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A New Activation Method for Electroless Metal Plating: Palladium Laden *via* Bonding with Self-Assembly Monolayers

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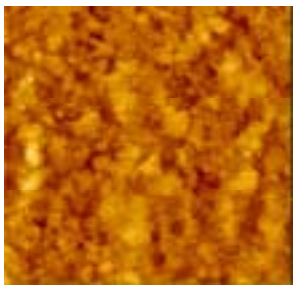
Abstract: A new activation method has been developed for electroless copper plating on silicon wafer based on palladium chemisorption on SAMs of APTS without $SnCl_2$ sensitization and roughening condition. A closely packed electroless copper film with strong adhesion is successfully formed by AFM observation. XPS study indicates that palladium chemisorption occurred *via* palladium chloride bonding to the pendant amino group of the SAMs.

Keywords: Palladium chemisorption, amino group, SAMs, activation, electroless plating.

Electroless metal plating on non-metallic species is possible only in the condition that catalytic sites are created on the surface to be metallized[1]. For silicon wafers, these sites, usually containing palladium nuclei, are chemisorbed from solution *via* stannous chloride sensitization because of the low reactivity of the substrate surfaces[2,3]. However, the palladium nuclei formed in this way has poor adhesion to the substrate, easily invalidates and desorbs from the substrate[4].

Now we develop a novel method for palladium laden on the silicon surface based on covalently bonded self-assembled monolayers (SAMs) of aminopropyltriethoxysilane (APTS) without $SnCl_2$ sensitization and former roughening condition. The experimental procedure was carried out as follows: (1) forming APTS SAMs on the cleaned silicon surfaces; (2) introducing in an activation solution containing $PdCl_2$; (3)

Figure 1 AFM image of the electroless copper deposit on the silicon wafer



initiating electroless copper plating. After each step the wafers were rinsed with water.

The experiment results showed that the palladium laden in this way successfully initiated the uniform electroless copper deposit on the surface of the silicon wafers. AFM image in **Figure 1** shows that the copper film formed is closely packed, free of pinholes, with mean roughness about 15 nm over the range of 6 μm^2 and the size of a single copper particle about 60 nm. Moreover, the film has strong adhesion to the silicon substrate, and it can undergo ultrasonic treatment without loss.

As known, APTS, the common silanization reagent, can be quickly chemisorbed onto the surfaces of silicon wafers containing –OH group *via* strong covalent bonds of Si-O-Si and thus the surfaces of the wafers are modified with a homogeneous compact ultrathin SAM (-Si-$CH_2CH_2CH_2$-NH_2) film, with outwards pendant -NH_2 groups[5]. X-ray photoelectron spectroscopy (XPS) study shows that the N1s peak of the –NH_2 of APTS monolayer is at 401.3 eV, which is consistent with reported data[5]. While after treatment of activation solution and water rinsing, the peak value was shifted to 402.1 eV. This suggests that the amino groups have strong affinity to palladium in the activation solution containing $PdCl_2$. The surface element analysis using auger electron spectra (AES) also showed that the activated surfaces contain Pd and Cl. On the contrary, Pd and Cl can not be observed on the surfaces without SAMs pre-modification. Based on the above results, we could conclude that palladium chloride is bonded to the amino groups of APTS SAMs.

The advantages of this new method over the conventional one, which is based on $SnCl_2$ sensitization, are as follows: elongating storage time of initiator, enhancing adhesion of the deposited metal on the silicon surface without roughening condition. More over, it can be extended to the other substrates with hydroxylated surfaces and has great significance in the field of electroless metal plating.

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