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# A Solid Ag Film Deposited from Solution on Self-assembled Mercaptopropyltrimethoxysilane (MPTS) Monolayer

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**Abstract:** Mercaptopropyltrimethoxysilane (MPTS) bearing mercapto groups was used to form self-assembly monolayers (SAMs) on glass substrates by solution extraction. SEM, XRD and rubbing test analysis illustrated that the Ag film on the SAMs-modified glass was more durable than that on the commonly-modified glass and that the crystallinity of Ag film on the SAMs-modified glass was identical with those of the Ag film on the commonly-modified glass and pure Ag.

**Keywords:** SAMs, electroless plating Ag, morphology, structure.

Electroless plating method has been widely applied, particularly in microelectronics, radioelectronics, computer engineering and aerospace techniques, because electroless method allows uniformly thick coatings on the articles of any profiles of metallic, dielectric and semiconducting materials. This method gives us the possibility to regulate physical-chemical properties of the coatings (electrical conductivity, chemical, mechanical and magnetic properties, *etc*) in the wide range and plating of the three dimensional articles[1-4]. The first industrial process of coating on flat glass has been silvering by electroless plating. In this process, silver is precipitated on the glass from an aqueous solution[5]. Since then electroless plating on glass has induced a wide variety of research activities during the past decade. Commonly before counducting silvering the glass surface is degreased in acid Cr (VI) solution *etc*., then was sensitized in Sn (II) solution and rinsed with distilled water, activated with silver nitrate solution. The coating obtained by these methods can satisfy the common use. However, partly attributed to the low durability of its coating, the application of this extremely cheap process is limited. The vacuum deposition and CVD (chemical vapor deposition) coating methods emerging lately solved this problem in some degree[6], yet these techniques are not suitable for the plating of articles having profiles, especially for those inner, hardly-accessible surfaces. Consequently with the aim to circumvent this difficult problem, finding a way to combine high quality coating with electroless plating

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method becomes one of the provocative objectives.

Based on the previous reports about colloid Au to react with the mercapto groups of sulfide or other chemicals to form the label beacon[7-10] as well as our studies on assembly of molecules[11], a new method for electroless plating Ag on glass by modifying glass with silane bearing mercapto groups was reported in this paper. X-ray photoelectron spectra (XPS), scanning electron microscopy (SEM), auger electron spectroscopy (AES) analysis and X-ray diffraction (XRD) investigations demonstrated that a solid Ag film was deposited on the glass solid modified with mercaptopropyltrimethoxysilane (MPTS).

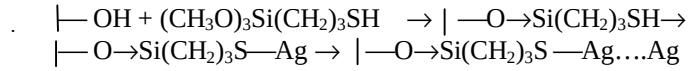
**Typical Experimental Procedure**

The commercially available r-mercaptopropyltrimethoxysilane (MPTS) from the Shuguang Chemicals Factory (Nanjing, China) was distilled under reduced pressure before use. The soda glass wafers (1×3.5 cm) were commercially available. Benzene was dried over molecular sieves before use. Chloroform, acetone, absolute ethanol, $SnCl_2.2H_2O$, $AgNO_3$, $NH_3H_2O$, glucose and tartaric acid were of analytical grade.

The commercially obtained glass slides were firstly washed with water and acetone, immersed in washing liquid for 30 minutes, taken out from the liquid and rinsed carefully with tapping water, distilled water and double-distilled water in turn, then dried under nitrogen flow and, therefore, the pretreated glass slide was prepared. The pretreated glass slide was sensitized in Sn(II) solution (2g/L $SnCl_2.2H_2O$) for 5 min, rinsed with distilled water and activated with $AgNO_3$ solution (10g/L), was changed to glass slide 1. After reacting with the MPTS solution of benzene with the concentration of $5\times10^{-3}$ mol/L, incubated at room temperature for 6 hours, taken out and washed with benzene, chloroform, acetone, absolute ethanol and double-distilled water, then dried under nitrogen flow, extracted with Soxlet apparatus with benzene, the pretreated glass slide was turned into glass slide 2.

The main plating solution according to the document[12] composed of silver solution A and reduction solution B. Solution A contained $AgNO_3$-3.5 g, $NH_4OH$-moderate quantity, NaOH-15 g and $H_2O$-600 mL. To make up solution A, firstly silver nitrate was dissolved in water, ammonia was dropped under constant agitation until the precipitate $Ag_2O$ dissolved completely, then sodium hydroxide was added and the solution turned black. Finally ammonia was dropped under constant agitation until the solution became clear. Solution B contained glucose-4.5 g, tartaric acid-4 g, ethanol-100 mL and $H_2O$-1000 mL. Glucose and tartaric acid were dissolved with 100 mL water and boiled for 10 min, after cooling ethanol the remaining water was added, then reduction solution B was ready. When used, solution A and B were mixed at the volume ratio 1 to 1, four kinds of glass substrates prepared in item 1.2 were placed in plating gutter at room temperature. The proposed scheme involved the surface silanized reaction and electroless plating Ag is shown in **Figure 1**.

