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Fabrication of flexible microelectrodes using Cold HV sputtering

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Flexible biocompatible microelectrodes are highly required for bio- and medical applications. Reliability of microelectrodes is associated with adhesion of metallic electrodes to polymeric flexible substrate. Therefore studying the fabrication process of microelectrodes based on different methods of metallization is of great interest. In the present work we showed the feasibility of microelectrode fabrication on polyimide substrate using its metallization by the method of Cold HV sputtering. The fabrication process includes formation of 0.1-0.5 μm Pd layer on polyimide substrate, photolithography defining the electrodes, deposition of about 1.0-1.5 μm gold layer on Pd electrodes by electroplating, removal of photoresist and Pd layer from the area unprotected by Au. Polyimide samples with deposited Pd layer were studied by SEM and XPS methods. Scaly structure of Pd layers explains their high electrical resistance (specific resistance of 20-200 μΩ·cm) and limits the Pd films application as interconnects. Along with this, Pd layers are characterized by very good adhesion to polyimide (metallized samples successfully passed Scotch peeling test and allowed numerous folding without adhesion disturbance) which provide a good advance as a seed layers for electroplating. Excellent Pd adhesion to polyimide was shown to be associated with Pd/polyimide chemical interaction.

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1. Introduction

Microelectrodes on flexible biocompatible polyimide (PI) substrate are needed for bio-medical applications, particularly in the neuroprosthetic systems designed for intracortical use [1, 2] or for peripheral nerves or muscles [3, 4]. Electrodes are usually made of noble metals such as Au and Pt deposited by electron beam evaporation or sputtering. In order to obtain good adhesion of an electrode to PI surface, an adhesion layer such as Cr or Ti with thickness typically of 20-50 nm should be sputter deposited before Au or Pt deposition [1-7].

Preliminary treatment of PI in plasma and using Ti alloys instead of the pure metal were proposed for adhesion improvement [8, 9]. To make better adhesion of 120 nm platinum film a 15 nm TiW layer was used [8]. This process is followed by a 400 nm gold deposition on top of the Pt/TiW. Prior to metal sputtering, RF oxygen plasma at 150 W for 3 min was applied. As was shown in [9] a low-stress silicon nitride adhesive film allowed for a titanium seeded gold layer (150 nm Au/30 nm Ti) to be deposited by electron beam evaporation on PI (cured Pryalin PI2545) surface with good adhesion. This metallization scheme overcomes many previous adhesion problems experienced with the etching of small features. The PI surface was roughened in oxygen plasma before nitride deposition.

Treatment of PI in oxygen plasma before its vacuum metallization has been shown to increase drastically adhesion strength also in the Cr/PI interface [7, 10, 11]. The treatment in O_2 plasma changes considerably both the surface morphology and chemical nature of the PI surface. Imide ring in the PI was opened to make additional C-O and C-OH bonding so that C=O bonding in the oxygen plasma etched sample decreased. The hydrophilic C-O bonding on the surface of PI films is believed to be suitable for enhanced adhesion between polyimide thin films and metal [10]. The formation of new carbon–oxygen structures as a result of polyimide treatment in atmospheric dielectric barrier discharge plasma led to the adhesion enhancement [11]. The treatment of PI surface in O_2 inductively coupled plasma followed by in-situ sputter-deposition of 100-nm-thick Cu seed layers on the sputter-deposited 50-nm-thick Cr adhesion layer allowed Au electroplating on Cu seed [7].

In electroless metallization of PI, before Pd activation, PI treatment in alkaline solutions [12 - 14] or in plasma [15 - 18] is necessary. The generation a high density of amino groups on treated PI surface is critical for successful metallization, however the mechanism by which Pd(0), the agent actually initiating the electroless deposition, bonds to the aminated surface is still unclear [17]. Treatment in O_2 plasma followed by modification of PI film by plasma graft polymerization with 1-vinylimidazole caused the significant increase of metal adhesion which is believed to be the consequence of domination of $N(C{=}O)_2$ species on the modified surface [18].

