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(54) METHOD FOR CHLORINE PLASMA MODIFICATION OF SILVER ELECTRODES

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(57) **ABSTRACT**

A method for the modification of a surface of a silver electrode wherein the surface is treated with a chlorine plasma is described. Control of the power, flux density and timing provide the manner to modify the silver surface, and so implant the chlorine atoms and ions into the silver. The present invention provides a method to produce thin-film silver electrodes with a very controlled surface. Such electrodes can provide quantitative quality of measurement. The present invention extends to a method for the modification of a surface of any metal wherein the surface is treated with a plasma.

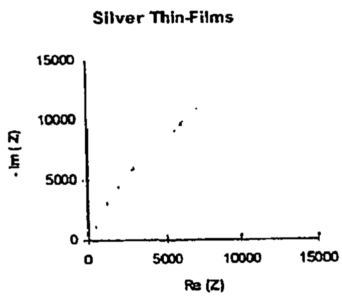

Figure 1a

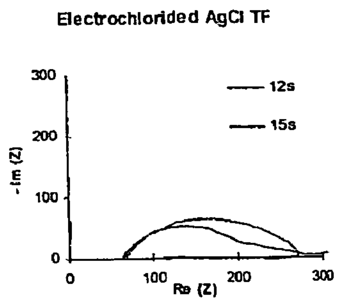

Fig 1b

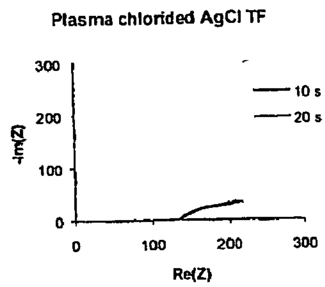

Fig 1c

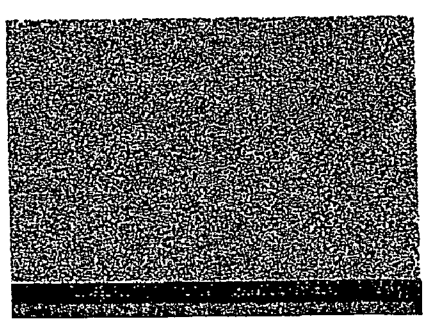

Figure 2 a

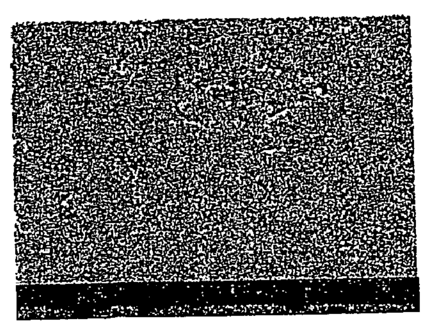

Fig 2b

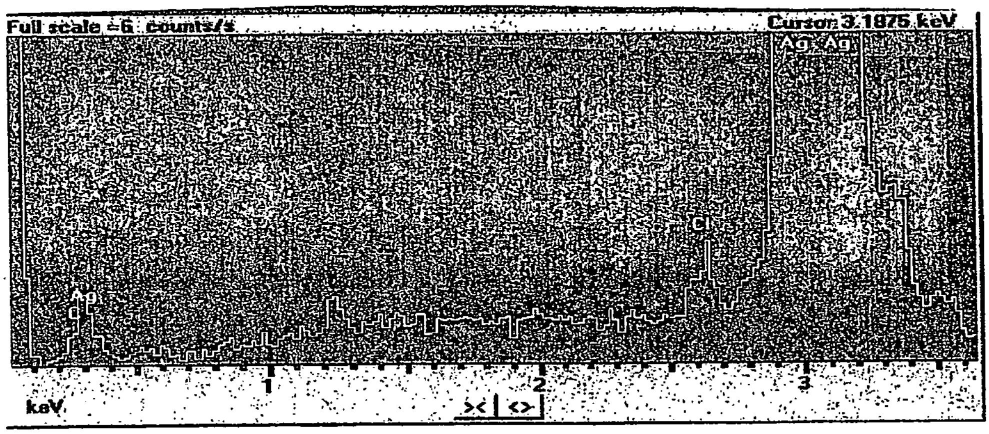

Figure 3

Figure 4

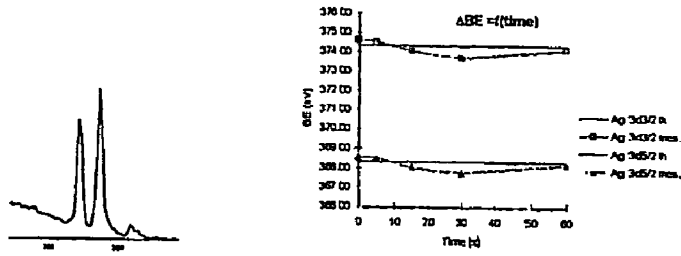

Figure 5

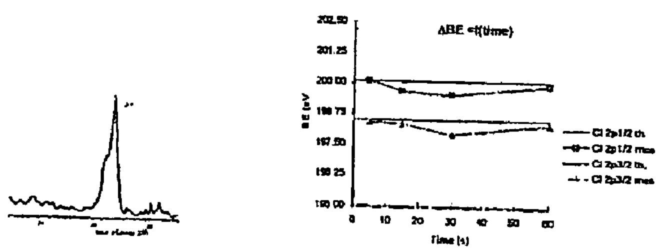

Figure 6

METHOD FOR CHLORINE PLASMA MODIFICATION OF SILVER ELECTRODES

[0001] This invention relates to the modification of metal electrodes and in particular to the chlorine plasma modification of silver electrodes.

[0002] Silver electrodes coated with silver chloride layers (Ag/AgCl electrodes) have for many years formed the basis for medical electrodes due to the excellent charge transfer characteristics and non polarisability of the silver chloride material. The main applications of Ag/AgCl electrodes concern amperometric (current sensitive) and potentiometric (voltage sensitive) sensors. Indeed, Ag/AgCl layers have formed the basis for many electrocardigram (ECG) electrodes and have been incorporated into both sensing devices and reference electrodes.

[0003] One common way of producing Ag/AgCl electrodes is the electrochemical technique whereby chloride ions are deposited on the silver surface reacting therewith to form a silver chloride layer(AgCl). Sintered Ag/AgCl electrodes have been used in the past as well as serigraphic inks. The latter is known as "thick film" technology and combines a mixture of silver and silver chloride particles trapped in a polymer. A common alternative to these methods is chemical chloriding, which is a technique applied in both thin and thick film technology.

[0004] The thicker the film of silver chloride (AgCl) formed on the silver electrode the less sensitive the electrode becomes. As such, thin film technology is becoming an essential key of sensing and bio-sensing, due to the concept of miniaturisation. Increasingly microscopic scale devices allow for more accurate readings. Therefore, Ag/AgCl electrodes have been designed and adapted to thin-film technology in order to be used as micro-sensors.

