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Electrochemical behavior of amorphous metal–silicon–carbon nanocomposites based on titanium or tungsten nanophase☆

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ABSTRACT

Electrode behavior of nanocomposite films containing titanium- or tungsten-based conducting nanophase embedded in dielectric silicon–carbon matrix, deposited onto glassceramics substrate, is studied by cyclic voltammetry and electrochemical impedance spectroscopy. As the films' resistivity decreases, their electrochemical behavior gradually changes from that of "poor conductor" to the nearly metal-like behavior. In particular, the differential capacitance increases, the charge transfer in a model redox system $[Fe(CN)_6]^{3-/4-}$ accelerates, which may be explained by the increasing number of metal-containing clusters at the film/electrolyte solution interface.

1. Introduction

Amorphous carbon electrodes, in particular, metal-containing amorphous carbon nanocomposites, attract attention during last decade as electrode materials being possibly a cheaper alternative to diamond electrodes [1–3]. Unlike graphite-like carbon, wide-gap diamond-like carbon with predominant sp^3-hybridization of C—C bonds demonstrates suppressed charge transfer in electrochemical reactions. However, the wide-gap diamond-like carbon acquires electrochemical activity after the introducing to its bulk, during the film deposition, of metals, e.g., platinum [4], as well as nitrogen [5,6]. Many carbide-forming metals, being introduced into carbon matrix, form carbide nanoparticles [7], which does not prevent the composite being well conducting because the conductivity of metal carbides often approaches that of the metals. The metal-carbide-nanoparticle-containing composites are characterized by specific range of the particle size (1–10 nm) and narrow size distribution function.

Addition of nitrogen increases both the film conductivity and the electrochemical activity; high electroactivity can be also imparted by the mere increase of sp^2-carbon content in the films of, e.g., tetrahedral carbon (ta-C) by means of their vacuum annealing at 700–900 °C or C^+ ion implantation up to a doze of 10^{15}–10^{17} ion/cm^2 [8].

The metal-containing nanocomposite films with plasma-deposited carbon matrix were studied in ref. [9]. At the metal (W, Cr, or Hf) content of 12–25 at%, the film resistivity was as low as $\sim 10^{-3}\ \Omega$ cm; the hydrogen overvoltage gradually decreased as the W or Cr content increased.

In this work the electrode behavior of nanocomposite films containing titanium- or tungsten-based conducting phase, deposited onto glassceramic substrates, was studied in indifferent electrolyte (1 M KCl or 2.5 M H_2SO_4) solutions, as well as in the presence of model redox couple ($[Fe(CN)_6]^{3-/4-}$) by electrochemical impedance spectroscopy and cyclic voltammetry methods.

2. Experimental

2.1. Films growth and their characterization

The nanocomposite films, with thickness $d = 0.5$–$1.0\ \mu$m, were grown on the polished polycrystalline dielectric sub-

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Table 1
Dependence of electrochemical characteristics of Ti-containing composite films on their surface resistance

Ti (at%)	r_{surf} (Ω/□)	ρ (Ω cm)	r_0 (Ω cm^2)	Potential window (V)	Background current (μA cm^{-2})
33.2	14	1.4×10^{-3}	4.3	2.7	20
21.5	70	7×10^{-3}	6.5	3.0	30
16.3	340	3.4×10^{-2}	8.8	2.9	2
13.4	713	7.1×10^{-2}	32.5	2.8	1
11.5	9000	0.9	620	3.5	1

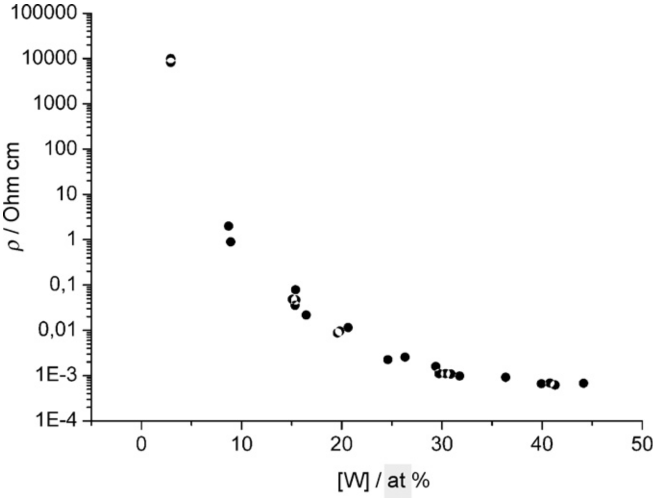

Fig. 1. The film resistivity as a function of tungsten content (at%).

strates of glassceramics (“sitall”) substrates[2] by simultaneous deposition from two sources. The silicon–carbon matrix was deposited by the decomposing of polyphenylmethylsiloxane $(CH_3)_3SiO(CH_3C_6H_5SiO)_3Si(CH_3)_3$ in a dc directional discharge plasma. Tungsten (or titanium) was introduced into the growing matrix by magnetron sputtering of the corresponding metal target. To control the deposition energy, microwave potential was applied, at a frequency of 1.76 MHz, to the metallic substrate holder.

