

(19)



(11)

EP 2 045 365 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

08.04.2009 Bulletin 2009/15

(51) Int Cl.:

C25D 3/02 (2006.01)

C25D 3/56 (2006.01)

(21) Application number: **08460009.7**

(22) Date of filing: **28.03.2008**

(84) Designated Contracting States:

**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HR HU IE IS IT LI LT LU LV MC MT NL NO PL PT
RO SE SI SK TR**

Designated Extension States:

AL BA MK RS

(30) Priority: **02.04.2007 PL 38211507**

(71) Applicant: **Uniwersytet w białymstoku
15-097 Białystok (PL)**

(72) Inventors:

- **Wojciech, Olszewski
15-453 Białystok (PL)**
- **Szymanski, Krzysztof Rafal
15-337 Białystok (PL)**

(54) **Electrolyte and the method of depositing metal layers especially of iron, cobalt, nickel, copper and zinc**

(57) The electrolyte and the method of depositing metal layers, especially of iron, cobalt, nickel, copper and zinc to be used in electrotechnics and electroplating technology.

The method of depositing metal layers, especially of iron, cobalt, nickel, copper and zinc by electrolytic deposition from the electrolyte (4) being a mixture mainly of acetone, hydrochloric acid, positive ions of the metal being deposited, is characterized in that at the initial stage of the process at least one anode (1) is being dissolved in the electrolyte (4) containing, at the initial stage, 90-99

% of acetone, 1-10 % of water and 0.5-3 % of concentrated hydrochloric acid (36 % solution HCl in water). Then the metal layer is deposited on the surface of cathode (5) and the concentration of ions of the metal, being deposited in the electrolyte (4), is set automatically.

The electrolyte is characterized in that it contains 90-99 % of acetone, 1-10 % of water and 0.5-3 % of concentrated hydrochloric acid (36 % solution HCl in water).

EP 2 045 365 A1

Description

[0001] The subject of invention is the electrolyte and the method of depositing metal layers, especially of iron, cobalt, nickel, copper and zinc, used in electrotechnics and/or electroplating technology.

[0002] There are ways of obtaining metallic coats by depositing single-component or multi-component electrolytic layers. In the processes of depositing electrolytic metal layers used on industrial scale, very sophisticated procedures are applied. Most manufacturing processes take place with the use of water electrolytes in which the concentration of positive ions is about 1 Mol/dm³.

[0003] The application of nonaqueous electrolytes is also known for deposition of metals, which cannot be deposited from water solutions - alkaline metals, magnesium, aluminium and rare earths. Similarly to water electrolytes, nonaqueous electrolytes are composed of many substances and the compositions are set for the deposition of a particular ion. Nonaqueous electrolytes are prepared from organic solvent, a dissociating compound providing the ionic transport, and the appropriate cation. In the publication [Yu.Ya. Fialkov, A.N. Zhitomirskii, and Yu.A. Tarasenko, "Fizicheskaya Khimiya Nevodnykh Rastvorov" (Physical Chemistry of Nonaqueous Solutions), Leningrad: Khimiya (1973)] deposition of copper from acetone solutions of its salt and cadmium from the saturated solution CdJ₂ is described. The authors also claim that in the case of low solubility of salts in organic solvents, cations tend to precipitate from the solution. In subsequent works, e.g. [T.V. Troepolskaya, G.A. Vagina, I.R. Abdullin, N.V. Utyaganov, S.G. Vul'fson and A.N. Vereshchagin, A. E. Arbuzov, "Electrochemical reduction of rare-earth chelates with certain - diketones", Journal Russian Chemical Bulletin 39 (1990): 2481] it is stated that actinides, Cu, Ni, Co and Tl precipitate from electrolytes containing the solutions of appropriate salts in diketones and in trifluoroacethylcamphor. The processes of electrochemical deposition of rare earths from acetone electrolytes are described by [Guan Fu-yu and Gao Xiao-xia, "Voltammetric study on the reduction of rare earths in acetone", J. Chin. RE Soc. 8 (1990): 166 (in Chinese)].

[0004] The deposition of metals from electrolytes composed mainly of acetone was also confirmed, for example in the publication of [V.N. Titova, V.A. Kozakov, N.V. Petrova and S. Biallozor, "The influence of solvent on the kinetics of silver electrodeposition", Journal of Analytical Chemistry 381 (1995): 227]. It described the precipitation of silver from acetone solution of AgNO₃ where ionic conductance was achieved by adding LiClO₄.