[0005] However, the present thin film methods of producing Ag/AgCl electrodes in general have been found not to be satisfactory. The technique of chemical chloriding thin films is a delicate task which is difficult to control and often results in the formation of a silver chloride film which is too thick and does not have uniform properties throughout. The thicker the silver chloride layer the higher the electrical impedance of the electrode which reduces the sensitivity. Also, chemical chloriding simply involves the surface absorption of chlorine on the silver electrode and as such does not always provide an AgCl film with a strong adhesion to the surface of the silver electrode.

[0006] Depositing chloride ions on the silver electrode using electroplating is also a difficult process to control and the resulting Ag/Cl layer is often be too thick and lacking in uniformity. It has also been shown that this technique does not provide good adhesion of the AgCl layer to the silver electrode and also induces surface cracking, both of which reduce the effectiveness of the electrode.

[0007] The present invention is directed to overcoming these problems and provides a method which can more closely control the formation and thickness of the silver chloride layer. The method also provides a silver chloride layer which is more uniform and stable in structure, thereby providing a more sensitive, stable and accurate reading.

[0008] According to a first aspect of the present invention there is provided a method for the modification of a surface of a silver electrode wherein the surface is treated with a chlorine plasma.

[0009] Control of the power, flux density and timing provide the manner to modify the silver surface, and so implant the chlorine atoms and ions into the silver. Different control parameters provide different silver surfaces, e.g. thicker or thinner, as desired or necessary.

[0010] Preferably, the silver electrode is in the form of a silver thin-film. More preferably, the silver electrode is fabricated by the evaporation of silver onto a glass plate to form a silver thin-film. The glass plate is preferably cleaned and coated with a thin metallic sub-layer prior to the addition of silver. Preferably, the sub-layer is a chromium or nichrome sub-layer and is coated on the glass plate using a sputtering system.

[0011] Typically, the sputtering system can be a Nordiko NM200/RFG1250 sputtering system using an inert plasma and a chromium target. Preferably, the inert plasma is argon plasma.

[0012] The modification of the surface of the silver electrode can take place in a plasma chamber. A surface of the silver electrode is bombarded with the chlorine plasma. Preferably, the modification of the silver electrode takes place in a reaction ion etching (RIE) radio-frequency (RF) plasma chamber. Preferably, the chamber is pumped down prior to the modification of the silver electrode.

