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(71) **Applicant: POLITECNICO DI TORINO** [IT/IT]; Corso Duca degli Abruzzi, 24, 10129 Torino (IT).

(72) **Inventors: FERRARIS, Monica**; c/o Politecnico Di Torino, Corso Duca degli Abruzzi, 24, 10129 Torino (IT). **BALAGNA, Cristina**; c/o Politecnico Di Torino, Corso Duca degli Abruzzi, 24, 10129 Torino (IT). **PERERO, Sergio**; c/o Politecnico Di Torino, Corso Duca degli Abruzzi, 24, 10129 Torino (IT).

(74) **Agent: LISA, Elisabetta** et al.; c/o Praxi Intellectual Property S.p.A., Corso Vittorio Emanuele II, 3, 10125 Torino (IT).

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(54) **Title:** METHOD FOR THE APPLICATION OF AN ANTIVIRAL COATING TO A SUBSTRATE AND RELATIVE COATING

(57) **Abstract:** A method for the application of an antiviral coating to a substrate and an antiviral coating thereof, the method comprising: co-sputtering on said substrate at least a first glass, ceramic, or glass-ceramic material, or matrix, and at least a plurality of nanoclusters of a second metallic material, said co-sputtering comprising: a simultaneous bombardment on the first and on the second target, with a first ion beam incident on said first target with a power ranging between 90 and 110 Watts and a second ion beam incident on said second target with a power ranging between 0.5 and 1.5 Watts, said second ion beam being switched on and off according to a periodic sequence with a duty cycle ranging between 97% and 98%; or a simultaneous bombardment on the first and on the second target, with a first ion beam incident on said first target with a power ranging between 190 and 210 Watts, and a second ion beam incident on said second target with a power ranging between 0.5 and 1.5 Watts, said second ion beam being switched on and off according to a periodic sequence with a duty cycle ranging between 25% and 35%.

WO 2019/082001 A1

"METHOD FOR THE APPLICATION OF AN ANTIVIRAL COATING TO A SUBSTRATE AND RELATIVE COATING"

DESCRIPTION

The present invention relates to a method for the application of an antiviral coating to a substrate and to a coating for covering a substrate, said coating being produced with such method. A subject-matter of the present invention is also an air filter formed by an air permeable substrate and covered with the antiviral coating produced according to said method.

It is known that the development of methods and materials for the conferment of biocidal properties to any surface that must not be contaminated by microorganisms (for example, surfaces of medical and surgical instruments, surfaces of filters for air conditioning plants, etc.) is the core of an extensive research. In particular, in the last twenty years different materials and methods have been developed for conferring antibacterial properties to a substrate, while the problem of the conferment of antiviral properties has been studied less.

In the documents US7559968B2, WO2002100448 and EP1310288A1, for example, the application of a material containing an antibacterial agent (e.g. triclosan, silver-based substances, etc.) on a substrate of a woven or non-woven fabric is described. In some cases, as in WO2002100448, the antibacterial component is applied by means of a carrier such as, for example, alcohol, glycols or water, which impregnate the substrate. In other cases, as in US20060008539, on the other hand, the antibacterial component is applied by means of a painting (or "coating") procedure, and the use of an inorganic carrier, as the porous silica gel, is provided for. In patent applications US20120294919A, US20130129565, US20130129565 and WO2007147832, the application of coatings made of metal ions having notoriously antibacterial properties such as silver, copper and zinc, is described. Such application is carried out by means of the various techniques, some of which involve the use of photocatalytic elements (US20130129565), others include the use of thermal plasma torches in radio frequency

(US20130129565). Still, others are based on the co-deposition (or "co-sputtering") in radio frequency (RF) of a metal with antibacterial properties, and silica. Co-sputtering techniques for the application of an anti-bacterial coating to a substrate are also described in the following articles: *[Ferraris M. et al. "Chemical, Mechanical, and Antibacterial Properties of Silver Nanocluster–Silica Composite Coatings Obtained by Sputtering, Advanced Engineering Materials, 7, 12, 2010]; [Ferraris et al. "Silver nanocluster–silica composite coatings with antibacterial properties", Materials Chemistry and Physics, 120, 123-126, 2010]*. In such articles, in particular, co-sputtering techniques for making antibacterial coatings consisting of silver nanoaggregates are mentioned. Said nanoaggregates are also known in the field with the English term "nanoclusters". The use of both metallic nanoclusters and the art of co-sputtering allows obtaining coatings with high mechanical and thermal resistance to wear and ageing, while obtaining at the same time antibacterial properties active for an extended period of time.

