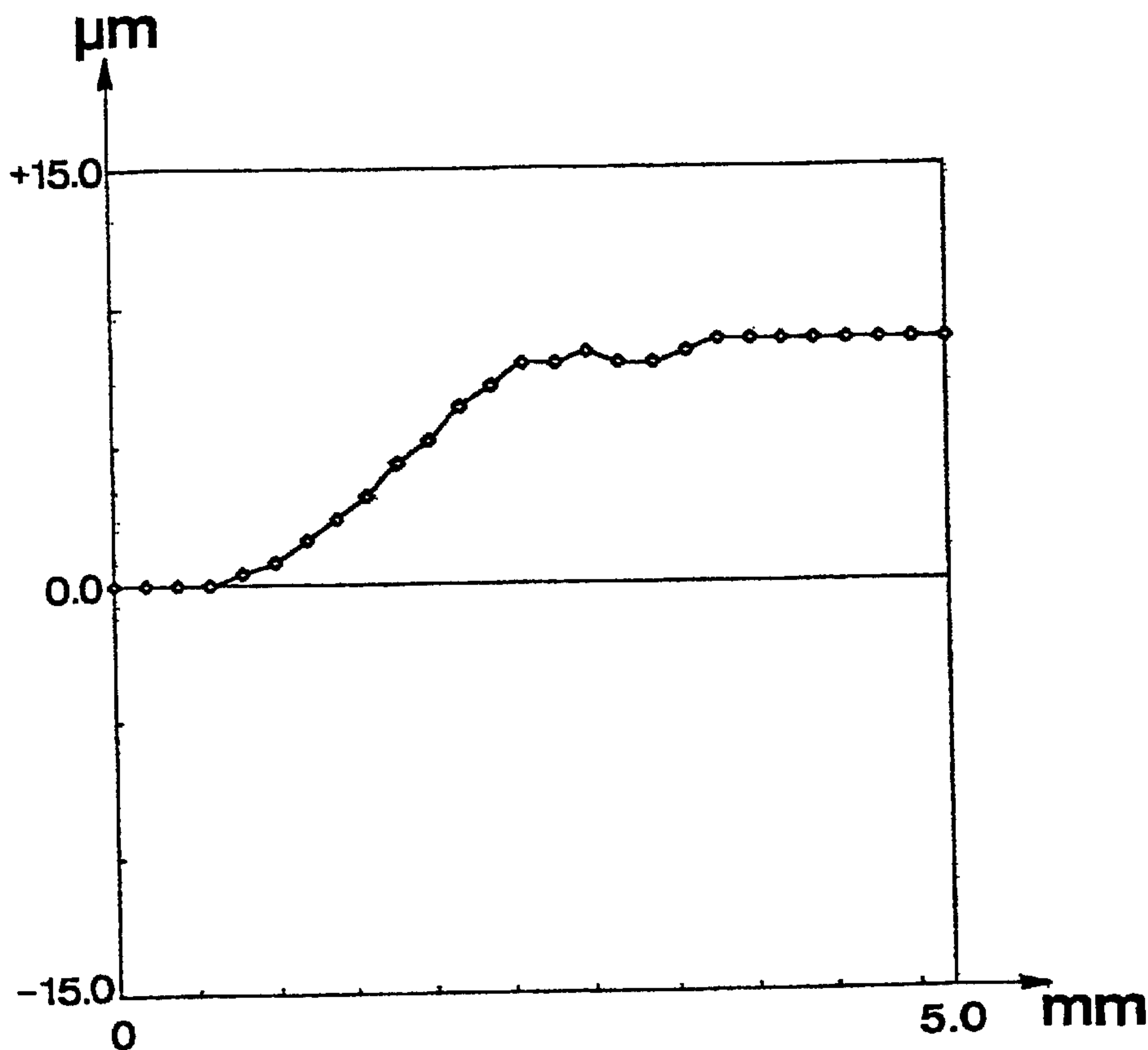




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(54) Titre : PROCÉDE DE PREPARATION DE FILMS VITREUX EPAIS EN SILICE OU A BASE DE SILICE SELON LA  
 TECHNIQUE SOL-GEL, ET FILMS EPAIS AINSI OBTENUS  
 (54) Title: SOL-GEL PREPARATION OF SILICA OR SILICA-BASED VITREOUS FILMS



(57) Abrégé/Abstract:

A sol-gel process allowing the preparation, on a substrate, of glassy films of silicon oxide or mixed oxides based on silicon oxide, of thickness above 1 micrometer, generally between 2 and 20 micrometers. They are characterised by absence of defects, and are particularly suitable as waveguides in flat optical devices.

Abstract

A sol-gel process allowing the preparation, on a substrate, of glassy films of silicon oxide or mixed oxides based on silicon oxide, of thickness above 1 micrometer, generally between 2 and 20 micrometers. They are characterised by absence of defects, and are particularly suitable as waveguides in flat optical devices.

## **Sol-Gel Preparation Of Silica Or Silica-Based Vitreous Films**

The present invention relates to a sol-gel process for the preparation of thick glassy films of silicon oxide, or based on silicon oxide and to the thick films thus  
5 obtained.

In the technology of solid state, with the term "film" is meant a thin layer of a material having a thickness generally comprised between a few tens of nanometers (nm) and a few tens of micrometers, the layer being supported over a substrate of another material, generally of flat geometry.

10 The term "thick" typically refers to films of thickness greater than 1  $\mu\text{m}$ .

Thick glassy films, deposited over a suitable substrate, are the object of extensive research in view of their foreseen use in the field of telecommunications, particularly telecommunications on optical and electro-optical cables.

