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(54) Title: ANTIMICROBIAL GLASS AND GLASS CERAMIC SURFACES AND THEIR PRODUCTION

(57) Abstract: The application relates to an article having an antimicrobial surface with a metal ion concentration, especially a Ag-concentration in a depth of about 0 µm to about 2 µm of the article measured from the surface higher than 0,6 wt.%, preferably 0,8 wt.% most preferably 1 wt.%.



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Antimicrobial glass and glass ceramic surfaces and their production

Field of the Invention

5 This invention relates to glass and glass ceramic substrates, glazes and enamels with antimicrobial surface properties, a method to prepare such surfaces and the applications of antimicrobial substrates. The antimicrobial efficacy is generated by one or more metal ions which are implanted on and/or into the glass or glass ceramic surface. Application fields are e.g. food contact, kitchen ware, bathroom
10 ware, displays, touch display, food displays, food production, pharmaceutical production, pharmaceutical packaging, medical devices, fresh water treatment, storage and conduction, food storage, cutting boards, counter tops, refrigerator shelves, white goods, table ware, hospital equipment.

15 Background of the Invention

From JP2001192234 a inline spray technology of solutions which contain silver or zinc salts for antimicrobial or water repellent characteristics onto a soda lime glass-surface is known. Zn was only applied for water repellance and not to
20 provide an antimicrobial effect to the glass substrate. The combination of Zn and Ag-Ions to provide antimicrobial properties for a glass surface are not mentioned. Only the spraying of Ag as an antimicrobial agent onto the surface at 250 °C with a concentration of 0,1 wt% in water is mentioned in this application.

25 Because by the spraying technology only a non perfect wetting of the surface of the substrate with the antimicrobial agents could be achieved, with the process disclosed in JP 2001192234 the antimicrobial effect of the surface is not perfect homogenous.

30 In JP 316320 an ion exchange process with fused salts for soda lime glasses is described. This process has the disadvantage that it cannot be conducted as a continuous process. Furthermore additional cleaning steps are required to remove

the salts from the surface. Furthermore as a substrate in the state of the art mainly soda lime glasses or alkaline containing glasses are used.

Antimicrobial glass-powders have been made known from several patent applications. For example WO 03/018498 describes a antimicrobial glass-powder comprising a iod-content greater than 10 ppm. From WO 03/018499 a antimicrobial glass powder has made known comprising a glass with a phosphor content lower 1 weight-% within the glass-composition.

From US 5,290,544 water-soluble glasses comprising a concentration of more than 0,5 weight -% Ag have been made known. This glasses provide for antibacterial effect due to the release of the Ag-ions out of the glass-matrix. The glass has a high B₂O₅ and a low SiO₂ – content.

From US 6,143,318 phosphat-glasses containing silver has been made known, which also provide an antimicrobial effect.

Antimicrobial borophosphatglasses or borosilicatglasses are described in JP10218637, JP08245240, JP07291654, JP03146436, JP2000264674 or JP2000203876.

Glasses with an antimicrobial effect and a phosphor-content of more than 1 weight-% are known from WO 01/03650.

Coatings for anti-microbial refrigerator shelving have been shown in WO 02/40180. According to WO 02/40180 an anti-microbial agents is added to a matrix containing an epoxy-acrylate resin, an adhesion promoter and a free-radial photo initiator. The matrix comprising the anti-microbial agents is then deposited as a coating onto the glas-substrate. The coating has a thickness of approximately 20 microns. In order to make the coating more stable, especially to prevent abrasion, the coating is cured, especially with UV-light.

Antimicrobial interior refrigerator-articles such as antimicrobial refrigerator shelves according to WO 02/40180 have the disadvantage, that their production is time consuming and furthermore although the shelves are cured an abrasion cannot totally prevented.

5 From WO 02/32834 an antibacterial glazing is made known comprising a antibacterial metal-ions.

10 EP 0942351 B1 shows a glass-substrate for a touch screen sensor. The surface of the glass substrate shows an antibacterial effect due to a coating comprising silver metal ions.

15 EP 1270527 shows a product with a glass layer. In that glass layer a antibacterial metal ion was obtained by an ion exchange from an alkali metal ion or alkali earth metal ion, which exists in that glass layer. EP 1270527 further shows that the antibacterial metal ions form a rich layer having a high concentration on the surface of the glass layer. No temperature dependence of the ion exchange reaction with regard to the glass substrate type is given.

20 A disadvantage of low processing temperature is that the processing times are very long and/or a long term release of silver ions is difficult to achieve. The Ag ions are removed out of the surface very fast in a washing processes. Also the processing times are very long as the diffusion of the silver into the glass takes a longer time at lower temperatures.

25 US 2002/001604 shows an glass article, wherein an antibacterial, antifungal or antialgal component has been diffused from a surface into the inside of a surface protion of this article. For a silver colloid dispersion having a silver component for a soda lime glass a antibacterial surface after a heat treatment for about 500°C for 30 minutes was found. The application does not describe how other glass
30 substrates such as borosilicate-glasses can be provided with a antibacterial surface, nor how deep metals ions have been diffused into the surface or how the process parameters must be choosen to provide a antimicrobial surface for which

by a ASTM 2180-test a reduction of microorganisms by two log scales is shown. The processing times of 30 minutes are very long and not suitable for fast mass production. Combinations of different antimicrobial ions are not described.

5 **Summary of the Invention.**

In view of the foregoing and other limitations and disadvantages of the prior art, it is an object of the present invention to provide an improved process for the production of antimicrobial glass and glass-like substrates.

10 Examples for microbials are bacteria, fungus, yeast, mold, algae and virus.

It is a further object to provide a material with a defined antimicrobial component such as Ag, Zn, Cu, Sn, I, Cr, Te, Ge with a antimicrobial effective concentration at the surface of the substrate, especially the surface of a glass substrate. Which also long term efficacy and efficacy after cleaning and washing.

15 In a preferred embodiment the material with a defined antimicrobial component such as Ag, Zn, Cu, Sn, I, Cr, Te, Ge has a concentration profile which shows a high concentration at least at one surface of the substrate, preferably the concentration of antimicrobial ions decreases towards the mid of the substrate depth.

20 For special applications the material has a concentration profile with a relatively low concentration of antimicrobial components, such as Ag, Zn, Cu-ions at at least one surface of the substrate. The concentration of antimicrobial ions increases direct under the surface for a short distance and then decreases to zero.

25 It is another object to provide a process for preparing a transparent, essentially colorless substrate, especially glass- or glass like substrate having an antimicrobial effective concentration of metal ions in at least one selected surface region thereof.

Yet another object is to provide articles of manufacture having at least one substantially flat glass or glass-like surface having a contact-killing, non-leaching antimicrobial effective amount of metal ions contained therein.

5 In a specific form non leaching means that in a Hemmhof Testing (EN 1104) no significant antimicrobial efficacy against e.g. *Aspergillus Niger* and *Bacillus Subtilis* can be detected.

10 The Hemmhof-Test is an Agar-Diffusion test according to EN 1104. In that test the sample is placed in Agar, which contains a defined germ concentration. Measured is the distance around the sample where no germ growth occurs in mm.

15 Another object is to provide articles of manufacture, and particularly articles of manufacture that are intended for use as food contacting articles, wherein the articles have at least one food contacting surface that is comprised of a transparent, essentially colorless glass or glass-like material having an antimicrobial effective concentration of metal ions in at least one surface region thereof that is to come into contact with food.

20 In the case of Ag-Ions as antimicrobial agents normally the antimicrobial effect decreases while the coloring increase if the amount of Ag is constant, it is advantageous that the antimicrobial substrate is essentially colorless for short term effects.

25 The reason is that the color mainly come from metallic silver cluster. Only ionic silver has antimicrobial properties. Therefore the yellow discolorisation is a sign for decreased short term antimicrobial-efficacy.

30 For long term antimicrobial efficacy of the surfaces in specific applications it can be advantageous to have beside ionic silver also metallic silver as nanoparticles in the glass matrix. In this case the nanoparticles should be close to the surface, so

that they can release silver ions. The nano particles are acting as a release system.

Nevertheless for specific applications such as cook tops, refrigerator shelves,
5 glass tubes a substrate having a specific color can be favorable.

If this color is induced by the generation of ion diffusion and formation of nano particles like silver this color can be varied by a variation of the number and size of the nano particles. In the case of silver the nano particles typically have particle
10 sizes which are lower than 30 nm, preferred lower than 20 nm , more preferred lower than 10 nm, most preferred lower than 5 nm

It is a further object of the invention that with the inventive process all different sort s of substrate, especially glass-substrate and glass-ceramic-substrates can be
15 provided with an antimicrobial surface, and the process is not limited e.g. to a float glass substrate.

With the inventive process alkali containing floatglass such as e.g. Borosilicate-glasses (e.g. Borofloat 33, Borofloat 40, Duran, of SCHOTT-GLAS, MAINZ) as
20 well as alkaline free glass (e.g. AF37 or AF45 of SCHOTT-GLAS, Mainz), Alumosilicate-glasses (e.g. Fiolax, Illax, of Schott Mainz), Alkline Earth Alkaline glasses (e.g. B270, BK7 of SCHOTT-GLAS, Mainz) and in a more specific application Soda lime float glasses should be used as substrates. In preferred
25 embodiment display glasses such as D263 of SCHOTT-DESAG, Grünenplan can be used as substrate. In principial the inventive process is applicable with all technical and optical glasses as a substrate material.