The deposited films possess a number of interesting properties. They are characterized by the high adhesion to a wide variety of materials, including plastics, low values of internal stress, variable electrical resistivity over the wide range—from amorphous insulators up to the values typical for amorphous metals, etc. The smoothness of the films is dependent on the thickness and for the films thinner than 1 μm is about several angströms on the scan area about 1 μm × 1 μm [10].

The details of growth procedures and the film structure and physical properties are described at length in ref. [11].

The surface resistance r_{surf} was measured by standard dc four-point probe method at room temperature. Prior to the measurements, the samples were etched, through peephole mask of required configuration, in Ar–microwave discharge plasma (13.56 MHz). To decrease the contact resistance, the pads were coated with Au-sublayer. The contacts were made with Ag-paste. To stabilize the contact properties, the samples were heated at 180 °C for 10 min in argon atmosphere.

The film resistivity ρ, calculated from r_{surf} and d, depends on the metal concentration drastically; it decreased with the increasing of the metal concentration as shown for W-containing films in Fig. 1, being related to the percolation of the metal phase [12].

2.2. Electrochemical measurements

Electrical (Ohmic) contacts to the films were made at the electrode periphery using the Ag-paste. The sample (the working surface area ~0.2 cm^2) was mounted at a glass holder. A three-electrode glass cell contained, apart of the working electrode, the platinum-wire auxiliary electrode and Ag, AgCl (1 M KCl) reference electrode (all potential values in the paper are given against this electrode).

Potentiodynamic curves and cyclic voltammograms were recorded either in indifferent electrolyte solution (to measure the potential window width) or in 0.01 M $K_3[Fe(CN)_6]$ (or $K_4[Fe(CN)_6]$) + 1 M KCl solution (to determine the transfer coefficients) at a potential scan rate v of 5–100 mV/s, by using a PI-50-1 potentiostat equipped with a PR-8 programming unit and a PDA-1 x–y recorder.

The electrochemical impedance spectra were measured over the 1 Hz to 20 kHz frequency range using a Solartron (model 1280B) spectra analyzer; at higher (up to 100 kHz) frequencies, using an R-5021 ac bridge. The measurements were carried out in the indifferent electrolyte (1 M KCl) solution and in the presence of the $[Fe(CN)_6]^{3-/4-}$ redox couple, with different ratios of the oxidized and reduced forms, at a background of 1 M KCl. In the processing of experimental results, the Ershler–Randles equivalent circuit was used. The elements of the equivalent circuit were calculated by the comparing of the experimentally measured impedance spectra with the theoretically calculated ones for this equivalent circuit; the root-mean-square error did not exceed 10^{-3} to 5×10^{-4}.

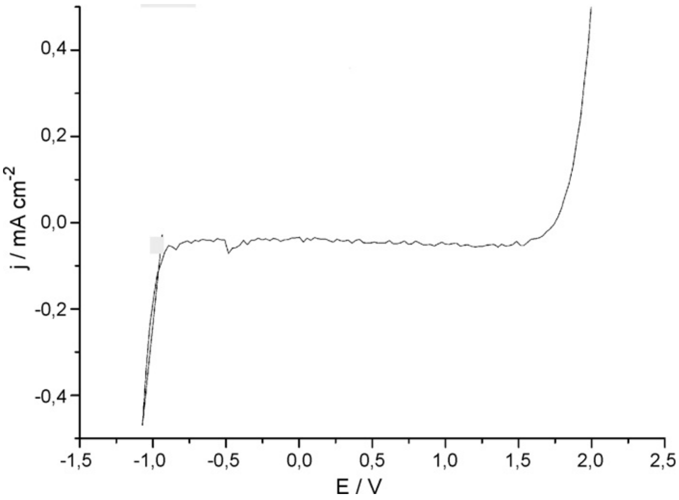

Fig. 2. Estimation of the potential window width: the potentiodynamic curve at Ti-based-composite electrode (13.4 at% Ti) in 2.5 M H_2SO_4 solution.

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[2] Sitall is glassceramics obtained by the glass bulk crystallization. It is chemically stable, heat-resistant, insulating. Being electrochemically inert, it is well suitable as substrate for deposition of electroactive materials.