Thin Solid Films 520 (2012) 4174–4179

Contents lists available at ScienceDirect

Thin Solid Films

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

Observation of room-temperature formation of carbon nanotubes as a result of the detachment of a gold nanolayer from a glass substrate

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ARTICLE INFO

Available online 21 April 2011

Keywords:
Thin layer
Carbon nanotubes
Gold
Ion exchange
Glass surface
Adhesion

ABSTRACT

The glass surface morphology after the detachment of a 50–200 nm-thick gold layer deposited on a glass substrate was investigated by the scanning electron microscopy for the three types of glass substrates: smooth plate glass surface without pre-treatment, chemical etched glass and glass surface modified by surface ion exchange process. It was found that the boundaries' morphology of the detached gold fragments depends essentially on the microrelief of surface for each kind of the glass substrate. It was confirmed by X-ray energy dispersive spectroscopy that carbon nanotubes are formed near the detachment boundaries of the gold nanolayer's fragment from glass substrate and consequent storage of these samples in the air at room temperature.

In the authors' opinion, the observed mechanochemical effect associated with the detachment of thin gold layer fragment from glass substrate leads to the increase of the gold catalytic activity and to carbon nanotubes formation in the air that contains carbon impurities. This assumption is confirmed, in particular, by the formation of carbon nanotubes after the detachment of thin gold layer fragment from the glass substrate surface and storage in an ethylene atmosphere.

1. Introduction

The processes of thin layer coatings on glass surfaces currently attract particular attention. It is connected with the possibility to change and control some important physical properties of glasses: optical properties, mechanical characteristics, hydrophilicity, which are significant for decoration and other applications. The investigation of the adhesive capacity of thin films on glasses is also very important for the glass application.

In the present research work it was set the task of investigation of thin gold layer detachment from the glass substrate, which special features may be a substantial factor in context of adhesive properties of the interfacial boundary Au/glass substrate. The authors have been interested in the study of the morphology of gold layer detachment boundaries depending on microrelief of the glass substrate surface formed owing to surface treatment, namely, by chemical etching or ion exchange process.

Of special importance and interest is the unexpected observed phenomena of room-temperature nanotubes formation on the surface of gold layer after its fragment detachment from glass substrate. This observation of nanotubes' formation sets the additional task to perform the nanotubes' characterization in their content, thickness, location and other features. Such investigation seems to be important taking into account the close attention of scientists to carbon nanotubes because their unique properties (electronic, mechanical, structural, physico-chemical and others) [1–8]. The development of catalytic methods involving gold as a catalyst for the preparation of carbon nanotubes is also of interest.

2. Experimental details

In the presented investigation 4 mm-thick soda lime glass plate samples (GOST 111–2001) were used as substrates. The glass substrate surface was modified by two methods. The first method (A) is the Na^+/Li^+ ion exchange process with the surface ion exchange paste (SIEP) [9,10]. After the glass surface was degreased and washed in warm running water (~30–40 °C) a SIEP layer was pasted with stencil use. After removal of the stencil, the glass samples with the surface SIEP layer were held at ~300 °C for 15–20 min. The dried paste layer was then washed with tap and distilled water. The glass samples modified by the surface ion exchange process were named as samples A. The second method (B) of the glass surface treatment is the chemical etching by the paste containing hydrofluoric acid for 5 min. at room temperature as described in [11]; the chemically etched glass samples were denoted as samples B. Smooth glass samples without surface treatment were investigated for comparison (samples C).

The thin gold layers have been deposed on glass surface in the special magnetron equipment Auto Fine Coater JFC-1600 (Jeol, Japan)

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doi:10.1016/j.tsf.2011.04.095

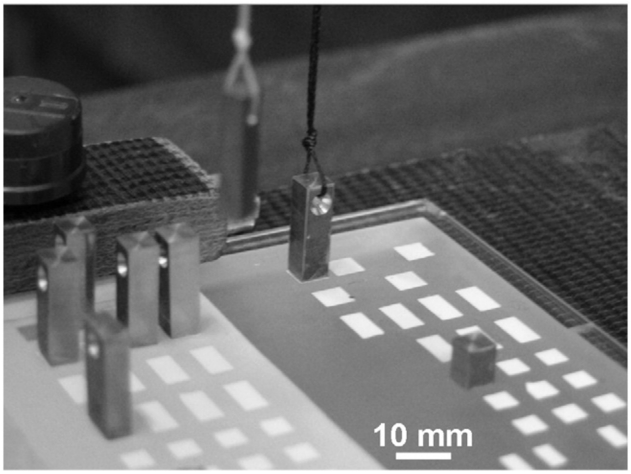

Fig. 1. Photograph of the glass sample used in the experiment of gold nanolayer detachment from the glass substrate.

at the sputtering current 40 mA; the sputtering time has been amounted 60 s, 120 s and 240 s for deposition of 50, 100 and 200 nm thick gold nanolayers, respectively. The study of glass and gold surface morphology has been carried out by the scanning electron microscope JSM-6460RV (Joel, Japan) equipped with installation of the elemental analysis by X-ray energy dispersed spectroscopy (X-ray EDS). The SEM and X-ray EDS measurements have been carried at the electrons' accelerating voltage 20 keV and 15 keV, accordingly. The EDS mapping of an investigated surface micro area has been measured with the scanning matrix 1024*768 points for next X-rays lines: the carbon map — the line $K_{\alpha 1}$, E = 0.28 keV; the silicon map — the line $K_{\alpha 1}$, E = 1.74 keV; the gold map — the line $M_{\alpha 1}$, E = 2.12 keV. The total measurement's time of the separate experimental map was about 60 minutes.

