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Investigations on the invalidated process and related mechanism of PEG during copper via-filling process

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ABSTRACT

The invalidated process and related mechanism of PEG during copper via-filling process were investigated by means of electrochemical polarization and electrochemical impedance (EIS) measurements, and infra-red spectrum (IR) measurement was employed to analyses the invalidated products of PEG. The results suggest that the adsorption strength of PEG on cathode surface and its inhibition to copper reduction decrease gradually with the increase of passed charges (PC). Both the anodic and the cathodic electrifying process can cause the invalidation of PEG, but their invalidated courses are different. PEG will further polymerize to form new PEG with bigger MW on the anode surface, which causes the dispersive ability of plating solution to decrease. As a result, super-filling behavior cannot be obtained and many small wales formed on the specimen surface during copper via-filling process. Inversely, PEG will decompose to form new PEG with smaller MW on the cathode surface, which results in the decrease of PEG adsorption ability and inhibition. As a result, super-filling behavior cannot be obtained and the brightness of the specimen surface decreases during copper via-filling process. The decomposition of PEG is easily to happen than its polymerization when the anodic and cathodic reactions happen in the same plating solution simultaneously. So the main invalidated product of PEG during copper via-filling process is PEG with smaller MW.

1. Introduction

Copper electrodeposition is used in the damascene process for the high density interconnections of integrated circuit (IC) chips and printed circuit boards (PCBs). In this process, copper is directly filled into the via by electroplating using specific plating additives [1–4]. These additives function synergistically to cause bottom-up fill or super-fill, which requires that the rate of copper electrodeposition at the bottom of the microvia (MV) must exceed that at the via opening and at the board surface, resulting in the void-free and seam-free filling of via and trench [1]. This interesting filling behavior not only occurs in the submicrometer vias of wafers [1–3], but also in the microvias of PCBs [5–7]. In practice, the plating additives used for the copper metallizationin IC chip fabrication are the same as those employed in PCB fabrication, no matter what feature size is chosen.

To accomplish super-fill, small concentration of Cl^- and organic additives, usually referred to suppressor (such as polyethylene glycol, PEG), accelerator (such as bis(3-sulfopropyl) disulfide, SPS), and leveler (such as Janus green B, JGB) are included in the bath [1–8], in which PEG takes an indispensability role during via-filling process. The inhibiting effect and related mechanism of PEG have been extensively studied [9–13], but the researchers usually ignore the stability of PEG during copper via-filling process. Therefore, to better understand the effect of PEG, the investigations about its invalidated process and mechanism related to the amount of passed charges (PC) are very necessary.

In this paper, the invalidated process and related mechanism of PEG during copper via-filling process were firstly investigated by means of electrochemical polarization and electrochemical impedance (EIS) measurements, and infra-red spectrum (IR) measurement was employed to analyses the anodic and the cathodic invalidated products of PEG. Based on the analyses above, the invalidated mechanism of PEG during copper via-filling process was proposed.

2. Experimental methods

Basic measuring solution (BMS) was composed of 1 mol L^{-1} $CuSO_4{\cdot}5H_2O$, 0.56 mol L^{-1} H_2SO_4 and 50 mg L^{-1} Cl^-. The molecular weight (MW) of PEG used in this paper are 12,000. In order to investigate the electrochemical behavior of PEG invalidated

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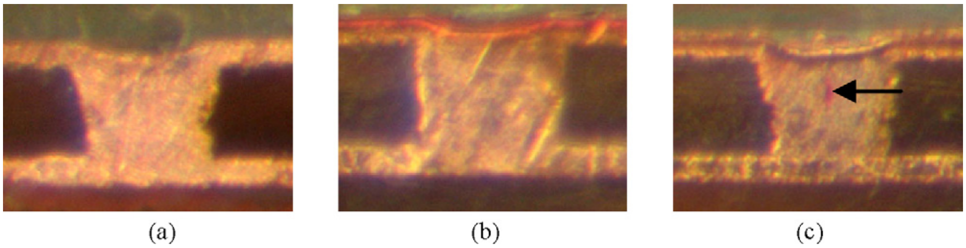

Fig. 1. Cross-sectional photos of copper via-filling prepared in the solutions containing PEG pre-treated by different anodic PC, (a) 0 Ah L^{-1}, (b) 40 Ah L^{-1} and (c) 80 Ah L^{-1}.

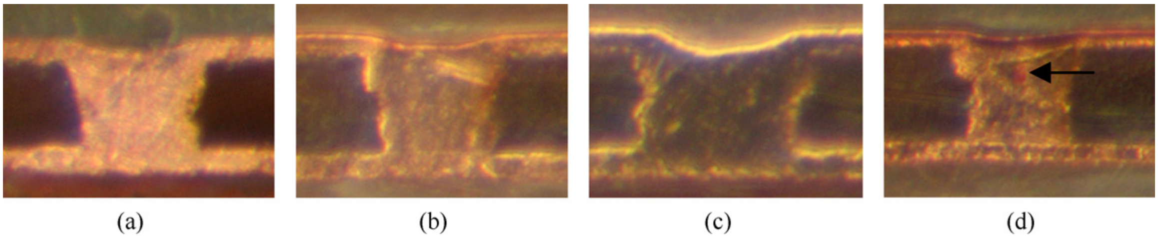

Fig. 2. Cross-sectional photos of copper via-filling prepared in the solutions containing PEG pre-treated by different cathodic PC, (a) 0 Ah L^{-1}, (b) 40 Ah L^{-1}, (c) 80 Ah L^{-1} and (d) 100 Ah L^{-1}.