[0005] In the American patent US4701244, deposition of particular metals from organic electrolytes was revealed, e.g. tin and lead, titanium, zirconium and niobium. Plating bath contained, among others, additives such as benzal acetone.

[0006] There are also methods in which the deposited cation is brought from anode. For example Kamada and

others reported that the layers of titanium oxide and niobium oxide precipitated from acetone solutions, where the metal got to the solution as a result of anodic dissolution [K. Kamada, M. Mukai, Y. Matsumoto, "Anodic dissolution of tantalum and niobium in acetone solvent with halogen additives for electrochemical synthesis of Ta₂O₅ and Nb₂O₅ thin films", Electrochimica Acta 49 (2004): 321].

[0007] In the German patent DE 3411320, the method of separating tantalum from organic electrolytes is claimed where anodic dissolution of tantalum is applied. In this process nonaqueous electrolytes and an atmosphere of inert gas are used.

[0008] In the German patent WO 2004/031449, the method of controlling the size during the electrochemical deposition of metal or semimetal oxide nanoparticles is claimed. In the mentioned method various electrodes are used, for which time dependence of potential or current density is programmed for nanoparticle size control.

[0009] The method of depositing metal layers, especially of iron, cobalt, nickel, copper and zinc, according to the invention, by electrolytic deposition from the electrolyte being a mixture mainly of acetone, hydrochloric acid, positive ions of metal being deposited, is characterized in that at the initial stage of the process at least one anode is dissolved in an electrolyte containing 90-99% of acetone, 1-10 % of water and 0.5-3% of concentrated hydrochloric acid (36 % solution of HCl in water). The concentration of ions of the metal being deposited in the electrolyte is set automatically when the anode is being dissolved, and then on the surface of cathode the metallic layer is deposited.

[0010] It is advantageous in the method of depositing metal layers, especially of iron, cobalt, nickel, copper and zinc, in order to produce a multi-component layer on the surface of cathode, when two or more anodes of different metals are dissolved.

[0011] Electrolyte used for production of metallic layers, especially iron, cobalt, nickel, copper and zinc, on different metallic substrates, according to the invention containing mainly acetone, hydrochloric acid positive ions of metal being deposited, is characterized in that it contains 90-99% of acetone, 1-10% of water and 0.5-3% of concentrated hydrochloric acid (36% solution of HCl in water).

[0012] The method of depositing metal layers, especially of iron, cobalt, nickel and zinc with the use of electrolyte, according to the invention, has attributes of universal applicability - a range of different metals can be deposited from the electrolyte of the same initial composition and the same current characteristics - what may be of great importance for applications. There is no need to prepare the electrolyte containing a particular cation. With the use of an appropriate anode, proper concentration of deposited metal is created automatically. Concentration of a positive ion in the electrolyte during the stage of deposition of metal is about 0.03 Mol/dm³, as was determined with the methods of optical spectroscopy. It is

a value over one order of magnitude lower than the concentration of ions of metal in typical sulfate electrolytes, used in processes of depositing electrolytic layers. Layers obtained in the process are well adhered to the surface and are shiny. These are two important features for practical application. The thicknesses of obtained layers measured by means of optical and electron microscopy are around 400 nanometers.

[0013] During the preparation of electrolyte, there is no need to provide strictly water-free composition, as some amount of water is an essential component of the electrolyte. Therefore, there is no need to apply expensive methods of disposing traces of water present in organic reagents, which is usually reported to be a necessary condition in the case of nonaqueous electrolytes. Moreover, the preparation of electrolyte in order to start the process is easier as it is unnecessary to add salts of metal to the electrolyte solution. These two features constitute an unquestionable advantage of the method, which makes it attractive for industrial applications.

[0014] In the method of depositing metal layers, according to the invention, the main constituent of the electrolyte (over 90%) is acetone, which is rather neutral for the natural environment. The content of positive ions at the final stage of the process of the deposition of layers, is about ten times lower than the concentration of positive ions in commercial, acid electrolytes. Furthermore, the quantities of positive ion of metal being deposited, are grams per litre, which helps to reduce costs connected with the preparation of the electrolyte.

[0015] Electrolytes based on acetone are of special importance in the case of radiochemistry, in processes of the preparation of radioactive sources. For example, the application of electrolyte based on acetone in a commercial process of Mössbauer sources preparation, in which a metallic layer of cobalt is being deposited, would decrease the concentration of radioactive constituent of ^{57}Co in a solution by one order of magnitude, which would be important for radiation safety.