As mentioned above, following numerous researches relating to the development of antibacterial coatings, very little is known about the development of techniques specifically designed for obtaining coatings with antiviral properties. In particular, whilst it is true that some of the known techniques mentioned above, such as those described in US7559968B2 and US20130129565, can be used to produce coatings with generic biocidal properties (i.e., with antibacterial properties and, at the same time, antiviral properties and antifungal properties), to the best of our knowledge, there aren't any known methods capable of conferring antiviral properties by means of co-sputtering. The techniques for the creation of antiviral coatings presently known (e.g. US7559968B2, US20130129565), are not capable of achieving a wear resistance equal to that obtainable by means of co-sputtering. On the other hand, techniques of co-sputtering, notoriously capable of achieving a high resistance to wear, have never been used to create antiviral coatings.

The object of the present invention is therefore to provide a method which could allow obtaining a coating having, at the same time, both antiviral properties and a high resistance to thermal and mechanical wear.

Such object is achieved by the present invention by means of a co-deposition or co-sputtering process of a first glass, ceramic, or glass-ceramic material, or matrix, and a plurality of nanoclusters of a second metallic material, in which the incident powers of a first ion beam on the first material and of a second ion beam on a second material are mutually different and specifically determined in order to confer antiviral properties to the obtained coating. Furthermore, the antiviral effect is achieved by means of an appropriate setting of useful work cycles (or "duty cycles"), i.e. of the regular sequences of switching on and off the ion beam incident on the second material. The method of the present invention may further provide for the co-sputtering of more than two materials and, in particular, can provide for the co-deposition of more than one metallic material (for example, of a third metallic material and/or a fourth metallic material). In this case, simultaneously to the ion beam bombardment on the first and second target, a bombardment occurs also on a third target made of a third metallic material, and/or on a fourth target made of a fourth metallic material, etc.

Thus, the method of the present invention comprises a co-sputtering on said substrate of at least a first glass, ceramic, or glass-ceramic material, or matrix, and of at least a plurality of nanoclusters of a second metallic material, said co-sputtering taking place by means of cathodic pulverization of at least a first target made of the first material and of at least a second target made of a second material. The parameters used to obtain the antiviral effect are then set in such a way that the co-sputtering, in turn, comprises:

- a simultaneous bombardment on the first and on the second target, with a first ion beam incident on said first target with a power ranging between 90 and 110 Watts, and a second ion beam incident on said second target with a power ranging between 0.5 and 1.5 Watts, said second ion beam being switched on and off according to a periodic sequence with a duty cycle ranging between 97% and 98%; or
- a simultaneous bombardment on the first and on the second target, with a first ion beam incident on said first target with a power ranging between 190 and 210 Watts, and a second ion beam incident on said second target with a power ranging between 0.5 and 1.5 Watts, said second ion beam being switched on and

off according to a periodic sequence with a duty cycle ranging between 25% and 35%.

The duration of the bombardment with the first ion beam and the second ion beam ranges between 15 and 80 minutes. Finally, here the first material is specified preferably as silica, while the second and/or third and/or fourth material, etc., is preferably a metal chosen from copper, zinc and silver.

Furthermore, the present invention relates to an antiviral coating for covering a substrate, comprising at least a plurality of nanoclusters of a second metallic material and at least one glass, ceramic, or glass-ceramic material; said coating having a thickness ranging between 15 nm and 500 nm. The antiviral coating of the present invention may further comprise a third and/or fourth metallic material, etc. Said at least one metallic material is preferably chosen from copper, zinc and silver. On the other hand, the first material is preferably silica. An air filter comprising a substrate which is permeable to air, said substrate being covered with the antiviral coating having the features described above, further forms a subject-matter of the present invention.

These and further features of the present invention will be made clearer on reading the following detailed description of some preferred embodiments of the present invention, to be construed by way of example and not limitation of the more general claimed concepts, as well as by way of examples concerning experimental tests performed on the present invention.

In a first embodiment thereof, the method of the present invention comprises:

- co-sputtering of silica and a plurality of silver nanoclusters on a substrate, said co-sputtering occurring by means of cathodic pulverization of at least a first target made of silica and at least a second target made of silver.

Said co-sputtering, in turn, comprises:

- a simultaneous bombardment on both the silica target and the silver target, with a first ion beam incident on the silica target with a power ranging between 90 and 110 Watts, and a second ion beam incident on the silver target with a power ranging between 0,5 and 1,5 Watts, said second ion beam being switched on and off according to a periodic sequence with a duty cycle ranging between 97% and 98%.

The plasma generating the first ion beam is obtained by means of a radio frequency alternating current, while the plasma generating the second ion beam is obtained by means of a radio frequency continuous current or alternating current.

In a second embodiment thereof, the method of the present invention comprises:

- co-sputtering of silica and a plurality of silver nanoclusters on a substrate, said co-sputtering occurring by cathodic pulverization of at least a first target made of silica and at least a second target made of silver.