15 In the past, telephone communications and data transmissions were realised by transforming the signal into electronic impulses that were transmitted by means of cables of an electrically-conductive material, generally copper.

20 Nowadays, in particular for long distances, transmissions on electrical cables have been almost completely replaced by transmissions on optical fibers. As known, the optical fibers are glassy fibers whose structure comprises at least a central part, called nucleus, and an outer part, called mantle, made of glasses having slightly different chemical compositions; the different chemical composition gives rise to a difference in the refractive index of the two materials that allows confining the optical signal in the nucleus. Commonly the mantle is made of pure silicon oxide, whilst the nucleus is made of a mixed oxide based on silicon oxide containing from a few  
25 percent to about 10% by mole of different oxides such as germanium oxide.

Optical fibers offer several advantages over electrical cables as means for information transmission, such as a lower level of noise and lower signal attenuation, as well as a higher amount of information transmitted per unit time, resulting in a higher transmission rate.

30 Despite these advantages, it has not been possible so far to fully exploit the potential of optical communications; in fact, a complete communication system requires devices for processing signals, for instance for transforming voice into signal at the two ends of the cable in telephonic transmissions, or for amplifying the signal along the fibre, that is rendered necessary due to unavoidable attenuation of

the same signal. More generally, the so-called operation of signal commutation that is needed for delivering the same signal in the network requires suitable devices.

To this end, traditional electrical devices (electronic switches) presently are used, and generally any operation on the signal requires a conversion into an electrical signal, followed by a possible further conversion back to optical signal. In these operations time and signal quality are lost. As a consequence, a strong need is felt for optical or electro-optical devices capable of guiding an optical signal, as well as of performing on it commuting operations comparable to those operated by electronic devices on electrical signals.

The main features that optical devices must have, are:

- material of very high transmittance, requiring absence of inclusions and mechanical defects;
- possibility of controlling through chemical composition the refractive index, that must be at least a few percent units higher than that of surrounding materials;
- flat geometry, for easy fit into automated production lines;
- thickness of a few  $\mu\text{m}$ , preferably between 2 and 20  $\mu\text{m}$ .

In order to ease integration of these devices into production and communication lines, the substrate should preferably be made of silicon or silicon oxide.

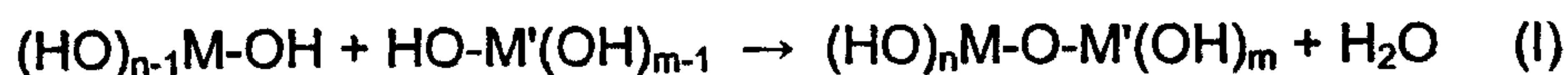
Such devices presently are produced according to physical techniques, among which thermal oxidation of silicon, and those known as Sputtering, Chemical Vapor Deposition and Flame Hydrolysis, can be cited. Another method consists in the vacuum deposition on a silicon substrate of microparticles of silicon oxide obtained according to the Flame Hydrolysis technique.

However, these productions are complex, requiring costly working chambers and tools; some of these, such as silicon thermal oxidation, have a limit in the film thickness that can be obtained, while others are exceedingly slow and are often characterised by low productivity and too high costs, so as not to allow an actual industrial exploitation of optical devices.

The most economically promising technology for massive production of glassy films on substrates is sol-gel. Under the terminology sol-gel are gathered different procedures for the preparation of oxides of one or more elements in form of porous bodies, ceramics or glasses.

While differing from each other in the specific details, all sol-gel procedures share the following steps:

- preparation of a "sol", a solution or suspension in water, alcohol or hydroalcoholic mixtures of precursors of the elements whose oxide is to be prepared. Generally used as precursors are the alkoxides, of formula  $M(OR)_n$ , where M represents the element whose oxide is desired, the group -OR is the alkoxide moiety, and n represents the valence of element M; soluble salts of the element M, such as chlorides, nitrates and exceptionally oxides, may be used in place of alkoxides. During this phase the precursors begin to hydrolyse, that is, alkoxide moieties or other anions bonded to element M are replaced by -OH groups;
- sol gelation, requiring from a few seconds up to some days, depending on chemical composition and temperature of the solution; during this phase hydrolysis of the possibly remaining precursor is completed and condensation occurs, consisting in the reaction of -OH groups belonging to different molecules with formation of one free water molecule and an oxygen bridge between atoms M, M' (alike or different), according to the reaction:



- The product obtained in this phase is called alcogel, hydrogel depending on the cases, or more generally "gel" as widely used in the English-language literature;
- gel drying. In this phase the solvent is removed by simple evaporation or through hypercritical transformation into gas inside an autoclave; there is obtained an extremely porous dry body, that may have an apparent density ranging from about 10% to about 50% of the theoretical density of the oxide of that composition;
- dry gel densification by thermal treating at a temperature generally between 800 °C and 1200 °C depending on the gel chemical composition and on the parameters of the previous process phases. In this phase the porous gel densifies obtaining a glassy or ceramic compact oxide of theoretical density, with a linear shrinkage of about 50%.

If the gelation phase is not too fast, it is possible to lay a liquid film of sol on a substrate, eventually resulting in a oxide-supported film. Obtaining an oxide film on a substrate in this way is, however, easily feasible only for a thickness up to some tenths of micrometer. Up to such values of thickness, cohesive forces in the film are

weak, and forces adhering the film on the substrate prevail, so that during the densification phase there is not in-plane shrinkage of the film and densification only involves its thickness decrease. At values of thickness above one micrometer, on the other hand, inner cohesive forces of the film become prevailing, and during  
5 densification in-plane shrinking of the film takes place as well. The result is film fragmentation into "islands" spread over the substrate surface and poor adhesion of the film to the substrate.