As was shown above, metallization processes providing desirable metal / PI adhesion are complicated and consist of a few stages. As adhesion of metallic electrodes to polymeric flexible substrate is a factor considerably affecting the reliability of microelectrodes [19], studying the alternative metallization processes is of great interest.

In the present work we showed the feasibility of microelectrode fabrication on polyimide substrate using its metallization by the method of Cold High Voltage (HV) sputtering [20]. This method was successfully applied for pretreatment of the polymer surfaces before bonding [21] and seems to be very promising for achievement of high adhesion strength of polymers with different materials.

2. Experimental

The Pd layers were deposited on the surface of the PI (Kapton 38 µm thickness film) by Cold HV sputtering. No preliminary pretreatment of PI samples except cleaning by acetone was done.

Cold HV sputtering process was carried out in a diod-type apparatus schematically shown in Fig.1. Glow discharge is established in the working chamber in an atmosphere of ionizable fluid, maintained at reduced pressure between the cathode (target) and the anode. Cathode atoms emitted by the bombardment of plasma ions move towards the substrate, mounted in the same chamber. While conventional magnetron sputtering is characterized by substrate temperatures and particle energies in the ranges of 150-200 C and 1-10 eV, respectively, a unique patented design of chamber in Cold HV sputtering provides a combination of low substrate temperature (30-150 C) and high particle energy (10-100 eV) [20] . The typical values of Cold HV sputtering parameters are shown in Table 1.

Table 1. Cold HV sputtering parameters.

Process parameter	Typical range
Surface - Cathode sputtering voltage	2-4 kV
Discharge density	0.5-5.0 mA/cm^2
Cathode working area	20-100 cm^2
Pressure inside the chamber	1-6 mTorr

In the present work Pd-metallization of PI was realized by sputtering of the flat quadrate Pd-target (S = 25 cm^2) on the distance near 10 cm from PI-film. Anomalous glow discharge is used for sputtering Pd-target. Sputtering voltage, discharge density, cathode working area and pressure inside the chamber were 3,2 kV; 0,6 mA/cm^{-2}; 25 cm^2 and 6 mTorr(Ar atmosphere). Substrate temperature was near 60 C. The times of Cold Pd-deposition were 3; 1; 0.5; 0,25 h (Samples #1,2,3,4, respectively).

Adhesion of Pd layers to PI surface was evaluated using Scotch peeling test and numerous folding of metallized samples to an angle of 180°. Electrical resistance of Pd layers was measured by In-line Four Point Probe (Lucas/Signatone^{TM}).

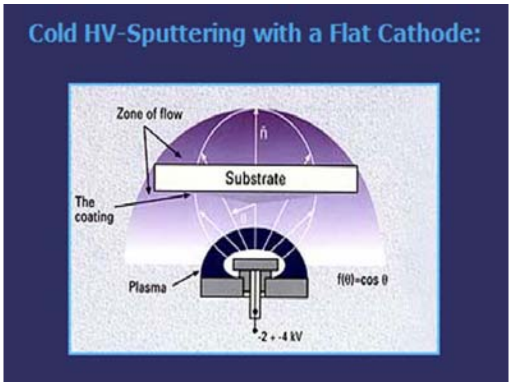


Fig.1. Schema of apparatus for Cold HV- Sputtering

The structure of Pd layers was studied using SEM JSM-6300 in low vacuum mode at 10 keV, at a working distance of 9.6-9.8 mm. The thickness values of Pd layers were measured using SEM and Profilometer Alpha-Step 500. Profilometer was also used for measurement of the photoresist layers thickness and Au/Pd electroplate sandwiches layers on the fabricated electrode structures.

Pd/PI interface was investigated by X-ray Photoelectron Spectroscopy (XPS) technique. XPS measurements were performed in UHV (2.5x10 $^{-10}$ Torr base pressure) using 5600 Multi-Technique System (PHI, USA). The samples were irradiated with an Al K_α monochromated source (1486.6 eV) and the outcome electrons were analyzed by a Spherical Capacitor Analyzer using the slit aperture of 0.8 mm in diameter. The samples were analyzed at the surface and after sputtering. Neutralization of positive charging was used when necessary. All peaks of the charged samples were referenced to C1s peak at 285 eV. High resolution measurements with pass energy of 11.75 eV are presented. Sputtering was carried out with 4kV Ar$^+$ Ion Gun.

