Applied Surface Science 363 (2016) 122–127

Contents lists available at ScienceDirect

Applied Surface Science

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

Fabrication and characterization of flaky core–shell particles by magnetron sputtering silver onto diatomite

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ARTICLE INFO

Article history:
Received 25 July 2015
Received in revised form 23 October 2015
Accepted 15 November 2015
Available online 29 November 2015

Keywords:
Diatomite
Core–shell structure
Magnetron sputtering
Silver film
Infrared emissivity

ABSTRACT

Diatomite has delicate porous structures and various shapes, making them ideal templates for microscopic core–shell particles fabrication. In this study, a new process of magnetron sputtering assisted with photoresist positioning was proposed to fabricate lightweight silver coated porous diatomite with superior coating quality and performance. The diatomite has been treated with different sputtering time to investigate the silver film growing process on the surface. The morphologies, constituents, phase structures and surface roughness of the silver coated diatomite were analyzed with SEM, EDS, XRD and AFM respectively. The results showed that the optimized magnetron sputtering time was 8–16 min, under which the diatomite templates were successfully coated with uniform silver film, which exhibits face centered cubic (fcc) structure, and the initial porous structures were kept. Moreover, this silver coating has lower surface roughness (RMS 4.513 ± 0.2 nm) than that obtained by electroless plating (RMS 15.692 ± 0.5 nm). And the infrared emissivity of coatings made with magnetron sputtering and electroless plating silver coated diatomite can reach to the lowest value of 0.528 and 0.716 respectively.

1. Introduction

Diatomite, mineralized from unicellular photosynthetic diatom, has unique micro/nanoscale porous silica structures with a variety of shapes (sphere, flaky, cylinder-shaped, etc.), showing promising application in micro-nanotechnology and attracted extensive research efforts during the past two decades [1–3]. Among these researches, some take advantage of the chemical stability, thermal resistance and large specific surface area characteristics of diatomite, such as using diatomite as adsorbents and filter aids for purifying water [4], lightweight building materials [5] as well as catalyst carrier [6,7], and some use the shape diversity of diatomite, taking diatomite as forming templates to fabricate diverse light-weight functional core–shell particles by depositing functional coatings onto their surface. Nowadays, as the core template, diatomite has been coated with the metal/alloy films by various deposition techniques, such as electroless plating Ni–Fe–P [8], electroplating Ni–Fe [9], and thermal decomposition $BaZn_{1.1}Co_{0.9}Fe_{16}O_{27}$ [10]. The as-prepared functional particles showed great potential application in electromagnetic wave absorbing and shielding fields [8–10]. In order to explore further application of diatomite in low infrared emissivity area, the low-emissivity coatings (such as silver, copper or aluminum, etc.) [11–14] need to be deposited onto the diatomite surface. However, the above mentioned film deposition technique either cannot achieve pure low-emissivity metal coating materials on diatomite templates or the coating quality is not good enough for low-emissivity application with some drawbacks, such as high roughness, poor uniformity and low adhesion. So in this study, we propose to use magnetron sputtering method to deposit silver onto diatomite.

As a vacuum film deposition technique, magnetron sputtering has been widely used to deposit uniform functional films on various plate substrates [15,16]. The thin metal films prepared by magnetron sputtering have similar performances with original metal materials, such as infrared emissivity. However, method of sputtering film on micro particles is seldom reported since the particles are in micron scale dimensions and with curved surface. Among these meaningful reports [17–20], most of them focused on the redesigning or upgrading magnetron sputtering apparatus. Senos et al. [17] have equipped a cylindrical chamber in a DC magnetron sputtering system with rotation and vibration movement to modify small particles. Shen et al. [18] have developed a magnetron sputtering system with a special designed ultrasonic vibration generator implemented to deposited metal films (Co, Ni, Cu and Ag) on cenosphere particles. Taguchi et al. [19] have used barrel-sputtering

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http://dx.doi.org/10.1016/j.apsusc.2015.11.148
0169-4332/

Table 1
Parameters of magnetron sputtering silver process.

Process	Values
Ar. pressure	0.8 Pa
Vacuum degree	5×10^{-3} Pa
Temperature of sample platform	Room temperature
Rotation speed of sample platform	10 r/min
Argon flow rate	42 sccm
Sputtering power	150 W
Sputtering time	4–24 min

system to obtain various surface coating metals on spherical particles. And Eisenmenger-Sittner et al. [20] have optimized a coating vessel equipped with three rotatable powder containers inside to intermix the microspheres in magnetron sputtering system. Thus the application is aiming to make the particle templates keep rolling during the sputtering process. Obviously, this method is likely confined to the particles with spherical shape and smooth surface. And it is not suitable for the diatomite particles, owing to their non-spherical shapes, low density and porous substructures.

Given all that, in this study, a new magnetron sputtering approach assisted with photoresist positioning was proposed and used to deposited silver films onto diatomite, and the properties of the obtained silver-coated diatomite were investigated in detail. Moreover, the infrared emissivity of such silver-coated diatomite was compared with that of silver-coated diatomite by electroless plating.

