Influence of the gold sub-layer on the catalytic properties of magnetron sputtered Pt and Ir thin films

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Abstract: The paper presents a research on the influence of the gold sub-layer in composite magnetron sputtered Au-M (M = Pt,Ir) films on their catalytic activity toward the hydrogen evolution (HER), oxygen evolution (OER) and oxygen reduction (ORR) reactions in sulphuric acid solution. The test samples are deposited on glass substrates upon 25 nm thick adhesive titanium layer. The thickness of the underlying Au is 240 nm and that of the top functional metal (Pt or Ir) is 10 nm. The properties of the sputtered films are studied using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and electrochemical methods of cyclic voltammetry and quasi steady state polarization curves. The performed morphological and electrochemical investigations reveal that the specific catalytic efficiency of the composite Au-Pt and Au-Ir films is superior compared to that of the pure metals which allows for essential reduction of the catalytic loading at preserved performance.

Keywords: platinum; gold; iridium; iridium oxide; magnetron sputtering; bi-functional catalysts

1. INTRODUCTION

One of the key goals of catalyst manufacturing for hydrogen energy systems (fuel cells, water electrolysers, and bi-functional reversible cells) is the development of new materials with improved cost efficiency. It is possible to design catalysts with enhanced activity and selectivity by alloying two or more metals [1, 2]. The bimetallic catalysts have demonstrated enhanced activity compared to the corresponding monometallic ones. They are extensively used in many catalytic and electrocatalytic applications [3].

One of the approaches to produce bimetallic surfaces is to replace either the sub-monolayer or the over-layer coverage of the single crystal with an ad-metal. The electronic and chemical properties of a metal in a bi-metallic surface may change due to two important factors - formation of hetero-atom bonds changing the electronic environment (ligand effect) and change in the orbitals overlap affecting the geometry of the bimetallic surface (strain effect). Both factors lead to shift in the surface d-band, resulting in decrease or increase of the adsorbate binding energy [4, 5, 6, 7, 8, 9]. Sinfelt and Rodriguez [4, 7] have shown how two metals interacting on a surface can form compounds with structures not seen in the bulk alloys. By

experimental and density functional theory (DFT) modeling it has been found that the monolayer ad-metal can interact with the host metal substrate by: i) occupying the top-most surface sites to produce a surface monolayer; ii) diffusing into the subsurface region to form the subsurface monolayer; and iii) alloying with surface to produce inter-mixed bimetallic surfaces. DFT modeling results have indicated that the modification on the surface d-band center is significantly different for the three types of bimetallic structures [1, 2, 3, 10].

Since the surface catalyzed reactions are extremely sensitive to the atomic-level details, the choice of the method for preparation of smooth thin layers with good mechanical strength is essential for tuning of the catalytic activity and utilization. Usually the catalysts are powders consisting of metal nanoparticles deposited on catalytic support with high surface area. There are various catalyst preparation techniques such as wet chemical reduction, sol-gel, thermal decomposition of metal salts, electrochemical deposition, underpotential deposition etc. [11-22]. The choice of the method depends also on several strict criteria such as efficiency, reproducibility, time consumption, cost as well as the technological availability in regard to the application. In the last decade the method of plasma enhanced physical vapour deposition (PVD), also called direct current magnetron sputtering (DCMS), has been introduced as an

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alternative of the classical methods for catalysts preparation [23, 24]. The magnetron sputtered catalysts are deposited as thin compact (mono, bi- or poly-metallic and/or oxide) films upon selected substrate materials and could have extremely low precisely controlled metal loading [25-27].

Platinum is the best known pure metal catalyst for hydrogen evolution (HER), hydrogen oxidation (HOR), and oxygen reduction (ORR) reactions, while it is not so efficient with respect to the oxygen evolution (OER). In order to increase the catalytic activity and reduce the cost of catalysis Pt is often alloyed with cheaper metals from the transition series such as Ni, Co, Fe and etc. or with other noble metals (Ru, Ir, Os) which improve not only the efficiency but also the stability of the composite catalysts [16, 19, 20, 21, 27, 28]. The most commonly studied catalysts for OER are Ir, IrO_x, RuO_x [29-31].

