

Method for implanting single or multiply charged ions into a surface of a
treated object and device for implementation of the method

Field of the invention

5 The present invention concerns a surface treatment method for an
object, especially but not exclusively made of synthetic sapphire, by means
of a single or multiply charged ion beam. This method aims to reduce
undesirable reflections from the surface of an object, for example made of
synthetic sapphire, and to improve long-term the light transmission of such
10 a material in the visible wavelength spectrum. The method according to the
invention is particularly intended to be applied to the anti-reflective surface
treatment of a synthetic sapphire watch crystal in order to improve its light
transmission characteristics. In these conditions, the surface of the watch
crystal has good anti-reflective properties in the visible light range. More
15 generally, the present invention applies to any type of electrically
conductive, semi-conductor or electrically insulating material, for the
purpose of improving the surface mechanical features, in particular
resistance to scratches, of objects made using such materials by means of
the ion implantation method according to the invention.

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Background of the invention

Sapphires or corundums are formed of aluminium oxide crystals
(Al_2O_3) whose colour is determined by the presence of trace impurities
(oxides) in these materials. It is thus known that the presence of titanium
25 and iron gives a sapphire a blue colour, the presence of vanadium a violet
colour and the presence of chromium a pink colour. Finally, the presence of
iron in a sapphire gives the latter a yellow or green appearance.

This colouration can be explained by the fact that the impurities cause the appearance of energy levels in the forbidden gap of corundum, which modify the transmission and absorption spectra of the material and therefore its colour.

- 5 Sapphire can be heat treated; stones that are too light or too dark or have too many inclusions are heated. This heat process enhances the colour and improves the brilliance of the stones by dissolving the trace impurities present in the stone.

10 The laboratory manufacture of synthetic sapphires and rubies has been known since the beginning of the 19th century. The chemical composition and physical properties of these synthetic stones are the same as those of natural stones. Synthetic stones can, however, be distinguished from natural stones by their generally curved crystallisation lines, at least as regards the oldest manufactured synthetic stones.

- 15 Because of its high scratch-resistance, synthetic sapphire is used, in particular, for making watch crystals or lenses in optical cameras, especially in smart phones. Nowadays, the production of synthetic sapphires is carried out on an industrial scale.

20 It is well known that a synthetic sapphire surface reflects around 15% of incident light, which hinders the reading of information displayed by a watch dial, a flat computer or mobile telephone screen.

 The light reflectivity value of a synthetic sapphire surface is obtained using Fresnel's equations which, for a light ray passing through a dioptré at an angle of incidence of 90° , give the following reflection (R) and
25 transmission (T) coefficients:

$$R = ((n_2 - n_1) / (n_2 + n_1))^2$$

$$T = 4n_1 n_2 / (n_2 + n_1)^2$$

where n_1 and n_2 are the reflection indices of the mediums separated by the dioptre.

Taking account of the principle of energy conservation, one obtains
5 $R+T = 1$.

For air ($n_1 = 1$) and synthetic sapphire ($n_2 = 1.76$), one obtains, with the above formulae: $R = 0.0758$, $T = 1-R = 0.9242$. In other words, 7.6% of the visible light that falls perpendicularly on a synthetic sapphire surface is reflected, and 92.4% of this light is transmitted.

10 For a strip of synthetic sapphire formed of an entry face and an exit face which extend parallel to and remote from each other, the optical losses are two times higher and are thus around 15%. This high reflection of ambient light makes it difficult to read the information displayed, for example, by a watch dial (hands, date indication, decorations) located
15 under the synthetic sapphire watch crystal.

There are anti-reflective methods consisting in depositing metal oxides which are relatively complex and expensive to implement. For example, for watch crystals, one of the methods used consists of the vacuum deposition (10^{-5} torr) of metal oxide thin films. In dust-free
20 enclosures of the white room type, the watch crystals are first cleaned in cleaning lines and then ultrasonic dried. These watch crystals are then mounted on supports which are inserted into vacuum chamber Bell jars. The vacuum inside these vacuum chamber Bell jars allows the evaporation by sublimation of a metal oxide at a lower temperature than under
25 atmospheric pressure. Evaporation can be achieved by Joule heating the metal oxide or by bombarding the oxide using an electron gun. The quality of the vacuum, the speed of evaporation and the thickness of the deposited films must be perfectly controlled. These thicknesses must of course be uniform.

