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Solvent Soluble Ti^{4+} and Si^{4+} Complex Solutions for Titanium Silicon Oxide Layer Formation on Glass for Increasing Copper Plating Adhesion Strength

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Abstract

Due to its industrial potentials, copper plating on glass has been explored through a variety of methods. The formation of a Cu film on a glass substrate is considered a fundamental technology in substrate-related industries; however, it has slow progress. The reason is pure Cu cannot adhere on to glass substrates directly, usually pre-depositing of an adhesion layer, such as Cr, Ti, or TiW, is required. In this study, an organic solution primarily composed of ethyl lactate and γ-butyrolactone, containing titanium (Ti) and silicon (Si) complexes, was used to coat borosilicate glass. Once coated, annealing the coated substrates resulted in the formation of a mixed Ti and Si oxide layer, 15~30 nm thick, depending on the coating conditions. The formed layer was able to adsorb Pd ions upon submersion in an arginine-Pd complex solution, catalyzing an electroless copper deposition reaction. A 100~300 nm thick electroless copper film was formed on the Ti/Si layers. The electroless Cu film was later dried, and at last the copper layer was plated to 15~30 μm by electroplating. Upon annealing a second time, the Ti, Si and Cu reacted to form adhesive chemical bonds between the three metals, giving the copper coated glass substrates with an average 90º vertical copper film peel strength of 7 N/cm, while maintaining a nanometer-scale smooth interface. This suggests Ti and Si were significantly responsible for the adhesion strength, compared to layers containing only Ti. The presence Si content generally resulted in higher adhesion strength than only Ti.

Keywords: Glass plating, Ti-Si solution, liquid processing, copper

1. Introduction

Dielectric materials have been of great interest in recent years due to their potential application in novel magnetic, catalytic, electronic, and nonlinear optical devices including multi-chip module packaging and printed circuit board manufacturing. Due to its industrial potentials, various methods have been reported for copper plating on glass [1]. The formation of Cu film on a glass substrate is considered a fundamental method in substrate-related industries, though progress has been slow. The reason is, pure Cu cannot adhere to glass substrates directly, usually glass surface modification and an adhesive layer like Cr, Ti, or TiW is required between glass and Cu for strong adhesion. Lee et. al applied copper paste directly on to glass substrate, resulting in thin copper films with some degree of adhesion post-thermal treatment [2]. Silver has been demonstrated to activate glass surfaces in a single-step method prior to conventional electroless plating [3], zinc oxide has also been found to serve as an adhesion layer, yielding reasonable results [4]. In addition, photopatterning of zinc compound has been demonstrated [5]. Regarding the metallization of glass with copper, the use of Ti complex solutions in organic solvent solutions has been accomplished [6]. The inclusion of copper in the titanium solutions was found to become catalytically active upon reduction in borohydride solution, enabling copper plating without requiring palladium as a catalyst, where high adhesion was attained post-thermal treatment [7]. Furthermore, direct patterning via photolithography using photoactive Ti-

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