This work concerns the preparation of thin composite catalytic films in which an essential part of the efficient but expensive Pt and Ir is substituted by dense Au sub-layer using the method of magnetron sputtering and investigates the influence of the Au sub-layer on the catalytic activity toward the partial electrode reactions proceeding in sulphuric acid solution.

2.   EXPERIMENTAL
2.1 Formation of the catalytic layers

Five different test samples are sputtered using a magnetron sputtering machine Nordiko 2550, equipped with 3 targets of high purity (99.999%) metals. The functional catalytic films are deposited on glass substrate upon 25 nm thick Ti sub-layer serving as an adhesion promoter. Three of the test samples are pure metals - Pt, Au, and Ir. Pt and Ir are deposited at previously optimized sputtering conditions ensuring high porosity (resp. high active surface per unit geometric area) combined with good mechanical stability of the films **[27, 32].** The Au deposition at this stage is not optimized and the film is much denser. The composite Au-M catalysts consisting of two consecutive functional layers sputtered at conditions identical to those used for the single films. The total thickness of all samples is fixed to 250 nm as the top M-layer is 10 nm thick.

2.2 Test procedure
Physical characterization. The surface structure and morphology of the sputtered catalysts are studied by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The diffraction data are collected using X-ray diffractometer Philips ADP15 with Cu-Kα (λ=1.54178 Ǎ)

radiation at a constant rate of $0.2^0.s^{-1}$ over an angle range 2Θ=10-90⁰. The XPS spectra are recorded with ESCALAB MK II (VG Scientific, England) electron spectrometer. The photoelectrons are excited with twin anode X-ray source using Al Kα (*h.v* = 1253.6 eV) radiations.

Electrochemical tests. The electrochemical characterization of the sputtered Au-M films is performed in Ar-saturated 0.5M H_2SO_4 at room temperature by conventional electrochemical techniques of cycling voltammetry and quasi-steady state polarization curves. The cyclic voltammograms (CV) are recorded in the potential range between hydrogen and oxygen evolution at temperature of 20 ºC and scan rate of 100 mV s⁻¹. The quasi steady state polarization tests are carried out in a potentiodynamic mode with scan rate of 1 mV s⁻¹. The experiments are performed with Galvanostat/Potentiostat POS 2 (Bank Electronik, Germany) in a standard three electrode electrochemical cell using Ag/AgCl reference electrode and Pt-wire as counter electrode. The working area of the test electrodes is 0.5 cm⁻².

3.   RESULTS AND DISCUSSION
3.1 Surface analysis

The XRD spectra of the films are presented in Figure 1. The patterns of Au, Au-Pt and Au-Ir films show poly-crystalline structure of all metals with preferential [111] orientation which is more characteristic for Au. On the spectrum of the multi-layered catalysts, alloying is not registered.

