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Properties of tin/plasma polymer nanocomposites

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ABSTRACT

Thin composite layers (tin in plasma polymer matrix) were prepared in a stainless steel vacuum chamber. An RF powered magnetron with tin target was used to excite the discharge and to activate the monomer species (*n*-hexane). The gas mixture introduced comprised Ar and *n*-hexane vapours. The properties of the films and chemical composition were characterized by AFM (surface morphology), TEM and Electron tomography (bulk structure characterization), XPS and FTIR spectroscopy (chemical composition analyses). Current–voltage characteristics were measured to examine the electrical properties of the layers and their dependence on the deposition parameters.

1. Introduction

Metal/dielectric nanocomposite films have been studied during the second half of the 20th century [1]. Later metal/polymer and metal/hard carbon (C:H or a-C:H) composite films were also considered [2–5]. Recently, magnetron DC and RF sputtering from a metallic target in a working gas mixture of argon and active (hydrocarbon) gas have been used to deposit metal/hydrocarbon nanocomposite films [6,7].

Nanocomposite films of metal or metal oxide with polymer matrix represent a class of promising materials. The main research attention has been paid to their excellent electrical and optical properties. The aim of this work was to investigate the relationship between the electrical properties of tin/hydrocarbon plasma polymer nanocomposite films and their deposition parameters and structure.

2. Experimental

The stainless steel chamber was pumped by a Roots 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 the needle valve. The container was kept at 35 °C to maintain a constant vapour pressure during the experiments. The *n*-hexane fraction r_{hex} (ratio of partial pressures: $r_{hex} = p_{nhex}/(p_{nhex} + p_{Ar})$) in the working gas mixture was varied from 0% to 10%. 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 (50 W power was used). The sample to target distance was 40 mm. For each experiment the substrate set consisted of silicon wafer (for XPS and AFM), carbon foil covered Cu grid (for TEM and Electron tomography), gold-coated glass slide (for FTIR) and a glass slide with pre-evaporated aluminium electrodes for current–voltage characteristics measurement.

TEM images and 3D reconstruction, based on electron tomography of the films deposited on carbon foil on a Cu grid, were acquired by a Tecnai G2 Sphera TEM at the operating voltage of 200 kV. Diffraction patterns were taken on a transmission electron microscope (JEOL). AFM characterizations were performed using an Integra Probe Nanolaboratory (NT-MDT). FTIR measurements of the layers deposited on gold-coated glass slides were performed on Bruker Equinox 55 (reflection–absorption spectra were taken). The XPS measurements presented in this work were carried out in the Fraunhofer Institut für Angewandte Polymerforschung, Potsdam, Germany. The XPS apparatus was a (KRATOS 165) instrument with analyser operated in FAT mode. The photoelectron spectra were referenced to the C1s peak at 285 eV. A PC driven voltage source

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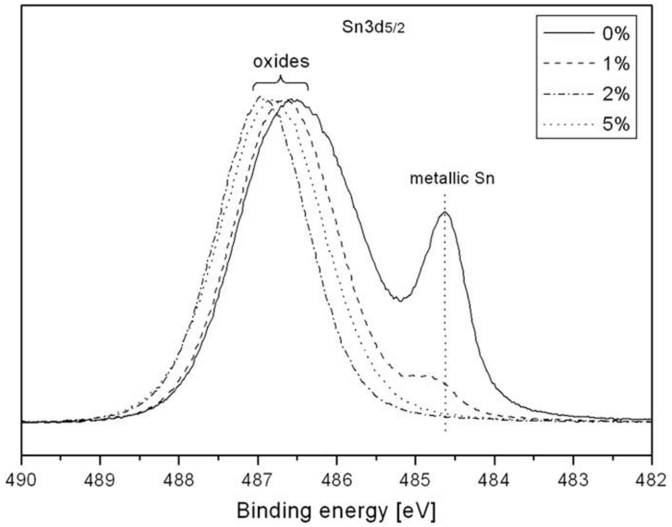

Fig. 1. XPS Sn_{3d} high resolution spectra development with increasing *n*-hexane fraction in working gas mixture.

(Keithley 230) and current meter (Keithley 617) were used to measure the current–voltage characteristics.

3. Results and discussion

For the independent variable, the amount of *n*-hexane in the working gas mixture was taken. Relatively small changes in the composition of working gas mixture lead to significant changes in the film structure, chemical composition and electrical properties, as described in appropriate paragraphs below.