[0016] The electrolyte containing low concentration of hydrogen ions can easily be diluted by the inactive basic constituent which is acetone. It allows to control the process of taking the electrodes out with thin layers of metals. Therefore, it is possible to remove from the bath layers of thickness under 1 micrometer with ease. Low concentrations of ions enable simple replacement of a deposited ion. Hence, it is possible to obtain multi-layers by use of electrolysis processes based on acetone electrolytes. So it is possible to deposit layers containing more than one component simultaneously.

[0017] The method of depositing metal layers, especially of iron, cobalt, nickel and zinc, according to the invention, is presented on the drawing on which a schematic system with the application of two electrodes (anodes) in order to deposit two-component layer, has been shown.

[0018] Anode 1, 2 is a metal, from which ions of metal are supplied to the electrolyte 4 and then a layer is being

formed on the surface of cathode 5. In the initial stage of the process, ions from anode 1, 2 go to the solution of electrolyte 4. The process is performed at room temperature. During the whole process, the power supply unit 3, 6 allows to keep constant current density ca. 5 mA/cm^2 . After a few or over a dozen minutes, a metallic layer is deposited on the surface of cathode 5.

Examples of implementation of the invention

[0019]

Example 1: A cathode in the form of a circle having a diameter of $\phi=15 \text{ mm}$ made of copper. An anode made of iron. Electrolyte 4.75 ml of acetone, 0.04 ml 36% of hydrochloric acid, 0.22 ml of water. Process performed at room temperature, DC current of $I=9 \text{ mA}$. After ca. 30 min a solid, shiny layers of iron of about 400 nanometers is being deposited.

Example 2: A cathode in the form of a disk of a diameter of $\phi=15 \text{ mm}$ made of iron. An anode made of copper. Electrolyte 4.75 ml of acetone, 0.04 ml 36% of hydrochloric acid, 0.22 ml of water. Process performed at room temperature, DC current of $I=9 \text{ mA}$. After ca. 10 min a solid, shiny layers of copper is being deposited.

Example 3: A cathode in the form of a circle of a diameter of $\phi=15 \text{ mm}$ made of copper. Two anodes, one made of iron, second made of nickel. Electrolyte 4.75 ml of acetone, 0.04 ml 36% of hydrochloric acid, 0.22 ml of water. Process performed at room temperature, DC current on iron anode of $I=5 \text{ mA}$. On nickel anode of $I=3 \text{ mA}$. After ca. 25 min a two-component layer is being deposited, by one anode -layer rich in iron, by another anode - layer rich in nickel.

[0020] The method of depositing layers and multi-layers of 3d metals is of great practical importance for electronics and spintronics. Special importance for electronics and in particular for production lines manufacturing integrated circuits has the deposition of Cu (the so called Damascene process). Layers of 3d ferromagnetic metal alloys obtained by electrochemical methods are used on the industrial scale in production of magnetoresistive sensors. Because of low concentrations of ions in the electrolyte composed mainly of acetone with a small amount of hydrochloric acid and water, this method can be applied for radioactive sources preparation, e.g. sources with ^{57}Co isotope used in Mössbauer spectroscopy.

Claims

1. The method of depositing metal layers, especially of iron, cobalt, nickel and zinc by their electrolytic dep-

osition on the surface of cathode from the electrolyte, being a mixture composed mainly of acetone, hydrochloric acid, positive ions of the metal being deposited supplied from the anode, **characterized in that** at the initial stage of the process at least one anode (1) is being dissolved in the electrolyte (4) containing 90-99 % of acetone, 1-10 % of water and 0.5-3 % of concentrated hydrochloric acid (36 % solution HCl in water), and the concentration of ions of the metal being deposited in the electrolyte (4), is set automatically.

2. The method of depositing metal layers, especially of iron, cobalt, nickel, copper and zinc according to claim 1, **characterized in that** the two anodes of different metals (1,2) are being dissolved, in order to produce on the surface of cathode (5) a multi-component layer.
3. Electrolyte to produce metallic layers, especially of iron, cobalt, nickel, copper and zinc on different metallic substrates, containing mainly acetone, hydrochloric acid, positive ions of the metal being deposited, **characterized in that** it contains 90-99 % of acetone, 1-10 % of water and 0.5-3 % of concentrated hydrochloric acid (36 % solution HCl in water).