With the inventive process glass ceramics such as e.g. Lithiumaluminosilicate Glass ceramics (e.g. Ceran, Robax, Zerodur of SCHOTT-Glas Mainz) or
30 Magnesiumaluminosilcate Glass ceramics or Mica Glass ceramics can be used as substrates.

In a most preferred embodiment, the parameters of the process are chosen in such a way, that the antimicrobial surface provided by the inventive process fulfill the antimicrobial requirements according to ASTM E2180-01 and/or JIS Z2801.

- 5 In a further preferred embodiment the antimicrobial surface fulfils ASTM E2180-01 and/or JIS Z 2801 and shows no "Hemmhof" formation according to EN 1104 and fulfils the non leaching results required for food contact materials according to German Law (LMBG) and/or drink water requirements as the German drinking water law (Trinkwasserverordnung) § 11 which allows for a release of Ag at
- 10 maximum of 0,08 mg/l.

Substrates can be e.g. flat glass, glass tube, glass lenses, ampulles, kapulles, bottles, cans, glass screens and other randomly shaped glass parts.

- 15 Further substrates can be e.g. glass ceramics in flat or curved form.

It is a further object of the invention to provide a process for preparing antimicrobial colored and non colored glass ceramics.

- 20 Preferably by the inventive process are antimicrobial glasses, which where produced by a float process and non float processes are provided.

Detailed Description

- 25 In a first step to obtain a antimicrobial surface a metal ion precursor material is applied to the surface of the substrate, especially the glass or glass-like substrate in any convenient manner, such as, for example, by dipping, spraying, screening, brushing or the like techniques.

- 30 The metal ion precursor material is a dispersion or solution or mixture of a metal ion precursor in suitable solvents, liquids or dilution substances.

The metal ion precursor can be e.g. Inorganics like Nitrates, Chlorides, Sulfates, Phosphates, Sulfides or Oxides. Also metal-organic or metallic precursor materials like nanoparticles can be used. The can be dissolved and/or dispersed in a solutions.

5

In a preferred embodiment totally soluble precursors are used to achieve most homogeneous distribution of the antimicrobial agents on the glass surface.

10

The penetration depth into the glass for different precursors and precursor formulations are different e.g. for silver salts it was found that the penetration depth decreases from Ag_2SO_4 , AgNO_3 , Ag_2O , to Ag_3PO_4 . By mixing the precursors specific diffusion profile properties can be achieved. The salts are also different with respect to color formation by nano particles. Normally AgNO_3 and Ag_2SO_4 show stronger color formation than Ag_2O and Ag_3PO_4 .

15

Therefore by choosing mixtures of precursor antimicrobial long and short term efficacy (ion profiles) and color formation can be designed and optimized.

20

After the metal ion precursor material, containing antimicrobial metal ions such as Ag, Zn, Cu, Sn, Cr, I, Te, or Ge and/or compounds with these metals is applied to at least one surface of the substrate, the substrate is heated to a temperature sufficient that during the heating process the antimicrobial precursors and solvents are decomposed and/or evaporated and the antimicrobial ions are penetrating or bonding into/to the substrate, e.g. the glass surface by diffusion and/or ion exchange.

25

30

This can be done in a one step process or in a two step process of multistep temperature time process e. g. to achieve specific antimicrobial ion distributions and profiles in the glass or glass like material. The process can be combined with other temperature treatments of the substrate which might be necessary like forming processes and/or mechanical strengthening processes and/or coating processes and/or decoration processes.

In a two step process the substrate, which is preferably amorphous glass is heated to a first temperature sufficient to drive off any volatiles contained in the antimicrobial metal ion precursor, which lies in a first embodiment within the range from about a temperature depending on the solvent and precursor-material from about 30 °C – 250°C and then heating the resulting substrate to a second temperature, which lies in a first embodiment within the range from $T(g)$ -300°C to about $T(g)$ +250°C for a short period of time, e. g. in a first embodiment from about 1 min. to about less than 30 min. $T(g)$ is the transformation temperature of the glass and depends on the glass composition. In preferred embodiment the temperature ranges from $T(g)$ –200°C to $T(g)$ + 200°. The transformation temperature $T(g)$ is well known for a man skilled in the art and e.g. described in VDI-Lexikon Werkstofftechnik (1993), pages 375 – 376. In a more preferred embodiment the temperature ranges from $T(g)$ –100°C to $T(g)$ + 150°.

By the above mentioned process one can obtain an article, especially a glass-substrate having a antimicrobial surface with a metal ion concentration in a depth of about 0 µm to about 2 µm of the article measured from the surface higher than 0,05 preferably higher than 0,5 wt%, more preferably higher than 1,0 weight-%, most preferably higher than 2 weight-%.

In a preferred embodiment an article is obtained having an antimicrobial surface with a metal ion concentration in a depth of about 0 µm to about 2 µm of the article measured from the surface higher than 0,8 wt%, preferably higher than 1,0 weight-%, most preferably 1,2 weight-% , wherein the ratio of the concentration of the metal ions in a depth of about 1 µm to the concentration at in a depth of about 10th µm is greater than 5, preferably greater than 10 , most preferred greater than 100.

The most preferred metal ion to be used for preparing a antimicrobial surface according to the invention is silver (Ag). But also other ions such as Zn or Cu or Sn or Cr or I or Te or Ge or combinations of these ions are possible

Combinations of ions can be advantageous if a broad antimicrobial effect against bacterial, yeast and fungus wanted to be achieved or synergistic effects wanted to be used.

So e. g. a combination between Ag- and Cu-precursor increases the antimicrobial efficacy against bacteria and fungus and also has an additional advantageous effect on avoiding the color generation by silver nano particles.

Different antimicrobial ions profiles can be achieved by the selection of the glass type, precursor types, surface preprocessing, the temperature time processing and post processing of the surface. Depending of the application and the time dependence of the antimicrobial efficacy following profiles are e. g. possible:

- a) constant decreasing ion concentration from surface into bulk
- b) constant increasing ion concentration from surface into bulk
- c) mixed forms of a) and b) especially nearly constant profiles

These profile can also include different types of antimicrobial ions. In general the type related profiles are different between each other because the diffusion and/or ion exchange rates are different.

In a more preferred embodiment providing for a long term-release of antimicrobial ions the process parameters are chosen such, that the ratio of the average concentration of the antimicrobial metal ions from the surface to 0,5 μm depth to the concentration of the metal ions from about 2 μm to about 5 μm is smaller than 0,5 preferred smaller than 0,1, most preferred smaller than 0,01.

In a preferred embodiment with low leaching at relatively high overall metal ion concentration the average concentration of antimicrobial metal ions in the first 50 nm are reduced to the average concentration between 50 nm and 1 μm by about more than 1% more than preferred more than 5 % most preferred more than 10 %.

In a most preferred embodiment providing for a long term-release of antimicrobial ions the process parameters are chosen such, that the ratio of the concentration of the metal ions in a depth of about 20 nm compared to the concentration of the

metal ions in a depth of about 1 μm is smaller than 1 to 1,1 preferred smaller than 1 to 5 most preferred smaller than 1 to 10 and wherein the ratio of the concentration of the metal ions in a depth of about 10 μm to the concentration of the metal ions in a depth of about 1 μm is smaller than 1 to 5 preferred smaller than 1 to 10 most preferred smaller than 1 to 100.

In a most preferred embodiment providing for a high antimicrobial efficacy at the start conditions the process parameters are chosen such, that the ratio of the concentration of the antimicrobial metal ions in a depth of about 20 nm compared to the concentration of the metal ions in a depth of about 1 μm is greater than 1,1 to 1 preferred greater than 5 to 1 most preferred greater than 10 to 1 and wherein the ratio of the concentration of the metal ions in a depth of about 10 μm to the concentration of the metal ions in a depth of about 1 μm is smaller than 1 to 5 preferred smaller than 1 to 10 most preferred smaller than 1 to 100.

The precursor of antimicrobial metal ions comprises a metal compound, typically a salt, complex or the like, dissolved or otherwise dispersed in a compatible carrier material, wherein the metal compound is capable of exchanging antimicrobial metal ions for metal ions.

Precursors are e.g. inorganic salts of antimicrobial ions, e. g. nitrates, preferably silver nitrat, chlorides, or organic salts such as acetates or mixtures thereof.

The carrier material or vehicle is a liquid or liquid-based material that is capable of dissolving or otherwise dispersing or suspending the metal compound. The carrier material can be water based or alcohol based.

Also organic oils or inorganic oils such as silicon oils as a carrier material or as vehicle are possible materials.

Any residue from the dried precursor material that is not decomposed and burned off the substrate during the ion exchange and/or diffusion heating step, generally is

completely removed during the ensuing antimicrobial tempering process or can be washed off easily.

5 The concentration of the source of antimicrobial metal ions in the precursor material may vary over wide limits depending, in part, on the particular metal compounds and the particular carrier materials involved. However, the identity and relative concentrations of the source of metal ions and the carrier material in the precursor materials are important only to the extent that the precursors are capable of exchanging or otherwise implanting an antimicrobial effective
10 concentration of metal ions into the surface regions of the substrate during the present treatment process. Typically, a concentration of Ag, Cu, Zn, Cr, I, Te, Ge compounds in the range of from about 0.01 to about 10.0%, by weight, and preferably from about 0.1 to about 5.0%, by weight, and more preferably from about 0.25 to about 2 % by weight based on the total weight of the metal
15 compound and carrier material, will be adequate to provide an antimicrobial effective concentration in the surface regions of a glass or glass-like substrate in accordance with the invention.