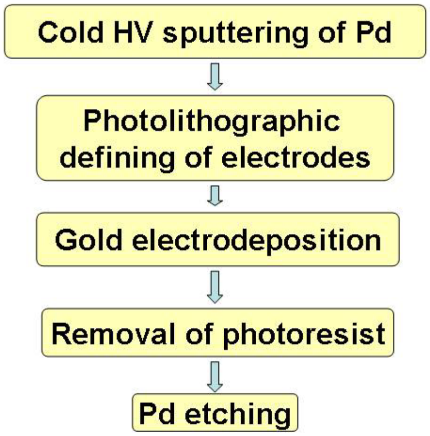


Fig. 2. The flow of electrode microfabrication process.

Feasibility of electrode fabrication on PI substrate with Pd metallization was studies using replication of structures with lines scaled down to 5 µm. The flow of electrode microfabrication process is shown in Fig. 2. Photolithographic defining of electrodes was carried out using photoresist AZ1518 (cured at 120 C and developed in conventional developer AZ 726). Au plating was done from sulfite/thiosulfate/phosphate bath containing stabilizing and wetting additives (pH 6.5). Photoresist was removed in acetone and Pd was removed by the selective electrochemical dissolution in electrolyte containing Cl^- [22] and by selective chemical etching in the mixture of concentrated acids HCl : HNO_3 : CH_3COOH 1 : 10 : 10 v/v.

Replicated structures were studied using optical microscope Olympus MX50 equipped with camera Infinity 1 CCB.

3. Results

Adhesion tests

PI with Pd layers successfully passed Scotch peeling test and allowed numerous folding without adhesion disturbance. 1-2 µm Au layers were electrodeposited on the surface of Pd without exfoliation and passed the Scotch peeling test as well. These results demonstrate good adhesion of Pd layers deposited by Cold HV sputtering to polyimide.

Electrical resistance

The sheet resistance of the Pd layers (Rs) versus their deposition times are presented in Fig. 3. The average Pd thickness values and the calculated values of specific resistivity (ρ) are shown in Table 2. As seen from the reported data, the average ρ values of Pd layers varied in the range of 25 -115 µΩ·cm depending on Pd layer thickness, while bulk Pd is characterized by ρ equal to 10.8 µΩ·cm [23] that is about 2.5 times lower than measured ones.