30

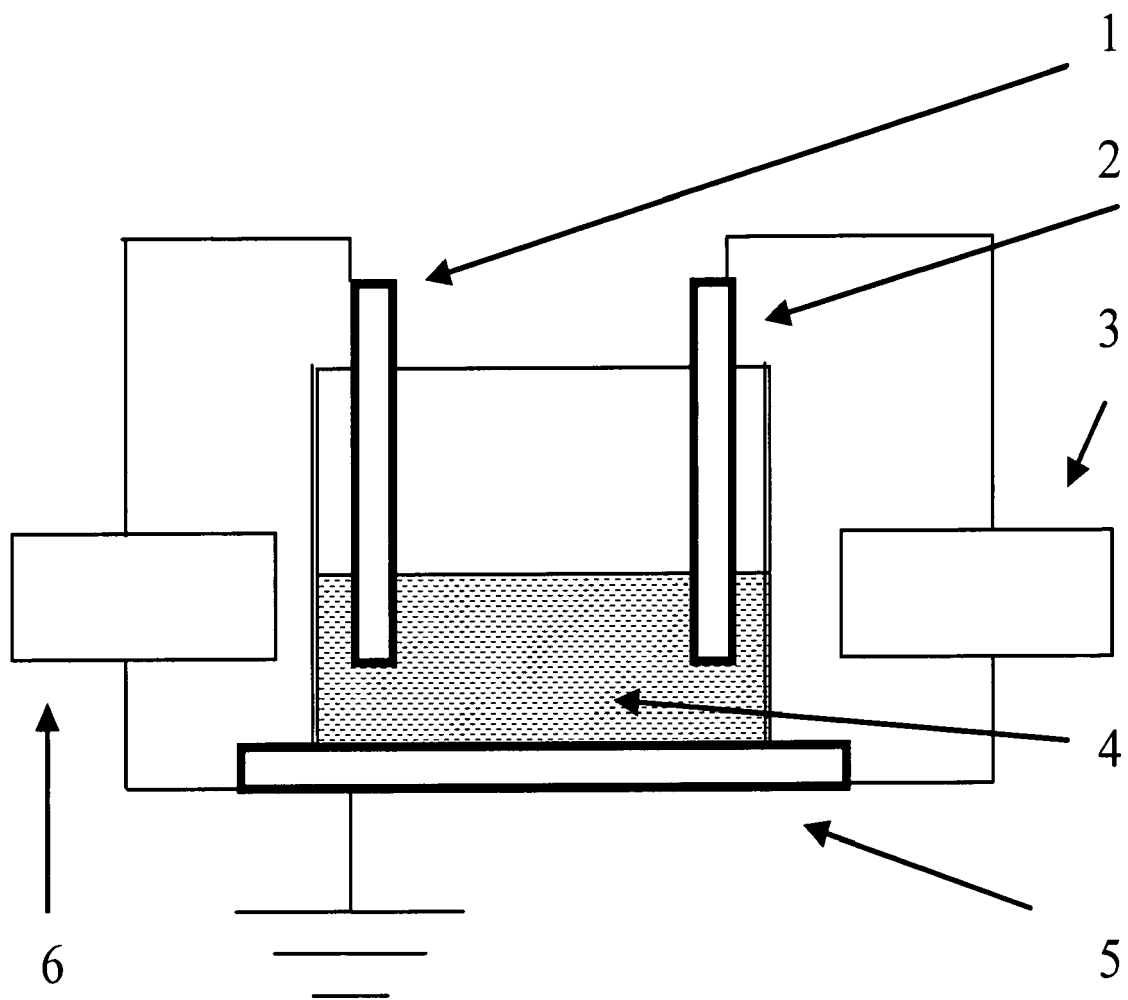
35

40

45

50

55





EUROPEAN SEARCH REPORT

Application Number
EP 08 46 0009

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
D,X	KAMADA K ET AL: "Anodic dissolution of tantalum and niobium in acetone solvent with halogen additives for electrochemical synthesis of Ta2O5 and Nb2O5 thin films" ELECTROCHIMICA ACTA, ELSEVIER SCIENCE PUBLISHERS, BARKING, GB, vol. 49, no. 2, 15 January 2004 (2004-01-15), pages 321-327, XP004474653 ISSN: 0013-4686	1-3	INV. C25D3/02 C25D3/56
Y	* abstract * * page 322, left-hand column, paragraph 3 * * page 322, right-hand column, paragraphs 2,3 * * page 323, left-hand column, paragraph 2 * * page 323, right-hand column, line 8 - page 324, left-hand column, paragraph 1 * * page 324, right-hand column, paragraph 4 * * page 325, left-hand column, lines 8-16 * * page 326, right-hand column, lines 4-13 * ----- SU 420 703 A1 (ROSTOV UNIV) 25 March 1974 (1974-03-25) ----- -& DATABASE WPI Week 197507 Thomson Scientific, London, GB; AN 1975-12105W XP002510210 & SU 420 703 A (ROSTOV UNIV) 30 August 1974 (1974-08-30) * abstract * ----- -/--	1-3	TECHNICAL FIELDS SEARCHED (IPC) C25D
X	SU 420 703 A1 (ROSTOV UNIV) 25 March 1974 (1974-03-25)	1,3	
Y	-& DATABASE WPI Week 197507 Thomson Scientific, London, GB; AN 1975-12105W XP002510210 & SU 420 703 A (ROSTOV UNIV) 30 August 1974 (1974-08-30) * abstract *	2	
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 14 January 2009	Examiner Zech-Agarwal, Nicole
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

 3
EPO FORM 1503 03.82 (P04C01)



EUROPEAN SEARCH REPORT

Application Number
EP 08 46 0009

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
Y	DE 198 40 842 A1 (HENKEL KGAA [DE]) 9 March 2000 (2000-03-09) * abstract * * column 2, line 5 - column 3, line 25 * * column 3, line 62 - column 4, line 20 * -----	1-3	
A	DE 18 11 204 A1 (COMMISSARIAT ENERGIE ATOMIQUE) 21 August 1969 (1969-08-21) * page 3, paragraph 5 - page 4, paragraph 1 * * examples * -----	1,3	