This thickness of about 1  $\mu\text{m}$  represents a technological limit for sol-gel technique, as indicated for instance in "Sol-Gel Science: The Physics And Chemistry  
10 Of Sol-Gel Processing", Brinker and Scherer, Academic Press, 1990, a comprehensive review of the knowledge in the field. As already stated above, films prepared in this way are defined thin or thick when they have a thickness below or above about 1  $\mu\text{m}$ , respectively.

For the production of thick films through the sol-gel technique it has been  
15 proposed to prepare a sol containing, in addition to normal precursors, a dense material in the form of nanospheres, that is, spheres of dimensions of about 10 nm. This approach is exposed in the paper "Sol-Gel Derived Thick Coatings And Their Thermomechanical And Optical Properties", Menning et al., SPIE Vol. 1758, Sol-Gel Optics II (1992), pages 125-134. This technique however can hardly be implemented  
20 practically; besides, despite the fact that the first papers on the technique were published more than five years ago, actual feasibility of thick films by this route has not been proven yet.

Another proposed approach is to prepare thick films through repeated  
depositions of thin films; any single layer must be densified before deposition of the  
25 subsequent layer. An example of this kind of procedure is given in "Deposition Of Thick Silica-Titania Sol-Gel Films On Si Substrates", Syms et al., Journal Of Non-Crystalline Solids, 170 (1994), pages 223-233. According to the literature, by this way it is possible to prepare multilayer thick films. On the other hand, as stated in the cited paper, in order to obtain films of good mechanical and optical  
30 characteristics any single layer must have a thickness not greater than about 0.25  $\mu\text{m}$ , so that the production of a film of thickness about 10  $\mu\text{m}$  requires about 40 deposition and densification steps.

Thus, the production of large amounts of flat waveguides by the sol-gel route still is an open problem.

It thus is an object of the present invention to provide a sol-gel process for the preparation of thick glassy films of silicon oxide or based on silicon oxide, as well as to provide glassy supported films of thickness higher than 1  $\mu\text{m}$ , preferably between 2 and 20  $\mu\text{m}$ .

5 In accordance with this invention, a sol-gel process for the preparation of a vitreous film of silicon oxide or of a mixed oxide containing silicon oxide and having a thickness greater than 1  $\mu\text{m}$ , comprises the steps of: preparing a sol comprising a soluble silicon precursor and optionally a soluble precursor or precursors of the elements Ge, C, Sn, Pb, P, As, Sb, B, Al, Ga, Bi, Ti, Zr, S and Hf, in which the molar  
10 ratio of the soluble silicon precursor to any other soluble precursors is at least 1:1, and in which the sol contains at least 10 mols of  $\text{H}_2\text{O}$  per each mole of the soluble precursor or precursors and an acid capable of causing hydrolysis of the precursor or precursors, the acid having a concentration between 0.03 and 0.5 N; completely hydrolysing the precursor or precursors; adding to the sol from 0.7 to 3.0 mols of  
15  $\text{SiO}_2$  per mole of the silicon precursor and any optional precursor(s); forming a film of the sol on a substrate; gelling the sol film through solvent evaporation; and densifying the gel film thus obtained through thermal treatment.

According to another embodiment the sol-gel process for the preparation of a vitreous film of silicon oxide or of a mixed oxide containing silicon oxide includes the  
20 step of preparing a sol from a solution or a suspension of one or more precursor elements in water, alcohol or a hydroalcoholic mixture, the one or more precursor elements comprising silicon and, optionally, one or more other elements selected from germanium, aluminum, boron, titanium and zirconium; the molar ratio of the silicon precursor to the sum of the optional other precursor elements being greater  
25 than or equal to 1:1, and the sol comprising a water solution and an acid containing at least 10 moles of  $\text{H}_2\text{O}$  per each mole of the one or more precursor elements and having a pH between 0.3 and 1.5, to form the sol. The precursor element or elements are hydrolysed, and 0.7 to 3.0 moles of  $\text{SiO}_2$  per mole of the precursor element(s) are added. A film of the sol is formed on a substrate, the sol film is gelled  
30 through solvent evaporation, the gelling being initiated by introducing the sol film into an oven preheated to a temperature from 300° C. to 400° C, and the resulting gel film is densified through thermal treatment to form a vitreous film.

The invention now will be described in detail with reference to the accompanying drawings, in which:

Figure 1 shows the result of a profilometric test on a sample of the invention before the densification operation, showing sample thickness variations along a line that crosses the film edge;

5 Figure 2 shows the result of a profilometric test on the same sample of Figure 1 after densification;

Figure 3 is a schematic view of a sample of the invention, obtained according to the interferometric technique in order to put in evidence possible defects of substrate-film interface; and

10 Figure 4 shows another image of the same sample and with the same view of Figure 3, with the only difference that the image in Figure 4 has been obtained according to the "dark field" technique, as explained below.

In the first phase of the process according to the invention there is prepared an extremely diluted sol of a silicon alkoxide or of a mixture of alkoxides corresponding to the desired glassy composition. In mixed oxides, the molar ratio  
15 between silicon oxide and oxides of other elements may be 1:1 or higher in the case of germanium, while it is generally not lower than 5:1 when elements such as titanium, aluminium or boron are employed.