[0013] According to another aspect of the present invention there is provided a method for the modification of a surface of a metal wherein the surface is treated with a plasma.

[0014] Preferably, the plasma is in the form of a stream and is formed from a reactive gas. More preferably, the reactive gas is a halogen such as chlorine gas.

[0015] The modification of the metal surface can take place in a plasma chamber. A surface of the metal is bombarded with the plasma stream. Preferably, the modification of the metal takes place in a reaction ion etching (RIE) radio-frequency (RF) plasma chamber. Preferably, the chamber is pumped down prior to the modification of the metal.

[0016] The method is suitable, for example, for the treatment of metal electrodes and in particular for the treatment of silver electrodes in the form of a thin-film, possibly fabricated by the evaporation of the metal onto a glass plate.

[0017] The invention extends to any metal item, e.g. an electrode, having a surface modified as herein described.

[0018] The invention will be more clearly understood by way of description thereof with reference to the accompanying drawings in which:

[0019] **FIG. 1**(*a*) is a graph of the impedance spectrum of silver thin-film before treatment according to the present invention;

[0020] **FIG. 1**(*b*) is a graph of the impedence spectra of silver thin-film after electrochloriding in a 0.5M KCl solution; **FIG. 1**(*c*) is a graph of the impedence spectra of silver thin-film after treatment according to the present invention;

[0021] **FIG. 2**(*a*) is a SEM view of the surface of silver thin-film after electrochloriding (x 2.5k);

[0022] **FIG. 2**(*b*) is a SEM view of the surface of silver thin-film after treatment according to the present invention (x 15k);

[0023] **FIG. 3** is a graph of EDX measurements realised on silver thin-film showing spectra of Ag (white) and AgCl (red);

[0024] **FIG. 4** is a graph of XPS spectra of silver thin-film modified according to the present invention;

[0025] **FIG. 5** are graphs showing Ag 3d5/2 and Ag 3d5/2 binding energy shifts; and

[0026] **FIG. 6** are graphs showing Cl 2p3/2 and Cl 2p3/2 binding energy shifts.

[0027] To aid in the understanding and advantages of the present invention, experimental testing was undertaken on a silver electrode modified according to the present invention (2) and compared to identical testing on a non-coated silver electrode, and on a silver electrode with chloride ions deposited thereon using the technique of electroplating (1).

[0028] For the purposes of this experiment, all the silver electrodes used were fabricated by evaporating silver in a form 99.99% pure(for example, 99.99% purity, Goodfellow, Cambridge U.K. type silver)to form a silver thin-film on top of a BDH plain microscope glass slide. Evaporation was carried out using an electron-beam chamber (Leybold L560E$^-$ Beam), at an evaporation rate of 100 Å/s^9, under high vacuum (2.10^{-5} mbar). Prior to the evaporation stage, the glass sides were cleaned and then introduced into a Nordiko NM200/RFG1250 sputtering system, using an argon plasma and a chromium target. A sub-layer of chromium was deposited on the glass slide and this improved the adhesion of the silver thin-film to the glass slide when deposited thereon. The silver electrodes thus formed (electrode samples) were then further treated as follows:

[0029] (1) Electrochemical Chloriding—Electroplating

[0030] A portion of the electrode samples were encapsulated in an electrochemical cell, allowing an active electrode surface of 0.96 cm^2. The electrodes were dipped into a 0.5M potassium chloride (KCl) solution. An anodic current of 0.98 mAmps was applied for several time durations (5s, 7s, 10s, 15s, 20s and 25s). The chloride ions in the KC1 solution migrated to the positive silver electrode and were deposited thereon. The chloride ions reacted with the silver and formed a layer of silver chloride (AgCl). The electrochemical chloriding was performed using AutoLab™ instrumentation, for example a General Purpose Electrochemical System (GPES) and Frequency Response Analyser (FRA).

[0031] (2) Plasma Modification

[0032] Another portion of the electrode samples were modified according to the present invention with a chlorine plasma stream. The plasma stream used was a pure chlorine plasma stream, in a Reaction Ion Etching (RIE) radio-frequency (RF) plasma chamber. Typical operating parameters for the plasma chamber are given below in Table 1.

