

SAMs-Directed Metallization and its Application in Fabrication of Core-Shell nanocomposites

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Abstract. Molecular assembly technology has attracted much research attention due to its flexible applications in modulation of surface property and construction of nanostructures and devices. Herein, a well-defined surface metallization technique has been achieved via anchoring electroless catalysts onto substrates' surfaces with the pendant active groups of self-assembled monolayers. This method affords a means to control surface functionality at molecular level and has advantages over the conventional Sn-Pd methods, such as convenient operation, good reproducibility, increased longevity of the activated initiator and improved adhesion of metal deposition to substrates. Therefore, it has great significance in the fields of developing bottom-up combined micro/nano-fabrication technique. This metallization process has been successfully performed on hollow ceramic particles to fabricate light-weighted core-shell functional materials.

Introduction

Molecular assembly technology has attracted much research attention due to its flexible applications in modulation of surface property and construction of advanced materials and nano-structures and even devices over the past decade [1-3]. Self-assembled monolayers form spontaneously by the adsorption of a surfactant with a specific affinity of its headgroup to a specific substrate. These ordered molecular assemblies potentially enable to tailor the surface properties for multifarious applications by simply selecting the terminal pendent functional group, which is useful in surface modification strategies due to their diversified reactions. Recently, self-assembly technique has been developed to conveniently construct metallic micropattern or conductive wires on wafers in combination with electroless plating, based on SAMs-bound catalysts for activating electroless reactions[4-7].

Metal-ceramic composites have been attracted considerable attention and research interest over the last few years as they can improve application properties of the substrates, such as hardness tensile, compressive strength, wear and abrasion resistance[8~13]. Even more, tunable optic properties have been achieved in a highly predictive manner for metal-coated core-shell structures by varying the metallic shell thickness and core size[14]. This leads to a research hotspot to design and realize advanced functional material. However, problem remains in solution chemistry. Colloidal self-assembly technique limits the efficiency and large-scale variation of shell thickness. As to the traditional electroless plating technique, though it is a promising method for forming uniform metal coating on any kind of activated substrates regardless of the shape, size and conductivity in principle, it is difficult to obtain objective products of uniform shell coated core structures, without free metallic species or core template. This difficulty in control of electroless deposition is in part because of the unsatisfactory Sn-Pd combined activation process. The electroless catalyst, palladium nuclei, formed in this way has poor adhesion to the substrates and its desorption from particle substrates is subject to occur under stir. This may cause failure in initiating uniform metal deposition or decomposition of the concerned electroless bath and further result in free metal deposits and free substrate particles. Besides, the Sn-Pd activation method requires multifarious steps and special pretreatment, leading to

inconvenience in practice. It is desirable to develop alternative surfaces activation approaches that require less process steps towards highly selective, well-defined surface metallization.

Herein, a well-defined surface metallization technique has been achieved on hollow ceramic particles via anchoring electroless catalysts onto substrates' surfaces with the pendant active groups of self-assembled monolayers. The light-weighted product was obtained, with nanocrystalline copper as shell, hollow ceramic particle as the core.

Experimental

Firstly, a given amount of hollow ceramic spheres were cleaned and hydroxylated in a freshly prepared piranha solution ($\text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 = 70 : 30$, v/v) at 85°C for 15 min, and then thoroughly rinsed with deionized water and dried at 105°C for use. Afterwards, thiol-terminated SAMs were formed on the silicon surfaces by immersing the hydroxylated wafers in a dehydrated toluene solution containing 1×10^{-3} mol/L 3-mercaptopropyltrimethoxysilane (MPTS) for 45min at room temperature. After thorough rinse with toluene, acetone and water in turn, the MPTS-coated particles were activated by dipping them in a chloride-rich Pd(II) colloidal solution for 15 min followed by rinsing with water. Electroless copper deposition was carried out by introducing the activated particles in the copper electroless plating solution, containing NaOH 12 g/L, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 13 g/L, $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ 29 g/L, HCHO 9.5 ml/L at ambient temperature. Finally, the product was separated by filtration and rinsed with pure water three times, dries at 40°C in a vacuum oven.

The surface modification with catalyst species was identified on an AES-350 type auger-electron spectrometer. The metal-deposited products were characterized by XRD, TEM, SEM-EDS and AES, respectively. XRD patterns were recorded using a D/Max RA X-ray diffractometer, TEM image was obtained with a Hitachi JEOL transmission electron microscope, and SEM-EDS analysis of the product was carried out on a LEO 1550 scanning electron microscope.

Results and discussions

SEM and TEM image of the Cu-metallized product was shown in Fig. 1. It can be clearly seen that the product resembles spherical morphology of ceramic hollow microspheres, and its surface coating layer is composed of copper particles. These suggest that a single metal-coated sphere was cored with a single microsphere.

