



Experimental and computational study of morphological and electrical properties of tin/plasma polymer nanocomposites

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ABSTRACT

Composite tin/n-hexane plasma polymer films were prepared by means of RF magnetron sputtering of tin target in Ar:n-hexane mixture and characterised by various analytical techniques. Their chemical composition was examined by XPS, current-voltage characteristics were measured, and their structure was investigated by conventional TEM and electron tomography. The acquired three-dimensional reconstructions were morphologically analysed by a self-made computer analytical tool, which estimated the mean form factor and the average effective radius of the reconstructed metal inclusions.

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1. Introduction

Metal/dielectric nanocomposite films have been studied since the second half of the 20th century [1] and still remain in the focus of research attention thanks to their interesting mechanical, optical and electrical properties. The potential of these materials has not been exhausted yet (sensors, switching devices, data storage, etc.) and therefore the nanocomposites are still studied intensively [2–8].

Various deposition techniques (e.g. evaporation and metal sputtering with plasma polymerization) were used to prepare the nanocomposite films [6,9], the RF magnetron sputtering of metal in reactive gas is one of them. Properties of layers prepared by this method are very sensitive to deposition conditions. We focused our attention on the investigation of the relation between deposition conditions, morphology and electrical properties of the deposited layers.

In most of existing computer simulations, a simplified assumption is applied that metal objects in composites are symmetrical, spherical or ellipsoidal, which is valid for films with small amount of metal. However, there exist composites – the tin/plasma polymer film being one of them – where metal objects are irregular. We examined these irregularities and electrical properties of the deposited thin layers with the help of the computer models.

2. Experimental

The nanocomposite thin films were prepared by a tin magnetron sputtering with simultaneous plasma polymerization in a stainless

steel deposition chamber, which was pumped by a diffusion pump with a rotary backing pump. The working gas mixture of n-hexane vapours (Sigma-Aldrich purity 95%) and argon (Linde, purity 99.9999%) was introduced through two needle valves, the n-hexane (liquid) was in a glass container connected to one of the needle valves. The n-hexane fraction r_{nhex} (ratio of partial pressures: $r_{\text{nhex}} = p_{\text{nhex}} / (p_{\text{nhex}} + p_{\text{Ar}})$) in the working gas mixture varied from 1% to 3%. The total working gas pressure for all experiments was 6 Pa. A balanced magnetron with Sn target was powered by an RF generator (Dressler Cesar 133) with a matching network. The power changed from 65 W to 90 W, the sample to target distance was 40 mm. To avoid the impurities in the discharge during experiments, several measures were carried out. The chamber was pumped down to the pressure 10^{-3} Pa before each experiment. The n-hexane was frozen by the liquid nitrogen and the air from the glass container was pumped away. This procedure was done twice in a row before the whole set of the measurements. The discharge was switched on in pure argon for 5 min before each experiment, to sputter away the impurities from the surface of the target (the chamber has to be vented and opened to insert the sample). We used a silicon wafer for XPS analysis, carbon-covered Cu grid for TEM and electron tomography, and Al₂O₃ wafer with screenprinted gold electrode system for current-voltage measurements, which were carried out using PC driven voltage source Keithley 230 and electrometer Keithley 617 used as ammeter. The voltage source, ammeter and PC were switched on 2 h before the measurement to thermally stabilise. The electrical scheme and the scheme of the screenprinted electrodes are shown in Fig. 2. TEM images and electron tomography of thin films were carried out on a Tecnai G2 Sphera TEM at the operating voltage of 200 kV. Several single-axis tilted series were acquired with 1° angular step in the tilting range $|\pm 68|^\circ$ at ~ -600 nm nominal defocus. The tilted series were aligned by the Imod reconstruction package [10], and this

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alignment was further refined by typically two rounds of re-projection matching [11]. Three-dimensional reconstructions were then computed by the Imod package and visualised by the Amira software (Mercury Computer Systems, San Diego). The XPS measurements were performed with the hemispherical analyzer operated in FAT mode (Phoibos 100 from company Specs). The photoelectron spectra were referenced to the aliphatic C1s peak at 285 eV, the elemental composition was calculated from survey spectra. The high resolution photoelectron spectra were acquired to understand the chemical bonds on the surface of the samples.

3. Results and discussion

3.1. XPS results

The stability of the elemental composition of the samples was estimated from the measurements 1 day and 45 days after deposition. The chemical composition is relatively stable in wide range of powers (from 65 W to 90 W) delivered to the magnetron, and there was no clear tendency. The carbon content was close to 30% for all powers in the mentioned range, oxygen close to 40% and tin 30% (the values differed by 5% at the most). There are several possible sources of the observed strong oxidation. The residual atmosphere in the chamber can contain oxygen species that are released from the walls of the reactor during discharge. We tried to avoid this effect by good vacuum conditions before the experiment (see Section 2). Secondly, the n-hexane itself could be another source of oxygen or water vapours. The freezing/pumping procedure should get rid of the air and most of the water vapours in the glass container. As the tin target was cleaned by a discharge in pure argon, the last possibility (to the author's best knowledge) is the oxygen from the atmosphere. We were not able to control this parameter, as we do not have any special storage box with controlled humidity and atmosphere. Provided the measures described above are good enough, the major source of the oxygen is the atmosphere during the storage of the sample. Unfortunately the chemical composition of the samples could not be measured immediately after deposition, so the ageing during the first day of the storage is not known. After 45 days we observed a slight increase of carbon content (several percent), while the tin content decreased. This is probably related to surface contamination from the environment (the samples were stored in an ordinary PE box, without any special care). Furthermore, the oxidation of the tin in Sn3d high