The chemical state of the sputtered films is examined by XPS analysis. The high resolution Au4f-Pt4f and Au4f-Ir4f photoelectron spectra are presented in Figure 2 (a,b). The peak analysis and the performed fitting procedure indicate that Au, Pt and Ir present as pure metals (the registered amount of oxides on the Pt and Ir surface is negligible). The Pt4f peak is clearly seen in the spectrum of the Au-Pt (Figure 2a). It is situated at binding energy 71.5 eV. The Au4f peak is also well recognized. For the pure Au it is situated at 83.3 eV, while for the Au-Pt sample its position is at 84.3 eV. Berg at al. **[33]** have performed high-resolution photoelectron spectroscopy measurements of Au over-layers on Pt (100) surfaces and have found contributions to the Au 4f7/2core level spectrum from Au atoms in four different local environments in the surface: Au atoms at the Pt interface (83.32±0.02eV) , surface Au atoms with (1×1) symmetry (83.50±0.02eV), surface Au atoms with a (1×7) symmetry (83.63±0.02eV), and bulk-like Au atoms at (83.87±0.02) eV. In our case the observed essential shift in the Au 4f7/2core level spectrum of the Au-
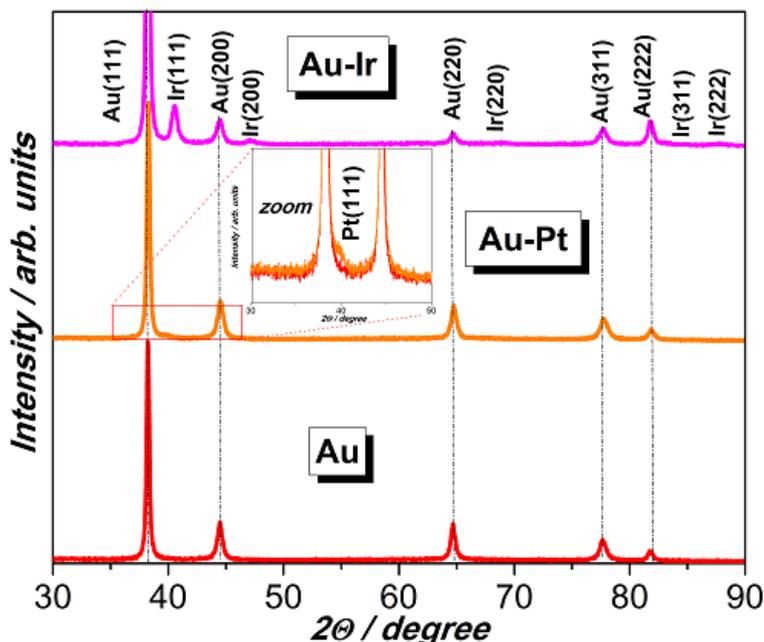
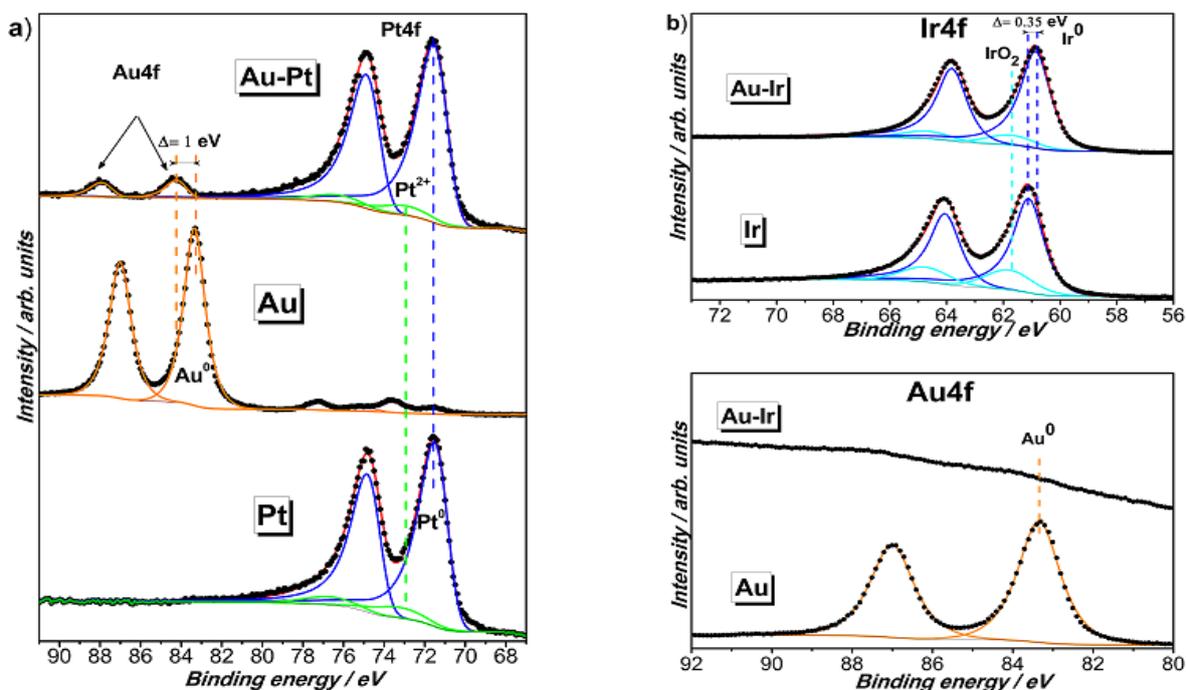**Figure 1.** XRD spectra of the Au, Au-Pt and Au-Ir catalytic films.

Figure 2. High resolution Au4f-Pt4f (a) and Au4f- Ir4f (b) photoelectron spectra of the sputtered catalytic films

Pt film to higher binding energy implies formation of Au-Pt interlayer on the Au-Pt boundary.