There are other, less expensive, types of vapour phase depositions (also known as physical vapour deposition or PVD) which consist in depositing magnesium fluoride MgF_2 (optical refractive index 1.38) or cryolite Na_3AlF_6 (optical refractive index 1.35). The refractive indices of these materials are close to one another, but their scratch-resistance properties are inferior to those of synthetic sapphire. PVD depositions made on synthetic sapphire to improve its anti-reflective properties can be scratched, or peel off, thereby completely removing any advantage that could be obtained for synthetic sapphire.

'Synthetic sapphire' means a material transparent to visible light. Synthetic sapphire is formed of aluminium oxide (Al_2O_3). In physical terms, synthetic sapphire is a very hard crystalline material (hardness equal to 9 on the Mohs scale) belonging to the corundum family and which has a very high refractive index equal to 1.76.

More generally, the present invention concerns any type of material such as, but not limited to, synthetic sapphire, polycarbonate, mineral glass or ceramics. The treated materials may be electrically conductive, or semiconductors, or electrically insulating.

Other known surface treatment techniques consist of implanting ions in the surface of a treated object.

These ion implantation methods consist of the surface bombardment of the treated object, for example by means of a source of single or multiply charged ions of the electronic cyclotron resonance type. This type of device is also known as an ECR ion source.

An ECR ion source makes use of electron cyclotron resonance to create a plasma. Microwaves are injected into a volume of low pressure gas intended to be ionised, at a frequency corresponding to the electronic cyclotron resonance defined by a magnetic field applied to an area located inside the volume of gas to be ionised. The microwaves heat the free

electrons present in the volume of gas to be ionised. By thermal agitation, these free electrons will collide with the atoms or molecules and cause their ionisation. The ions produced correspond to the type of gas used. This gas may be pure or compound. It may also be a vapour obtained from a solid or
5 liquid material. The ECR ion source is capable of producing single charged ions, i.e. ions whose degree of ionisation is equal to 1, or multiply charged ions, i.e. ions whose degree of ionisation is higher than 1.

Within the scope of the present Patent Application, we are concerned with a single or multiply charged ion source of the ECR type.
10 Very briefly, and as illustrated in Figure 1 annexed to the present Patent Application, an ECR ion source, designated as a whole by the general reference numeral 1, includes an injection stage 2 into which is introduced a volume 4 of gas to be ionised and a hyperfrequency wave 6, a magnetic confinement stage 8 in which a plasma 10 is created, and an extraction
15 stage 11, which allows the ions from plasma 10 to be extracted and accelerated by means of an anode 11a and a cathode 11b between which a high voltage is applied.

The aspect of ion beam 12 produced at the exit of multiply charged ECR ion source 1 is illustrated in Figure 2 annexed to the present Patent
20 Application. It is noted that this ion beam 12 tends to diverge at the exit of ECR ion source 1, which can be explained by the fact that the ions, which all have the same electrical sign, tend to repel each other. Since ion beam 12 tends to diverge at the exit of ECR ion source 1, this causes problems of inhomogeneity of ion distribution at the surface of the treated object.

25 Another problem linked to surface ion implantation of a treated object concerns the gradual appearance of electrostatic potential at the surface of the treated object as the single or multiply charged ions are deposited. Indeed, the higher the number of ions implanted in the surface of the treated object, the higher the electrostatic field, and the more the surface of
30 the treated object tends to repel the ions arriving from the ECR ion source,

which also causes problems of inhomogeneity in the method for ion implantation of the treated object. In the case where the treated object is electrically conductive, this problem is less present insofar as at least some of the free or weakly bound electrons of the material from which the treated
5 object is made can recombine with the implanted ions. However, in the case where the treated object is made of a non-electrically conductive material, the phenomenon of recombination between electrons and single or multiply charged ions does not occur, and it is difficult to guarantee homogeneous ion distribution at the surface of the treated object.

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Summary of the invention

It is an object of the present invention to overcome the aforementioned problems, in addition to others, by providing a method for implanting ions into the surface of a treated object that can ensure, in
15 particular, the homogeneous distribution of said ions in the surface of the object.