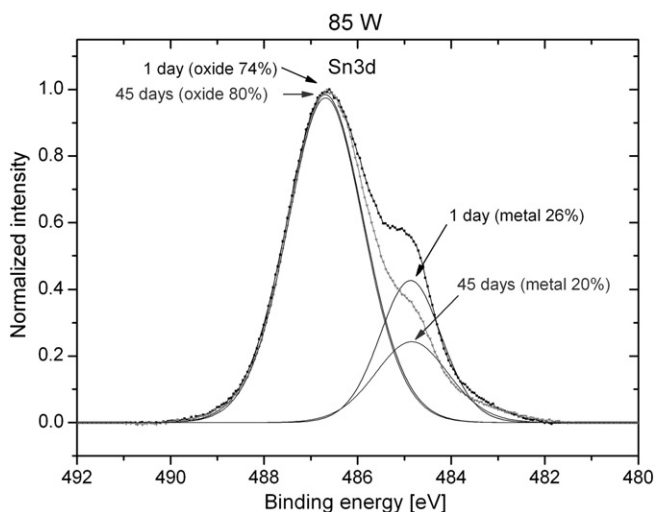


Fig. 1. Example of the high resolution X-ray photoelectron spectra of nanocomposite thin film, sample deposited at 85 W, 1% of n-hexane. The metal fraction after one day (black points) on the surface decreases due to oxidation after 45 days (grey points).

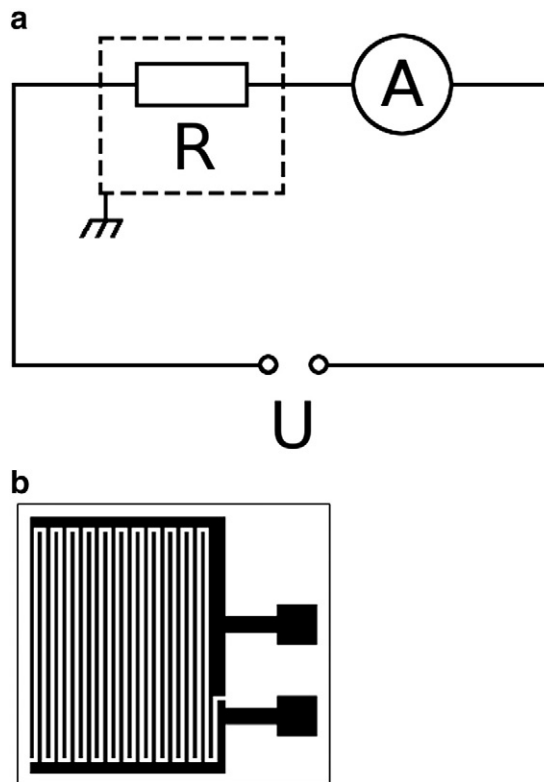


Fig. 2. a) Scheme of the electrical arrangement: U – computer driven voltage source, A – amperemeter, R – measured resistive load, b) scheme of the gold screenprinted electrodes on the Al_2O_3 wafer (size of the Al_2O_3 substrate was 1×1 cm).

resolution peak after 45 days of storage could be clearly observed (see Fig. 1). As the hydrogen is not observable by the XPS, we cannot distinguish whether the Sn3d peak change is caused by oxidation only, or if the humidity is involved. The overall chemical composition of the surface does not seem to change significantly, however, there may be changes that take place during the first day after deposition. The oxidation during ageing is evident.

3.2. Electrical properties

In our previous work [12] we used a sandwich arrangement of the thin film and electrodes for electrical properties measurement. As the films are intended to be used as a gas sensing device, this arrangement is not very suitable. For this reason we swapped to another type of substrate – two screen printed golden electrodes on alumina (Al_2O_3), creating a meander-like structure. If unwrapped (not physically possible – only a mind experiment), the meander length would be 19 mm and the electrode separation would be 150 μm . This type of substrate was used for all current-voltage measurements mentioned in the following text. The contacts were masked during deposition to allow connection to the measuring device. With increasing the amount of n-hexane in the working gas mixture, the film character changed from a material with relatively low sheet resistance ($1.2 \times 10^6 \Omega/\text{sq}$) at 1% to insulating material at 3% of n-hexane in working gas mixture. The sheet resistance was $5.7 \times 10^{12} \Omega/\text{sq}$ in the case of the 3% of n-hexane, while the substrate with empty electrode system (i.e. no thin film on it) showed sheet resistance $5.8 \times 10^{12} \Omega/\text{sq}$, which is in the order of the measurement's accuracy. Although the ammeter Keithley 617 is able to measure units of pA in ideal conditions, for the measurements presented here this was not the case – we observed noisy readings (changes in the order from several tens to hundreds of pA). The measurement error is then larger than 10% in the last two cases mentioned above (sample deposited at 3% of n-hexane and empty

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