Electroless Metallization of Hydrogen-Terminated Silicon Surface Functionalized by Viologen

W. H. Yu, E. T. Kang* and K. G. Neoh
Department of Chemical Engineering
National University of Singapore
Kent Ridge, Singapore 119260
*Tel.: +65-6874-2189; Fax: +65-6779-1936
Email address: cheket@nus.edu.sg

The manipulation and control of the chemical and physical characteristics of silicon surfaces have been carried out for many years because of their crucial importance to the modern microelectronics industry. A stable densely-packed organic layer covalently bonded to the silicon surface can be used, for example, as passivation layers in MEMS and microfluidic devices, as components in hybrid electronic and sensing devices, and as adhesion promoter for metals with the substrate. One approach to surface functionalization is through the formation of self-assembled monolayers (SAMs) on the native oxide layer. Recently, there have been a number of reports on direct covalent bonding of organic monolayers to a silicon surface, in the absence of the native oxide layer[1,2]. However, the covalent attachment of functionalized organic layers to the hydrogen-terminated silicon (H-Si) surface is yet to be explored in detail. On the other hand, viologen, or 1,1'-disubstituted-4,4'-bipyridinium salt, is one of the electrochromic materials. Numerous studies on 4,4'-bipyridine and its derivatives as photochromic, electrochromic, and molecular electronic materials and devices have been carried out[3]. The response of the viologen-modified films to photoirradiation and bleaching in air or under vacuum has been reported[4]. For example, the viologen grafted low density polyethylene (LDPE) film was proposed to be used as a "smart" window, as the transmittance of the modified film could be altered by UV irradiation[4]. In addition, photo-reduction of palladium and gold ions adsorbed on the viologen-modified dielectric SiLK® coating on silicon to their respective metal atoms had also been studied[5].

In the present work, electroless metallization of palladium, gold, and copper on the hydrogen-terminated (100)-oriented single crystal silicon surface functionalized by viologen (1,1'-substituted-4,4'-bipyridinium salt) is carried out. The surface functionalization approach involves a two-step process whereby glycidyl methacrylate (GMA) was first graft-polymerized onto the hydrogen-terminated silicon surface (the GMA-g-H-Si surface). The NH_2-terminated viologen molecules (structure shown in Fig. 1) are then coupled to the epoxide groups of the grafted GMA chains. The chemical composition and topography of the viologen-modified Si surfaces (the viologen-GMA-g-H-Si surfaces) are determined by X-ray photoelectron spectroscopy (XPS) and atom force microscopy (AFM), respectively.

Pd(II) and Au(III) ions in acid solution could be adsorbed onto the viologen-GMA-g-H-Si surfaces. Viologen can exist in three interconvertible intrinsic redox states, *viz*., the viologen dication, the viologen radical cation, and the direduced viologen[3]. Previous studies have shown that the emergence of the UV-vis absorption bands at 615 and 410 nm was due to the formation of viologen radical cations upon UV irradiation[4]. The grafted viologen species in the reduced form (viologen radical cation and/or direduced viologen) can be act as reducing agents upon exposure to the palladium(II) and Au(III) ions. Photo-induced reduction of the palladium or gold ions on the viologen-GMA-g-H-Si surface to their respective metal atoms could be readily achieved. The viologen-GMA-g-H-Si surfaces with the photo-reduced palladium metal could be used to catalyze the electroless deposition of copper. The 180°-peel adhesion strength of the electrolessly deposited copper with the viologen-GMA-g-H-Si surface is much higher than that of the electrolessly deposited copper with the pristine H-Si surface. For the pristine H-Si surface, electroless deposition of copper requires the prior sensitization of the substrate surface by $SnCl_2$ for palladium adsorption. Thus, not only did the surface grafted viologen molecules provide the chemisorption sites for the photo-reduction of the Pd catalyst, they also served as adhesion promoters for the electrolessly deposited copper.

References:

1. M. R. Linford, P. Fenter, P. M. Eisenberger, and C. E. D. Chidsey, *J. Am. Chem. Soc.* **117**, 3145 (1995).
2. J. M. Buriak, *Chem. Reviews*, 102, 1271 (2002).
3. P. M. S. Monk, *The Viologens: Physicochemical Properties, Synthesis and Applications of the Salts of 4,4'-Bipyridine*; John Wiley & Sons, Chichester, UK (1998).
4. J. T. Sampanthar, K. G. Neoh, S. W. Ng, E. T. Kang, and K. L. Tan, *Adv. Mater.,* **12,** 1536 (2000).
5. W. H. Yu, Y. Zhang, E. T. Kang, K. G. Neoh, S. Y. Wu, and Y. F. Chow, *J. Electrochem. Soc.*, submitted, 2002.

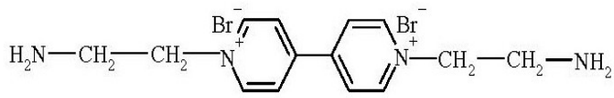

Fig. 1 Structure of the NH_2 terminated viologen 1