Applied Surface Science 258 (2012) 7982–7988

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

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

Production of porous PTFE–Ag composite thin films by pulsed laser deposition

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ARTICLE INFO

Article history:
Received 6 January 2012
Received in revised form 13 April 2012
Accepted 24 April 2012
Available online 30 April 2012

Keywords:
Pulsed laser deposition
Polytetrafluoroethylene (PTFE)
Silver (Ag)
Composite film
Resistance
Sensor technology

ABSTRACT

The suitability of pulsed laser deposition technique for preparation of polytetrafluoroethylene (PTFE) and silver (Ag) composite thin films was demonstrated. Disk-shaped targets combined from silver and Teflon with various percentages were ablated with pulses of an ArF excimer laser. The chemical composition of the deposited layers was estimated based on deposition rates determined for the pure PTFE and Ag films. EDX and SEM analyses using secondary electron and backscattered electron images proved that the morphology of the layers is determined by the PTFE which is the main constituent and it is transferred mostly in form of grains and clusters forming a sponge-like structure with high specific surface. The Ag content is distributed over the surface of the PTFE structure. Contact angle measurements showed that with increasing the amount of Ag in the deposited layers the surface significantly enhanced the wetting properties. Conductivity experiments demonstrated that when the average silver content of the layers was increased from 0.16 to 3.28 wt% the resistance of our PTFE–Ag composite films decreased with about three orders of magnitudes (from $\sim$10 MΩ to $\sim$10 kΩ). The properties of these films suggest as being a good candidate for future electrochemical sensor applications.

1. Introduction

Polymer–metal compounds are an important group of composite materials. The role of metals is mainly the enhancement of different properties of the polymeric matrix material. The electrical, optical and dielectric behaviors of the polymer composites are very sensitive to small changes in the metal content and in the size and shape of the particles. Over the years various methods have been developed for production of composite materials used in different areas of science and technology. For example, Fu et al. showed that the interfacial conductivity of Ag–PTFE composite coating produced by electrodeposition for fuel cell applications is close to that of the pure Ag coating. On the contrary, the contact resistance of the composite coating is lower than that of pure Ag coating [1]. Higher bronze content in the power-pressed bronze–PTFE composite improved tribological properties of the corresponding transfer film, i.e., reduced friction coefficient and prolonged wear life [2].

Polymer composites are good candidates for sensor materials, which have the roles of providing information on physical, chemical and biological parameters of our body or any other studied environment. Although polymers can be stand-alone components responsible for sensing [3,4], they can also be used for immobilizing the active components of the sensors [5,6]. Choudhury et al. proved that PANI/Ag nanocomposites exhibit remarkable improvement of electrical conductivity and dielectric properties compared to pure PANI. The AC conductivity of PANI/Ag nanocomposites was increased by two orders of magnitude with respect to pure PANI. In contrast to pure PANI sensor, the PANI/Ag based sensor responded rapidly and reversibly in the presence of ethanol [7].

Due to the good mechanical, thermal and chemical stability, Teflon (PTFE-polytetrafluoroethylene) is a very promising basic material to be used in sensor devices [8–14]. Thin PTFE films can be deposited by a variety of techniques depending on the film quality requirements and the substrate that is being coated [15,16]. Previous experiments demonstrated that under adequate conditions the pulsed laser deposition (PLD) method allows the production of stoichiometric, compact PTFE films [17–19]. It was also proved that through PLD technique Teflon layers having sponge like morphology with high specific surface can also be produced resulting in a drastically increased sensitive area for the deposited thin films [20,21]. PLD has already been used for fabrication of biosensors as well. Saha et al. deposited nanoporous cerium oxide (CeO_2) thin film onto platinum (Pt) coated glass plate which has been utilized for immobilization of glucose oxidase and successfully exploited for glucose biosensing [22]. PLD method is being effectively used in metal thin layer preparation, too. Since silver exhibits the highest electrical and thermal conductivities among all the metals, the combination of PTFE with silver could yield functional materials having enhanced electrical properties [1,7,23,24]. In present work we demonstrate that PLD technique is also suitable for the deposition of Teflon–Ag composite thin films. Our aim is to prove, that

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http://dx.doi.org/10.1016/j.apsusc.2012.04.151

Fig. 1. The ablated target containing 75 vol% PTFE and 25 vol% Ag.