In the XPS spectra of Ir and Au-Ir (Figure 2b) the Ir4f peak is well recognized. At the same time the Au4f peak is only slightly hinted which most probably is due to the morphology of the functional top layer.

The Ir4f peak for the pure Ir is situated at 61.19 eV, while for the Au-Ir sample it is shifted in negative direction (60.75 eV). The reasons for the registered differences in the binding energy changes of both systems (Au-Pt and Au-Ir) are not very clear and should be further investigated. For instance the morphology and/or density of the top functional layer could have an influence.

3.2 Electrochemical measurements

The obtained cyclic voltammograms of the catalysts under study are presented in Figures 3 (a,b) for the systems containing Pt and Ir, respectively. Figure 3a shows the effect of the partial substitution of Pt by Au. On the Pt and Au CV curves the characteristic curve peaks typical for the pure metals are clearly depicted – hydrogen
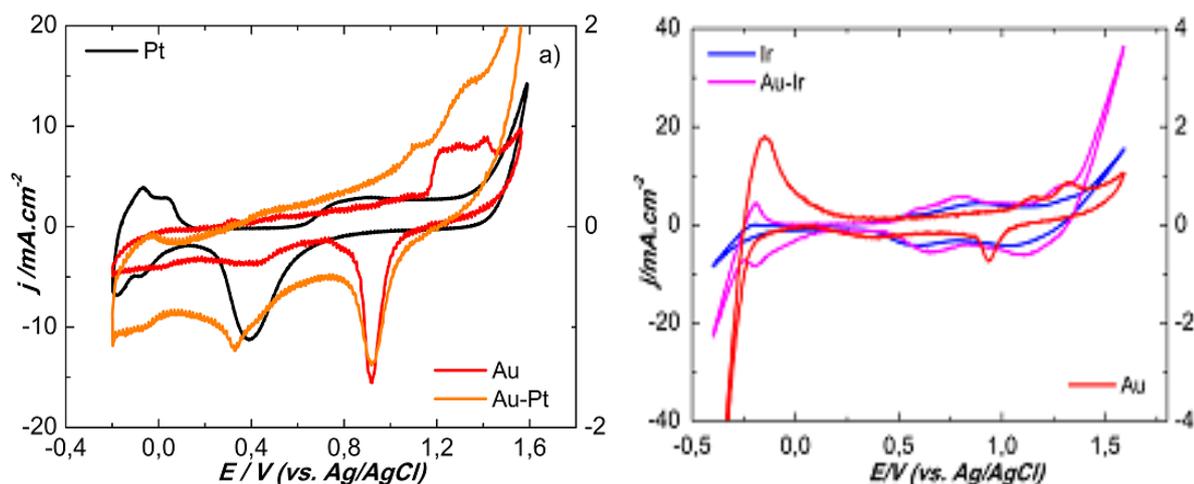
Figure 3 Cyclic voltammograms of Au-Pt (a) and Au-Ir (b) in 0.5M H_2SO_4; potential ranges (a) -0.2 to 1.6 V and (b) -0.4 to 1.6 V; scan rate 100 $mV.s^{-1}$.
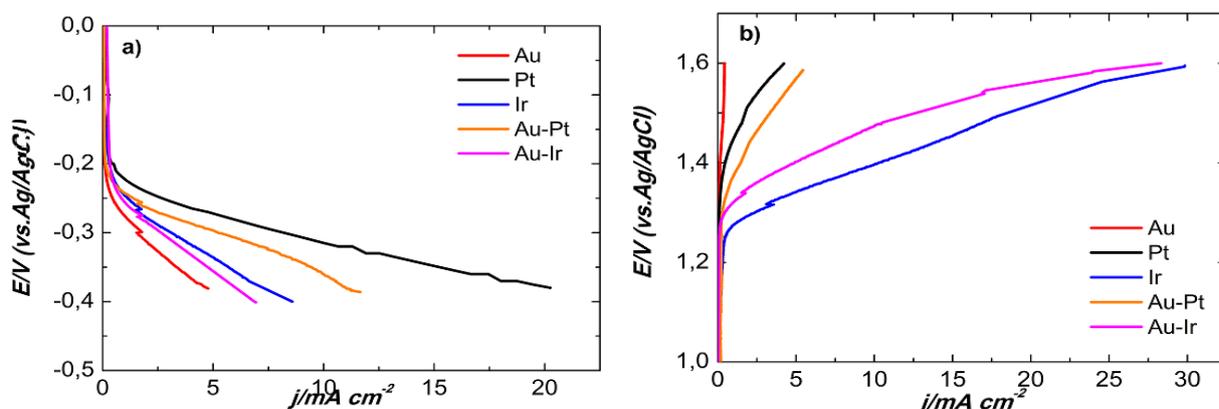