This sol preferably is of very low concentration and is obtained using at least 10 mols of H<sub>2</sub>O per mole of alkoxides, preferably from about 20 to about 100 mols of  
20 H<sub>2</sub>O per mole of alkoxides, and more preferably from about 30 to about 40 mols of H<sub>2</sub>O per mole of alkoxides. Preferred alkoxides are those where the alcoholic moiety comes from methyl or ethyl alcohol, as these alkoxides are easily hydrolysed and the resulting alcohols may be easily removed by evaporation. Taking silicon as an example, silicon alkoxides may also be defined as silicic acid ortho-esters, and are  
25 known in the field as TMOS, which is the acronym for Tetra-Methyl-Ortho-Silicate, Si(OCH<sub>3</sub>)<sub>4</sub>, and TEOS, the acronym for Tetra-Ethyl-Ortho-Silicate, Si(OCH<sub>2</sub>CH<sub>3</sub>)<sub>4</sub>. H<sub>2</sub>O is added as a solution of an acid of concentration such as to yield a pH value between 0.3 and 1.5. The preferred acid is HCl: in this case the acid concentration is between 0.03 and 0.5 N and preferably between 0.04 and 0.2 N.

30 Alkoxides hydrolysis is an equilibrium reaction; as the invention process necessarily requires that hydrolysis at this stage be completed, and that no traces of alcohol remain in the subsequent phases, hydrolysis is pushed to its stoichiometric completion by distilling the forming alcohol. Distillation is generally performed under pumping, keeping the pressure in the hydrolysis container at a level below 10 mbar,

and preferably between 3 and 5 mbar. This phase may be accelerated and favoured by operating at a temperature between 30 and 40 °C. Hydrolysis is stopped when the volume of alcohol recovered in a suitable flask is about 110% of the volume of alcohol stoichiometrically produced by alkoxides hydrolysis; recovering an over-stoichiometric volume takes into account the amount of water that may evaporate along with alcohol as an azeotropic mixture, thus ensuring total alcohol removal.

To the thus-obtained sol there are added from about 0.7 to 3 mols of SiO<sub>2</sub>, preferably about 2 mols of SiO<sub>2</sub> per each starting silicon alkoxide mole. In a preferred embodiment of the invention, SiO<sub>2</sub> compound is in the form of extremely fine powders, such as the compound obtained by flame hydrolysis. SiO<sub>2</sub> by flame hydrolysis is a particular form of extremely pure powdery silica, with particles of granulometry of about 10 nm, and it is produced feeding SiCl<sub>4</sub> to an oxyhydrogen flame. This product is commonly available on the market and may be obtained for instance from Degussa AG under the tradename Aerosil OX-50. Homogeneous dispersion of flame hydrolysis SiO<sub>2</sub> into the sol may be favoured by mechanical or ultrasonic stirring.

The thus-obtained sol is deposited on a substrate according to known techniques, e.g. by means of dip-coating or spin-coating, the first one consisting in dipping in and extracting from the sol, at a constant pre-set speed, the substrate kept in vertical position, and the second one in pouring a pre-set amount of sol on the substrate while spinning this latter, at a speed generally between 500 and 5000 rpm.

The sol films thus obtained on the substrate are preferably caused to gel suddenly through quick solvent evaporation. Gelation consists in the condensation of -OH groups bonded to different atoms of silicon or of other possibly present elements, according to reaction (I) given above. Oxygen bridges between two atoms of metal, silicon or germanium are formed, eventually resulting in the formation of an oxidic gel.

Instantaneous gelation is obtained in the simplest way by sudden heating of the film from room temperature to a temperature of about 300-400 °C, for instance introducing the substrate with the film into a pre-heated oven. The film may then be left in the oven for a few minutes, to enhance its mechanical strength. Once extracted from the oven, the film is stable and can be left exposed to air indefinitely.

This film is constituted by a dry gel, having the same chemical composition of the final oxide, but with a porous structure.

The last process phase is densification of the film, that is realised in subsequent thermal treatment steps. They comprise, in turn, the following: thermal treatment between 500°C and 800°C in an oxidising atmosphere in order to remove through combustion possible traces of organic compounds, alcohol or alcoholic moieties present in the gel; film dehydration or purification through thermal treatment at a temperature between 500°C and 800°C, and maintaining film and substrate at that temperature for a time between 10 minutes and 1 hour in a flow of a gaseous mixture comprising up to 10% of HCl in an inert gas; heating of the film on the substrate at a temperature between 500°C and 800°C in a pure inert gas flow to realise film washing; and film and substrate heating at a temperature between 1200°C and 1400°C in an inert gas flow.

As known in the field, the dry porous gel obtained is generally subjected, as a first preparation step of the densification procedure, to a thermal treatment in an oxidising atmosphere, for instance between 300 °C and 1000 °C, preferably between 500 °C and 800 °C in air or oxygen, in order to remove through combustion the remaining traces of organic compounds, alcohol or alcoholic moieties, that can have been left in the gel pores.

A subsequent step consists in a film dehydration or purification treatment, in order to remove the -OH groups possibly remaining in the film after gelation, solvent evaporation and combustion removal of organic moieties. In a first embodiment of the process of the invention this is obtained by flowing in the gel pores a gaseous dry dehydrating agent, such as HCl possibly diluted in an inert gas. Alternatively, the same procedure is realised by using HCl diluted in H<sub>2</sub> in the inert gas.

When the substrate is made of silicon, the gaseous mixture of HCl in an inert gas further can contain hydrogen with a molar ratio 1:100 between HCl and hydrogen.

Once the pre-set temperature in the above the range is reached, substrate and film are kept at such a temperature for a given time, generally between 10 minutes and 1 hour in the presence of a dehydrating atmosphere.