The precursor concentration can further on limited by the solubility in the chosen solvent.

20 In a further preferred embodiment of the invention the inventors found out, that depending on the temperature time profile and the starting surface concentration of the ions different concentration profiles from surface to interior of the substrate can be generated, because during the heating process the antimicrobial precursors are decomposed and the antimicrobial ions are penetrating the glass
25 surface by diffusion and/or ion exchange. If the temperature and time are too high the antimicrobial ions are penetration too deep the bulk material so that the antimicrobial surface effect is too low. If temperature and time are too low fixed antimicrobial ions in the surface can be too low so that the antimicrobial effect is
30 removed e.g. after cleaning with water.

Especially by use of Ag-ions as antimicrobial agent in the case of float glass additionally a yellowing can occur which is caused by the formation of metallic silver nano particles or clusters. The formation of Silver nanoparticles is supported by Sn and/or Fe impurities and the overall redox state in or on the glass surface. Redox partners like Fe^{2+} or Sn^{3+} are reducing the silver ions. The reduced silver forms silver nanoparticles/clusters which absorb light at about 420 nm which causes a yellow coloring. Therefore the usage of Zn and/or Cu or a mixture of Ag and Zn and/or Cu as an antimicrobial metal ions is preferred if a colorless antimicrobial substrate should be provided. The synergistic antimicrobial effect of different ions is advantageous. An advantageous synergistic antimicrobial effect can be achieved as the mechanisms and locations of reaction of e. g. Ag and Zn-ions are different. Furtheron a combination of Ag and Cu-salts in the solution is advantageous for the reduction of discoloration especially at higher process temperature where Cu-ions have a higher diffusion rate.

According to a further improved embodiment, the inventors found out, that the first temperature sufficient to drive off any volatiles contained in the antimicrobial metal ion precursor in the two step-process can lie within a temperature range from about 40 to about 250°C. This temperature depends e. g. on the precursor-material or the solvent.

In the first embodiment in a second step the antimicrobial ions are implanted on and/or in the surface of the glass. The inventors found out, that in the further improved embodiment, the temperature of the second step depends on the glass type and furthermore the temperature dependent diffusion coefficients of the antimicrobial ions, which are used to produce the antimicrobial surface. The inventors found out that, the temperature dependent diffusion coefficient of the ions is not only dependent from the sort of the ions, but also from the substrate material used. Therefore the temperature-region for the second process step is also substrate-dependent. The ion exchange and/or diffusion temperature for the second process-step is chosen preferably to be in the range from about 200°C lower than the glass transformation temperature (T_g) of the substrate, especially

the glass substrate to about 200°C higher than the glass transformation temperature (T_g) of the substrate, especially the glass substrate. More preferably the temperature of the second process step is chosen from about 100°C lower than the glass transformation temperature of the substrate material to about 100°C higher than the glass transformation temperature of the substrate material, most preferably about 50 °C lower than the glass transformation temperature point of the substrate material to about 50°C higher than the glass transformation temperature point of the substrate material. The period of time in which the substrate is heated up to the ion exchange / diffusion temperature which lies in the range given above for the second process step is according to the further embodiment of the invention from about 1 min to about 30 min., preferably from about 1min. to about 15 min most preferable from about 1min to about 5 min.

In an improved embodiment of the invention, the antimicrobial surface of a substrate can be prepared in a one step-process. In a one step process, the substrate is heated up to a temperature sufficient that the antimicrobial ions are implanted on and/or in the surface of the substrate, especially the glass or glass-like substrate. The temperature depends on the substrate type, especially the glass type and furthermore the temperature dependent diffusion coefficients of the antimicrobial ions, which are used to produce the antimicrobial surface. The inventors found out that, the temperature dependent diffusion coefficient of the ions is not only dependent from the sort of the ions, but also from the substrate material used. Therefore the temperature-region for this process-step is substrate-dependent. The ion exchange and/or diffusion temperature for the is chosen preferably to be in the range from about 200°C lower than the glass transformation temperature of the substrate, especially the glass substrate to about 200°C higher than the glass transformation temperature of the substrate, especially the glass substrate. More preferably the temperature of the second process step is chosen from about 100°C lower than the glass transformation temperature of the substrate material to about 100°C higher than the glass transformation temperature of the substrate material, most preferably about 50 °C lower than the glass transformation temperature (T_g) of the substrate material to about 50°C higher

than the glass transformation temperature of the substrate material. The period of time in which the substrate is heated up to the ion exchange / diffusion temperature which lies in the range given above for the second process step is according to the further embodiment of the invention from about 1 min to about 30 min., preferably from about 1 min to about 15 min most preferable from about 1 min to about 5 min. Also by heating up the substrate to the ion exchange temperature the volatiles of the ion precursor material are driven off the substrate. The one step process has the advantage of a shorter processing time than the two step process.

In the case float glass is used as a substrate material much high silver concentrations can be implanted into the glass without discoloration if the surface layer with e. g. contains Tin or is in an disadvantageous redox state is removed or cleaned. The tin containing layer is introduced within the production process of the floatglass. The thickness of the tin-layer is e. g. about 10 – 20 nm on the atmosphere side in the float bath and on the bath side several micrometer thick. Further impurities like iron ions are in the whole glass. The Redox equilibrium of polyvalent ions (e. g. between Fe^{2+} and Fe^{3+}) is moved to the reduced side especially in the first micrometers of the glass surface. Also the viscosity (lower viscosities on the reduced side) and therefore the diffusion rate of Ag^+ is influenced by the redox equilibria in the surface region. As it is advantageous that Ag^+ does not diffuse to deep into the glass a removal of the surface layer which has normally a lower viscosity is advantageous.

So depending on the side which shall be treated with the antimicrobial layer different removal technologies have to be used.

The removal and cleaning of the surface-layer can be done e.g. by chemical, etching or mechanical removal. Chemical etching can be done with different inorganic or organic acids and/or bases and with combinations of them. Acids can be e.g. HF, HCl, HNO_3 . Bases can be alkaline or earth alkaline hydroxide (e.g. NaOH). Additionally oxidizing treatments with e.g. H_2O_2 or the use of Peroxy-salts

like Earth alkaline peroxides (e. g. CaO_2 or ZnO_2) or heating in O_2 -containing atmosphere can be done to avoid discoloration effects by reduction.

In the case of float glasses in oxidizing heat treatment in oxygen containing atmosphere can significantly reduce the yellowing effect. This is due to the redox state change in the glass surface which influence the reduction potential of Ag-ions and the diffusion rate of Ag-ions in the glass.

To avoid silver induced discoloration further compounds which contain and introduce polyvalent ions on or in the glass surface can be used to reduce the discoloration effect. Polyvalent ions can be e.g. of element Ti, Cu, Ce, Cr, Mn, V, Bi, Mo, Nb, Co, Zn, As and Sb. By combination of these ions with e.g. NO_3 -salts and processing parameters is possible to reduce discoloration by changing diffusion rates and mechanical strength. Precious metals such as Pd, Pt and Au could be added as salts or oxides to the glass. The advantage of such precious metal combinations could be seen by oxidation of reduced silver to metallic silver.

Mechanical removal can be done by standard grinding and polishing techniques in inline or off line production processes. Low cost touch polishing processes are preferred.

For the float bath side mechanical removal is preferred as the tin containing layer can be several micrometer thick.

On the float bath side typically less than 200 μm are removed preferred less than 100 μm most preferred less than 10 μm less than 1 μm

On the atmosphere side typically less than 50 less than 10 less than 1 μm less than 100 nm are removed.

If the surface layer of float glass is removed extremely high silver salt concentrations can be applied with solutions and/or dispersions on the surface and temperature treated without any discoloration of the glass. No discoloration was found up to surface concentrations of more than 15 wt%.

Since the usage of alkaline containing glasses such as soda lime float glass with a temperature of the glass transformation point from about 525°C to 545°C as a substrate is preferred, the process is not restricted on soda lime glass or alkaline containing glasses and the related ion exchange process, because the diffusion coefficients of the different antimicrobial ions are high enough at the selected processing temperatures and times, so that they can penetrate the glass surface also of other glasses, such as Borosilicate glasses (e.g. BF33, BF40 from SCHOTT), Aluminosilicate Glasses (e.g. FIOLAX, ILLUX from SCHOTT) alkaline free Aluminosilicate glasses (e.g. AF37, AF45 from SCHOTT). The softening point of Borosilicate-glasses lies within the range from about 460°C to about 600°C, for Aluminosilicate-glasses from about 550°C to about 700°C and for alkaline free Aluminosilicate glasses from about 650°C to about 800°C.

Surprisingly the process is not only limited to Alkaline containing glasses where an ion exchange process between e. g. Sodium and Silver supports the movement of silver ions into surface. Obviously also by normal diffusion process the silver ions will penetrate the surface if temperatures are high enough.

Also glass-ceramics can be used as substrate-material. In the case of glass ceramics as a substrate material the inventors found out that the processing temperature of the diffusion step of the metal-ions into the glass surface is dependent from the ceramization temperature of the glass ceramic and the T_g of the residual glass phase. Preferably the processing temperature lies in a region from about 300 °C lower than the crystallization temperature and about 200 °C higher than crystallization temperature. More preferred are temperatures in a range from about 200 °C lower than crystallization temperature to 100 °C higher than crystallization temperature. Most preferred are temperatures which lie in the range from about 50 °C lower than crystallization temperature to about 50°C higher than the crystallization temperature.