TABLE 1

1 to 100 mTorr:
5 to 500 Watts (per cm^2):
1 to 50 sccms (standard cm^3) of chlorine:
1 ms to 5 seconds plasma time

[0033] Operating Parameters for preparing, for example, a low impedance electrode for a suitable system, are:

[0034] 10-20 mTorr

[0035] ~170 Watts 5-10 sccms

[0036] 1 second plasma time

[0037] Experimental Testing

[0038] The above treated electrode samples (electrochemical electrode and, plasma electrode) and the standard non-treated electrodes were then subjected to the following tests:

[0039] Electrochemical tests;

[0040] X-Ray Photoelectron Spectroscopy

[0041] (XPS) investigations;

[0042] Energy Dispersive X-Ray Spectroscopy (EDX) analysis; and

[0043] Scanning Electron Microscopy (SEM) analysis.

[0044] All the electrochemical tests and measurements were carried out with an AutoLab apparatus (GPES and FRA). A 5 mV AC voltage was applied using a range of frequency from 10,000 Hz to 0.1 Hz for all these tests and measurements were carried out in a phosphate buffer solution (PBS), to which 0.9% NaCl was added.

[0045] XPS investigations were carried out on a KRATOS XSAM 800 apparatus. The X-ray source was run with MgKα X-rays at 240W (13.8 kV, 18 mA).

[0046] SEM pictures were taken from a SEM/EDX system, an Hitachi S3200N microscope interfaced with an Oxford Instrument Link ISIS EDX spectrometer.

[0047] As a standard, the non-treated electrode samples were first characterised by electrochemistry and SEM. The silver thin-films (Ag TF) deposited by evaporation technique have a very smooth surface and react poorly with the electrolyte (large impedance), as shown in **FIG. 1**(*a*).

[0048] After electrochemical chloriding of the electrode samples, SEM analysis shows large granules at the surface of the silver layer, giving a very rough surface topography. Islands of silver chloride have grown, generating a non-uniform surface as shown in **FIG. 2**(*a*) at which the electrolyte can react easily. Once the Ag/AgCl reduction/oxidation couple is formed, a nearly non-polarisable electrode is obtained. The presence of AgCl layer which acts as a bridge between the electrode and the electrolyte and the roughening of the electrode surface are directly linked to the overall electrode impedance. As shown in FIG **1**(*b*) a reduced impedence of a factor of 100 is realised for the sample electrodes treated in this manner (electrochemical electrode). The impedence of the electrochemical electrode was tested at intervals of 12 and 15 seconds and show that the impedence of this electrode increases with time which is an indication that the AgCl layer is not stable.

[0049] For the electrode samples treated according to the present invention (plasma electrodes) with a chlorine plasma stream, a similar reduction in impedence is also observed. This treatment apparently created a singular physical reaction between the silver layer and the chlorine atoms, molecules and ions present within the plasma. The impedance is also lower than that of the sample electrodes by a factor of 100 as shown in **FIG. 1**(*c*), and this can be achieved only if a "bridge" behaving compound, able of exchanging charges with the electrolyte, is created.

[0050] SEM analysis of the plasma electrode show pictures of a "cauliflower" like structure similar to that of the electrochemical electrode. However, in the case of a plasma electrode the layer formed thereon is thinner, more uniform and more controllable. The layer so-formed includes what appears to be a combination of an AgCl film, a chloride form of chlorine (Cl) and individual chlorine atoms which are embedded in the surface of the silver.

[0051] The similarity in behaviour and structure obtained after the two treatments (1) and (2)above possibly suggest that a similar AgCl film was created in each case. However, EDX measurements of the plasma electrode, shown in **FIG. 3**, show the presence of remaining chlorine atoms in the surface of the silver electrode, which supports the feasibility of creating an AgCl film using this treatment.

[0052] XPS measurements were carried out on several sample electrodes treated with plasma streams other than chlorine plasma in order to determine the chemical nature and physical structure of the AgCl thin film formed from the second treatment process. The plasmas used were from similar reactive gases such as fluorine (Fl) as AgCl can be approximated to behave as any other form of silver halide; their electronic structure being very similar. The XPS results show energy peaks related to the Ag 3d and the Cl 2p electronic orbits as shown in **FIG. 4**.

[0053] The shifts in energy are related to changes within these electronic orbits. First of all, as shown by EDX measurements chlorine peaks on spectra show that the surface modification compound remains at the surface of the electrode sample after plasma treatment. Then, both chlorine and silver peaks are shifted towards lower energies. **FIGS. 5 and 6** compare the value of these peaks to pure silver and chlorine theoretical peaks, as referred in literature [ref. *Web+XPS Handbook*]. Silver halides (AgI and AgF) Ag $3d_{5/2}$ peaks show a ±0.27eV shift compared to pure silver. The silver peak of the plasma treated sample electrode is shifted by about ±0.4 for the same Ag $3d_{5/2}$ peak. The energy shift spread is similar to the other silver halides tested. AgCl can be expected to behave in a similar manner to other forms of silver halide as the electronic structure of each are very similar. Nevertheless, the exact values can not be deducted using the energy peak values of the other silver halides, but does provide a close enough idea of the expected energy shift range. Furthermore, quantification of the different elements existing at the surface of the silver thin-film, showed that silver and chlorine are the main species (respectively 75% to 80% and 12% to 17%), and only very few contaminants are present (i.e. carbon and oxygen). Thus, only few oxide forms of silver must be created, leaving the shift in the peaks under the influence of the chlorine ions.