2. Materials and methods

2.1. Pretreatment of diatomite

The diatomite used in the experiment is *Coscinodiscus* diatomite C292, which was provided by the Linjiang Sailite Diatomite Co., Ltd. The raw diatomite is in pink-white color, and it was purified with sedimentation process so as to remove impurities and fractured diatomite [21]. The purified diatomite was then filtered with sieve and dried in oven at 200 °C for 1 h, and the color became white. The morphology test result under SEM showed that the diatomite particles are about 30–50 μm in diameter, and about 2–5 μm in thickness. The mass density is about 2.15 g cm^{-3}.

2.2. Magnetron sputtering with photoresist assisted positioning

The magnetron sputtering silver onto diatomite assisted with photoresist positioning method is mainly taking advantage of the sensitive principle of the photoresist: After UV irradiation, the positive photoresist can be removed by its developer solution, while the negative photoresist can resist the etching of developer solution, meanwhile can be dissolve in its stripper solution. The diagram of the whole process was shown in Fig. 1. The positive photoresist, developer solution and negative photoresist used in the experiment are the BP212-37S, KMPPD238-II, and BN-308-450 from Kempur Microelectronics Inc.

At the beginning, the cleaned 50 mm × 50 mm × 5 mm Aluminum substrate was covered with tinfoil, and a positive photoresist coating was added with a spin coater. Then the purified diatomite powder were sprayed onto the coating surface while it is till sticky, after which the sample was heated to 100 °C for 1.5 min to solidify the positive photoresist and fix the diatomite. The unstuck diatomite was blown away with compressed air flow and monolayer diatomite was achieved on the substrate. Then the sample was ready for first time magnetron sputtering process, and the experimental parameters are shown in Table 1.

When the first time magnetron sputtering of silver was finished, the cooled sample was taken out from the magnetron sputtering equipment. Then a negative photoresist coating was spin coated onto the sputtered sample and heated at 100 °C for 1.5 min to solidify. After solidification, the tinfoil with the coating was removed from the aluminum substrate, and the tinfoil was peeled off, leaving the positive photoresist exposed and treated with UV irradiation for 20 min (using UV CURER KW-4AC from Chemat Technology Inc.). Then, the coating film was immersed in the 1:1 mixed solution of photoresist developer and ethyl alcohol to remove the positive photoresist, leaving the uncoated side of diatomite exposed for the second time magnetron sputtering. After sputtering, the sample was further immersed in negative photoresist stripper solution to dissolve the negative photoresist, and the silver-coated diatomite was dispersed in the photoresist stripper solution. The particles was collected with strainer and cleaned with ethyl alcohol for the following inspection and infrared coating paint preparation.

2.3. Characterization

The microscopic morphology of the coated diatomite was examined with a scanning electron microscope (SEM, Cambridge CamScan CS3400). Oxford Link 860 energy dispersive spectrometer (EDS, collocating with Cambridge CamScan CS3400) was used for ingredients analysis. The phase structures of the surface coating was studied with the X-ray diffraction (XRD, Rigaku D/Max-3) with Cu-Kα radiation at 40 kV voltage, 40 mA current, step size 0.02°, scanning rate 8°/min and scanning area around 20–100°. Surface roughness of the coating was characterized by an atomic force microscope (AFM, Dimension Icon type, U.S. Veeco company), with a scanning area of 4 μm × 4 μm. The root-mean-square (RMS) roughness values were calculated from AFM images. Infrared emissivity at the wavelength of 8–14 μm was measured by using an IR-2 Infrared Emissometer (Shanghai Chengbo High Tech Co., Ltd.). The measurement error of infrared emissivity is less than 0.001.

3. Results and discussion

3.1. Morphology characteristics of diatomite after magnetron sputtering silver

The morphology of magnetron sputtering silver coated diatomite was shown in Fig. 2, from which we can see that the diatomite after magnetron sputtering for 4–24 min, can all keep their initial shapes with delicate nano-pores, and the coating surface on diatomite is uniform and clean. However, with sputtering time growing, more target atoms bombarded by energetic ions ejected from the solid target, the deposited silver tends to thicken and pile up around the nano-pores, thus the coating surface on diatomite become uneven with peaks and valleys in different height, which will significantly influence the film consistency. And if the sputtering time were too short, like, less than 4 min, the cladding thickness of silver coating would be small. Therefore, considering the property of coating surface and replication of microstructure, in this situation, sputtering time around 8–16 min is preferred. And, from the EDS results of the ingredients of surface coating shown in Fig. 3, it is found that the main components are Ag and diatomite's original component element Si. Based on the analysis, the diatomite was deposited with a certain thickness of silver films successfully.

3.2. Comparison with electroless plating of silver

To further illustrate the coating quality of the magnetron sputtering silver on diatomite, we took the silver-coated diatomite obtained by electroless plating process as a contrast, since electroless plating technique is the most common method for fabricating