3.1. XPS measurements

With increasing content of *n*-hexane in the mixture, the elemental composition of the resulting layer changed. The tin amount (in atomic %) decreased from 37% to 16% with increasing *n*-hexane fraction in the working gas mixture from $r_{hex} = 0\%$ to $r_{hex} = 5\%$. The carbon species revealed the opposite tendency: its amount increased from 22% to 58%. The oxygen content ranged from 41% (at $r_{hex} = 0\%$) to 26% (at $r_{hex} = 5\%$). The XPS measurements showed that the tin is present as a mixture of metallic and partially-oxidized material (see Fig. 1). For $r_{hex} = 0\%$, the Sn_{3d} peak indicates the metallic component at 484.6 eV. For $r_{hex} = 1\%$, there still is a “metallic shoulder.” As the fraction of *n*-hexane in the working gas mixture increases, the metallic component disappears and the tin is present in the form of non-stoichiometric oxides. The oxide components of various samples show a small shift, which is still not satisfactorily explained.

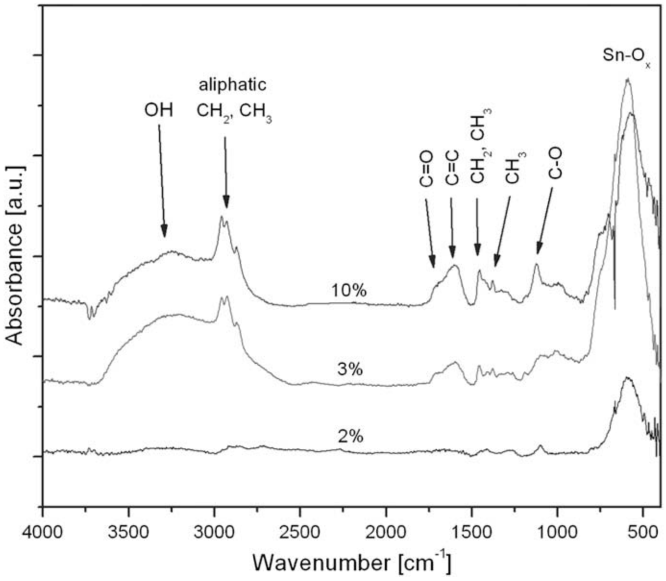

Fig. 2. FTIR spectra of Sn/C:H composite films for various *n*-hexane fractions in working gas mixture.

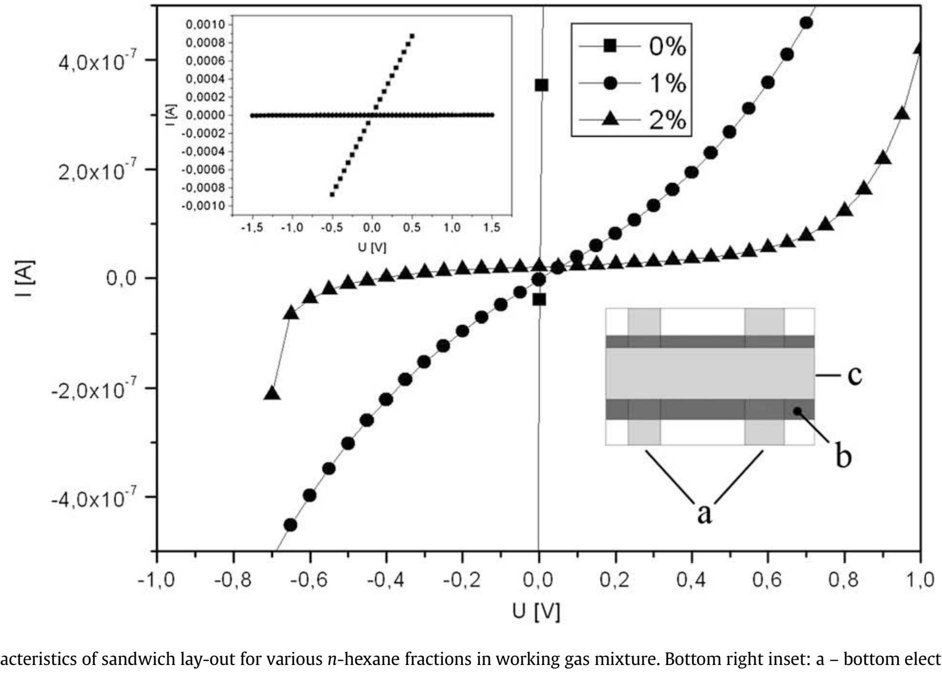

Fig. 3. Current–voltage characteristics of sandwich lay-out for various *n*-hexane fractions in working gas mixture. Bottom right inset: a – bottom electrodes, b – composite film, c – top electrode.