Figure 4. Quasi-steady state polarization curves - HER (a) and OER (b) of the sputtered catalytic films in 0.5M H_2SO_4; scan rate 1 $mV.s^{-1}$.

adsorption/desorption on Pt (0.0 to - 0.4V), formation of oxygen coverage on both metals (> 0.65V), and oxygen reduction (around 0.4V and 0.9V, respectively). The Au-Pt CVs show that the deposition of 10 nm Pt on the top of 240 nm Au layer results in a rather complex cyclic voltammogram. All current peaks characteristic both for Au and Pt are well recognized. Particularly clear are the oxygen reduction peaks situated at 0.9 V and 0.4 V. Figure 3b illustrates the effect of partial substitution of Ir layer by Au. The CV curve of the pure iridium shows all characteristic current peaks resulting from reversible changes in Ir valent state: from metallic iridium to iridium in second, third and forth oxidation state Ir/Ir^{2+} (0.50 to 0.63 V), Ir^{2+}/Ir^{3+} (0.63 to 0.92 V), Ir^{3+}/Ir^{4+} (1.16 to 1.34 V). The CV curve of the composite Au-Ir sample is identical in shape. The reversible current peaks are slightly smaller, while the oxygen evolution starts a bit earlier and is more intensive.

To evaluate the catalytic efficiency of the sputtered composite films toward the proceeding partial electrode reactions, quasi steady state polarization curves are recorded.

Figure 4 (a,b) shows the hydrogen evolution (HER) and oxygen evolution (OER) reactions. As expected, the HER is most intensive on the pure Pt film. The next best catalyst is the composite Au-Pt. It should be stressed out that the Pt content in both samples is very different (the platinum content in the gold-platinum film is 25 times less than that in the "pure" platinum film). Since Pt is much more expensive than Au, the cost efficiency of the catalysis in the case of Au-Pt is strongly improved. Ir and Au-Ir catalysts are less active to HER compared to both Pt-containing samples as the reaction rate is not proportional to the thickness of the top iridium film.

The OER reaction is most intensive on the pure Ir film which facilitates the oxygen evolution stronger than Au-Ir. However, the difference in the reaction rate on both samples is much lower than the difference in the thickness of the functional iridium layer (250 to 10 nm). On the other hand, the

composite Au-Pt sample demonstrates higher catalytic efficiency toward the oxygen evolution compare to pure Pt, despite the difference in the Pt loading, implying strong synergetic effects between both metals. This assumption is supported by the XPS analysis (Figure 2a).

It is well known that Pt is a very active catalyst toward the ORR. The quasi steady state cathodic polarization curves of the pure Pt and Au-Pt recorded in the potential range where ORR takes place are presented in Figure 5. The achieved current densities and the values of the Tafel slopes are summarized in Table **1.** They show some catalytic activity of Au-Pt and indicate different mechanism of the reaction compared to that on the pure Pt, which is in accordance with the results from the CV curves. In order to investigate the mechanism of ORR and to find out if Au-Pt could be used as a bi-functional reversible oxygen electrode catalyst, further experiments on RDE are currently in progress.
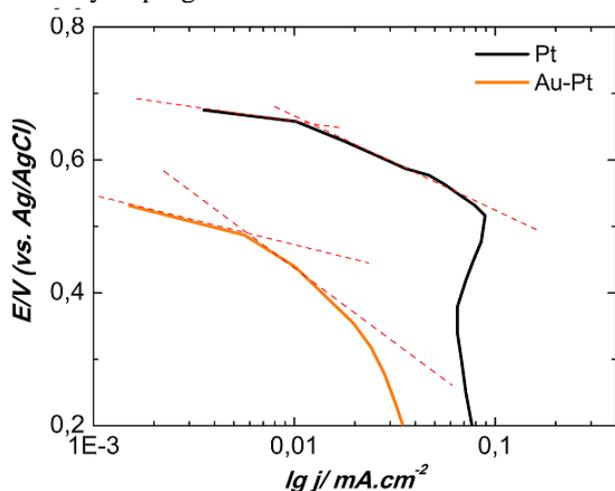

