Initiation electroless nickel plating by atomic hydrogen for PCB final finishing

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HIGHLIGHTS

- We proved that atomic hydrogen could be prepared on the copper surface.
- The lifetime of atomic hydrogen on the copper surface is less than 23s in the air.
- The prepared atomic hydrogen could start electroless nickel plating.
- Atomic hydrogen is prior to Pd in starting electroless nickel plating for ENIG.

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ABSTRACT

In this work, atomic hydrogen generated from decomposition of formaldehyde, is used to replace of Pd catalyst, because, according to Brenner and Hersch's model, atomic hydrogen as reaction intermediate can start electroless nickel plating. As the plated copper was removed out of the alkaline formaldehyde solution, its open circuit potential and Raman spectra were also studied, showing that the existence of atomic hydrogen adsorbed on the copper can last for a while until the formation of Cu_2O. Then it was verified that electroless nickel could be started successfully by short-lived atomic hydrogen. The obtained nickel layers separately initiated by atomic hydrogen and Pd were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDX); their anti-corrosion was also studied by potentiodynamic polarization and electrochemical impedance spectroscopy. The results demonstrate that atomic hydrogen is superior to Pd in starting electroless nickel plating for PCB final finishing.

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1. Introduction

Cu is selected and widely used in printed circuit board (PCB) manufacturing to link electrical components due to the excellent electrical conductivity and easy processing [1,2]. However, copper is apt to corrode in the atmosphere and copper wires need surface finishes to maintain its conductivity [3,4]. There are many types of Cu surface finish for PCB industry [5–8]. Due to anti lead laws in EU, China, California, etc., demands for electroless nickel immersion gold (ENIG) have been dominating the market for decades [9,10]. The electroless nickel of ENIG is the protective layer to the copper and is the surface to which the components are actually soldered to [11]. Electroless plating nickel is an autocatalytic process which needs to be activated by Pd, but Cu itself without Pd is inactive to hypophosphite [12,13]. At present, Pd as an activator is indispensable to ENIG for PCB.

Due to the ever-increasing price of Pd, it is urgent to find a Pd-free method to replace Pd-activation process of ENIG [14,15]. Because of the autocatalytic behavior of electroless nickel plating, the Ni-activation method for Cu substrate has been intensively studied [12,16,17]. There are mainly two ways about Ni-activation method: 1) Ni^{2+} is reduced to Ni in high concentrated thiourea solution to form a Ni-S film on Cu substrate [12,17]; 2) Ti^{3+} as a reducing agent directly reduce Ni^{2+} to form Ni layer [16]. These two ways have successfully realized Pd-free activation, but both have inevitable drawbacks. The first method will cause the Cu pattern diminished and introduced thiourea into the process, which is not easy to wash away from Cu surface and is poisonous to electroless plating nickel. The second method employs Ti^{3+} as a reducing agent, which is not stable and is easy to oxidize, and Ti^{3+} is too expensive to satisfy large-scale production. Except

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for the Ni-activation method, using direct electroless nickel plating on the copper patterns by the addition of hydrazine or dimethylamine borane (DMAB) as second reducing agent into the plating bath was also investigated [18–20]. However, there is an intrinsic drawback in this method that hydroxyl ion in alkaline solution, which is indispensable for hydrazine and DMAB providing reducibility, is hard to coexist with Ni^{2+}. In this work, we try to solve this problem. We do not directly add reducing agent into the plating bath, but divide it into two independent parts: alkaline solution with reducing agent and plating solution containing Ni^{2+}. In this way, the coexisting problem can be solved perfectly; the stability of the plating bath is also greatly enhanced because the plating solution need not be alkaline.

Herein, formaldehyde is chosen as reducing agent; it is not the only candidate but these soluble substances which could be decomposed with atomic hydrogen attached on the copper surface, such as hydrazine [21], DMAB [22], and glyoxylate [23], are all available. Because electro-oxidation of formaldehyde on the copper surface has been studied widely and deeply, choosing formaldehyde as research object is in favor of clarifying the issue.

2. Experimental

2.1. Initiation electroless nickel plating by atomic hydrogen

The samples with a thickness 30 μm copper pattern were made by direct current with a current density of 2.08A dm^{-2} [24]. Before activation, samples need to be degreased in acetone and be etched in 5 wt.% H_2SO_4 solution to remove oxides. After washed with deionized water, the pretreated samples were immersed into the activating solution containing 0.2 mol dm^{-3} NaOH and 0.2 mol dm^{-3} HCHO at 25 °C for 20 s, which can cause decomposition of formaldehyde and generation of atomic hydrogen adsorbed on the Cu surface [25,26]. Then the activated sample with hydrogen atoms need to be quickly moved into the plating bath at 88 °C. The bath contains 20 g dm^{-3} $NiSO_4 \cdot 6H_2O$, 25 g dm^{-3} NaH_2-$PO_2 \cdot H_2O$, 20 ml dm^{-3} lactic acid, 5 ml dm^{-3} propionic acid and 2 mg dm^{-3} KI. In addition, the traditional Pd-activation bath was also studied for a comparison.

