Journal of Industrial and Engineering Chemistry 35 (2016) 158–166

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

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

Gold nanoparticles embedded in carbon film: Micromorphology analysis

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ARTICLE INFO

Article history:
Received 16 August 2015
Received in revised form 9 December 2015
Accepted 19 December 2015
Available online 29 December 2015

Keywords:
Au NPs @ a-C: H films
Plasma enhanced chemical vapor deposition
AFM
Fractal analysis
Three-dimensional surface micromorphology

ABSTRACT

In this paper the sputtered gold nanoparticles (NPs) deposited by Radio Frequency-Plasma Enhanced Chemical Vapor Deposition (RF-PECVD) method on the glass substrates in trace of amorphous hydrogenated carbon (Au NPs @ a-C: H) were analyzed to study the three-dimensional (3-D) surface texture. The prepared Au NPs @ a-C: H films were used as research materials. The synthesis of samples was carried out in different powers from 80 to 120 W while all other parameters were kept constant. The X-ray diffraction patterns and UV–vis spectra were applied to study the structure and Localized Surface Plasmon Resonance (LSPR), respectively. An atomic force microscope in a non-contact mode was used to record the sample surface images then the fractal geometry was studied. The images were numerically processed to calculate the Areal Autocorrelation Function (AACF), which was used to determine the anisotropy ratio S_{tr}, and to compute the Structure Function (SF). The log–log plots of the latter were used to calculate fractal properties of the studied surfaces, such as fractal dimension D, and pseudo-topothesy *K*. The analysis of 3-D surface texture was helpful in optimizing the functional performance of the thin film.

Introduction

Over the last decades, continuing efforts have been directed toward understanding fundamental concepts and models based on the modern theories in manufacturing process, control, and tests of thin films [1–4].

Extensive integration of interdisciplinary research of nanomanufacturing processes establishes safety standards to develop robust protocols for technological transition of nanoscience to practical products of thin films [5–9].

The engineering surface design of thin films requires a simultaneous need for high-resolution and high-sensitivity techniques for characterization of thin film microstructures at the nanometer level and thus to relate material structures to material properties [10–15].

The three-dimensional (3-D) surface morphology of engineering surfaces is in correlation with the manufactured method and can be classified as: isotropic (Gaussian or non-Gaussian) or anisotropic [16–18].

The 3-D engineering surface texture of thin films was characterized by fractal [2,7,9,10] and multifractal [1,3,5,12,14,15] geometry, which may be directly applied to AFM data [19]. AFM method can discriminate between a large diversity of interactions felt by the scanning tip in the vicinity of a surface (electrical, magnetic, adhesive, friction, etc.) [18].

It is known that the statistical self-similarity of fractal 3-D surfaces of thin films is highlighted only in a restricted range of spatial scales [17,19].

In several past decades, for the preparation of metal nanoparticles (NPs) numerous physical and chemical techniques such as: RF-sputtering, RF-PECVD, hydrothermal reduction, and sol–gel

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http://dx.doi.org/10.1016/j.jiec.2015.12.029
1226-086X/

method have been developed that allows fine control of chemical composition and the introduction of lowest concentrations of finely dispersed dopants [20–23].

This work aims to synthesize the Au NPs @ a-C: H films by RF-PECVD deposition method on the glass substrates, to study the structure of films using XRD pattern, to discuss the LSPR peaks position by UV–vis spectra, also to characterize the 3-D surface texture using AFM data in connection with the statistical, and fractal analyses.

Materials and methods

Materials and preparation of thin films

Using RF-PECVD system with 13.56 MHz radio frequency power supply hydrogenated carbon films with sputtered gold nanoparticles were prepared. The reactor in this method consists of two different area size electrodes. The smaller electrode which was used as a powered electrode was Au plate. The other one was grounded via the body of the stainless steel chamber. The deposition was performed at room temperature without any harmful chemical reaction on the glass substrate. The evacuation of chamber was done to a base pressure of 10^{-3} N/m^2 prior to the deposition, then the pressure was increased to ambient pressure by acetylene gas. Acetylene as both reactive and bombarding gas was used in the RF plasma system. In this method deposited film is a compound of the sputtered target materials and the reactive gas in classical reactive sputtering. By changing power the sputtering process was investigated and nanoparticles gold/carbon composite films were grown with different percentage of gold content and different sizes. AFM and SEM image also XRD patterns were used to study the process of formation of gold nanoparticles in the prepared films. Details of prepared samples are given in Table 1.

Characterization of the properties of thin films

The XRD pattern on the samples was recorded by X-ray diffractometer using Cu-kα radiation of wavelength λ = 1.54 Å for 2θ range from 20° to 90° by Bruker make (Model D8) operated at 40 kV and 30 mA.