To this end, the present invention concerns a method for implanting single or multiply charged ions into a surface of a treated object, this method including the step that consists in directing towards the surface of
20 the treated object, an ion beam produced by a source of single or multiply charged ions of the ECR type, the method also including the step that consists in producing at least one primary electron beam and in directing this primary electron beam so that it passes through the multiply charged ion beam.

25 According to a complementary feature, the method of the invention also includes a step that consists in producing a secondary electron beam by reflecting the primary electron beam onto a target once the primary electrons have pass through the ion beam, the target being oriented such

that the secondary electron beam falls onto the surface of the treated object.

According to another feature of the invention, the treated object is made of a non-electrically conductive material. The material from which the
5 treated object is made is chosen from the group formed by natural and synthetic sapphires, mineral glasses, polymers and ceramics.

According to another feature of the invention, the treated object is made of an electrically conductive material. It particularly concerns crystalline or amorphous metal alloys and precious and non-precious
10 metals.

According to yet another feature of the invention, the material from which the treated object is made is chosen from the group formed by natural and synthetic sapphires, mineral glasses, polymers, crystalline or amorphous metallic alloys, ceramics and precious and non-precious metals.

15 According to yet another feature of the invention, the atoms that can be implanted in the surface of the treated object by means of the single or multiply charged ECR ion source are chosen from the group formed by nitrogen N, carbon C, oxygen O, argon Ar, helium He and neon Ne.

According to yet another feature of the invention, the nitrogen atoms
20 are obtained by ionisation of a dinitrogen precursor gas, the carbon atoms are obtained by ionisation of a methane precursor gas, and the oxygen atoms are obtained by ionisation of a dioxygen precursor gas.

According to yet another feature of the invention, the surface temperature of the treated object is measured remotely and in real time. A
25 temperature sensor well suited for measuring the surface temperature of a sapphire object is that sold by the French company LumaSense Technologies under the reference IN 5/9 Plus.

According to yet another feature of the invention, the electrical potential of the surface of the treated object, or the electrical potential of a table that supports the treated object, is measured in real time.

As a result of the present invention, it is thus possible, in particular,
5 to control the charge of the multiply charged ions before they impinge on the surface of the treated object.

It is clear that by directing at least one primary electron beam towards the beam of positively charged ions (or cations), at least some of the electrons will recombine with the cations in the beam. This
10 recombination will cause a reduction, or cancellation of the electrical charge of the cations, such that, very often, it is the neutral particles, carried by their kinetic energy, which will impinge on the surface of the treated object.

Reducing or cancelling out the electrical charge of the single or multiply charged ions of the beam has two very positive consequences: on
15 the one hand, the ions are less likely to repel each other electrostatically, so that the ion beam diverges less; on the other hand, the electrical potential of the surface of the treated object and/or the electrical potential of the table on which the treated object is placed, is lower, so that the surface of the treated object and the table are less likely to repel the ions arriving from the
20 ECR source. It is therefore possible to more precisely control the kinetic energy of the atoms (whether electrically charged or not) that impinge on the surface of the treated object, and thus to more precisely control the quality of the coating formed on the surface of the treated object.

Control of the quality and homogeneity of the surface coating of the
25 treated object is further improved by the use of a beam of secondary electrons obtained after the primary beam electrons have rebounded onto a target, whose orientation is chosen such that the secondary electrons impinge on the surface of the treated object. On falling onto the surface of the treated object, these secondary electrons recombine with the multiply
30 charged ions implanted in the surface, reducing or cancelling out the

electrostatic charge of said ions, which also contributes to a reduction in the electrostatic potential of the surface of the treated object and of the table that supports it, and thus to a reduction in the phenomenon of multiply charged ions being repelled by said surface.

5 Finally, controlling the electrical potential of the surface of the treated object and/or the temperature of said object further improves the precision of control of the kinetic energy of the atoms (whether ionised or not) impinging on the surface of the treated object.

10	<u>Brief description of the drawings</u>
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Other features and advantages of the present invention will appear more clearly in the following detailed description of an example implementation of the method according to the invention, this example being given simply by way of non-limiting illustration in conjunction with the
15 annexed drawing, in which:

- Figure 1, cited above, is a schematic view of a single or multiply charged ECR ion source according to the prior art.