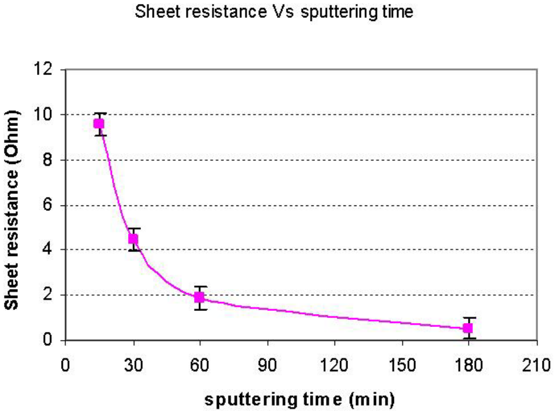


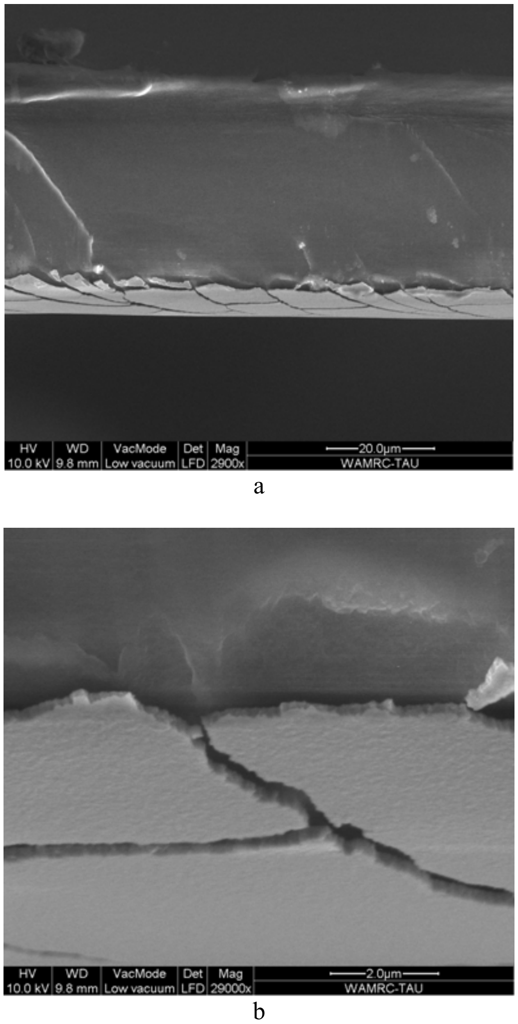
Fig. 3. Sheet resistance of Pd layers versus deposition time.

Table 2. Thickness and Specific resistivity of Pd layers.

Deposition time, min	Thickness, nm	Specific resistivity, µΩ·cm
15	120	114.4
30	150	66.5
60	250	46.4
180	480	25.8

Structure of Pd layer

Pd layers are characterized by scaly structure as can be seen in Figs. 4. Areas of Pd are separated by the cracks the width of which reaches about 0.5 µm for the layer with thickness of about 0.5 µm (Fig. 4b). This structure explains, likely, their high specific resistivity.



a

b

Fig. 4. Cross section of the film deposited for 0.25 h at 3.2 kV, 60 C, substrate-cathode distance 10 cm and 6 mTorr Ar for 3 h. a – Magnification 2900; b- Magnification 29000.

XPS results

Samples with Pd layer deposited for 3 h (Sample #1) and 0.25 h (Sample #4) were investigated using XPS. XPS spectra were collected from the surface of Pd layer before and after sputtering and from backside of polyimide film with Pd layer deposited for 3 h.

Figs. 5 -7 show high-resolution Pd3d, N1s and C1s spectra respectively. It should be noted that these spectra for Samples #1 and #4 before sputtering were identical.

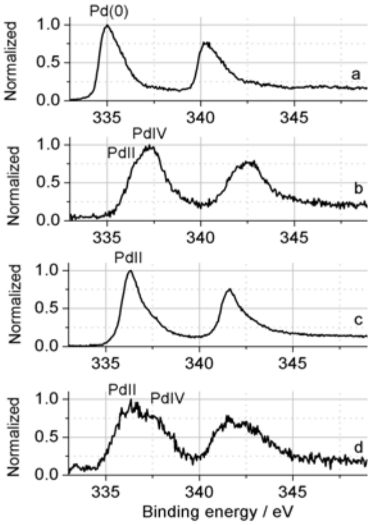


Fig. 5. Pd3d spectra: Pd film deposited on polyimide for 3 h (a), Pd film deposited on polyimide for 3 h and sputtered for 32 min (b), Pd film deposited on polyimide for 0.25 h and sputtered for 8 min (c), back side of polyimide film after deposition of Pd for 3 h (d)

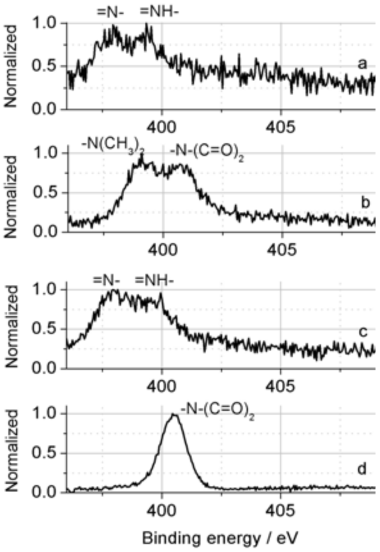


Fig. 6. N1s spectra: Pd film deposited on polyimide for 3 h (a), Pd film deposited on polyimide for 3 h and sputtered for 32 min (b), Pd film deposited on polyimide for 0.25 h and sputtered for 8 min (c), back side of polyimide film after deposition of Pd for 3 h (d)