Before realising the final densification phase, substrate and film are heated at a temperature between 400 °C and 1000 °C, preferably between 500 °C and 800 °C, in a flowing inert gas, such as 99.99% pure helium, to wash the film.

The densification phase then involves heating substrate and sample in a flowing inert gas. Specifically, substrate and film are brought to temperatures between 1200 °C and 1400 °C in a 99.99% pure helium during a time preferably between 10 and 30 minutes.

5 A sol composition for the preparation of a silicon oxide or silicon oxide-based film having a thickness greater than 1 µm thus comprises: a sol comprising a soluble silicon precursor and optionally a soluble precursor or precursors of the elements Ge, C, Sn, Pb, P, As, Sb, B, Al, Ga, Bi, Ti, Zr, S and Hf, in which the molar ratio of the soluble silicon precursor to any other soluble precursor(s) is at least 1:1;  
10 at least 10 mols of H<sub>2</sub>O per each mole of the silicon precursor and any other precursors; and an acid capable of causing hydrolysis of the precursor(s), the acid having a concentration between 0.03 and 0.5 N.

Alternatively, a sol composition for the preparation of a silicon oxide or silicon oxide-based film can comprise: a sol comprising a soluble silicon precursor and  
15 optionally a soluble precursor or precursors of the elements Ge, C, Sn, Pb, P, As, Sb, B, Al, Ga, Bi, Ti, Zr, S and Hf, in which the molar ratio of the silicon precursor to any other soluble precursor(s) is at least 1:1; at least 10 mols of H<sub>2</sub>O per each mole of the soluble precursor(s); an acid capable of causing hydrolysis of the at least one soluble precursor, that acid having a concentration between 0.03 and 0.5 N; and  
20 from 0.7 to 3.0 mols of SiO<sub>2</sub> per each mole of soluble precursor(s); in which composition the soluble precursor(s) are hydrolysed.

The process of this invention is fully compatible with silicon oxide substrates. When the substrate is made of silicon, using HCl mixtures in helium may give rise to microerosions, known in the field as "pittings", on the same substrate surface. To  
25 avoid this, it is possible to resort to mixtures where the inert gas contains hydrogen along with HCl, with an acid/hydrogen ratio that varies depending on the treatment temperature, according to the conditions indicated in a paper of G. A. Lang, published on RCA Review of 1963, Vol. 24, page 448. This paper shows that the volume percent of HCl that may be present admixed with hydrogen without giving  
30 rise to pitting becomes higher the higher the temperature: as an example, pitting may be avoided with mixtures containing a HCl volume up to about 1.5% of the volume of hydrogen working at about 1200 °C; up to about 3% at about 1240 °C; and up to about 5% at about 1270 °C.

Objectives and advantages of the present invention will be better appreciated by reading the following examples, that are meant to illustrate the invention but by no means are to be considered as limiting its scope. In the Examples from 1 to 5, the preparation and check of a silicon oxide film on a substrate according to the invention is shown, while in Example 6 is shown the preparation of a film by using a starting sol of different composition.

**EXAMPLE 1: Preparation of a porous film on a substrate**

50 grams of TEOS are added to 150 cc of HCl solution 0.1 N in a flask. The thus-obtained solution is made homogeneous by subjecting it to simultaneous mechanical and ultrasonic stirring during about 10 minutes. A clear monophasic solution is obtained. The solution is heated at 40 °C; after 1-2 minutes, extraction of ethyl alcohol formed by TEOS hydrolysis is begun, maintaining the sol at a temperature of 20 °C in the flask, connected, through a Rotavapor™, to a pump that brings the pressure in the reaction flask to about 5 mbar. The condensing pipe of the Rotavapor is kept at a temperature of about -20 °C to ensure complete condensation of the formed alcohol. The pump is disconnected from the system when in the collecting flask there is measured about 56 cc of liquid, essentially consisting of ethyl alcohol. 28.8 grams of Aerosil OX-50™ Degussa are added to the thus-obtained sol, and the mixture is made homogeneous by ultrasonic stirring during 10 minutes. By using the thus-obtained sol, some films are prepared through the dip-coating technique, dipping and extracting from the sol a silicon substrate at a speed of 0.5 cm per second. The sol film is instantaneously gelled, placing it into an oven preheated at 400 °C and keeping it in the oven for about 10 minutes. On this film, not yet densified, a profilometric test is carried out by using a Rodenstock™ RM-600 profilometer. This technique allows performance of nondestructive tests to investigate a surface profile; tests may either be performed along one single line, obtaining the surface heights variations along the chosen line, or scanning the surface along parallel lines, thus obtaining the surface heights variations of the whole surface. In the present example a single-line mode profilometric test was performed. The result is shown in Fig. 1, reporting film thickness in microns on the vertical axis and displacement in millimeters on the film plane on the horizontal axis. The horizontal axis zero value corresponds to the border of the zone reached by the

sol during dipping of the substrate in the same sol. The resulting film thickness, apart from the edge zone, is of about 10  $\mu\text{m}$ .

#### EXAMPLE 2: Porous film densification

5 The sample prepared as given in Example 1 is cleaned from traces of possibly remaining organic compounds, and densified according to the following thermal treatment:

- heating from room temperature to 800 °C in helium at a heating rate of 4 °C per minute;

10 - treatment in a 10% anhydrous HCl-90% helium mixture during half an hour at 800 °C;

- heating in helium up to 1370 °C at a heating rate of 4 °C per minute;

- rapid cooling, taking about 6 hours, down to room temperature.

