Applied Surface Science 257 (2011) 8067–8071

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Electroless plating of copper on surface-modified glass substrate

Wei Su[a,*], Libei Yao[a], Fang Yang[a], Peiyuan Li[b,**], Juan Chen[a], Lifang Liang[a]

[a] College of Chemistry and Life Science, Guangxi Teachers Education University, Nanning 530001, China
[b] College of Pharmacy, Guangxi Traditional Chinese Medical University, Nanning 530001, China

ARTICLE INFO

Article history:
Received 29 January 2011
Received in revised form 9 April 2011
Accepted 21 April 2011
Available online 28 April 2011

Keywords:
Electroless deposition
Copper
Amine modification
Glass substrate

ABSTRACT

This work focuses on developing a novel convenient method for electroless copper deposition on glass material. This method is relied on the formation of amino (NH_2)-terminated film on the surface of glass substrate, by coating polyethylenimine (PEI) on glass matrix and using epichlorohydrin (ECH) as cross-linking agent. The introduced amino groups can effectively adsorb the palladium, the catalysts which could initiate the subsequent Cu electroless plating, onto the glass substrate surface. Finally, a copper film is formed on the palladium-activated glass substrate through copper electroless plating and the surface-coppered glass material is therefore acquired. X-ray diffraction (XRD), atomic force microscope (AFM), scanning electron microscopy (SEM) images combined with energy diffraction X-ray (EDX) analysis demonstrate the successful copper deposition on the surface of glass substrate.

1. Introduction

Metallic dielectric materials have been of great interest in recent years due to their potential application in novel electronic, magnetic, catalytic, and nonlinear optical devices such as multi-chip module packaging and printed circuit board fabrication [1–4]. Among various types of metal, copper is the optimum one for its low bulk resistivity, good thermal stability and low-temperature coefficient of resistance [5,6], consequently, increasing attention has been given to copper-metalized dielectrics [7–10]. Conventional approaches, including photolithography, electron lithography, focused ion beam lithography (FIBL), vacuum evaporation, sputtering, plasma treatment, electroplating, and electroless plating, have been used for the fabrication of the copper-metalized dielectrics [11–14]. Among them, electroless plating has attracted much attention in the microelectronics industries [15,16]. Electroless plating is an autocatalytic redox process where metal ion from solution onto the substrate is reduced to metal without application of any electric current [12]. The driving force for the reduction of metal ions is provided by a chemical reducing agent in solution [17]. However, to initiate this autocatalytic metallization process, a catalyst is generally necessary to lower the activation energy of metal formation by serving as a temporary electron bridge between the reducing agent and metallic ions [18]. Provided by the catalyst particles are deposited onto the substrates, the subsequent electroless plating process will be activated for a large amount of metals [18]. As a result, the deposition process of catalyst particles is essential for the electroless of copper and other metals on various substrates.

Because the catalyst cannot chemically bond with the untreated insulating surface, surface modification of the glass substrate is necessary for strongly binding the catalyst onto the glass substrate. To date, a number of surface modification methods have been studied. Hereinto, modification with nitrogen-containing groups on the surface of substrate has attracted much attention. Hozumi and coworkers prepared an amino-terminated organosilane self-assembled monolayer (SAM) on a PI substrate for embedding palladium ions catalyst using UV irradiation [9]. Badyal et al. used pulsed plasma-chemical functionalization to produce a pyridine functionalized surface for binding palladium as catalyst [19]. Kimura et al. produced a poly(vinyl pyridine) (PVMP) layer on the glass substrate through photochemical cross-linking reaction with the assistance of UV-irradiation [20]. These methods, based on UV-irradiation and plasma technology, are generally combined with higher energy and cost consumption. As a result, a simple and cost-effective approach to fabricating copper-metalized dielectrics remains to be developed.

In this paper, we describe a convenient and low-cost method for the preparation of a surface-coppered dielectric, where glass was employed as a matrix. This convenient and low-cost method can fabricate metallic layers on substrates at low temperature, without the need for UV-irradiation and plasma technology. Palladium is selected as catalyst to initiate the reduction of copper cations. This novel method is achieved by coating polyethylenimine (PEI) film on glass substrate to offer the amine groups for the adsorption of palladium ions (Pd^{2+}), combined with the reduction of Pd nanoparticles by dimethylamine borane (DMAB) and the subsequent electroless plating of copper. This integrated tech-

* Corresponding author. Tel.: +86 7713908065.
** Corresponding author.
E-mail addresses: aaasuwei@yahoo.com.cn (W. Su), lipearpear@yahoo.cn (P. Li).

0169-4332/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2011.04.100

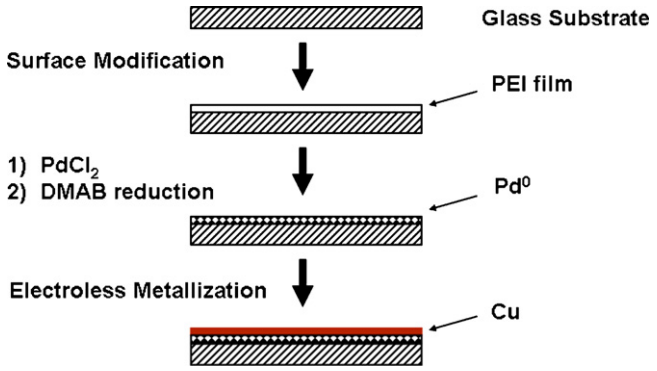

Fig. 1. Schematic illustration for the process of electroless copper deposition on glass substrate.

nique, which can reduce the number of manufacturing steps and obtain excellent copper-metalized glass materials, can be readily extended to the metallization of other substrates.