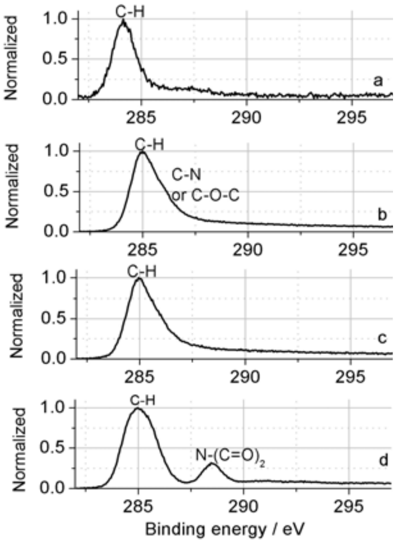


Fig. 7. C1s spectra: Pd film deposited on polyimide for 3 h (a), Pd film deposited on polyimide for 3 h and sputtered for 32 min (b), Pd film deposited on polyimide for 0.25 h and sputtered for 8 min (c), back side of polyimide film after deposition of Pd for 3 h (d)

Figs.5a, 6a and 7a illustrate the data for Sample #1 before sputtering. Along with metallic Pd (Binding Energy, BE, is 334.9 eV [24], Fig.1a), nitrogen atoms of quininoid imine (=N-) (BE 398.1 eV) and of the benzenoid amine (=NH-) (BE 399.4 eV) were detected as well (Fig. 6a). Imine and amine are characterized by BEs 398.4 and 399.6 eV, respectively [25]. Considerable deviation of hydrocarbon chain (BE 284.18 eV instead of 285 eV in C1s spectrum, Fig.7a) can be presumably explained by the Pd-N=C- bonding. C1s and N1s BEs equal to 284.2 eV and 398.1 eV, respectively, were reported for citosan-supported imine palladacycle containing fragment with the similar bonding [26].

Pd3d spectra for sputtered Samples #1 and #4 (Figs.5b and 5c, respectively) and for back side of Samples #1 before sputtering (Fig.5d) can be considered as superposition of spectra for PdII and PdIV. Pd-O and O-Pd-O BEs are 336.3eV and 337.8 eV, respectively [27]. PdIV component is more pronounced in the spectrum in Figs.5b than in the spectrum in Fig.5c, that is more prolong deposition lead to more deep ionization of Pd. The presence of PdII and PdIV in low concentration (about 0.8 at.%) on back side of as prepared Sample #1 can be presumably explained by diffusion of ionized metal species in gas phase in chamber during Pd deposition. This is verified by the fact that after cleaning (sputtering) of Sample #1 back side Pd signal inside the polyimide substrate was not found.

On the sputtered Pd surfaces, the N1s signals of tertiary amine (-N(CH_3)$_2$) at about 399.15 eV and of imide (-N(C=O)$_2$) at 400.5 eV [28] are found on Sample #1(Fig. 6b), while imine (=N-) and benzenoid amine (=NH-) are observed on Sample #4 (Fig. 6c). The shoulder near 285.5

eV in C1s spectra (Figs. 7b and 7c) indicate the presence of C-O-C bonding [29] and amine CH-N bonding [28].

N1s and C1s spectra of polyimide substrate before sputtering (back side) contain peaks attributed to imide (-N(C=O)$_2$) species – at 400.5 eV and at 288.5 eV, respectively [28].

Thus, the results of XPS analysis show that during Pd deposition the transformation of imide group in amine and imine groups as well as ionization of Pd occur. Interaction of species leads to the formation of Pd-N=C- bonds at the Pd/polyimide interface that causes high metal adhesion to the polymeric substrate.

Electrode fabrication

The replication of microstructures was carried out following the procedures described in the experimental section on Sample #3 with Rs of about 2 Ω /sq. The Rs value of Pd layer was essentially higher than that of Cu PVD seed (0.1 – 1.3 Ω /sq.) [30]. Nevertheless it allowed Au electroplating in the photoresist moulds defining the opened conductive structures. Electroplating for 20 min resulted in the deposition of Au layer with thickness of 1.2-1.4 µm.