15 Profilometric tests similar to the one previously described are carried out on the thus densified film. The test result is represented in Fig. 2, similar to Fig. 1, and shows a film thickness of about 8  $\mu\text{m}$ .

#### EXAMPLE 3: Substrate and film check

20 The dense film sample obtained in Example 2 is inspected with an interferometric microscope (Zeiss, Mod. "Axiovert")<sup>TM</sup>. The results are shown in Fig. 3: focussing the microscope at the interface between the perfectly transparent film and the silicon substrate, black spots corresponding to silicon surface defects are noted. The image in Fig. 3 shows a line, L, representing the edge of film F on substrate S: the silicon oxide film lies on the upper part of the image.

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#### EXAMPLE 4: Film check

30 The same sample of Example 3 is now inspected in "dark field", using the same view direction and the same Zeiss Axiovert microscope. The "dark field" technique consists in lighting the sample with light directed towards the centre of the viewing field and with an incidence degree on the sample of about 45°. In these conditions, if a sample surface has no defects, light is not reflected in the observation direction and the sample looks black; vice versa, if the sample has defects, these diffuse light in any direction, comprising the observation direction, so that the appearance of shining spots or areas in the microscope field reveals a non-

perfectly planar surface. The results of this inspection are shown in Fig. 4. It thus can be noted that defects are present on the substrate 5 alone, while film F, corresponding to a zone with no bright spots or zones, results completely free of defects.

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**EXAMPLE 5: Thick films production with no substrate defects generation**

A sample obtained according to the procedure of Example 1 is densified according to the following thermal treatment:

- heating from room temperature to 800°C in oxygen at a heating rate of 4 °C a minute;

10

- treating at 800°C with a gaseous mixture containing one mole of HCl per 100 mols of H<sub>2</sub> per 2500 mols of inert gas, such as N<sub>2</sub> or He;

- heating in helium up to 1370°C at a heating rate of 4°C a minute.

By inspecting the thus-obtained sample with the microscope, according to both the "clear field" and "dark field" techniques, no defects are detected.

15

**COMPARATIVE EXAMPLE 6**

The procedures of Examples 1 and 2 are repeated, with the only difference that the HCl concentration for preparing the starting sol is lowered to 0.01 N. The result is a broken film showing poor adhesion onto the substrate.

20

The analysis of tests results shows that the process of the invention allows the obtainment of thick supported films. In particular, Fig. 2 shows that by the invention process a film about 8 µm thick has been obtained having side dimensions of several millimeters. Figures 3 and 4 show that, although the substrate surface presents a few point defects (black spots in Fig. 3), the oxidic film formed according to the invention process has an upper surface with no defects (lack of bright spots in the upper part of the image in Fig. 4, corresponding to the zone where the film is). In this image, defects at the film-substrate interface, that is, under the film, are no longer visible, because in the "dark field" technique this interface is no longer lighted, being shielded by the mirror plane represented by the intact film. Silicon surface defects are avoided if, in the last part of the densification process, a HCl-hydrogen mixture in inert gas instead of HCl alone in inert gas is used, as explained in the cited paper of G. A. Lang and as shown in Example 5. Films obtained according to

25  
30

the process of the invention are hence endowed with good optical surfaces, allowing their use in optics.

Finally, despite the fact that the sol-gel technique has been known and investigated for a number of years, and despite the fact that the single steps of the present process of the invention previously may have described in the specialised literature, the process of the invention, allows the obtainment of the above described results, that could not be obtained before by experts in the sol-gel field.

The embodiments of the present invention in which an exclusive property or privilege is claimed are defined as follows:

1. A sol-gel process for the preparation of a vitreous film of silicon oxide or of a mixed oxide containing silicon oxide and having a thickness greater than 1  $\mu\text{m}$ , the process comprising the steps of:

preparing a sol comprising a soluble silicon precursor and optionally a soluble precursor or precursors of one or more of the elements Ge, C, Sn, Pb, P, As, Sb, B, Al, Ga, Bi, Ti, Zr, S and Hf, in which the molar ratio of the soluble silicon precursor to the sum of any other optional soluble precursors is at least 1:1, and in which the sol contains at least 10 mols of  $\text{H}_2\text{O}$  per each mole of said soluble silicon precursor plus any other optional soluble precursors and contains an acid capable of causing hydrolysis of said silicon precursor and optional precursors, the acid having a concentration between 0.03 and 0.5 N;

completely hydrolysing said silicon precursor and any optional precursors;

adding to the sol from 0.7 to 3.0 mols of  $\text{SiO}_2$  per mole of said silicon precursor and optional precursors;

forming a film of the sol on a substrate;

gelling the sol film through solvent evaporation; and

densifying the gelled film thus obtained through thermal treatment.

2. A process according to claim 1, wherein, in said sol preparation step,  $\text{H}_2\text{O}$  is added in the form of a solution of an acid having such concentration as to produce a pH value between 0.5 and 1.5.

3. A process according to claim 2, wherein  $\text{H}_2\text{O}$  is added as a solution of HCl of concentration between 0.03 and 0.5 N.

4. A process according to claim 3, wherein  $\text{H}_2\text{O}$  is added as a solution of HCl of concentration between 0.04 and 0.2 N.

5. A process according to any one of claims 1 to 4, wherein said soluble precursors-hydrolysis step is undertaken in a hydrolysis container and is performed

up to stoichiometric completion by distillation of the alcohol formed in the hydrolysis, keeping the pressure in the hydrolysis container at a value below 10 mbar.