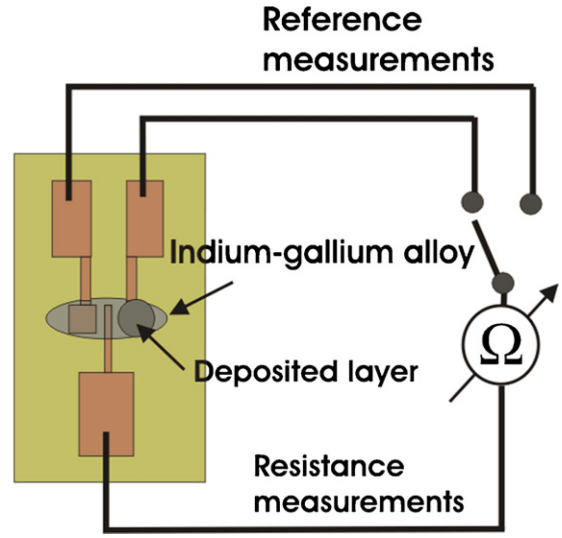

Fig. 2. The experimental arrangement for resistance measurements.

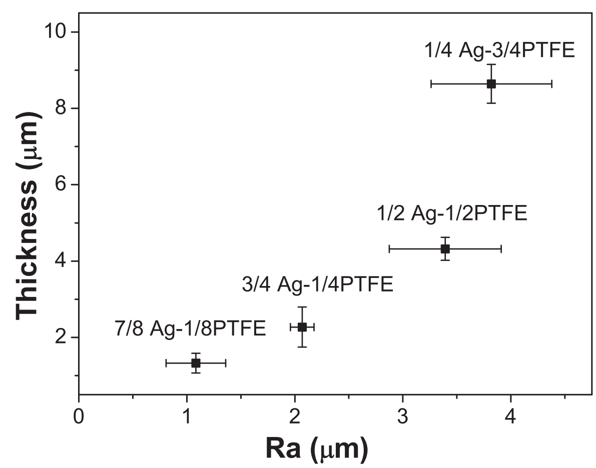

Fig. 3. The mean roughness (Ra) of the deposited layers as the function of the thickness of the thin films.

under suitable experimental conditions thin films with high specific surface and increased wetting and electric properties can be produced with special regard on their applicability in electrochemical sensor technology.

2. Materials and methods

The targets used for PLD experiments were silver plate (Goodfellow, thickness of 2 mm, purity 99.95%) and Teflon ($[C_2F_4]_n$) tablet pressed from powder (Goodfellow, grain size 6–9 μm) by a Graseby Specac 15011 hydraulic compactor at 520 MPa pressure. Disk form targets of six different compositions were prepared using different volumetric percentages of PTFE and Ag as shown in Table 1. These special disks were realized by using sectors of circles for the two materials as seen in Fig. 1.

The beam of an ArF excimer laser (λ = 193 nm, FWHM = 20 ns) was focused by a quartz lens (*f* = 40 cm) onto the surface of the target at 45° angle of incidence, the irradiated area was 1.4 mm^2 and the applied fluence was 8 J/cm^2 according to our previous study on deposition of PTFE films [20]. The number of laser pulses was 5000 in case of each sample with 10 Hz repetition rate. The laser pulses ablated the rotating target surface along a circle to avoid the formation of crater-like structures on the target which could influence the ablation and consequently the layer deposition process. Since the targets were composed of two sectors of circles (Ag and PTFE), for example, in case of 1/4 Ag– 3/4 PTFE target composition during 1 rotational period the silver and the PTFE were irradiated with ~12 and ~37 laser pulses, respectively. Since the deposition rate within one rotational period is much lower than the grain diameter of the deposited PTFE grains, the possibility of layer-by-layer deposition can be excluded. Thin films were deposited onto glass substrates placed onto a 150 °C heatable holder. The base pressure of the PLD

Table 1
Composition of the applied targets, the ablated material and deposited layers.

	Compositions					
Rational target composition						
PTFE	1	3/4	1/2	1/4	1/8	0
Ag	0	1/4	1/2	3/4	7/8	1
Volumetric composition of the ablated material						
PTFE vol%	100	99.1	97.4	92.5	84.2	0
Ag vol%	0	0.9	2.6	7.5	15.8	100
Approximated volumetric composition of deposited layer						
PTFE vol%	50	49.92	49.76	49.3	48.36	0
Ag vol%	0	0.16	0.48	1.4	3.28	100
Void vol%	50	49.92	49.76	49.3	48.36	0
Mass composition of the deposited layer						
PTFE wt%	100	98.4	95.6	87.8	75.5	0
Ag wt%	0	1.6	4.4	12.2	24.5	100