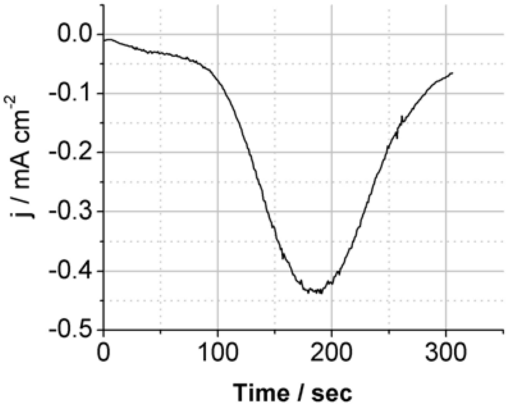
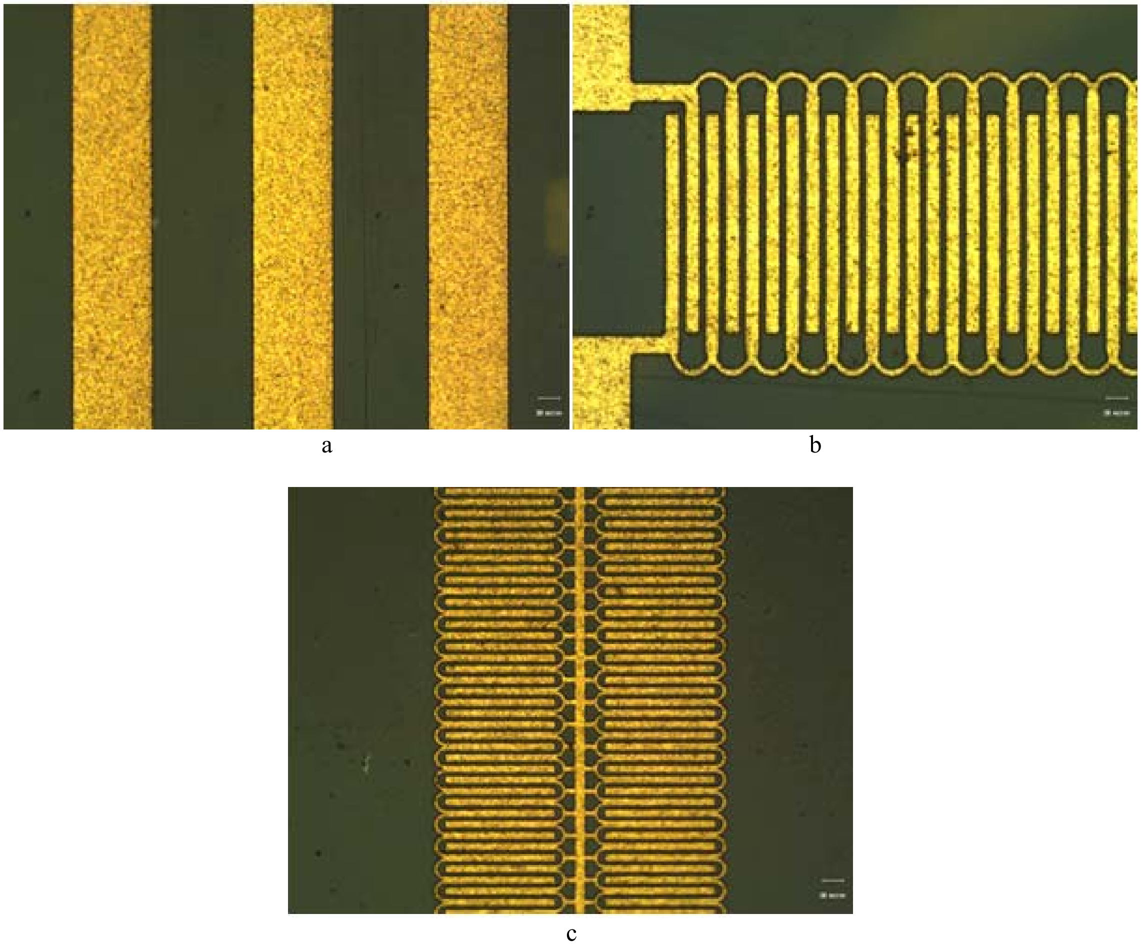