- Figure 2 is a schematic view which illustrates an ion beam at the exit of the single or multiply charged ECR ion source illustrated in Figure 1.

20 - Figure 3 is a schematic view of a device for implanting single or multiply charged ions into the surface of a treated object according to the invention.

- Figure 4 is a schematic view which illustrates an ion beam at the exit of the single or multiply charged ion source device according to the invention illustrated in Figure 3.

Detailed description of one embodiment of the invention

The present invention proceeds from the general inventive idea which consists in cancelling out all or part of the electrostatic charge of ions produced by a source of single or multiply charged ions of the ECR type before said ions impinge on the surface of the treated object. By reducing
5 the electrostatic charge of said ions, the latter repel each other less, so that the beam that they form diverges less. Likewise, the atoms (whether neutral or ionised) that impinge on the surface of the treated object are repelled less by the ions already implanted in said surface, so that a more homogeneous surface coating is obtained for the treated object. To achieve
10 this result, the present invention teaches directing an electron beam towards the ion beam. On passing through the ion beam, the electrons recombine with said ions and reduce or cancel out the electrostatic charge of the latter. To reinforce this effect, the present invention proposes placing a target on the path of the electrons once the latter have passed through
15 the ion beam, so that the electrons are redirected towards the surface of the treated object and also contribute to the reduction or cancellation of the electrostatic charges of the ions already implanted in the surface of the treated object. It is an object of the present invention to treat the surface of objects by implanting ions and cancelling out charges in order to improve
20 physical properties, especially mechanical properties (increased surface hardness of objects) and optical properties (reduced surface reflection of the objects made of transparent material).

Figure 3 is a schematic view of a device for implantation of single or multiply charged ions into the surface of a treated object according to the
25 invention. Designated as a whole by the general reference numeral 14, this ion implantation device includes an ECR ion source 1 of the same type as that illustrated in Figure 1.

According to the invention, there is associated with this ECR ion source 1 an electron gun designated as a whole by the general reference
30 numeral 16. As is known, an electron gun is a device for producing an

electron beam by extracting electrons from a conductive material to a vacuum in which they are accelerated by an electrical field.

In the case that concerns us, a cold field emission electron gun is preferably used. To this end, electron gun 16 includes an anode 18, for example made of graphite, in which is arranged an orifice 20, and a metal cathode 22 in the form of a very fine tip 24. A high electrical voltage is applied by means of an electric generator 26 between anode 18 and metal cathode 22. Under the effect of this high voltage, a very intense electrical field is produced by point effect at the end of metal cathode 22. This intense electrical field allows electrons to be extracted by tunnel effect from tip 24 of metal cathode 22 and to be accelerated to create an electron beam 28 which propagates as it passes through orifice 20 arranged in anode 18. For reasons that will appear below, the electrons emitted by electron gun 16 will be called primary electrons.

According to a variant, the extraction of electrons from tip 24 of metal cathode 22 can be heat assisted.

According to the invention, the electron beam 28 produced by electron gun 16 is oriented so that it passes through ion beam 12. On passing through ion beam 12, some of the primary electrons recombine with the ions, which causes a reduction, or cancellation of the electrical charge of said ions, so that, very often, it is neutral atoms (or at least atoms with a lower electrostatic charge) which, carried by their kinetic energy, will impinge on the surface of a treated object 30.

According to a complementary feature of the invention, there is arranged on the path of primary electron beam 28 a target 32, onto which fall the primary electrons that have not recombined with the ions after passing through ion beam 12. Target 32 is oriented such that a secondary electron beam 34, produced by the collision between the electrons of primary electron beam 28 and target 32, impinges on the surface of treated object 30 and a table 36 on which treated object 30 is placed. In this case

too, the electrons of secondary electron beam 34 cancel out or reduce the electrostatic charge of the ions implanted into the surface of the treated object.

According to yet another feature of the invention, the surface
5 temperature of treated object 30 is measured remotely and in real time by means of a temperature sensor 38. A temperature sensor well suited for measuring the surface temperature of a sapphire object is that sold by the French company LumaSense Technologies under the reference IN 5/9 Plus.