Typical glass ceramics which can be used are alkali containing glass ceramics like e. g. Lithiumaluminosilicate (LAS) glass ceramics like CERAN®, ROBAX® or

Zerodur ® (all trademarks of SCHOTT-GLAS, Mainz) but also alkaline free glass ceramics like Magnesium Aluminium silicates (MAS).

5 If the substrate after the diffusion step is cooled down rapidly (e.g. by blowing air) a glass-substrate can be mechanical strengthened. The process steps are the same process steps as described above for glass substrates as substrate material. In a specific form of the invention it is highly advantageous to define the temperature time profile of the diffusion step in such a way that rapid cooling generates a mechanical strengthened substrate. It is further on advantageous to
10 define the temperature profile in such a way that surface decoration treatments can be done parallel in the same process. It is most advantageous if all three processes (antimicrobial treatment, decoration treatment and mechanical strengthening treatment) can be done in one processes.

15 The inventors further found out in a most preferred embodiment of the invention that, if one uses a Ag-salt as a metal ion precursor, a combination of Ag-Salts as a metal ion precursor material with salts of other polyvalent ions can reach a reduction of the yellowing. For example a combination of a Ag-salt with e. g. a Cu-salts can reduce coloring. Most preferred salts have oxidizing properties like
20 Nitrates or Peroxides.

Also a combination of different ion-precursor materials can be used. This can be advantageous e. g. if the antimicrobial properties should be combined with water repellent properties. In this case Ag-salts as a precursor material and Zn-salts as a
25 further metal ion precursor material can be combined. Such a combination is most preferred in case a high antimicrobial effect should be achieved without coloring.

In such a case to achieve a high antimicrobial effect Ag-salts as a first metal ion precursor material can be combined with Zn-salts as a second metal ion precursor
30 material.

Furthermore by combination of different metal ion precursor materials an synergistic antimicrobial booster effect can also be achieved e.g. by combining different antimicrobial ions such as ions of e.g. Ag,Cu,Zn,Sn,I,Te,Ge,Cr.

5 In case a colored glass or glass ceramic is used discoloration effects are of lower importance. It is also possible to add specific coloring agents to the antimicrobial ion containing solution.

10 In a improved embodiment the inventors found out, that if a suspension is used as a carrier material for the metal ions the particle size of inorganic antimicrobial substances should be lower than 1um preferred lower than 0,5 um most preferred lower than 0,1 um. This is especially necessary if a homogenous, non speckeled surface should be achieved.

15 The application of the metal ion precursor material or materials onto the substrate, especially the glass substrate in a preferred embodiment of the invention is done at room temperature or temperatures slightly higher than room temperature. If a two step process is used the coating could be dried in a first tempering step.

20 In a preferred embodiment the concentration of a Ag-metal compound in a metal ion precursor material in the range of from about 0.01 up to about 4% by weight, and preferably from about 0.25 to about 1,5% by weight, based on the total weight of the metal compound and carrier material, will be adequate to provide an antimicrobial effective concentration in the surface regions of a glass or glass-like
25 substrate in accordance with the invention.

For Zn-metal or Cu-metal compounds Zn-metal or Cu-metal compound in a metal ion precursor material in the range of from about 0.01 up to about 20% by weight, based on the total weight of the metal compound and carrier material, will be
30 adequate to provide an antimicrobial effective concentration in the surface regions of a glass or glass-like substrate in accordance with the invention.

The term "antimicrobial effective concentration", as used in this specification and claims, means that ions, atoms, molecules and/or clusters of the antimicrobial metal which has been exchanged or otherwise implanted into the surface regions of the glass or glass-like substrate are present in the surface regions of the substrate in a concentration such that they are released from the surface of the substrate at a rate and in a concentration sufficient to kill, or at least to inhibit microbial growth, on contact. To achieve this in a preferred embodiment the release rate of the metal ions providing for the antimicrobial effect is such that it fulfills the requirements of the LMBG (German Food law) and shows not Hemmhof". This means that in a Agar-diffusion Test (the so called "Hemmhof"-test EN 1104) against *Aspergillus Niger* and *Bacillus subtilis* no release or diffusion from the antimicrobial surface should be seen.

As heating technologies for reaching the temperatures for the different process steps the following techniques could be used: standard roller furnaces, batch furnaces, IR-heating, laser heating, gasburner heating, microwave heating. Since only a surface treatment of the substrate is performed preferably only the temperature directly at the surface of the substrate has been monitored, e.g. risen. This can e.g. be done by specific heating technologies like IR or Laser heating.

Especially the Laser heating technology can be used to provide for structured antimicrobial surfaces e.g. for biological applications. They can be combined with standard heating technologies.

As used in this herein the term "non-leaching antimicrobial glass or glass-like surface" is meant to describe a glass or glass-like surface, e.g., ceramic or glass-ceramic surface, that contains antimicrobial metal ions that are released from the surface at a rate sufficient to render the surface antimicrobially effective, while at the same time being released slowly enough for the glass surface to remain antimicrobially effective for an extended period, even when subjected to washing, e.g., in a conventional dishwasher.

In preferred embodiment these surfaces pass the Hemmhof Test and the leaching requirements of German LMBG Law.

5 After the final heat treatment process a washing step of the glass surface can be conducted to remove debris from the coating solution from the glass and adjust the antimicrobial agent concentration directly at the surface e. g. to fulfill the required German LMBG constraints. Such a step is especially necessary if high antimicrobial agent concentrations have to be achieved inside the glass to generate a long term antimicrobial effect. The heat treatment is done with
10 solutions with so high antimicrobial ion concentrations that without washing the ion release directly from the outer surface is too high to fulfill e. g. Hemmhof test and LMBG requirements for food contact materials.

15 Beside the ion concentration and release also the specific surface area plays an important role with respect to the antimicrobial efficacy. The surface area can e. g. be modified by grinding and polishing processes and influences directly the ion release. This can also be combined with a different optical appearance like "frosted glass". Standard grinding technologies can be used like fixed or loose grain grinding or sand blasting. By increasing the surface area the overall amount
20 of antimicrobial ions can be reduced in the surface by achieving the same antimicrobial efficacy. This can be especially advantageous if additionally discoloration effects should be avoided.

25 The surface roughness (Ra) is e.g. for rough grinding surfaced is between 5 μm and 1 μm for fine grinding between 1 μm and 0,2 μm and for polishing down to about 2 nm. Variation of the surface roughness allows to modify the antimicrobial efficacy e. g. by keeping other process parameters like silver concentration and processing temperature and time constant.

30 The atmosphere during the temperature processes has an influence of the redox behaviour at and in the glass surface. Increased oxygen concentrations are reducing the discoloration which is introduced e.g. by the reduction of silver ions

and the formation of metallic silver nano particles. This effect increases with increasing processing temperature as the diffusion rate and depth of oxygen into the glass is growing. On the other side oxygen in the atmosphere supports the generation of metal oxides like Ag_2O at the glass surface. These Oxides are quite stable and are reducing the metal ion diffusion into the surface. These oxides are increasing the surface antimicrobial effect.

In a preferred embodiment the formation of these metal oxides are controlled in such a way that are homogenous spread on the surface and no surface layer can be seen with the human eye. Further on the oxides are fixed to the glass surface in such a manner that they cannot be removed by normal cleaning processes like wiping and normal washing. Surface modifications with respect to wetting properties or diffusion properties can be additionally done.

According to a further aspect of the invention an article comprising an antimicrobial surface prepared according to the invention is provided. Particularly the article comprising an antimicrobial surface according to the invention is an article which is intended to contact food. Such an article may be a tray, a shelf, a cooktop, a countertop, an eating or drinking utensil or a cutting board.

Also pharmaceutical packaging products with an antimicrobial surface or optical glasses for e. g. medical devices are provided according to the invention.

Other applications for applying the technique of providing a glass-article with an antimicrobial effect are:

Display glasses e.g. touch screens, Baby bottles, nutritional storing water treatment and tubing systems, windows, food display, optical lenses, laboratory glasses, especially from borosilicate glasses. Most preferred are antimicrobial glass-shelves, especially for refrigerator shelving.

Therefore one further aspect of the invention is to provide antimicrobial interior refrigerator-article such as antimicrobial refrigerator shelves, which avoid the disadvantages of the state of the art, especially the interior refrigerator-article should be easy to produce and furthermore have a high resistance against abrasion of the antimicrobial coating.

This aspect of the invention is solved by an interior refrigerator article comprising a glass article, wherein said glass article comprises an antimicrobial surface region, wherein said antimicrobial surface region is provided by an antimicrobial effective amount of metal ions in the surface region.

Preferably the interior refrigerator article is a refrigerator shelving.

The invention can be further on applied in the following fields if a glass substrate has a antimicrobial glass surface: food contact, food display, food production, hospital equipment, medical devices, water treatment, water storage, water conducting, health care, hygiene products, white goods, kitchen and bathroom ware, table ware. The invention can also be applied in the field of dental products e. g. for providing antimicrobial dental products.

The following examples are illustrative of the invention and are intended to give those of ordinary skill in the art a more complete understanding of how the present process and articles of manufacture are to be achieved and evaluated. The examples are intended to be purely exemplary of the invention and are not intended to limit the scope of what the inventors regard as their invention. Efforts have been made to ensure accuracy with respect to numbers (e. g., amounts, temperatures, etc.), but some errors and deviations should be accounted for. Unless indicated otherwise, parts or percentages are parts or percentages by weight, temperature is in °C or is ambient temperature, and pressure is at or near atmospheric.