process, 80 mg L^{-1} PEG was added into BMS (BMS + PEG). Then, BMS + PEG were pre-treated galvanostatically at 70 mA cm^{-2} until PC reached 0, 5, 20, 40 and 80 Ah L^{-1}, and these solutions were used for electrochemical measurements directly. During this process, a Cu–P alloy was used as the anode, and a copper plate was used as the cathode. In order to investigate the via-filling behavior of PEG anodic and cathodic invalidated process respectively, 800 mg L^{-1} PEG was added into the solution only containing 0.56 mol L^{-1} H_2SO_4 (H_2SO_4 + PEG). Then, H_2SO_4 + PEG were pre-treated galvanostatically at 70 mA cm^{-2} until the anodic PC reached 0, 40, 80 Ah L^{-1} and the cathodic PC reached 0, 40, 100 Ah L^{-1}, respectively. After that, a certain amount of $CuSO_4{\cdot}5H_2O$, Cl^-, SPS (3 mg L^{-1}) and JGB (1 mg L^{-1}) were added into the pre-treated H_2SO_4 + PEG, which were used for copper via-filling plating directly. During the electrifying pre-treatment above, H_2SO_4 + PEG was divided into the anodic part and the cathodic part by a membrane which can only allow small ions, such as Cu^{2+}, Cl^-, H^+ and so on, to pass through, but big PEG molecules and its invalidated products cannot pass through it. So the anodic and the cathodic invalidated products of PEG can be separated completely during the electrifying pre-treatment process. In order to investigate the structure conversion of PEG during the anodic and the cathodic invalidated processes, H_2SO_4 + PEG was also pre-treated by the same method mentioned above until the anodic and the cathodic PC reached 100 and 180 Ah L^{-1}, respectively. Then, the pre-treated H_2SO_4 + PEG were extracted by CH_2Cl_2 (chromatographic grade), and the extracted layer was evaporated to dryness by rotating evaporator. The obtained powder was used for infrared spectrum measurement directly. In the electrifying experiments mentioned above, a Ti net was used as the anode, and a copper plate was used as the cathode.

All the electrochemical measurements were performed using CHI660B electrochemical working station at room temperature. A standard three-electrode and two-circuit cell was used for the electrochemical measurement, which consisted of a copper plate (1 cm^2) as the working electrode, a Pt plate as the counter electrode (10 cm^2) and a saturated calomel electrode (SCE) as the reference electrode. The potentials given in this paper were all respected to SCE. Steady-state cathodic polarization measurements were recorded at scanning rate of 0.5 mV s^{-1}. EIS measurements were carried out at different potentials, separately, and before each measurement the system had been firstly polarized at the given potential for 60 s. The measuring frequency range was from 10 mHz to 10 kHz. All the measurements above were carried out without stirring. IR measurements (American Thermo Nicolet, AVATAR360) were used to detect the structure conversion of PEG reacting products.

Via-filling plating was performed galvanostatically at 20 mA cm^{-2} for 60 min at room temperature. A Pt net was used as the anode, and a PCB plate with via size 60 μm in depth and 80 μm in width was used as the cathode. Before each plating, the PCB plates were rinsed by deionized water and acid.

3. Results and discussion

3.1. Via-filling behavior analyses

Via-filling specimens were prepared in BMS containing SPS, JGB and PEG pre-treated by different anodic and cathodic PC, and the cross-sectional morphologies of the via-filling specimens are shown in Figs. 1 and 2, respectively. Fig. 1(a) and (b) show that the via can be filled successfully when the anodic pre-treated PC of PEG is less than 40 Ah L^{-1}, and a little void can be observed in the filled MV (Fig. 1(c)) after the anodic pre-treated PC reached 80 Ah L^{-1}. Fig. 2(a), (b) and (c) show that the via can be filled successfully when the cathodic pre-treated PC of PEG is less than 80 Ah L^{-1}, and a little void in the filled MV (Fig. 2(d)) appears after the cathodic pre-treated PC reached 100 Ah L^{-1}. The results above suggest that PEG begins to invalidate after PC

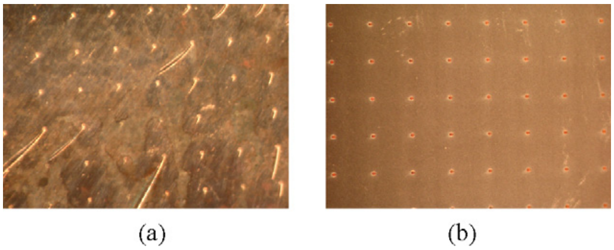

Fig. 3. Top-view photos of copper via-filling prepared in solutions containing PEG pre-treated by (a) anodic PC 80 Ah L^{-1} and (b) cathodic PC 100 Ah L^{-1}.