10 According to yet another feature of the invention, the electrical potential of the surface of treated object 30, or the electrical potential of a table that supports treated object 30, is measured in real time by means of an electric voltage measuring instrument 40.

The invention also concerns a device for implantation of single or
15 multiply charged ions into a surface of a treated object, this device comprising an ECR ion source 1, and an electron gun 16, ECR ion source 1 producing an ion beam 12 and the electron gun producing a primary electron beam 28, ECR ion source 1 and electron gun 16 being arranged such that primary electron beam 28 intercepts ion beam 12.

20 The single or multiply charged ion implantation device also includes a target 32 placed on the path of primary electron beam 28 once the latter has passed through ion beam 12. Target 32 is oriented such that a secondary electron beam 34, produced by the collision between the electrons of primary electron beam 28 and target 32, impinges on the
25 surface of treated object 30 and a table 36 on which treated object 30 is placed.

The single or multiply charged ion implantation device also includes a temperature sensor 38 for measuring remotely and in real time the surface temperature of treated object 30.

The implantation device of single or multiply charged ions also includes an instrument 40 for measuring the electrical potential of the surface of treated object 30 and/or of table 36 that supports treated object 30.

5 The aspect of ion beam 12 produced at the exit of ECR ion source 1 after interception by primary electron beam 28 is illustrated in Figure 4 annexed to the present Patent Application. It is noted that this ion beam 12 diverges very little, if at all, on exiting ECR ion source 1, which can be explained by the fact that the electrical charge of a large number of ions
10 (marked "+") is cancelled out or reduced by the recombination of electrons (marked "-") of primary electron beam 28 with ions of ion beam 12. Since the divergence of primary electron beam 28 is at least greatly reduced, the homogeneity of distribution of multiply charged ions at the surface of treated object 30 is substantially improved.

15 It is evident that the present invention is not limited to the embodiments that have just been described and that various simple modifications and variants can be envisaged by those skilled in the art without departing from the scope of the invention as defined by the annexed claims. It will be noted, in particular, that the ion implantation dose used lies
20 within a range comprised between $1 \cdot 10^{16}$ ions/cm² and $15 \cdot 10^{16}$ ions/cm² and that the single or multiply charged ion acceleration voltage is comprised between 7.5 kV and 35 kV. It will also be understood that the present invention applies more particularly, but not exclusively, to the surface treatment of sapphire objects (natural or synthetic sapphire) for the
25 production of watch crystals. As a result of the ion implantation method according to the invention, the amount of incident light reflected by such crystals is considerably reduced, which significantly improves the readability of information displayed by the indicator members (hands, date indication, decorations, etc.) placed under such crystals. The present invention also
30 applies to other types of materials (for example ceramics or crystalline or

amorphous metal materials) whose mechanical properties, especially scratch-resistance, are greatly improved when the ion implantation and charge neutralisation method is applied thereto. It will also be noted that the secondary electron beam includes both electrons from the primary electron
5 beam and electrons extracted from the target by the electrodes of the primary electron beam. It will be noted finally that, according to the invention, the ECR ion source is capable of producing single or multiply charged ions, i.e. ions whose degree of ionisation is higher than or equal to 1, wherein the ion beam can include ions that all have the same degree of
10 ionisation or can result from a mixture of ions having different degrees of ionisation.

Nomenclature

- 1. Electronic cyclotron resonance (ECR) ion source
- 2. Injection stage
- 4. Volume of gas to be ionised
- 5 6. Hyperfrequency wave
- 8. Magnetic confinement stage
- 10. Plasma
- 11. Extraction stage
- 11a Anode
- 10 11b. Cathode
- 12. Ion beam
- 14. Ion implantation device
- 16. Electron gun
- 18. Anode
- 15 20. Orifice
- 22. Metal cathode
- 24. Tip
- 26. Electric generator
- 28. Primary electron beam
- 20 30. Treated object
- 32. Target
- 34. Secondary electron beam
- 36. Table
- 38. Temperature sensor
- 25 40. Electric voltage measuring instrument

CLAIMS

1. Method for implanting single or multiply charged ions into a surface of a treated object (30), said method including the step that consists
5 in directing towards the surface of the treated object (30) an ion beam (12) produced by an ion source (1) of the electronic cyclotron resonance (ECR) type, the method also including the steps consisting in:

- producing at least one primary electron beam (28) and directing said
10 primary electron beam (28) so that it passes through the ion beam (12), and
- producing a secondary electron beam (34) by reflection of the primary
electron beam (28) onto a target (32) once said primary electron beam
has traversed the ion beam (12), the target (32) being oriented such
that the secondary electron beam (34) falls onto the surface of the
15 treated object (30).