**Figure 1** Scheme for the preparation of the silanized surface and the electroless plating Ag on glass.



## Results and Discussion

The quality of Ag coating on MPTS SAMs modified glass slide **2** and $SnCl_2$ solution sensitized glass slide **1** was examined with a Japan Hitachi-650 scanning electron microscope (SEM) as shown in **Figure 2-5**, respectively. From **Figure 2** and **3** about the micrographs of Ag coatings on glass slide **1** and **2**, although the Ag film on glass slide **2** (**Figure 2**) seems to be more uniform than that on the $SnCl_2$ solution sensitized glass slide **1** (**Figure 3**), it can be found that these two pictures exhibit no significant difference. However, the apparent difference in adherence stability to glass substrates of these two films was clearly detected when the samples were tested according to the commonly used methods[13]. Both samples were firstly treated at 200°C for 2 h in an oven. After

**Figure 2** SEM of Ag coating on glass slide **2** functionized with SAMs

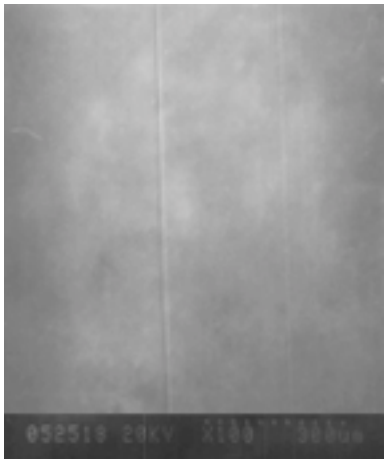


**Figure 3** SEM of Ag coating on glass slide **1** sensitized with $SnCl_2$ solution

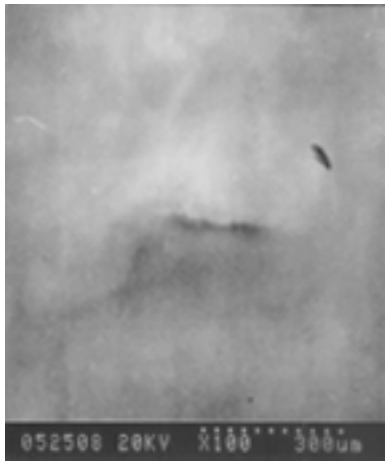


**Figure 4** SEM of Ag coating on glass slide **2** after treatment at 200°C for 2 h

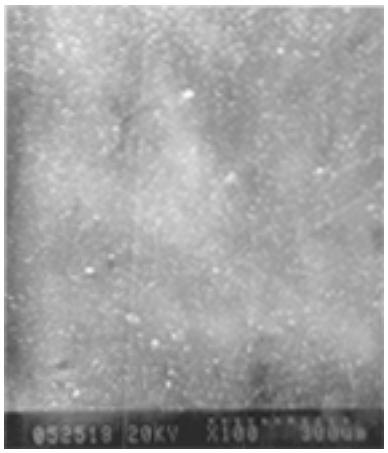
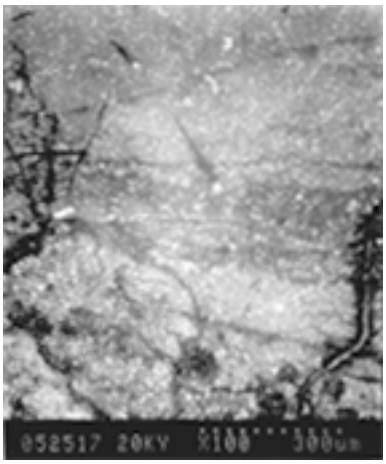


**Figure 5** SEM of Ag coating on glass slide **1** after treatment at 200°C for 2 h



the samples were cooled a piece of transparent adhesive tape was attached to the samples. Then the adhered adhesive tape was rubbed with a pencil eraser and pulled off using tweezers. The as-handled samples were examined again using SEM as shown in **Figure 4** and **5**. **Figure 5** demonstrates that the Ag coating on $SnCl_2$ solution sensitized glass slide **1** dealt at high temperature was easily exfoliated. However, it is very interesting that due to the formation of Ag-S chemical bonds between Ag layer and the the micrographs of Ag coatings on glass slide **1** and **2**, although the Ag film on glass slide **2** (**Figure 2**) seems to be more uniform than that on the $SnCl_2$ solution sensitized glass slide **1** (**Figure 3**), it can be found that these two pictures exhibit no significant difference. However, the apparent difference in adherence stability to glass substrates of these two films was clearly detected when the samples were tested according to the commonly used methods[13]. Both samples were firstly treated at 200°C for 2 h in an oven. After glass substrate modified with MPTS which guaranteed the excellent adherence of Ag layer to glass, the Ag film on MPTS SAMs modified glass slide **2** was difficult to be peeled off, thus the **Figure 4** still shows us a uniform Ag film SEM picture. XPS, AES, and XRD investigations (not shown here) further demonstrated that the solid Ag film deposited on glass slide **1** possessing little difference from the metal silver, meaning the electroless-plating Ag on SAMs is a novel approach to plate Ag on articles possessing complicated structures. A detailed discussion about the formation mechanism of Ag film on the MPTS SAMs modified glass slide **2** will be reported elsewhere.

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