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Nickel dependence of hydrogen generation, hydrogen co-deposition and film stress in an electroless copper process

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ABSTRACT

Hydrogen co-deposition in electroless copper is a cause of embrittlement, voids and blisters. Hydrogen release in the plating bath and its incorporation into the copper films were measured. The amount of hydrogen in the films was determined by monitoring its release over several days at ambient conditions. The mixed potential and the film stress were recorded during film deposition. Adding nickel ions in the plating bath lowers the mixed potential, and it reduces hydrogen incorporation from about 25 at.% to 0.01 at.%. However, the total amount of hydrogen generated per amount of plated copper remains unchanged. For films plated without nickel, the biaxial stress of the films and their hydrogen content are proportional with 3.2 ± 0.3 MPa/at. % H.

1. Introduction

Electroless (or chemical) copper plating is a key process in manufacturing printed circuit boards, establishing electrically conductive seed layers on insulating substrates for subsequent galvanic copper plating [1]. It frequently requires filling of vias in multilayer circuit boards. The scope of electroless copper plating technology is evolving to a broader range of substrate materials that allow for smaller structures, higher temperatures and higher signal frequencies [2]. On smooth substrates, copper film adhesion can be problematic.

In electroless plating, the reduction of metal ions and the oxidation of a reducing agent take place simultaneously at a catalytic surface. Van den Meerakker considered reactions without and with generation of hydrogen [3]. The two limiting cases are

$$Cu^{2+} + HCHO + 3OH^{-} \longrightarrow Cu + HCOO^{-} + 2H_2O \tag{1a}$$

and

$$Cu^{2+} + 2HCHO + 4OH^{-} \longrightarrow Cu + 2HCOO^{-} + H_2 + 2H_2O \tag{1b}$$

For Cu alone the oxidation of HCHO proceeds by Reaction (1b), while in the presence of metal ions such as Pd and Ni, Reaction (1a) is favored. Because OH^- ions are consumed, a high pH is required [4]. Deuterium marking has shown that oxidation of HCHO is initiated by breaking a C—H bond [5,6],

$$HCHO_{ad} \overset{Cu}{\rightarrow} H_{ad} + HCO_{ad}, \tag{2}$$

where, for clarity, the intermediate methylene glycol formation is not considered. Enyo proposed that Reaction (1a) avoids the production of molecular hydrogen via oxidation of hydrogen in the presence of Ni [1,7],

$$H_{ad} + OH^{-} \overset{Ni}{\rightarrow} H_2O + e^{-} \tag{3a}$$

Desorption of molecular hydrogen, either during or after the plating process, is a competing process with

$$2H_{ad} \longrightarrow H_2 \tag{3b}$$

As a third alternative, adsorbed hydrogen atoms may be incorporated into the deposit.

$$Cu + y\ H_{ad} \longrightarrow CuH_y \tag{3c}$$

Hydrogen co-deposition by Reaction (3c) has been recognized as a cause for the formation of voids, blistering and low ductility in electroless copper [2,8,9]. Diffusible (atomic or molecular) hydrogen is distinguished from non-diffusible or residual hydrogen that is part of organic or inorganic compounds [10]. Diffusible hydrogen accumulates in voids and strains the material through the gas pressure, thus reducing the ductility of the metal [11]. Compressive film stress is a co-determining factor in the initiation and growth of blisters [12]. The relationship between the number of hydrogen atoms embedded, the

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blister shape and the energetics of blister formation has been described and analyzed for a multilayer system [13]. While hydrogen is taken up by copper as atomic hydrogen, it is considered that molecular H_2, present in voids, influences the properties of the material [9]. For a deposit with 0.2 at. % hydrogen, the calculated pressure of H_2 in microvoids is 70 MPa [10]. Out-diffusion of hydrogen upon annealing at 150°C restores the ductility of the copper film [8].

Addition of nickel to the electroless copper process modifies the chemical reaction, and it should lower hydrogen production during plating [3]. Plating baths containing nickel ions show indeed less buildup of compressive film stress during plating [14,15]. Although, as expected, the addition of nickel eliminates film blistering, surprisingly the amount of hydrogen released to the bath during the plating process does not change noticeably [12]. The data presented here show that the amounts of hydrogen released during plating and incorporated in the deposit are independent, and that nickel ions in the plating bath are effective in reducing the latter. A direct chemical reaction path to copper hydride in competition with the electrochemical reduction of copper has been proposed [16,17].

2. Experimental

Copper was plated from a commercial electrolyte (Printoganth P Plus, Atotech Deutschland GmbH). This standard electrolyte contains 2 g/l (31.5 mM) Cu^{2+}, 0.4 g/l (6.82 mM) Ni^{2+} (both added as sulfates), 3.5 g/l (117 mM) HCHO as reducer and 9 g/l (529 mM) OH^- added as NaOH. The copper ions are complexed with 10.6 g/l (72 mM) tartrate ions, added as $KNaC_4H_4O_6$, and a stabilizer system based on dipyridyl is used [4]. The concentration of Ni^{2+} ions was varied between 0 and 800 mg/l. Film growth was initiated by activating the substrates with Pd^{2+} ions (200 mg/l) at 45 °C for 4 min. These ions were reduced on the substrate surface with a dimethylamine borane solution at 30 °C [18]. Plating was carried out for 20 min at 32°C, and the bath was constantly aerated. The concentrations of OH^-, HCHO and Cu^{2+} were monitored by titration and replenished as required. Dummy plating was carried out for freshly prepared plating baths and if the plating solution had not been used for several hours. The substrates were 50 mm × 50 mm glass-reinforced epoxy laminate (FR-4) sheets that were desmeared prior to plating. Stress measurements were carried out with Ni—Fe (alloy 42) dual-leg test strips with a thickness of 38 μm, purchased from Specialty Testing and Development Co. Inc. (York, PA).