Antimicrobial testing was done according to the standard Tests ASTM 2180-01 with following microorganisms: *Pseudomonas. aeruginosa*, *Staphylococcus aureus*, *Aspergillus. niger*, *Candida albicans*, *Echerichia Coli* , und *Salmonella choleraesius*

5 Antimicrobial testing according JIS Z2801 was done with *Echerichia Coli* and *P. aeruginosa*.

Tests were stated as "passes" if an microbial reduction of two log scales was detected.

10 Furtheron an antimicrobial testing was done by the Proliferation method which is described in in Bechert et al., Nature Medicine Vol 6 2000 1053-1056
In this test the surface proliferation of microorganisms is detected by measuring the optical density of a solution which is in contact with the surface which has to be tested. The Proliferation test was done in all cases with *S. epidermis*. The
15 Proliferation test was stated as passed if the measurement of optical density showed a retardation the increase in optical density.

In a first example a soda-lime float glass having the following composition in weight-% with regard to the total composition:

20	SiO ₂	72,00 weight-%
	Al ₂ O ₃	0,30 weight-%
	Na ₂ O	14,50 weight-%
	MgO	2,80 weight-%
	CaO	10,40 weight-%

25 with a T(g) of 565°C according to embodiment 1 of table 3 are coated by screening standard technology with a metal-ion precursor having oil as a vehicle and 1 weigth-% of AgNO₃ as a metal ion. The film thickness was between 10 - 20 um.
The coated substrate was set into a furnace at first temperature of 550 °C for 10
30 minutes. The samples was cleaned with rinsing water for 1 minute. No significant discoloration of the glass samples was detected.

Then the ASTM 2180-01 Test and JIS Z2801 test was performed and passed.

In a further example a soda-lime float glass having the following composition in weight-% with regard to the total composition:

5

SiO₂ 72,00 weight-%

Al₂O₃ 0,30 weight-%

Na₂O 14,50 weight-%

MgO 2,80 weight-%

10

CaO 10,40 weight-%

with a T(g) of 565°C according to embodiment 1 of table 3 are coated by screening standard technology with a metal-ion precursor having oil as a vehicle and 2 weight-% of AgNO₃ as a metal ion. The film thickness was about 15 µm.

15

The coated substrate was set into a furnace at first temperature of 650 °C for 10 minutes. The samples was cleaned with rinsing water for 1 minute. Strong yellow discoloration of the glass samples was detected.

Then the ASTM 2180-01 Test and JIS Z2801 test was performed and passed.

20

In a further example a Ceriumoxid polished soda-lime float glass having the following composition in weight-% with regard to the total composition:

SiO₂ 72,00 weight-%

25

Al₂O₃ 0,30 weight-%

Na₂O 14,50 weight-%

MgO 2,80 weight-%

CaO 10,40 weight-%

30

with a T(g) of 565°C according to embodiment 1 of table 3 are coated by screening standard technology with a metal-ion precursor having oil as a vehicle and 2 weight-% of AgNO₃ as a metal ion. The film thickness was about 40 µm.

The coated substrate was set into a furnace at first temperature of 650 °C for 10 minutes. The samples was cleaned with rinsing water for 1 minute. No yellow discoloration of the glass samples was detected.

- 5 In EDX profile measurement were done to determine the silver penetration: the following are the values in weight-% found by EDX-measurement in dependency from the depth:
- 1um 0,3 wt%; 3 um 0,4 wt%; 5 um 0,4 wt%; 7um 0,3 wt%; 9 um 0,3wt%; 11um 0,2 wt%; 13um 0,3 wt% 15um 0,2 wt% 17um 0,1 wt%, 19um 0,1wt%; 21 um lower
- 10 than detection lever 0,1wt%
- The error of the measurement is in the range of 0,1 wt%

Then the ASTM 2180-01 Test and JIS Z2801 test was performed and passed.

- 15 In a still further example a soda-lime glass having the following composition in weight-% with regard to the total composition:

	SiO ₂	72,00 weight-%
	Al ₂ O ₃	0,30 weight-%
20	Na ₂ O	14,50 weight-%
	MgO	2,80 weight-%
	CaO	10,40 weight-%

- 25 with a T(g) of 565°C according to embodiment 1 of table 3 was polished on the atmosphere side (removal of about 1um) and then coated by screening standard technology with a metal-ion precursor having oil as a vehicle and 1 weight-% of AgNO₃ as a metal ion. The film thickness was about 15 um.
- The coated substrate was set into a furnace at a first temperature of 650 °C for 10 minutes. The samples was cleaned with rinsing water for 1 minute. No significant
- 30 discoloration of the glass samples was detected.

Then the ASTM 2180-01 Test and JIS Z2801 test was performed and passed.

In a even further example a soda-lime glass having the following composition in weight-% with regard to the total composition:

5	SiO ₂	72,00 weight-%
	Al ₂ O ₃	0,30 weight-%
	Na ₂ O	14,50 weight-%
	MgO	2,80 weight-%
	CaO	10,40 weight-%

10

with a T(g) of 565°C according to embodiment 1 of table 3 are coated with a metal-ion precursor having oil as a vehicle and 2 weight-% of AgNO₃ as a metal ion after being cleaned with a 5-weight% HF-solution for 5 minutes and a Ultrasonic treatment.

15

The coated substrate was set into a furnace at a first temperature of 650 °C for 10 minutes and rapidly cooled down by air cooling. The samples was cleaned with water for 1 minute. No discoloration of the glass samples was detected.

20

Then the ASTM 2180-01 Test and JIS Z2801 test was performed and passed. The glass was significant mechanical strengthend.

In a further example a soda-lime glass having the following composition in weight-% with regard to the total composition:

25

	SiO ₂	72,00 weight-%
	Al ₂ O ₃	0,30 weight-%
	Na ₂ O	14,50 weight-%
	MgO	2,80 weight-%
30	CaO	10,40 weight-%

with a T(g) of 565°C according to embodiment 1 of table 3 are coated with a metal-ion precursor having oil as a vehicle and 2 weight-% of AgNO₃ as a metal ion after being cleaned with 5 % HNO₃-solution for 20 minutes and a Ultrasonic treatment followed by 10% NaOH solution for 10 minutes..

5

The coated substrate was set into a furnace at a first temperature of 550 °C for 10 minutes and rapidly cooled down by air cooling. The samples was cleaned with water for 1 minute. No discoloration of the glass samples was detected.

10

Then the ASTM 2180-01 Test and JIS Z2801 test was performed and passed.

The same glass of example 1 was treated at only 150 °C 10 minutes and cleaned with water for 1 minute. The sample did not pass ASTM 2180-01 and JIS Z2801-Teste and therefore showed no sufficient antimicrobial effect.

15

In a further example a soda-lime glass having the following composition in weight-% with regard to the total composition:

	SiO ₂	72,00 weight-%
20	Al ₂ O ₃	0,30 weight-%
	Na ₂ O	14,50 weight-%
	MgO	2,80 weight-%
	CaO	10,40 weight-%

25

with a T(g) of 565°C according to embodiment 1 of table 3 was surface polished on the atmosphere side and coated by screening standard technology with a metal-ion precursor having oil as a vehicle and 1 weight-% of AgNO₃ as a metal ion. The film thickness was about 15 um. The glass sheet was dried in an IR-furnace for 15 minutes. In a next step inorganic decoration paste was screen

30

printed on the tin bath side of the flat glass and also dried in an IR-furnace for 15 min.

Then the coated substrate was set into a furnace at a first temperature of 650 °C for 10 minutes and cooled down by air blowing rapidly. The samples was cleaned with rinsing water for 1 minute. No yellow discoloration of the glass samples was detected. The ASTM 2180-1 Test and the Proliferation Assay was passed. The mechanical strength was according the requirements for window glass and glass shelves.

In an further example of the invention for which the results are shown in table 1 silver nitrate was added to Oil Ferro C38 as a vehicle to obtain the metal-ion precursor in a concentration as mentioned in Table 1 in the column Ag-conc in solution. The metal ion precursor material as a solution was screen printed on a float glass surface with a glass composition given in table 3, embodiment 1. The film thickness was about 10 µm. The samples then were dried in a first process step at 80 °C for 30 minutes. Thereafter the samples were introduced to a lab furnace. In the lab furnace the coated and dried glass-substrates were tempered at a second process-temperature given in Table 1 in column Temp/Time for the time given in Table 1 in the column Temp/Time. Then they were removed out of the furnace and cooled in air.

The results are shown in Table 1. In Table 1 is also shown the average concentration of silver ions down to a depth of 2µm of the substrate which was measured in an Surface Electron Microscope with EDX-Analysis.

Table 1: Soda Lime Float Glass (Type: Example 1 in table 3)

Ag-conc in solution	Temp/Time	2um Ag surf. conc	discoloration (b< 4)	ASTM 2180 passed	Proliferation Test passed	JIS Z 2801 passed
0,5	400//10min		No		Yes	
0,5	450//10min		No		Yes	
0,5	650//10min		No		Yes	
0,6	490//10 min	0,9	No			yes
0,6	550//10 min	0,5	No			yes
0,6	650//10 min	0,3				
0,6	740//10min	0,2				
0,6	650//10 min	0,5	No	no		no
0,6	100°C//10 min	<0,1	No	No		No
1	480//10 min		No		Yes	
1	550//10min		No			
1	550//30min		No			
1	650//10min		Yes			
1	740//10min		Yes	No		
2,0	350//30 min		No		Yes	
2,0	450//30 min		No		Yes	
2,0	500//30 min		No	Yes		
2,0	550//10 min	1,8	No	Yes		
2,0	650//10 min	1,1	Yes	yes		yes
2,0	650//10 min	1,3				
2,0	650//20 min	0,6	Yes	no		no
2,0	740//10min	0,8	Yes			
4,0	400//30 min		No	Yes	Yes	
4,0	550// 10 min	3,6	No	Yes		

4	650// 10 min	2,4	Yes	Yes		
4	740//10 min	1,9	Yes	Yes		

The surface concentration was determined by EDX in a SEM.