The detachment of gold layer fragment has been realized at stationary vertical loading (see Fig. 1) applied to the metal holder glued to the gold nanolayer on glass substrate surface. The samples have been stored after gold layer fragment detachment at room temperature for two months in the air or 24 h in the ethylene atmosphere and then they have been studied by SEM.

3. Results and discussion

3.1. The glass surface morphology with and without the thin gold layer

The structure of the glass substrate surface may play often an important role in adhesion of thin films therefore it has been paid the special attention to the SEM study of the surface morphology of the glass substrate and the gold surface layer. The glass substrate surface without preliminary modification is practically smooth and does not display any features of microrelief right up to the magnification ×50,000 (see Fig. 2a). The surface morphology of the chemical etched glass substrate is characterized by hills, hollows, steps and kink sites formed as a result of moving away of glass components with the different rate from different surface areas (Fig. 2b).

The surface morphology of glass modified by ion exchange process with SIEP is conditioned by the formation of the glass surface layer with the system of microblocks and microcracks (Fig. 3c). The arising of such structure is caused by the surface ion exchange of ions Na^+ in glass on ions Li^+ diffusing to a glass surface from SIEP. This process is characterized by the product volume reduction in comparison with the initial volume; the shrinkage factor is ~5% [12]. The accumulation of mechanical stresses in the glass surface layer leads to the formation of microcracks (width is ~100–200 nm) and microblocks of breaking (~50–150 μm in size). The frontal surface areas of microblocks are smooth as well as the glass surface without surface modification. The stress relief with cracks in the modified glass surface layer is apparent in cross-section in the SEM micrograph (Fig. 2d).

The morphology of the glass surface with the thin gold layer is similar mainly to the surface morphology of glass without gold layer. The investigated samples with Au layer (50, 100 and 200 nm thick) were named as samples A–Au, B–Au, C–Au, correspondingly. The observed morphological feature of the gold layer deposition on samples A–Au is the formation of nucleation centres of volume growth

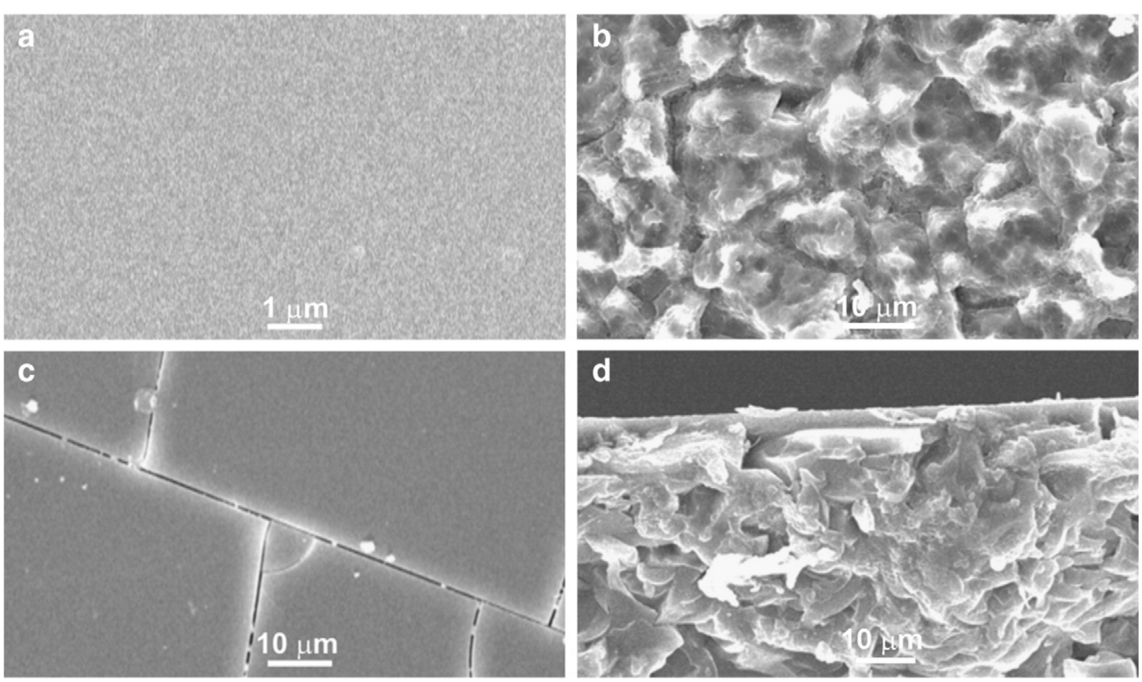

Fig. 2. SEM micrographs of the surface morphology of glass substrates: (a) without preliminary modification; (b) after chemical etching; top (c) and cross-section (d) SEM micrographs of the glass substrate after the ion exchange process with SIEP.