The amount of evolved gas was measured during and after electroless copper deposition. Similar to the method employed in Reference [2], gas evolving during deposition was trapped in an inverted funnel connected to a pipette and a pipette filler bulb. The sample was mounted on a stand that allows a magnetic stirrer to operate below the sample. Right after the plating start the liquid level in the pipette is adjusted to a fixed level. Gas evolving during plating displaces the liquid, and its volume can be read directly. A handle, attached to the sample holder, passes underneath the funnel. This handle is used to knock the sample to release hydrogen bubbles from the plating surface prior to each reading. A test without plating was carried out with a non-activated FR-4 surface under otherwise identical conditions. The amount of gas collected in this blank test was small (0.25 ml) compared to the amount in trials with plating (in the range from 3 to 9 ml).

Gas evolution from the electroless copper deposit after plating was measured by trapping the gas in an oil-filled gap (Fisherbrand 19 Mechanical Pump Oil) between the copper film and a glass plate. For good optical contrast, Oil Blue N dye was added to the oil. Electroless copper was deposited on both sides of the 50 mm square pieces of FR-4 glass-epoxy printed circuit board material. The plated area was restricted to a 35 mm wide square by covering the margin with 3 M 851 tape during the palladium activation step. This tape was removed prior to plating. Glass plates (50 mm square) were prepared with a 5 mm wide border around the outside edge (Fig. 1). This border consisted of one to four layers of electrical tape (each layer with a thickness of 150

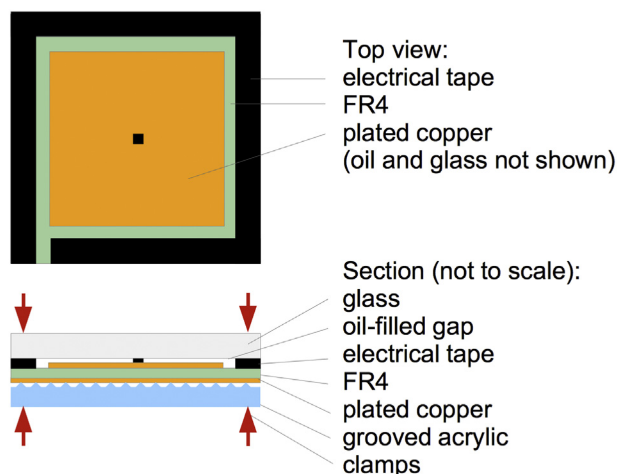

Fig. 1. Schematic of the device to measure hydrogen release after plating.

μm), depending on the expected amount of evolved hydrogen. The oil displaced by the evolved gas can seep out through a 2 mm wide gap in one corner of this border. Within 3 min from the end of plating, the FR-4 piece is rinsed with water, dried and covered with the glass plate and the oil. The back side of the plated FR-4 piece is covered with an acrylic sheet, and the setup is clamped. A pattern of grooves in the acrylic sheet allows gas evolving from the plated backside to dissipate freely. Photographs were taken at regular intervals to monitor the amount of gas, with the first photograph typically being taken within 6 min after the end of plating. Any bubbles visible in the first image are assumed to be trapped air, and this amount of gas is subtracted from all gas amounts found in the subsequent images. The contrast is sufficiently good to measure the area covered by gas bubbles with an image analysis program (ImageJ).

The average film stress was measured during and after plating with the dual-leg metal test strips mentioned above. The legs are coated with varnish on the opposite sides such that the Cu plates only on one side of each strip. Any film stress will bend the strips in opposite directions. Photographs were taken before, during and after plating. The lateral spread of the test strip legs was converted to substrate curvature, κ, allowing for the effects of gravity and buoyancy [19]. The curvature is converted to deposit stress with Stoney's equation,

$$\sigma = \frac{1 + hm(4 + 6h + 4h^2) + h^4hm^2}{1 + h}\frac{E_s h_s^2 \kappa}{6h_f(1 - \nu_s)},$$

where h_f, E_f and ν_f (h_s, E_s and ν_s) are the thickness, Young's modulus and Poisson's ratio of the film (substrate), and the coefficients $h = h_f/h_s$ and $m = E_f(1 - \nu_s)/[E_s(1 - \nu_f)]$ are correction factors for films of finite thickness [20]. Data during plating are analyzed with the assumption that h_f increases linearly with time.

The stress and lattice constant of the fully relaxed deposits on FR4 were measured several weeks after deposition with X-ray diffraction (XRD) with a custom-built diffractometer using CuK_α radiation with graphite monochromator and analyzer crystals. The data were analyzed with the $\sin^2\psi$ method that considers the interplanar spacing for different (*hkl*) as a function of the tilt angle ψ of the surface normal of the deposit with respect to the scattering vector [15]. The thickness and the Ni/Cu ratio of films plated on FR4 were determined by X-ray fluorescence (XRF, Olympus Innov-X Delta Premium DP-2000) [18]. The XRF data were calibrated against three samples for which the amount of deposited copper was measured by iodometric titration. Micrographs of film cross sections, prepared with focussed ion beam (FIB) milling, were obtained by scanning electron microscopy (SEM) with a FEI Nova Nanolab.

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