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Palladium catalyst synthesis through sol-gel processing for electroless nickel deposition on glass

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ABSTRACT

The method of palladium catalyst synthesis by spin-coating of silicate glass with stable isopropanol sol containing the products of controllable $SnCl_2$ hydrolysis with subsequent treatment in $PdCl_2$ solution has been developed. It has been shown that nanostructured Sn(II) hydroxycompounds film containing trace quantity of isopropanol was formed by sol-gel process. This film had an improved continuity and enlarged thickness, smoothed down the surface of the substrate and imparted to it high reductive ability resulting in the generation of palladium nanoparticles in the increased concentration. Mean size of palladium nuclei appeared to be about 4.9 nm against 6.4 nm and concentration gained 4500–5000 μm^{-2} contrary to 1700–2300 μm^{-2} as compared with the particles formed at the use of common aqueous $SnCl_2$ solutions in the processes of palladium activation of dielectrics for electroless nickel deposition. The increase in palladium nanoparticles concentration, improvement of their arrangement and diminution of their sizes provided the rise in palladium catalyst activity. That was revealed in the growth of the rate of nickel films electroless deposition by a factor of 4–6, the improvement of these films microstructure and adhesion to the glass, the enlargement of their thickness from 0.3 to 2.5 μm. Nickel films had good adhesion to the glass and were characterized by uniform, compact and fine-grained microstructure with a majority of grains smaller than 40 nm. The developed method of palladium catalyst synthesis was applied also for electroless nickel deposition on alumina ceramics and quartz.

1. Introduction

Silica-based materials, such as different silicate glasses, quartz monocrystals, silica membranes, fibers, nanoparticles, covered with thin metal films are widely applied. The sphere of their application includes the production of liquid crystal displays [1], waveguides or optical fibers in optoelectronics [2], solar cells [3], conductive contacts in different setups [4], metal coated silica nanoparticles in catalysis [5], membranes for hydrogen separation [6], coloured windowpanes, stained-glass windows and windscreens. Electroless deposition of metal films is an effective and low-cost method to impart the desired conductivity, optical properties (colour, reflectance, absorption, transmittance), catalytic activity. As compared with electrochemical plating and vacuum technologies this method provides the uniformity of metal coating thickness on the devices of different shape [2,5,6], cheap production equipment and low electric energy demand [3,4]. Its weak point is a low adhesion of metal films to silica-based materials because of their very smooth surface and the lack of functional groups which provide chemisorption of metal ions on the glass and are responsible for adhesive interaction.

In comparison with other metals nickel is most often used in the processes of electroless metal deposition from solutions owing to high corrosion and thermal stability of nickel films, their conductivity and ability to fulfil functions of a barrier and a sublayer for other metal coatings. The traditional process of electroless nickel deposition on a dielectric commonly includes four stages, such as 1) surface etching with aggressive acid or alkaline solutions to make a developed relief and provide damping in aqueous solutions, 2) treatment of a substrate with $SnCl_2$ aqueous slightly acid solution to impart reductive properties to the surface by adsorption of Sn(II) containing compounds, 3) treatment in $PdCl_2$ solution to activate the surface with palladium nanoparticles, 4) electroless nickel deposition [1–4,7–10]. The thickness of thus obtained nickel films on the glass does not exceed some tenth of micron. It is limited by weak metal adhesion to the substrate which is worse than in case of metal films obtained by vacuum technologies.

The most important reasons of this lack are the island-like microstructure of not continuous Sn(II) oxycompounds films and the effect of a great number of factors on their characteristics. The arrangement and thickness of the islands formed by Sn(II) containing nanoparticles are dependent on the morphology and energetics of a substrate, concentration of $SnCl_2$ in the solution and its pH, conditions and duration of its storage and of rinsing a substrate after processing in this solution and so on [7–10]. The irregularity and discontinuity of Sn(II) containing

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films causes the diminution of their contact area with the surface of a substrate and adhesion to it, the nonuniformity in sizes and the arrangement of palladium catalyst nanoparticles and of nickel nuclei accordingly. This nonuniformity can be also caused by partial loss of the reductive activity of Sn(II) containing film on the reason of Sn(II) oxidation in the air. The rate of nucleation and growth of nickel grains varies on different sites of a substrate thus causing the internal stresses, cracking and peeling of nickel films.

The increase in adhesion strength can be attained by traditional creation of a surface roughness that is needed for mechanical interlocking between a substrate and a deposited film by means of mechanical, physical or chemical treatments. Unfortunately, a surface roughness can cause a diminution of cohesive strength in the near surface layer and impossibility to produce fine submicron conductive elements with precise sizes and regular edges of conductors [11].

The increase in adhesion strength can be provided by the deposition of intermediate layers [8,12] or by modifying the surface of a substrate with some anchor groups, like different silane derivatives (γ-mercaptosilanes) [13]. Both methods demand expensive materials and additional operations.

To provide uniformity of the morphology and energetics of the substrate and to apply it the reductive properties required for palladium ions reduction the method of photoinduced metal deposition on semiconductive TiO_2 films was proposed in [14–16]. These films are formed from $TiO_2 \cdot nH_2O$ sols obtained by polybutyltitanate controllable hydrolysis in isopropanol with the addition of a certain water amount. The lacks of this method are the usage of rather expensive titanorganic compound and the necessity of TiO_2 film UV irradiation to generate electrons for palladium(II) reduction. The advantages of this method are the possibility to vary the thickness of TiO_2 films by multiple spin-coating with fast drying and a very small dependence of their homogeneity on the morphology and chemical nature of a substrate.