2.2. Electrochemical measurements

Except open circuit potential (OCP), all electrochemical measurements were carried out on an Autolab GN233 electrochemical workstation in a three-electrode cell. Sample, 1×1 cm^2, was employed as working electrode; Ag/AgCl electrode with saturated KCl was used as reference electrode; a Pt sheet, 5×5 cm^2, was used as counter electrode. OCP measurements were carried out in a two-electrode cell: working and reference electrode; Especially when sample was taken out of the solution, the measurements were carried out in liquid film attaching to copper surface instead of a cell.

2.3. Raman measurements

Raman spectra were collected on a JY Horiba LabRAM 800 spectrometer equipped with a liquid-nitrogen cooled detector. A 632.8 nm He-Ne laser of 2–5 mW provided the incident radiation. A $50 \times$ objective was employed for focusing the laser beam. The chosen conditions, a 200 μm confocal hole and a 600 grooves/mm grating, provided a Raman spectral resolution of 2–4 cm^{-1}. The Raman spectra were calibrated by using the Si 520.07 cm^{-1} shift.

2.4. Physical characterization

The morphologies of nickel layers were observed with a JSM-6700 F field-emission scanning electron microscope (FE-SEM) at an accelerating voltage of 10 kV. The EDX system mounted on the SEM was employed to determine the elemental compositions of the nickel layers. The hardness of Nickel layers was measured by time 6710 and the Depth of nickel layers was tested by XRF-1800. A simple corrosion test method was used to detect "black pad" phenomenon in ENIG. After EN plating, the 2 cm × 6 cm nickel sample was rinsed and dried, and was immersed into the 40% v/v nitric acid meanwhile a stopwatch was used to recording time during which the nickel sample turned black spontaneously [27].

3. Results and discussion

3.1. Preparation of atomic hydrogen on the copper surface

The mechanism of formaldehyde oxidation on copper surface has been extensively discussed [28–30]. Fig. 1 is the linear sweep voltammetry plots of plated copper in two kinds of solution: alkaline and alkaline formaldehyde solution. In the potential range from −1.0 V to −0.443 V, no anodic current is found in the alkaline solution; on the contrary, in the alkaline formaldehyde solution significant anodic current is found, demonstrating that plated copper is highly active for anodic oxidation of formaldehyde. It is worth to note that the potential of anodic peak in alkaline formaldehyde solution is at around −0.443 V, which is consistent with the initial potential of formation of Cu_2O in the alkaline solution [31,32]. This phenomenon indicates that Cu_2O is not active for electro-oxidation of formaldehyde, and copper will lose the catalytic activity, if it is covered by Cu_2O.

In order to identify the atomic hydrogen attached on the copper surface, the Raman spectra are discussed. Fig. 2 shows Raman spectra, which were measured as soon as copper was taken of formaldehyde alkaline solution. The band at 711 cm^{-1} is assigned to Cu—OH stretching mode. It has been reported that CuOH surface species is formed upon cathodic reduction of the copper electrode in alkaline solution [33]. The Raman band at 2875 and 2910 cm^{-1} is the characteristic band of symmetric and anti-symmetric stretching vibration band of H—C—H group of $CH_2(OH)_2$ [34]. The Raman band at 2050 cm^{-1} could be attributable to Cu—H or C—O
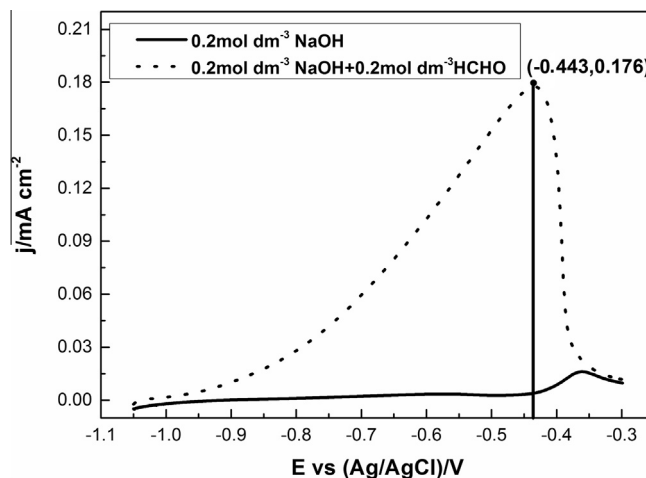

Fig. 1. Linear sweep voltammetry of plated copper in 0.2 mol dm^{-3} NaOH and 0.2 mol dm^{-3} NaOH + 0.2 mol dm^{-3} HCHO solution (scan rate 10 mV s^{-1}, scan range from −1.05 V to −0.3 V).