[0054] Chlorine was also detected in a chloride form, as the Cl $2p_{3/2}$ peaks are within the same region of binding energy as the alkali chloride, as shown in **FIG. 5**, with an energy shift of about −0.25eV. Even if this chloride shift is compared to a non-metal chloride form, one can still assume that the structure of AgCl and NaCl are close enough to give a very similar electronic distribution of the molecular orbits (M.O.), and hence an analogous shift value.

[0055] Discussion

[0056] These results support the idea that the chlorine ions within the plasma, react chemically with the silver surface and create a halide silver/alkali chloride structure type.

[0057] The texture and macro-appearance of the plasma electrodes are not similar to the electrochemical electrodes and this is clearly shown by comparison of **FIG. 2**(*a*) and **FIG. 2**(*b*). The plasma electrodes gave a matt yellowish colour, as described for abnormally electrochlorided electrodes in Crenner et al. When increasing the chloriding time for a given input power and chlorine flux, the colour of the sample electrodes turn from a white/yellowish shade to a brown/plum tint. It has been reported (Yalcinkaya and Power (1997), Janz and Ives (1968)and Beck and Rice (1984)) that the latter tint is characteristic of a further reduction of AgCl to free interstitial Ag, and that "the white allotropic form of AgCl does not correspond to the standard state for crystalline silver chloride". Actually, Neuman Michael (1995) 2^{nd} edition reported that "pure silver chloride is amber coloured and becomes dark grey because of fine particles of silver". These rough optical observations are consistent with the fact that none or poor crystalline AgCl would be expected to grow at the surface of the thin film, producing a matt yellowish colour. Further exposure to the chlorine plasma, which is highly reactive, could be susceptible to induce silver sputtering or etching (as it can be observed on the SEM pictures). Therefore, it is possible that an increasing number of silver particles could be trapped within the created silver chloride, leading to a darker colour specific to the interstitial silver.

[0058] The present invention provides a method for providing silver modification by chlorine, to produce thin-film silver electrodes with a very controlled surface. Such electrodes can provide quantitative quality of measurement.

1. A method for the modification of a surface of a silver electrode wherein the surface is treated with a chlorine plasma.

2. A method as claimed in claim 1 wherein the silver electrode is in the form of a silver thin-film.

3. A method as claimed in claim 2 wherein the electrode is fabricated by an evaporation of silver onto a glass plate.

4. A method as claimed in claim 3 wherein the glass plate is coated with a thin metallic sub-layer prior to the addition of silver.

5. A method as claimed in claim 4 wherein the sub-layer is a chromium or nichrome.

6. A method as claimed in claim 5 wherein the sub-layer is coated on the glass plate using a sputtering system.

7. A method for the modification of a surface of a metal wherein the surface is treated with a plasma.

8. A method as claimed in claim 7 wherein the plasma is formed from a reactive gas.

9. A method as claimed in any one of the preceding claims wherein the method is carried out in a plasma chamber.

10. A method as claimed in claim 9 wherein the plasma chamber is a reaction ion etching radio-frequency plasma chamber.

11. A method as claimed in claim 9 or claim 10 wherein the plasma chamber is pumped down prior to modification of the silver electrode or metal surface.

12. A method as claimed in claim 11 wherein the operating pressure in the plasma chamber is within the range 1 to 100 mTorr.

13. A method as claimed in any one of the preceding claims wherein the operating power is in the range of 5 to 500 Watts (per cm^2).

14. A method as claimed in any one of the preceding Claims wherein the operating flux density method is within the range 1 to 50 sccms of gas.

15. A method as claimed in claim 14 wherein the gas is chlorine.

16. A method as claimed in any one of the preceding Claims wherein the operating time is within the range 1 ms to 5 seconds plasma time.

17. A silver electrode whenever obtainable by a method as claimed in any one of claims 1 to 16.

18. A modified metal surface whenever obtainable by a method as claimed in any one of claims 7 to 16.

19. A silver electrode having a silver chloride surface layer provided by plasma modification.

20. A metal surface having a plasma modified surface.

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