Analysis of the available data shows the necessity and some means to improve the traditional method of palladium catalyst formation needed for electroless nickel deposition on the smooth and inert surface of the silicate glass. The demands for this method improvement are to preserve the smooth surface of the glass and to insure the formation of uniformly arranged palladium nanoparticles with high catalytic activity, high concentration and good adhesion. The use of sol which contains Sn(II) hydroxycompounds nanoparticles in isopropanol media seemed us to be prospective. This supposition was based on the ability of alcohol to improve the damping of the glass surface, to control $SnCl_2$ hydrolysis and oxidation, the sizes and concentration of Sn(II) compound nanoparticles in sol and in films and also to heighten the uniformity of Sn(II) containing layer and palladium particles concentration.

The aim of this work was to develop the synthesis of palladium nanoparticles catalytically active in electroless nickel deposition on the silicate glass surface through its processing in isopropanol Sn(II) containing sol on purpose to improve the microstructure and properties of nickel films.

2. Experimental

2.1. Substrate preparation

Pyrex glass slides were used as a model substrate simulating a wide range of silica-based materials applied nowadays.

The degreased glass plates were etched at 80 °C in Piranha (the mixture of H_2SO_4 and H_2O_2 at 3:1 volume ratio) [17].

2.2. Composition of Sn(II) containing solutions

Solutions were prepared with the use of 98 wt% pure (A.C.S. reagent, Aldrich) $SnCl_2 \cdot 2H_2O$ and 37 wt% solution of hydrochloric acid (A.C.S. reagent, Aldrich). Commonly used slightly acid $SnCl_2$ aqueous solution № 1 containing 0.11 mol/l of $SnCl_2$ and 0.1 mol/l of HCl was tried for comparison. New tin(II) containing solution № 2 (Table 1) was obtained as a result of controllable $SnCl_2$ hydrolysis in isopropanol. This solution comprised a small amount of water (0.6 mol/l) introduced with $SnCl_2 \cdot 2H_2O$ crystalline hydrate and hydrochloric acid used to control chemical processes and composition of the solution. Solution № 2 was prepared by dissolution of $SnCl_2 \cdot 2H_2O$ portion in a measured volume of 37 wt% HCl with the formation of transparent concentrated solution which was further diluted by dried distilled isopropanol.

2.3. Preparation of Sn(II) containing films

Films containing tin compounds were deposited on a glass surface by dip coating (time of the treatment 15 min) in case of aqueous solution № 1 and by three-step spin-coating in case of isopropanol solution № 2. The latter included next operations 1) 700–900 rev/min for 7–12 s – primary spreading of the solution layer; 2) 1300–1500 rev/min for 20–30 s – partial solvent evaporation, thin film formation; 3) 2700–3000 rev/min for 20–30 s – final solvent evaporation, gel-like Sn(II)-containing film formation. Then the films were completely dried with a warm air flow (40–50 °C) for 20–30 s. It was impossible to use spin-coating in case of the aqueous solution № 1 because of poor glass damping and low rate of water evaporation.

2.4. Formation of catalytically active Pd nanoparticles and their activity characterization

To obtain palladium catalyst on the glass surface coated with Sn(II) containing films the samples were treated in the slightly acid $PdCl_2$ solutions. Owing to the heightened reductive ability of films obtained by sol-gel processing in isopropanol solution № 2 concentration of $PdCl_2$ solution was diminished from $3.0 \cdot 10^{-3}$ to $1.2 \cdot 10^{-3}$ mol/l together with the decrease of the treatment time from 60 to 30 s.

Palladium particles formed at this stage appeared to display catalytic activity in the reaction of hypophosphite ions oxidation necessary to reduce nickel(II) ions and to obtain nickel films. The ability of the obtained Sn(II) containing films to generate palladium catalyst was estimated indirectly in a process of electroless nickel deposition because the rate of nickel films growth was dependant on the catalytic activity and the number of palladium nanoparticles formed. Nickel was deposited from the weak-acid acetate hypophosphite solution, containing (mol/l): $Ni(CH_3COO)_2$ (A.C.S. reagent, Aldrich) – 0.14; NaH_2PO_2 (A.C.S. reagent, Aldrich) – 0.42; CH_3COONH_4 (A.C.S. reagent, Aldrich) – 0.52; saccharin $5.5 \cdot 10^{-3}$ (A.C.S. reagent, Aldrich) at 40 °C.

2.5. Methods of investigation

Transmission electron microscopy (TEM) with LEO 906 E set was used to determine the sizes of Sn(II) containing nanoparticles formed in the bulk of the both solutions. Collodion supports were used to prepare nanoparticles for this investigation. TEM method was also used to study palladium nanoparticles formed on the glass surface after Sn(II) containing sols treatment. The samples for this study were prepared by the method of carbon replicas with palladium nanoparticles extraction. In this experiment carbon films were evaporated in vacuum onto the samples treated with solutions № 1 or № 2 and then with $PdCl_2$ solution. Carbon films containing palladium particles were detached from the glass in the hydrofluoric acid solution. Both methods of preparation provided to obtain the resolution on TEM photos about 1 nm.

Table 1
Composition of Sn(II) containing solutions.

Solution, №	Solvent	$SnCl_2$, mol/l	HCl, mol/l	H_2O, mol/l
1 [10,11]	Water	0.11	0.1	55.6
2	Isopropanol			0.6