As is apparent from table 1 the antimicrobial efficacy crucial depends on the silver ions concentration at the surface of the glass or the concentration of ions which can reach the surface e.g. by diffusion processes during the application. This "active" silver concentration depends on the following processing parameters:

- Silver precursor concentration in the solution;
- thickness of the solution film on the glass substrate,
- Temperature/Time regime of the whole processing.

The temperature/time regime is very important because if temperature and time are too low not enough antimicrobial ions can bond to or introduce the surface of the substrate and are washed off the substrate by simple cleaning processes. If temperature and time are too high, the antimicrobial ions will penetrate too deep into the glass and are no longer active in a sufficient amount at the surface in the application. In specific cases the surface might be tempered several times because of production reasons (e.g. a further tempering step to burn in a color or decoration layer) in such a case the overall integral temperature/time process has to be taken into account.

In a further example a concentration of 0,6 weight-% AgNO_3 and 2 weight-% ZnNO_3 was dispersed in C38 Oil as a vehicle for the metal ion precursor with a mixer. The metal ion precursor as a solution was then screen printed on the air side of the floatglass with a thickness of the layer of approx. 10 μm . The floatglass is also a Soda-lime glass with a composition according to embodiment 1 in table 3.

For different samples of sodalime-glass substrates, all of them comprising the glass composition according to embodiment 1 of table 3, which were treated with a metal-ion precursor material consisting of C38 Oil as a vehicle and different concentrations of AgNO_3 as metal ions and thereafter temperature-treated

in a furnace at 650 °C for different temper times e.g. 15 min and then again removed and cooled in air, the silver concentration profile over the depth of the substrate was measured. The results are shown in Table 2.

Table 2: SEM-EDX Analysis to evaluate the silver concentration profile over the depth of the substrate dependent from tempering time

ASTM -test AM- effect			AgNO ₃ conc. of the metal ion precursor in weight- %	temper time	Depth surface (Average of about first 2 μ m)	Depth 1 μ m	Depth 2 μ m	Depth 3 μ m	Depth 4 μ m	Depth 5 μ m
No			0,6 %	650//15 min	0,5	0,5	0,6	0,1	0	0
es			4 %	650//15 min	1,1	1,1	0,7	0,2	0,2	0
o			0,6	650//15 min	0,5	0,4	0,2	0,1	0	0
			2 %	650//15 min	1,3					
			4 %	650//15 min	2,4					
			0,6	650//10 min	0,3					
no			0,6	680//10 minmin15	0,2	0,2	0,3	0	0	0
yes	yes	yes	2	680//10min	0,8	0,7	0,2	0,2	0	0

- 5 As is apparent from Table 2 an antimicrobial effect or a so called AM-effect according to the this experiments for a surface concentration of about 0,8 wt% is sufficient to pass. This means, the parameters for the temper temperature, the duration of tempering as well as the concentration of Ag-ions in the precursor material have to be chosen according to the invention such, that a surface
- 10 concentration of Ag-ions of more than 0,8 weight -% results.

Then a antimicrobial effect, which is sufficient to pass the ASTM-test is achieved. As is apparent from table 1 a surface concentration greater than 0,8 weight-% is necessary for an antimicrobial effect, to pass the ASTM-Test.

Figure 1 shows the transmission spectra of floatglass samples which were tempered at different temperatures between 550 and 740 °C. The composition of the floatglass was according embodiment 1 in Table 3. The concentration was 4 weight-% AgNO₃ in the metal-ion precursor-solution. The samples were introduced into a furnace at different temperatures for 10 minutes, removed again and cooled down in air. Reference number 10 denotes a temperature of 500°C, 14 denotes a temperature of 600°C, 16 denotes a temperature of 650°C, 18 denotes a temperature of 680°C, 20 denotes a temperature of 700°C and denotes a temperature of 750°C. As is apparent from Figure 1 the higher the temperature for tempering the more a significant absorption bands can be seen which are caused by the absorption of silver nano particles.

In Figure 2 is shown the concentration-profile of Ag-ions implanted into the surface of the substrate by the inventive technique depending onto the temperature of the substrate. This measurement was done by EDX-Analysis. The first measuring point was taken at depth of about 5 µm from the glass surface. Ag concentration is plotted in arbitrary units. As can be seen from figure 2, the Ag-ions are penetrating the glass deeper with increasing temperature. Points 100 denotes a sample which was tempered with 650°C, points 110 denotes a sample which was tempered with 550°C and points 120 denotes a sample which was tempered with 740°C.

Figure 3 of the same sample as in figure 2 shows the silver concentration in the first 5 µm depth measured with WDX-Analysis. The WDX-Analysis has a higher spatial resolution than EDX-Analysis. The Ag diffusion in a bulk surface for 2 samples is shown. The first sample was a sample of a glass substrate coated with a metal-ion precursor- solution having a content of 0,6 weight-% AgNO₃. The points for sample 1 is denoted with 200. Sample 2 was coated with a metal-ion-precursor solution having a content of 2 weight-% AgNO₃. The points for sample 2 is denoted with 210. Both samples were tempered at 650°C for 15 min. As is apparent from Figure 3 the silver surface concentration is about 3 times higher for

the sample produced from the metal ion precursor solution having 2 weight-% AgNO_3 than from the metal ion precursor solution having 0,6 weight-% AgNO_3 . The glass-substrates for both samples are sodalime glass substrates with a composition according to table 3, embodiment 1. The significant difference in there near surface concentration of silver can be seen.

As is apparent from the foregoing paragraph the Ag-concentration to pass the ASTM test should be higher than about 0,8wt% Ag at the surface. This is measured preferably by EDX with a information depth of about 2 μm .

The silver salt concentration of the solutions is limited by the solubility of the silver salt. If the concentration is in the range of the solubility silver salt particles can be detected by SEM on the flat glass surfaces. E.g. in Oil C38 the solubility limit of AgNO_3 is around 3 wt%. Tempering should be done in oxidizing conditions to avoid reduction of silver.

To determine the ion-release out of the glass substrate with an antimicrobial surface provided by the process described above, the glass substrates were treated with a aqueous solution comprising 3 weight -% acetetic acid for 10 days and a temperature of 40°C. The release surface was 100 cm^2 .

As is apparent from the forgoing the release of Ag is lower than 0,08 mg/l, the value allowed according to the German law related to drinking water (so called Trinkwasserverordnung).

In the following table 3 further composition of glasses are given, which can be used to practice the invention:

Table 3: Glass composition for various embodiments (emb.) of the invention

	Emb. 1	Emb. 2	Emb. 3	Emb. 4	Emb. 5	Emb. 6	Emb. 7	Emb. 8	Emb. 9	Emb. 10	Emb. 11	Emb. 12
SiO ₂	72,00	73,50	64,10	80,80	69,90	79,00	50,40	61,20	76,50	64,30	71,20	69,10
B ₂ O ₃		10,00	8,40	12,70	11,20	10,40	13,40	7,90	5,00			1,00
Al ₂ O ₃	0,30	6,70	4,20	2,40		4,20	11,80	16,30	3,40	21,50	0,35	4,00
Li ₂ O										3,65		
Na ₂ O	14,50	6,60	6,40	3,50	9,70	4,60	0,10		8,10	0,70	14,10	12,70
K ₂ O		2,60	6,90	0,60	7,30	0,80						3,30
MgO	2,80							2,80			4,00	2,70
CaO	10,40	0,60			0,25	1,00		8,30			9,60	5,00
SrO							0,30					
BaO					1,50		24,00	3,50	5,00	2,40		2,20
ZnO			6,00							1,20		
TiO ₂			4,00		0,15					2,30		
ZrO ₂										1,60		
Sb ₂ O ₃										1,50		
Fe ₂ O ₃										0,15	0,10	
CoO										0,30		
NiO										0,40		
F									2,00			
α	5,40	5,40	7,20	3,30	8,30	4,05	4,54	3,77	5,60	4,20		
T _g	565	565	557	525	559	580	627	716	550	673		530
VA	1189	1189	1051	1270	968	1280	1215	1263		1305		1040
Temper ature	350,0	600,0 0	600,0 0	520,0 0	650,0 0	620,0 0	550,0 0	80,00	650,0 0	720,0 0	650	610
Time	30 min	3 min	5 min	3 min	10	10	10	10	10	15	10	10
Solution	water	Water	Water	C38	Water	Water	C38	Oil	Oil	C38	C38	C38

37

				Oil			Oil					
Conc Ag	2% Nitrat e	2% Nitrat e	1	2	2	2	2	1	1	1	1	1
Conc Zn			1Nitra te									
Conc Cu			0,2 Sulfat e					0,2 Sulfat				
Prolif- eration passed	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
Summe	100,0 0	100,0 0	100,0 0	100,0 0	100,0 0	100,0 0	100,0 0	100,0 0	100,0 0	100,0 0		

In table 3 T_g denotes the transformation temperature of glass and VA the processing temperature.