6. A process according to claim 5, wherein a pressure in the hydrolysis container is kept between 3 and 5 mbar.

7. A process according to claim 5 or 6, wherein the temperature in the hydrolysis container is kept at a value between 30°C and 40°C.

8. A process according to any one of claims 1 to 7, wherein said soluble precursors-hydrolysis step is continued until the distilled volume is about 110% of the theoretical volume of alcohol formed in the same hydrolysis.

9. A process according to any one of claims 1 to 8, wherein said film-gelation step is realised by introducing the substrate with the sol film into an oven preheated to a temperature between 300°C and 400°C.

10. A process according to any one of claims 1 to 9, wherein said film-densifying step comprises, in turn, the following steps:

thermal treatment between 500°C and 800°C in an oxidising atmosphere, in order to remove through combustion possible traces of organic compounds, alcohol or alcoholic moieties present in the gel;

film dehydration or purification through thermal treatment at a temperature between 500°C and 800°C, and maintaining the sol film and substrate at that temperature for a time between 10 minutes and 1 hour in a flow of a gaseous mixture comprising up to 10% of HCl in an inert gas;

heating of the sol film on the substrate at a temperature between 500°C and 800°C in a pure inert gas flow, to realise film washing; and

film and substrate heating at a temperature between 1200°C and 1400°C in an inert gas flow.

11. A process according to claim 10, wherein, in said dehydration step, a mixture of HCl diluted in H<sub>2</sub> in said inert gas is used.

12. A process according to claim 11, wherein, when the substrate is made of silicon, said gaseous mixture of HCl in an inert gas contains hydrogen with a molar ratio 1:100 between HCl and hydrogen.
13. A process according to claim 10, 11 or 12, wherein the inert gas is 99.99% pure helium.
14. A process according to any one of claims 1 to 13, wherein, in said sol-preparation step, there is used from 30 to 40 mols of H<sub>2</sub>O per each mole of said silicon precursor and optional precursors.
15. A process according to any one of claims 1 to 14, wherein, in said sol-preparation step, a mixture of soluble precursors of silicon and of germanium is used such that the mole ratio of silicon to germanium is equal to or higher than 1:1.
16. A process according to any one of claims 1 to 14, wherein, in said sol-preparation step, a mixture of soluble precursors of silicon and of one or more of titanium, aluminium and boron is used, such that the mole ratio of silicon to the one or more other elements is higher than 5:1.
17. A process according to any one of claims 1 to 16, wherein said soluble precursor or precursors is/are alkoxides of the elements.
18. A process according to claim 17, wherein, in said sol-preparation step, tetramethylorthosilicate or tetraethylorthosilicate is employed as the silicon alkoxide.
19. A sol composition for the preparation of a silicon oxide or silicon oxide-based film having a thickness greater than 1  $\mu\text{m}$ , the sol composition comprising:  
a sol comprising a soluble silicon precursor and optionally a soluble precursor or precursors of one or more of the elements Ge, C, Sn, Pb, P, As, Sb, B, Al, Ga, Bi, Ti, Zr, S and Hf, in which the molar ratio of the soluble silicon precursor to the sum of any other optional soluble precursors is at least 1:1;  
at least 10 mols of H<sub>2</sub>O per each mole of said silicon precursor plus any other soluble precursors; and

an acid capable of causing hydrolysis of said silicon precursor plus any other soluble precursors, the acid having a concentration between 0.03 and 0.5 N.

20. A sol composition for the preparation of a silicon oxide or silicon oxide-based film having a thickness greater than 1  $\mu\text{m}$ , the sol composition comprising:

a sol comprising a soluble silicon precursor and optionally a soluble precursor or precursors of one or more of the elements Ge, C, Sn, Pb, P, As, Sb, B, Al, Ga, Bi, Ti, Zr, S and Hf, in which the molar ratio of the soluble silicon precursor to any other soluble precursors is at least 1:1;

at least 10 mols of  $\text{H}_2\text{O}$  per each mole of the silicon precursor plus any other soluble precursors;

an acid capable of causing hydrolysis of the silicon precursor plus any other soluble precursors, the acid having a concentration between 0.03 and 0.5 N; and

from 0.7 to 3.0 mols of  $\text{SiO}_2$  per each mole of the silicon precursor plus any other soluble precursors;

wherein the precursor or precursors is/are hydrolysed.

21. A sol-gel process for the preparation of a vitreous film of silicon oxide or of a mixed oxide containing silicon oxide, the process comprising:

preparing a sol from a solution or a suspension of one or more precursor elements in water, alcohol or a hydroalcoholic mixture, the one or more precursor elements comprising silicon and, optionally, one or more of the other elements germanium, boron, aluminum, titanium and zirconium, the molar ratio of the silicon precursor to the sum of the optional other precursor elements being greater than or equal to 1:1, the sol comprising a water solution and an acid containing at least 10 moles of  $\text{H}_2\text{O}$  per each mole of the one or more precursor elements and having a pH between 0.3 and 1.5, to form said sol;

hydrolysing the one or more precursor elements;

adding to said sol 0.7 to 3.0 moles of  $\text{SiO}_2$  per mole of the one or more precursor elements;

forming a film of said sol on a substrate;

gelling the sol film through solvent evaporation, the gelling being initiated by introducing the sol film into an oven preheated to a temperature from 300° C. to 400° C.; and

densifying the resulting gel film through thermal treatment to form the vitreous film.

22. A process according to claim 21, wherein H<sub>2</sub>O is added as a solution of HCl of concentration between 0.03 and 0.5 N.

23. A process according to claim 22, wherein H<sub>2</sub>O is added as a solution of HCl of concentration between 0.04 and 0.2 N.