			TECHNICAL FIELDS SEARCHED (IPC)
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 14 January 2009	Examiner Zech-Agarwal, Nicole
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

3
EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 08 46 0009

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

14-01-2009

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
SU 420703	A1	25-03-1974	NONE
SU 420703	A	25-03-1974	NONE
DE 19840842	A1	09-03-2000	AT 237007 T 15-04-2003
		DK 1121477 T3 04-08-2003	
		WO 0014302 A1 16-03-2000	
		EP 1121477 A1 08-08-2001	
		ES 2196852 T3 16-12-2003	
		JP 2002524661 T 06-08-2002	
		PT 1121477 T 29-08-2003	
		US 6676821 B1 13-01-2004	
DE 1811204	A1	21-08-1969	BE 722261 A 14-03-1969
		FR 1557749 A 21-02-1969	
		GB 1192117 A 20-05-1970	
		LU 57372 A1 03-03-1969	
		NL 6816933 A 02-06-1969	

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 4701244 A [0005]
- DE 3411320 [0007]
- WO 2004031449 A [0008]

Non-patent literature cited in the description

- YU.YA. FIALKOV ; A.N. ZHITOMIRSKII ; YU.A. TARASENKO. *Fizicheskaya Khimiya Nevodnykh Rastvorov*, 1973 [0003]
- T.V. TROEPOLSKAYA ; G.A. VAGINA ; I.R. ABDULLIN ; N.V. UTYAGANOV ; S.G. VUL'FSON ; A.N. VERESHCHAGIN ; A. E. ARBUZOV. Electrochemical reduction of rare-earth chelates with certain - diketones. *Journal Russian Chemical Bulletin*, 1990, vol. 39, 2481 [0003]
- GUAN FU-YU ; GAO XIAO-XIA. Voltammetric study on the reduction of rare earths in acetone. *J. Chin. RE Soc.*, 1990, vol. 8, 166 [0003]
- V.N. TITOVA ; V.A. KOZAKOV ; N.V. PETROVA ; S. BIALLOZOR. The influence of solvent on the kinetics of silver electrodeposition. *Journal of Analytical Chemistry*, 1995, vol. 381, 227 [0004]
- K. KAMADA ; M. MUKAI ; Y. MATSUMOTO. Anodic dissolution of tantalum and niobium in acetone solvent with halogen additives for electrochemical synthesis of Ta₂O₅ and Nb₂O₅ thin films. *Electrochimica Acta*, 2004, vol. 49, 321 [0006]