2. Method according to claim 1, characterized in that the treated object (30) is made of a non-electrically conductive or semiconductor material.

3. Method according to claim 1, characterized in that the material
20 from which the treated object (30) is made is chosen from the group formed by natural and synthetic sapphires, mineral glasses, polymers and ceramics.

4. Method according to claim 2, characterized in that the material from which the treated object (30) is made is chosen from the group formed by natural and synthetic sapphires, mineral glasses, polymers and ceramics.

25 5. Method according to claim 1, characterized in that the material from which the treated object (30) is made is an electrically conductive material.

6. Method according to claim 2, characterized in that the material from which the treated object (30) is made is an electrically conductive
30 material.

7. Method according to claim 5, characterized in that the material from which the treated object (30) is made is chosen from the group formed by crystalline or amorphous metal alloys, ceramics and precious and non-precious metals.
- 5 8. Method according to claim 6, characterized in that the material from which the treated object (30) is made is chosen from the group formed by crystalline or amorphous metal alloys, ceramics and precious and non-precious metals.
- 10 9. Method according to any of claims 1 to 8, characterized in that the atoms that are implanted into the surface of the treated object (30) by means of the single or multiply charged ECR ion source (1) are chosen from the group formed by nitrogen N, carbon C, oxygen O, argon Ar, helium He and neon Ne.
- 15 10. Method according to claim 9, characterized in that the nitrogen atoms are obtained by ionisation of a dinitrogen precursor gas, the carbon atoms are obtained by ionisation of a methane precursor gas, and the oxygen atoms are obtained by ionisation of a dioxygen precursor gas.
- 20 11. Method according to claim 1, characterized in that the surface temperature of the treated object (30) is measured remotely and in real time.
12. Method according to claim 1, characterized in that the electrical potential of the surface of the treated object (30) or the electrical potential of a table (36) that supports the treated object (30) is measured in real time.
- 25 13. Method according to claim 12, characterized in that the surface of the treated object (30) is treated by means of at least one ion implantation dose that falls within a range comprised between $1 \cdot 10^{16}$ ions/cm² and $15 \cdot 10^{16}$ ions/cm² and in that the single or multiply charged ion acceleration voltage is comprised between 7.5 kV and 35 kV.
- 30 14. Device for implanting single or multiply charged ions into a surface of a treated object (30), said device comprising an ECR ion source (1) and an electron gun (16), the ECR ion source (1) producing an ion beam (12) and the electron gun (16) producing a primary electron beam (28), the

ECR ion source (1) and the electron gun (16) being arranged such that the primary electron beam (28) intercepts the ion beam (12), the single or multiply charged ion implantation device further comprising a target (32) placed on the path of the primary electron beam (28) once the latter has passed through the ion beam (12), the target (32) being oriented such that a secondary electron beam (34), produced by the collision between the electrons of the primary electron beam (28) which have not recombined with the ions of the ion beam (12) and the target (32), impinges on the surface of the treated object (30).

10 15. Device for implanting single or multiply charged ions according to claim 14, characterized in that the secondary electron beam (34) also impinges on a table (36) on which the treated object is placed (30).

 16. Device for implanting single or multiply charged ions according to claim 15, characterized in that the device also includes a temperature sensor
15 (38) for measuring remotely and in real time the surface temperature of the treated object (30).

 17. Device for implanting single or multiply charged ions according to claim 15, characterized in that the device includes an instrument (40) for measuring the electrical potential of the surface of the treated object (30)
20 and/or of the table (36) that supports the treated object (30).

 18. Device for implanting single or multiply charged ions according to claim 16, characterized in that the device includes an instrument (40) for measuring the electrical potential of the surface of the treated object (30) and/or of the table (36) that supports the treated object (30).