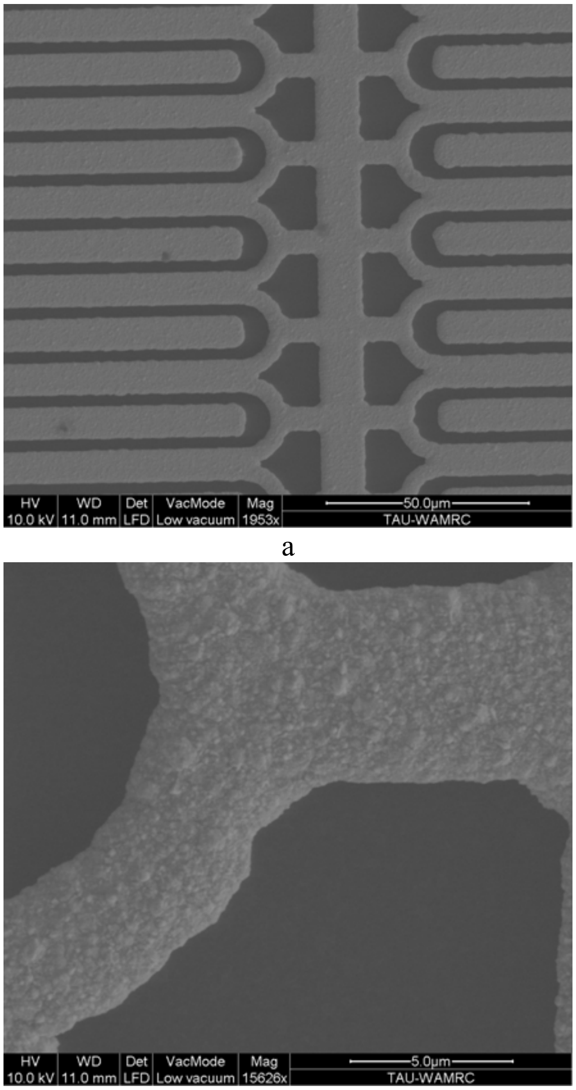
Fig. 8. Change of current during selective potentiostatic (0.7 V vs SCE) dissolution of Pd.


a

b

c

Fig. 9. Optical microphotographs of replicated electrode structures. Scale bar -20 µm, a – structure 1, b – structure 2, c- structure 3.



a

b

Fig. 10. SEM microphotographs of replicated electrode structure. a and b –the fragments of structure 3 at different magnifications (about 2000 and more than 15000, respectively)

The selective electrochemical dissolution of Pd from the unprotected by Au areas was conducted at constant potential of 0.7 V vs SCE in the cell with Pt counter electrode. The typical change of the current during dissolution is shown in Fig. 8. The process was stopped when the current began to decrease and the rest of Pd was removed by the chemical etching. The optical and SEM microphotographs of the formed electrode structures are presented in the Figs. 9a - 9c. and Figs.10a – 10b, respectively. The structures with the line width as low as 5 µm were replicated. No exfoliation of Pd layer from PI substrate or Au layer from Pd during fabrication process were revealed. It should be noted that in spite of scaly structure of Pd seed (Fig.4b), Au layer seems to be continuous; no cracks were observed on its surface (Fig.10b).

4. Summary

- ➢ Metallization of polyimide by Cold HV sputtering in combination with photolithography, electrochemical deposition and selective electrochemical and chemical etching allow fabrication of flexible electrodes with line width scaled down up to 5 µm.
- ➢ Excellent adhesion of metal layer to polyimide surface is associated with metal/polymer chemical interaction in the interface. The results of XPS analysis show that during Pd deposition the transformation of imide group into amine and imine groups as well as ionization of Pd occur. Interaction of species leads to the formation of Pd-N=C- bonds at the Pd/polyimide interface.
- ➢ Scaly structure of Pd layers explains their high electrical resistance (specific resistance of 20-200 µΩ·cm) and limits the Pd films application as interconnects.

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