, size distribution, surface roughness, and surface coverage of copper clusters considering the effect of individual additive on copper nucleation. Forming a thin and uniform copper film, which is proper for void-free copper fill of nanometer scale damascene structures, needs a copper nuclei density higher than $2 \times 10^{10} \text{ cm}^{-2}$ from theoretical calculation. The value of $1.8 \times 10^{10} \text{ cm}^{-2}$ was achieved

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