Said co-sputtering, in turn, comprises:

- a simultaneous bombardment on the silica target and the silver target, with a first ion beam incident on the silica target with a power ranging between 190 and 210 Watts, and a second ion beam incident on the silver target with a power ranging between 0,5 and 1,5 Watts, said second ion beam being switched on and off according to a periodic sequence with a duty cycle ranging between 25% and 35%.

The plasma generating the first ion beam is obtained by means of a radio frequency alternating current, while the plasma generating the second ion beam is obtained by means of a radio frequency continuous current or alternating current.

With both the first and the second embodiment of the method of the present invention it is possible to obtain an antiviral coating having a thickness ranging between 15 nm and 500 nm, said coating comprising: a silica matrix and a plurality of silver nanoclusters. Further, such coating may be used for covering an air permeable substrate, resulting in an antiviral material which can be used to make an air filter.

EXAMPLES

The antiviral effect of the composite coating formed by silver nanoclusters and a silica matrix has been assessed against the Respiratory Syncytial Virus following a protocol in two steps, structured in the following manner:

- STEP 1: a comparison was carried out among:

- the viral load on a sample of cotton fabric, hereinafter referred to as "reference sample", coated according to the method of the present invention and wetted with 10 ml of growth broth;
- the viral load on a control sample consisting of an uncoated cotton fabric wetted with the same solution mentioned in the previous point; and
- the viral load in the same solution mentioned in the preceding points and hereinafter called the control solution;

- STEP 2: tissue samples coated according to the method of the present invention were prepared using a silica target and a silver target and varying, depending on the sample, the parameters related to the time of co-sputtering, the powers of the ion beams incident on the silica target and on the silver target, as well as the duty cycle of the switching on and off of the ion beam incident on the silver target. Then, the behaviour of single samples was compared with that of the reference sample.

<u>Example 1 (STEP 1)</u>

On a substrate of cotton fabric, a coating made of a silica matrix and silver nanoclusters obtained by means of co-sputtering with a duration equal to 60 minutes was applied and carried out by means of a simultaneous bombardment on a silica target with an ion beam having a power equal to 200 Watts and on a silver target with an ion beam having a power of 1 Watt. The ion beam incident on the silver target has been switched on and off according to a periodic sequence with a duty cycle equal to 25%.

The coated sample showed a significant reduction of the plaque-forming units (62 PFU/ml) compared with those detected on the sample of uncoated fabric (2,482 PFU/ml) and the control solution (7,488 PFU/ml).

<u>Example 2 (STEP 2)</u>

On a group of 16 substrates of cotton fabric a coating made of a silica matrix and silver nanoclusters obtained by means of co-sputtering for a duration equal to 15 minutes was applied, on other 16 samples co-sputtering for a duration equal to 40 minutes was applied, on other 16 the duration of the co-sputtering was prolonged up to 60 minutes, and on other 16 yet up to 80 minutes.

For each of the samples, a different power for the plasma generating the ion beam incident on the silica target, a different power for plasma generating the ion beam incident on the silver target and different duty cycles regarding the ion beam incident on the silver target were used.

In the tables hereinafter, the tested parameters are summarized.

Sputtering Time (mins)	Applied Power		Duty Cycle
	SiO_2	Ag	
15	100	1	93.75%
			96.77%
			97.22 %
			97.56 %
	200	1	93.75 %
			96.77%
			97.56%
			25%
40	100	1	93.75%
			96.77%
			97.22 %
			97.56 %
	200	1	93.75 %
			96.77%
			97.56%
			25%

60	100	1	93.75%
			96.77%
			97.22 %
			97.56 %
	200	1	93.75 %
			96.77%
			97.56%
80	100	1	93.75%
			96.77%
			97.22 %
			97.56 %
	200	1	93.75 %
			96.77%
			97.56%
			25%

As a result of the comparison between the behaviour of single samples and the behaviour of the reference sample, it was observed that the biocidal properties of the coating are preserved when:

- the power of the ion beam incident on the silica target is equal to 100 W, the power of the ion beam incident on the silver target is equal to 1 W, and the ion beam incident on the silver target is switched on and off according to a periodical sequence with a duty cycle ranging between 97% and 98%; or
- the power of the ion beam incident on the silica target is equal to 200 W, the power of the ion beam incident on the silver target is equal to 1 W, and the ion beam incident on the silver target is switched on and off according to a periodical sequence with a duty cycle ranging between 25 % and 35 %.