Figure 5 Quazi steady state polarization curves of ORR of the sputtered catalytic films in 0.5M H_2SO_4; scan rate 1 mV.s^{-1}.

To distinguish better the effect of the Au sub-layer on both systems performance, in Table 1 are given also the values of the reaction rates for HER and OER at constant potentials, presented in current density and in specific activity (normalized to the thickness of the top functional layer). It is seen that there is no linearity between the thickness and the specific activity, which confirms the assumption for existence of synergism in the composite catalytic films. This is more clearly demonstrated in the case of Au-Pt.

4. CONCLUSIONS

The research performed proved that the method of DCMS can be used as precise technique for deposition of multi-layered catalysts with controlled thickness and tailored synergetic effects between the components. It was shown that the partial substitution of platinum and iridium by gold improves the specific activity and reveals possibilities for better utilization of the Pt and Ir catalysts and thus, for reduction of catalytic loading.

The polarization measurements showed an improved HER and OER activity of the Au-Pt films compared to pure Pt as well as an indication that it could behave as a bi-functional oxygen electrode for both ORR and OER.

The observed changes in the electrochemical performance of the composite films allow to assume a synergy between both metals, which is stronger in the case of Au-Pt. The synergetic effect is explained with formation of interfacial bimetallic layers and electronic interactions, confirmed by the registered shift in the binding of the metallic components. How exactly the BE shift affects the mechanism of the proceeding electrode reactions needs to be cleared in the ongoing research. The possibilities to enhance the observed synergetic effects by optimization of the layers order, number, and thickness will be also explored.

Table 1. Catalytic activity of the sputtered films.

Catalytic Films	Hydrogen Evolution Reaction (HER) E= -0.35 V		Oxygen Evolution Reaction (OER) E= 1.6 V		Oxygen Reduction Reaction (ORR)	
	$j/mA.cm^{-2}$	$js/mA.cm^{-2}.nm^{-1}$ Pt or Ir	$j/mA.cm^{-2}$	$js/mA.cm^{-2}.nm^{-1}$ Pt or Ir	*Tafel Slopes/ mV.dec^{-1}* b1	b2
Pt	15.16	0.060	4.27	0.017	42	145
Au-Pt	9.30	0.930	5.82	0.582	77	223
Ir	5.65	0.023	29.9	0.120	-	-
Au-Ir	4.67	0.467	28.6	2.86	-	-

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ВЛИЯНИЕ НА ПОДСЛОЙ ОТ ЗЛАТО ВЪРХУ КАТАЛИТИЧНИТЕ СВОЙСТВА НА ТЪНКИ МАГНЕТРОННО РАЗПРАШЕНИ ФИЛМИ ОТ Pt И Ir

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(Резюме)

Статията представя изследване на влиянието на златен подслой върху каталитичната активност на магнетронно разпрашени филми Au-M (M = Pt и Ir) спрямо парциалните електродни реакции на отделяне на водород (HER), отделяне (OER) и редукция (ORR) на кислород, протичащи в кисели водни електролити на сярна киселина. Филмите от Au-Pt и Au-Ir са отложени върху стъклена подложка, покрита със адхезивен слой от 25 nm Ti. Дебелината на всички проби е 250 nm – слой от 240 nm Au, върху който е отложен 10 nm функционален слой Pt или Ir. Свойствата на получените филми са изследвани чрез рентгеноструктурен анализ (XRD), рентгенова фотоелектронна спектроскопия (XPS), и електрохимичните методи – циклична волтаметрия и поляризационни криви. От проведените морфологични и електрохимични изследвания е установено значително увеличение на специфичната каталитичната активност на биметалните филми Au-Pt и Au-Ir, което позволява да се намали каталитичното натоварване като се запази ефективността на процеса.