2. Experimental

2.1. Materials

Deionized water of 18 MΩ resistivity was used for all experiments. Epichlorohydrin (ECH), dimethylformamide (DMF), HCl (37 wt%) and ethanol were purchased from Sinopharm Chemical Reagent Ltd. (China); dimethylamine borane (DMAB) was purchased from Shenyu Chemical Ltd. (China); $PdCl_2$ was provided by Beijing Jiuzhoumol Ltd. (China); electroless Cu bath was purchased from Nanjing Delei Technology Ltd. (China); polyethylenimine (PEI) was purchased from Aldrich Co., and all these reagent used as received unless otherwise noted.

2.2. Preparation of the copper film on glass substrates

The process for electroless copper deposition on glass substrate schematically is presented in Fig. 1. The modified glass substrate was obtained by coating PEI film on glass slide through a wet impregnation method, in which ECH was employed as cross-linking agent. Water-free PEI was dissolved in ethanol with a weight ratio of 1:2, and ECH was dissolved in DMF to prepare a 50 wt% solution. The above PEI and ECH solutions were mixed at different ratios of PEI to ECH under stirring, and then 5 g of this solution mixture was added to 20 g of methanol and stirred for 10 min before the glass slide was immersed in. After 12 h, the glass slide was taken out and dried at 60 °C for 6 h. Next, the modified sample substrate was activated at 50 °C for 60 min by immersion in an aqueous solution containing 0.25 g/L of $PdCl_2$ and 10 ml/L of HCl (pH = 1.4), followed by gentle rinsing with Milli-Q water. This activated substrate was then immediately immersed into a 0.5 M aqueous DMAB solution at 20 °C for 3 min to reduce the doped Pd ions. Finally, this activated substrate was immersed in a electroless Cu bath (pH = 14) at 50 °C for 60 min, followed by carefully rinsed with Milli-Q water and blown dry with N_2 gas, and the surface-coppered glass was obtained.

2.3. Characterization

ATR FT-IR spectra were obtained in the 2000–1200 cm^{-1} range using a Nicolet 670 Fourier transform infrared (FT-IR) instrument equipped with an attenuated total reflection (ATR) attachment. Contact angles were collected using an optical contact angle meter (Tracker, Teclis-IT Concept, France) with the drop sessile down mode. XPS measurement was performed on a Kratos Axis Ultra DLD multi-technique X-ray photoelectron spectroscopy with Mg Kα source at 14.0 kV and 25 mA. All the binding energies were referenced to the C 1s peak at 284.6 eV of the surface adventitious carbon. The electrical conductivity of cooper films was measured by a four-point probe (RTS-9, 4 probe). XRD patterns (2θ ranges from 35° to 80°) were recorded on a Rigaku D/Max 2500 PC diffractometer with Cu Kα radiation (λ = 0.154056 nm). The surface morphology of the films was observed by scanning electron microscopy (SEM, S-3400N, HITACHI) and atomic force microscope (AFM, Veeco Co.). For SEM imaging, Au (1–2 nm) was sputtered onto these grids to prevent charging effects and to improve image clarity. For AFM observation, the images were collected in air under ambient conditions using the tapping mode with a Nanoscope III/Bioscope scanning probe microscope from Digital Instruments. The chemical composition of the Pd catalyst and copper deposit were determined using energy diffraction X-ray (EDX, AMETEK Inc.) analysis attached to the SEM.

3. Results and discussion

3.1. Surface modification of glass substrate

The surface-modified glass substrate is prepared by the PEI solution treatment. ATR FT-IR measurements were conducted to investigate the structural change in the surface of glass substrate before and after PEI modification, and the results are presented in Fig. 2A. For the bare glass, a broad adsorption band in the

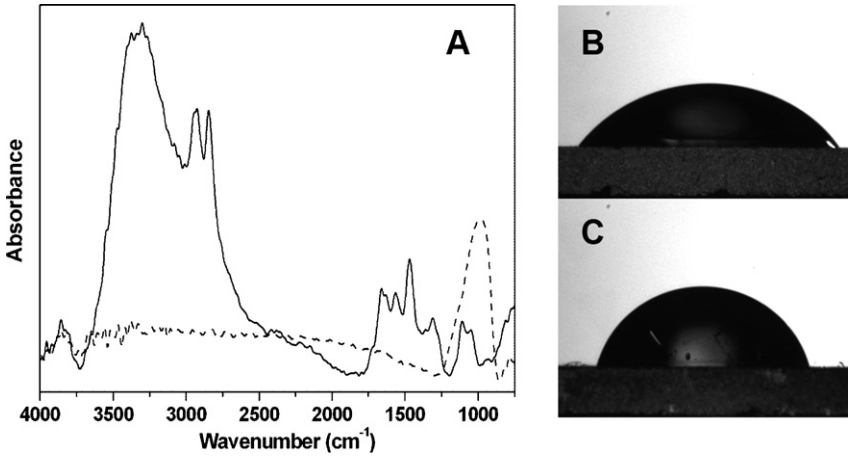

Fig. 2. (A) ATR FT-IR spectra in the 4000–750 cm^{-1} region of glass substrate before (dotted line) and after PEI modification (solid line), and photographs of a water droplet on the surface of glass substrate before (B, $\theta = 47.3°$) and after PEI modification (C, $\theta = 70.0°$).