CLAIMS

1. A method for the application of an antiviral coating to a substrate, the method comprising:
   - co-sputtering on said substrate at least a first glass, ceramic, or glass-ceramic material, or matrix, and at least a plurality of nanoclusters of a second metallic material, said co-sputtering occurring by means of cathodic pulverization of at least a first target made of the first material and at least a second target made of a second material;

   characterized in that said co-sputtering comprises:

   - a simultaneous bombardment on the first and on the second target, with a first ion beam incident on said first target with a power ranging between 90 and 110 Watts, and a second ion beam incident on said second target with a power ranging between 0.5 and 1.5 Watts, said second ion beam being switched on and off according to a periodic sequence with a duty cycle ranging between 97% and 98%; or
   - a simultaneous bombardment on the first and on the second target, with a first ion beam incident on said first target with a power ranging between 190 and 210 Watts, and a second ion beam incident on said second target with a power ranging between 0.5 and 1.5 Watts, said second ion beam being switched on and off according to a periodic sequence with a duty cycle ranging between 25% and 35%.

2. The method according to the preceding claim, wherein the duration of the bombardment with the first ion beam and the second ion beam ranges between 15 and 80 minutes.

3. The method according to claim 1 or 2, wherein the second material is chosen from silver, copper and zinc.

4. The method according to any of the preceding claims, wherein a bombardment also on a third target of a third metallic material occurs simultaneously to the bombardment on the first and on the second target.

5. The method according to the preceding claim, wherein the third material is chosen from silver, copper and zinc.

6. The method according to the preceding claim, wherein a bombardment also on a fourth target of a fourth metallic material occurs simultaneously to the bombardment on the first, the second and the third target.

7. The method according to the preceding claim, wherein the fourth material is chosen from silver, copper and zinc.

8. The method according to any of the preceding claims, wherein said first material is silica.

9. The method according to any of the preceding claims, wherein said first ion beam is generated by a plasma obtained by means of a radio frequency alternating current.

10. The method according to any of the preceding claims, wherein said second ion beam is generated by a plasma obtained by means of a radio frequency continuous current or alternating current.

11. An antiviral coating for covering a substrate, comprising at least:
    - a first glass, ceramic, or glass-ceramic material, or matrix; and
    - a plurality of nanoclusters of a second metallic material;

said coating having a thickness ranging between 15 nm and 500 nm.

12. The coating according to the preceding claim, wherein the first material is silica

and/or the second material is chosen from copper, zinc and silver.

13. The coating according to the preceding claims 11 or 12, comprising a plurality of nanoclusters of a third metallic material.

14. The coating according to the preceding claim, wherein the third material is chosen from copper, zinc and silver.

15. An air filter comprising an air permeable substrate, said substrate being covered by the antiviral coating according to any of the preceding claims 11 to 14.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2018/057639

A. CLASSIFICATION OF SUBJECT MATTER
INV. C23C14/06
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, COMPENDEX, INSPEC, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	IRFAN M ET AL: "Antimicrobial functionalization of cotton fabric with silver nanoclusters/silica composite coating via RF co-sputtering technique", CELLULOSE, vol. 24, no. 5, 23 February 2017 (2017-02-23), pages 2331-2345, XP036205944, SPRINGER [NL] ISSN: 0969-0239, DOI: 10.1007/S10570-017-1232-Y [retrieved on 2017-02-23]	1-14
Y	page 2332 - page 2333 page 2343, left-hand column -----	15

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[X] Further documents are listed in the continuation of Box C.

[ ] See patent family annex.

* Special categories of cited documents :

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Name and mailing address of the ISA/
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Hoyer, Wolfgang

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2018/057639

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	YOUNG-SEON KO ET AL: "Prompt and synergistic antibacterial activity of silver nanoparticle-decorated silica hybrid particles on air filtration", JOURNAL OF MATERIALS CHEMISTRY B, vol. 2, no. 39, 8 August 2014 (2014-08-08), pages 6714-6722, XP055476492, Royal Society of Chemistry [GB] ISSN: 2050-750X, DOI: 10.1039/C4TB01068J abstract -----	15
A	Balagna C ET AL: "Silver Nanocluster/Silica Composite Coatings Obtained by Sputtering for Antibacterial Applications" In: "Structural Nanocomposites", 20 November 2013 (2013-11-20), Springer, Berlin, Heidelberg [DE], XP055476562, ISSN: 1612-1317 ISBN: 978-3-642-40322-4 pages 225-247, DOI: 10.1007/978-3-642-40322-4_10, page 228, paragraph 1 page 231, paragraph 1 -----	1-15
A	YUN HAENG JOE ET AL: "Evaluation of Ag nanoparticle coated air filter against aerosolized virus: Anti-viral efficiency with dust loading", JOURNAL OF HAZARDOUS MATERIALS, vol. 301, 11 September 2015 (2015-09-11), pages 547-553, XP029307057, Elsevier [NL] ISSN: 0304-3894, DOI: 10.1016/J.JHAZMAT.2015.09.017 the whole document -----	15