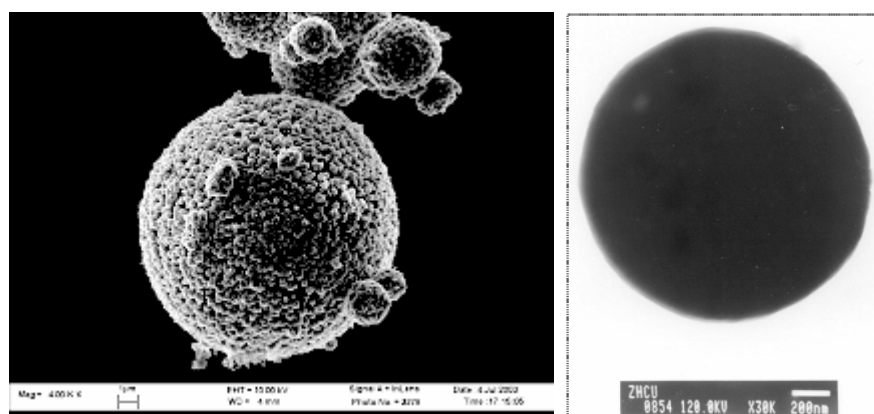


Fig.1 (Left) SEM and (Right) TEM micrograph of the Cu-coated microspheres

Fig.2 shows the XRD patterns of hollow ceramic particles and the products. By comparing Fig.2(a) with Fig2(b), we could see that there are diffraction peaks of fcc-structured crystalline copper in addition to that of ceramic particles in Fig.2 (b). It confirms that copper coating has been fabricated

on the microspheres. The crystalline size of the deposited copper particles is calculated to be 16.8 nm according to the peak of Cu(1 1 1) face based on Scherrer formula.

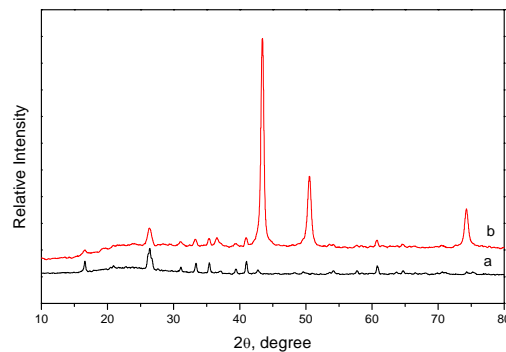


Fig.2 XRD pattern of: (a) core-template and (b) Cu-coated composites

The copper coatings can also be confirmed by the surface element analysis of the product using an Auger-Electron Spectrometer (AES). Randomly selecting several analytical microzones of the sample, all AES spectra showed the similar signal of copper element.

The above results indicate light-weighted metal composite was conveniently developed and the hollow ceramic microspheres were completely covered by a uniform copper layer. The metallization mechanism was studied by the surface element analysis herein. It is obvious in Fig.3(a) that MPTS was self-assembled on the surface of microspheres, mainly with bonds of (substrates Si or Al)-O-Si. Compared with Fig.3(a), Fig.3(b) presents the powerful evidence that besides Si, S, C and O, the Pd(II)-treated wafer contain Pd and Cl, which is the main components of Pd(II)-based catalytic species, similar to those chemisorbed onto thiol-terminated organosilane modified wafers [15]. AES results showed the SAMs-directed chemisorption of chloride-rich Pd(II) species via forming bonds of S-Pd. After treated with HCHO, a reducing reagent, element Cl disappeared, indicating the Pd(II)-based species was reduced to Pd, which is the ideal catalyst for electroless. That is the reason why immersing the activated particles into the electroless copper bath resulted in quick initiating copper deposition and autocatalytic redox reactions at the interface between the solid substrate and the liquid solution.

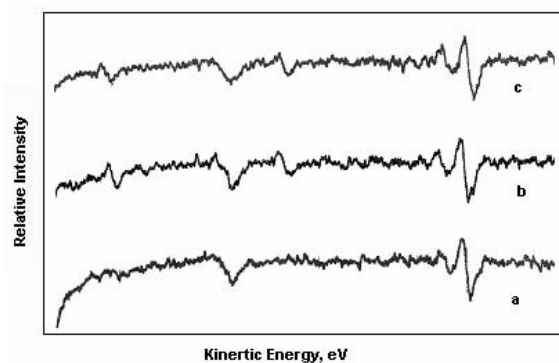
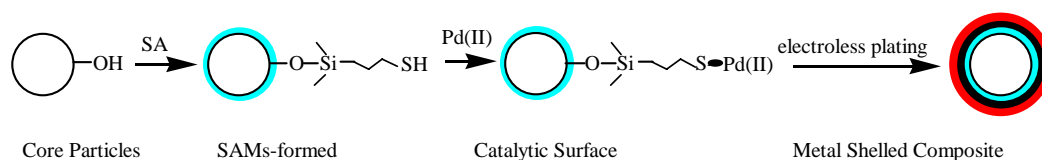


Fig.3 AES spectra of the surface of microspheres treated with:
(a) MPTS; (b) MPTS+ Pd(II); (c) MPTS+Pd(II)+HCHO

SAMs-directed metallization for fabricate core-shell materials was outlined as following:



Conclusions

SAMs-attached catalyst ultrathin layer has good uniformity and sturdiness in favor of inducing metal deposit of high quality. It offers a high degree of both flexibility and control in the binding of the electroless catalyst complex to the functionalized surface. The adhesion of the EL metal deposit can be potentially improved. Consequently, both of chemical etching and acceleration process were omitted. That is, the SAMs-directed metallization technique affords a means to control surface functionality at molecular level and has advantages over the conventional Sn-Pd activated one, such as convenient operation, good reproducibility, increased longevity of the activated initiator and improved adhesion of metal deposition to substrates. Therefore, it has great significance in the fields of developing bottom-up combined micro/nano-fabrication technique. This metallization process can be employed in fabrication of microstructures on wafers but also be successfully performed on particles to fabricate light-weighted core-shell functional materials.

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