In a further example an alkaline free glass according to embodiment 8 in table 3 was screen printed with C38 Oil with 2 wt% AgNO_3 . The sample was introduced into a furnace at 800 °C for 20 minutes and afterwards cooled down in air. The samples passed the antimicrobial proliferation test and the JIS Z2080 test.

In Figure 4 TOF-SIMS measurement of an untreated soda lime float glass surface (atmosphere side) according to example 1 in table 3 (standard float glass which is used most of the experiments is shown.

An increase of the tin concentration (Sn-concentration) at the surface can be seen. **The curve for the tin-concentration is denoted with reference number 300.**

Figure 5 shows an TOF-SIMS measurement of an example with reduced Ag-concentration in the first 50 nm and a Silver plateau down to about 2 μm . Samples is according Table 1 with a Ag-concentration in solution of 2wt%, a temperature of 650 °C and a temper time of 10 min.

5 Figure 6 shows the reduction of Yellowing of soda lime glass due to chemical etching. Soda lime Float glass was pretreated with in a 4% HF solution in a ultrasonic bath for different times and treated with a 2% solution of AgNO_3 . The samples introduced in a furnace for 10min at about 650 °C The color index b^* is the index for yellow color and therefore for the yellowing.

What is claimed is:

1. Article having a antimicrobial surface with a metal ion concentration, especially a Ag-concentration in a depth of about 0 μm to about 2 μm of the article measured from the surface higher than 0,6 wt%, preferably 0,8 weight-%, most preferably 1 weight-%.
2. Article according to claim 1 wherein the ratio of the concentration of the metal ions in a depth of about 1 μm to the concentration in a depth of about 10 μm is greater than 10.
3. Article according to claim 2 wherein the ratio of the concentration of the metal ions in a depth of about 1 μm to the concentration in a depth of about 10 μm is greater than 5.
4. Article according to claim 1, wherein the ratio of the concentration of the metal ions in a depth of about 1 μm to the concentration in a depth of about 5 μm is smaller than 0,5 and wherein the ratio of the concentration of the metal ions in a depth of about 5 μm to the concentration in a depth of about 10 μm is greater than 10.
5. Article according to claim 1, wherein the ratio of the concentration of the metal ions in a depth of about 30nm to the concentration in a depth of about 1 μm is smaller than 0,5 and wherein the ratio of the concentration of the metal ions in a depth of about 10 μm to the concentration in a depth of about 1 μm is smaller than 0,2.
6. Article according to one of the claims 1 to 5, wherein the metal ion concentration in a depth more than 10 μm of the article measured from the surface is lower than 0,1 wt%

7. Article according to one of the claims 1 to 6, wherein the concentration of the metal ions is such, that according to the JIS Z2801-test a reduction of microorganisms by two log scales is provided.
- 5 8. Article according to one of the claims 1 to 6, wherein the concentration of the metal ions is such, that according to the ASTM 2180-test a reduction of microorganisms by two log scales. Is provided.
- 10 9. Article according to one of the claims 1 to 6, wherein the concentration of metal ions is such, that in a proliferation test the OD parameter is higher than 15.
- 15 10. Article according to one of the claims 1 to 6, wherein the concentration of metal ions is such, that according to a Hemmhof test according EN 1104 no reduction of microorganime growth can be detected
- 20 11. Article according to one of the claims 1 to 6, wherein the concentration of metal ions is such, that according to a test according to the German "Lebensmittel " law the leaching rate of the metal ions is lower than 0,08 mg/ml
- 25 12. Article according to one of the claims 1 to 6, wherein the concentration of metal ions is such, that the leaching rate of the metal ions is lower than 0,08 mg/ml according to the German "Trinkwasserverordnung".
- 30 13. Article according to one of the claims 1 to 12, wherein the article comprises a glass- or glass ceramics or glass-like like emails substrate.
14. Article according to claim 13, wherein
said glass- or glass like structure is choosen from one of the following materials:
- alkali containing floatglass

- alkalin free glass
- alkaline earth glasses
- sodalime-floatglasses
- display glasses

5 glass ceramics

- borosilicate glass

15. Article, wherein said article is choosen from one of the following materials:

- alkali containing floatglass
- alkalin free glass
- alkaline earth glasses
- sodalime-floatglasses
- display glasses
- glass ceramics
- borosilicate glass

and said article contains within a depth of 10 μm from the surface a concentration of an antimicrobial metal ion in an amount sufficient to create a antimicrobial surface to said article.

16. Article according to one of the claims 1 to 15, wherein the antimicrobial metal ions are choosen from the group of Ag, Zn, Cu, Sn, I, Te, Ge, Cr

17. Article according to one of the claims 1 to 16, wherein the antimicrobial metal ion is Ag or a combination of Ag with Zn, Cu, Sn, I, Te, Ge, Cr.

18. Article according to one of the claims 1 to 17 wherein the transmission at a wavelength of about 420 nm is higher than 60 %, preferably higher than 70, more preferably higher 80 and 85 and wherein the article has a thickness of about 4 mm.

19. Article according to one of the claims 1 to 18 where in the substrat is used for home appliance applications, especially special for

oven doors

5

refrigerator shelves

freezer shelves

glass cooktops

microwave doors

hoods

10

glass panels

touch panels

glassceramic cooktops

20. Article according to one of the claims 1 to 18 where in the substrat is used for sanitary applications, especially for

15

glass boards

shower cabinets

wall and floor tiles

drinking glasses

20

sanitary assesories

personal scales

21. Article according to one of the claims 1 to 18 where in the substrat is used for pharmaceutical packaging applications .

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22. A method of preparing an article with an antimicrobial surface comprising the steps of

- a) depositing a liquid, a solution, a dispersion, a emulsion which contains at least one antimicrobial effective ion or a precursor of these ion on at least apart of the surface of said article by spraying, rolling, screen printing, printing, dipping, casting

30

b) heating the article to a temperature within a temperature range of from about 200°C lower than the transformation temperature of the material of the article to about 200° C higher than the transformation temperature of the material of the article for a period of from about 2 min to about 30 min, to introduce antimicrobial effective metal ions into any surface of the substrate on which said precursor was deposited,

23. Method according to claim 22, wherein the temperature range is about 200°C lower than the transformation temperature of the material of the article to about 200° C higher than the transformation temperature of the material of the article without the temperature range from about 600°C to about 650°C.

24. Method according to claim 22 or 23, wherein between the step of depositing a metal ion precursor onto the article and heating the article a further process step of heating the article to temperatures higher than evaporation temperatures of the volatile components to remove them from the surface is introduced.

25. Method according to one of the claims 22 to 24, wherein in step b.) the material of the article is heated to a temperature within a temperature range of from about 50°C lower than the transformation temperature of the article to about 200 ° C higher than the transformation temperature of the material of the article for a period of from about 2 min to about 15 min, to introduce antimicrobial effective metal ions into any surface of the substrate on which said metal ion precursor was deposited.

26. Method according to one of the claims 22 to 25, wherein the article comprises a glass- or glass-like substrate.

27. Method according to claim 26, wherein said glass- or glass like structure is chosen from one of the following materials:
- alkali containing floatglass
 - alkaline free floatglass
 - alkaline free glass
 - alkaline earth alkaline glasses
 - soda lime float glasses
 - display glasses
 - glass ceramics
 - lithium aluminosilicate glass ceramics
28. Method according to claim 27 wherein for a soda lime floatglass the tin containing surface layer is mechanically removed before onto the substrate metal-ion precursor is deposited.
29. Method according to claim 27 wherein for a soda lime floatglass the tin containing surface layer is chemically removed before onto the substrate metal-ion precursor is deposited.
30. Method according to one of the claims 22 to 29 wherein the glass surface area is increased or decreased by mechanical grinding and polishing to control the antimicrobial efficacy.
31. Method according to one of the claims 22 to 29 wherein the glass surface area is increased or decreased by chemical polishing or chemical treatments to control the antimicrobial efficacy.
32. Method according to claims 22 - 29 wherein the glass surface, especially the float glass surface is mechanically grinding and/or polishing to avoid coloring.

33. Method according to one of the claims 22-29 wherein the glass surface is , especially the float glass surface is washed and chemically etched to avoid coloring.

FIG. 1

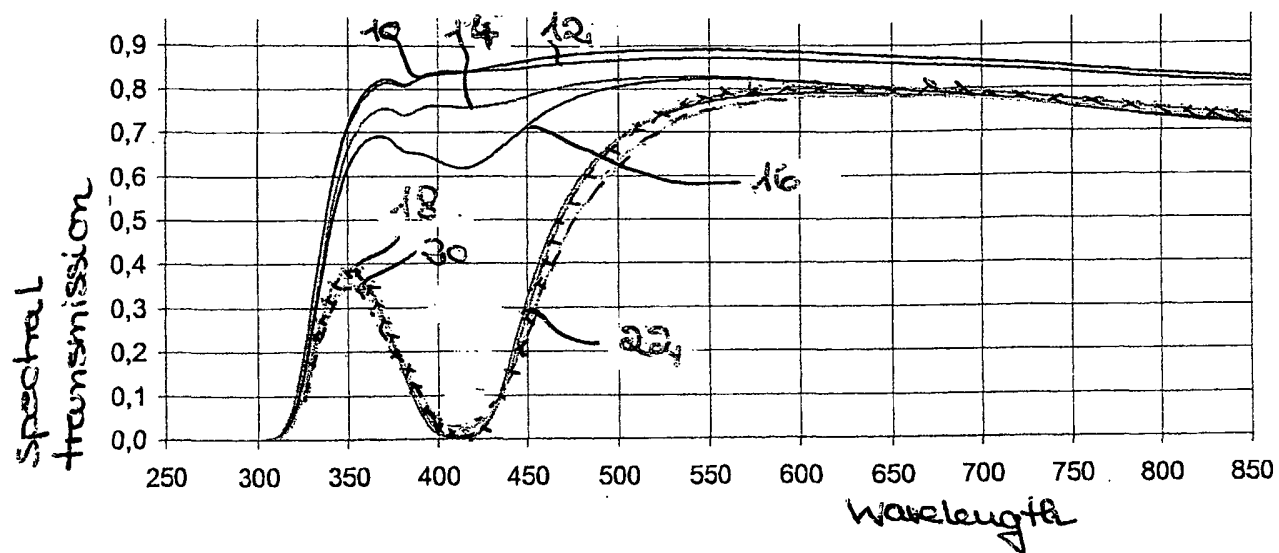


Figure 2 : concentration of Ag-ions depending from the depth at different temperatures. (First measuring point 5 μm depth)