The Localized Surface Plasmon Resonance absorption spectra of UV–vis spectrometer, was obtained by Stellar.net (Florida, USA) from 2 mm diameter optical fiber that transfers a non-polarized light beam (400–850 nm) through samples to a CCD detector.

AFM on non-contact mode was used to obtain the surface topography and roughness of the samples and the average size of gold NPs using a Nanoscope Multimode atomic force microscope (Digital Instruments, Santa Barbara, CA), with a scan speed of 10–20 μm/s. The experiments were carried out at room temperature (24 ± 1 °C) using cantilevers with the nominal properties for force–distance curve measurements specified in Ref. [24]. All images were obtained over square areas of 1 μm × 1 μm. Nanoparticles on the surface of samples were scanned by field emission scan electron microscopy (FESEM).

Table 1
Process details of prepared samples containing Au nanoparticles.

ID	Target	Sputtering parameters			Sputtering time [min]
		Basic pressure [N/m^2]	Work pressure [N/m^2]	Power [Watt]	
#1	Au	10^{-3}	2.5	80	30
#2	Au	10^{-3}	2.5	90	30
#3	Au	10^{-3}	2.5	100	30
#4	Au	10^{-3}	2.5	110	30
#5	Au	10^{-3}	2.5	120	30

Characterization of the film surface texture

AFM measurements of the surface topography produce discrete arrays of heights $z(x,y)$ whose distributions can be characterized in various ways. In this paper three main methods are used: statistical description that considers the shape of a distribution, fractal – that gives insight into its scaling properties, and functional – that studies the shape of a distribution arranged in a descending order.

According to Nayak [25], any surface can be treated as a real random process with its spatial variation described using the Areal Auto Correlation Function. Assuming that the surface is stationary and ergodic, its AACF can be computed through spatial averaging over a limited range of AFM samples. Even surfaces with apparent curvature and waveform (i.e., actually non-stationary) can be treated in this manner providing that their bow is previously removed exhibiting the so-called residual surface, i.e., the surface without the longest wavelength components.

AACF can then be computed using the following formula [26]:

$$R(\tau_x, \tau_y) = \frac{\langle (z(x,y) - \langle z \rangle) \cdot (z(x+\tau_x, y+\tau_y) - \langle z \rangle) \rangle}{S_q^2} \quad (1)$$

where, $\langle \ldots \rangle$—denotes the mean value, whereas (τ_x, τ_y)—discrete spatial lags along scan axes.

Topographical randomness of man-made surfaces usually extends over several orders of magnitude, assuming that surfaces have nearly identical properties regardless of the direction of the measurement. In fact, spatial correlation between data points may significantly vary with surface direction, which is referred to as the surface lay characterized using the surface anisotropy ratio S_{tr} [26]. More specifically, S_{tr} is defined as the ratio of extreme autocorrelation decay lengths τ with which the normalized AACF falls from 1.0 down to 0.2:

$$0 < S_{tr} = \frac{\tau_{a1}}{\tau_{a2}}\Big|_{R=1\to 0.2} \leq 1 \quad (2)$$

where, a1, and a2 are the axes of the fastest and the slowest AACF decay, respectively [26]. For $S_{tr} > 0.5$ the surface is said to be isotropic (the higher S_{tr} the more angle-independent surface), while for $S_{tr} < 0.3$, surface is said to be highly anisotropic.

As such, AACF characterizes spatial correlations between sample heights and their contribution to short-wavelength surface variation (roughness) exhibiting, for example, periodic patterns. Higher-orders regularities can be observed using alternative characteristics that include fractal parameters: fractal dimension D, pseudo-topothesy K, and corner frequency f_c derived from the Structure Function (SF). For stationary surfaces, their SF can be easily computed from AACF using the formula [27]:

$$S(\tau_x, \tau_y) = 2S_q^2(1 - R(\tau_x, \tau_y)) \quad (3)$$

Basically, fractals are virtual geometrical objects that appear identical regardless of the magnification scale, which can be characterized by a single parameter—fractal dimension D. However, no real structures can be fractal over an infinite range of scale lengths due to several restrictions: finite measurement resolution, finite sampling discrimination, finite observation time and range, and others. Hence, real objects actually exhibit self-affine properties rather than self-similar. Self-affinity expressed in terms of the pseudo-topothesy K corresponds to the way, how the amplitude scales with the specific observation length.

Thomas et al. [27] have shown that fractal parameters of self-affine profiles can be derived directly from the profile SF obtained after averaging along an arbitrary direction. Fig. 1 shows that the