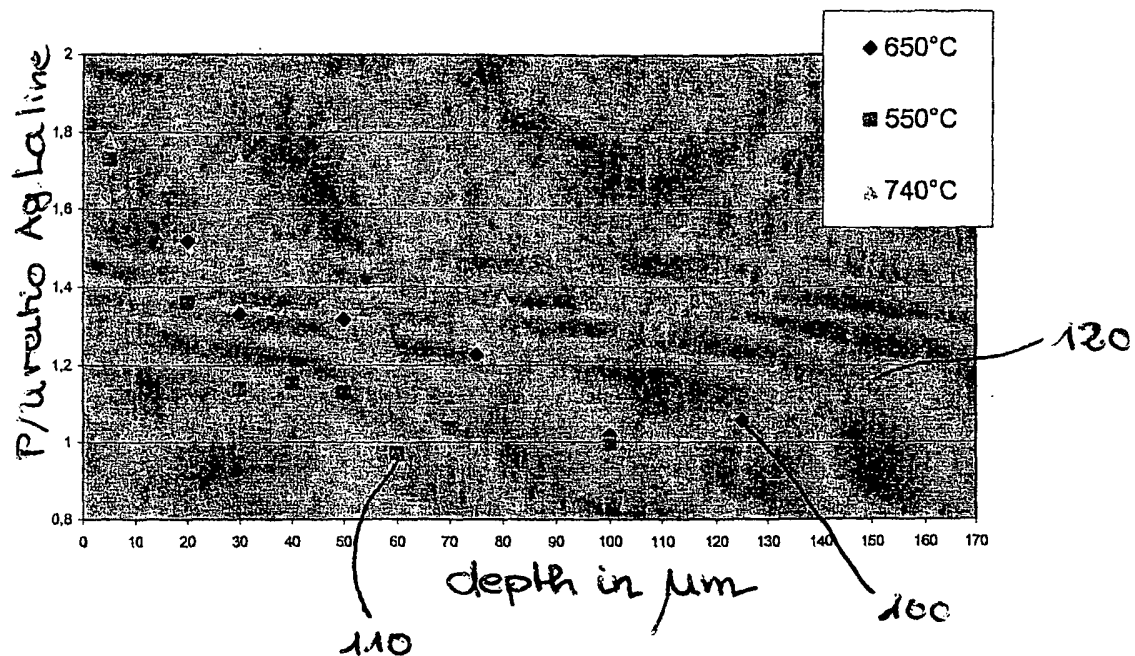


Figure 3: concentration of Ag ions depending from the depth for different substrates (First measuring point 1 μm depth)

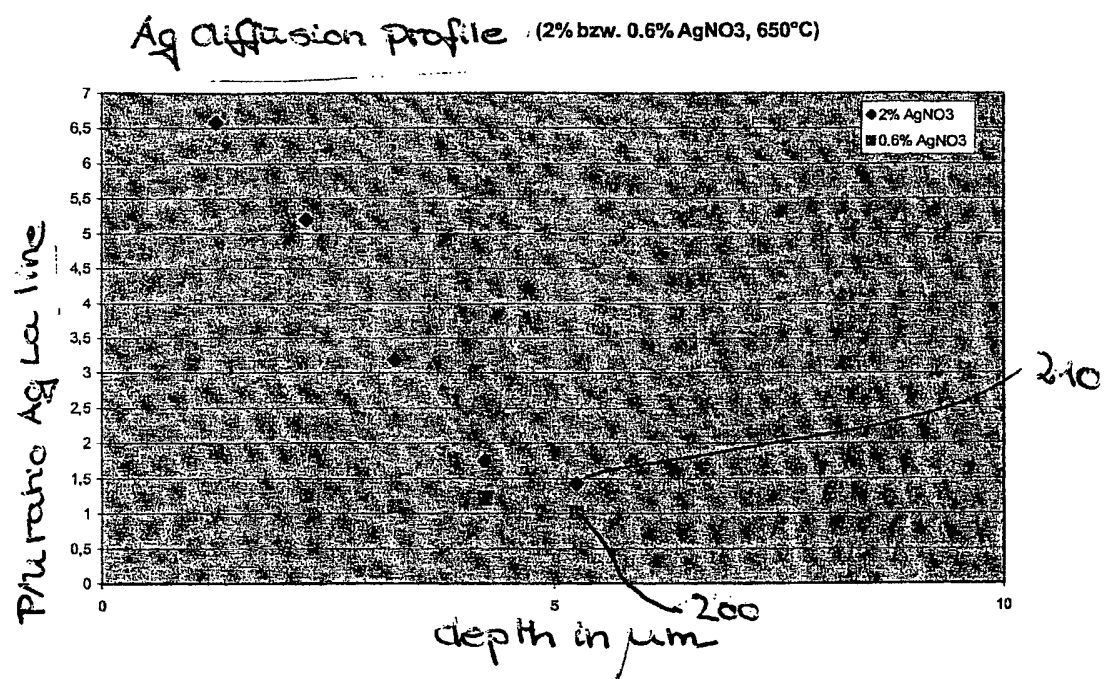


Fig. 4

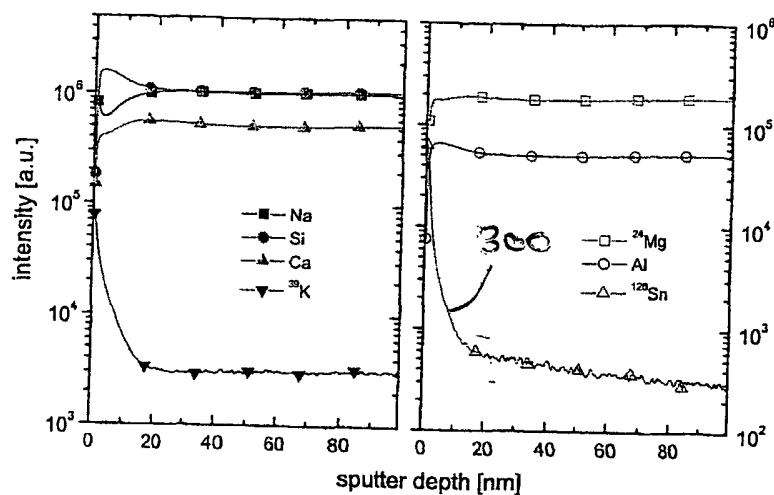


Figure 5 TOF-SIMS cleaned surface with reduced Ag-concentration in the first 50 nm and a Silver plateau down to about 2 μm .

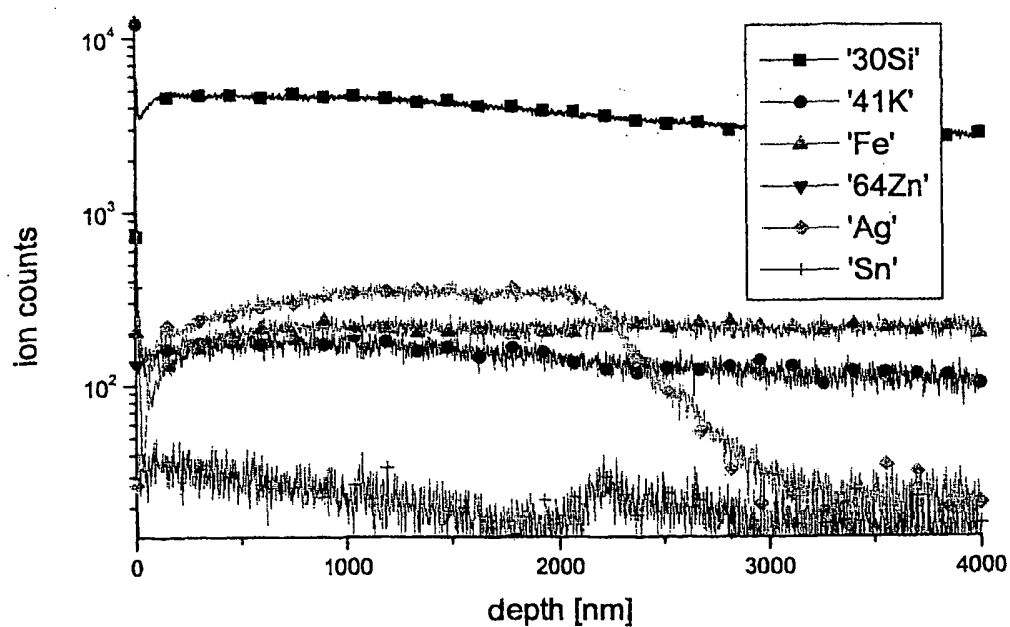


FIG. 6