24. A process according to claim 21, 22 or 23, wherein hydrolysis of said one or more precursor elements occurs in a hydrolysis container and is driven towards stoichiometric completion by distillation of alcohol formed in the hydrolysis, keeping the pressure in the hydrolysis container at a value below 10 mbar.

25. A process according to claim 24, wherein a pressure in said container is between 3 and 5 mbar.

26. A process according to claim 24 or 25, wherein the temperature in said hydrolysis container is kept between 30° C. and 40° C.

27. A process according to claim 24, 25 or 26, wherein hydrolysis is continued until the distilled volume is 110% of the theoretical volume of alcohol formed in the hydrolysis.

28. A process according to any one of claims 21 to 27, wherein said sol is prepared using from 30 to 40 moles of H<sub>2</sub>O per each mole of said one or more precursor elements.

29. A process according to any one of claims 21 to 28, wherein a mixture of precursor elements of silicon and of one or more of the other elements titanium, aluminum, zirconium or boron are used, and the molar ratio of silicon to the sum of the one or more other elements is greater than 5:1.

30. A process according to any one of claims 21 to 28, wherein a mixture of precursor elements of silicon and germanium is used, and the molar ratio of silicon to germanium is equal to or greater than 1:1.
31. A process according to any one of claims 21 to 30, wherein said one or more precursor elements are alkoxides of the elements.
32. A process according to claim 31, wherein, during sol preparation, tetramethylorthosilicate or tetraethylorthosilicate is used as the silicon alkoxide.
33. A sol-gel process for the preparation of a vitreous film of silicon oxide or of a mixed oxide containing silicon oxide, the process comprising:
- preparing a sol from a solution or a suspension of one or more precursor elements in water, alcohol or a hydroalcoholic mixture, the one or more precursor elements comprising silicon and, optionally, one or more of the other elements germanium, boron, aluminum, titanium and zirconium, the molar ratio of the precursor elements of silicon to the sum of the optional other precursor elements being greater than or equal to 1:1, the sol comprising a water solution and an acid containing at least 10 moles of H<sub>2</sub>O per each mole of the one or more precursor elements and having a pH between 0.3 and 1.5, to form said sol;
  - hydrolysing the one or more precursor elements;
  - adding to said sol 0.7 to 3.0 moles of SiO<sub>2</sub> per mole of the one or more precursor elements;
  - forming a film of said sol on a substrate;
  - gelling the sol film through solvent evaporation; and
  - densifying the resulting gel film through thermal treatment to form the vitreous film, the densifying step comprising:
    - treating the film with heat between 500° C. and 800° C. in an oxidizing atmosphere, to remove through combustion possible traces of organic compounds, alcohol or alcoholic moieties present in the gel;
    - dehydrating or purifying the film through thermal treatment at a temperature between 500° C. and 800° C., and maintaining the film and substrate at that temperature for between 10 minutes and 1 hour in a flow of a gaseous mixture comprising up to 10% by volume HCl in an inert gas;

heating the film on the substrate at a temperature between 500° C. to 800° C. in a pure inert gas flow to wash the film; and

heating the film and the substrate at a temperature between 1200° C. and 1400° C. in an inert gas flow.

34. A process according to claim 33, wherein a mixture of HCl diluted in H<sub>2</sub> in said inert gas is used in dehydrating or purifying the film.

35. A process according to claim 33 or 34, wherein, when the substrate is made of silicon, said gaseous mixture of HCl in an inert gas further contains hydrogen with a molar ratio of 1:100 between HCl and hydrogen.

36. A process according to claim 33, 34 or 35, wherein said inert gas and/or said pure inert gas is 99.99% pure helium.

37. A sol composition comprising:

(a) a solution or a suspension comprising at least one silicon alkoxide in water, alcohol or a hydroalcoholic mixture, the solution or the suspension comprising at least 10 moles of water per mole of silicon alkoxide; and

(b) an acid having a concentration between 0.3 N and 0.5 N, such that the sol has a pH value between 0.3 and 1.5.

38. A sol composition comprising:

(a) a solution or a suspension comprising at least one silicon alkoxide in water, alcohol or a hydroalcoholic mixture, the silicon alkoxide further comprising at least 0.7 mole to 3.0 moles of SiO<sub>2</sub> per mole of silicon alkoxide, and the SiO<sub>2</sub> being hydrolyzed;

(b) at least 10 moles of H<sub>2</sub>O per mole of SiO<sub>2</sub>; and

(c) an acid having a concentration between 0.03 N and 0.5 N, such that the sol has a pH value between 0.3 and 1.5.

39. A sol composition according to claim 38, wherein the SiO<sub>2</sub> is in a fine powder condition.

40. A sol composition according to claim 37, 38 or 39, further comprising at least one other element, each other element being germanium, aluminum, titanium or zirconium, and wherein the molar ratio of silicon to the at least one other element is greater than or equal to 1:1.
41. A substrate having a vitreous film deposited thereon, the vitreous film having a thickness greater than 1  $\mu\text{m}$  and obtained by a process as defined in any one of claims 1 to 18.
42. A substrate having a vitreous film deposited thereon, the vitreous film having a thickness greater than 1  $\mu\text{m}$  and obtained by a process as defined in any one of claims 21 to 32.
43. A substrate having a vitreous film deposited thereon as defined in claim 41 or 42, wherein the vitreous film has a thickness between 2 and 20  $\mu\text{m}$ .
44. A substrate having a vitreous film deposited thereon as defined in claim 41, 42 or 43, wherein the substrate is silica.

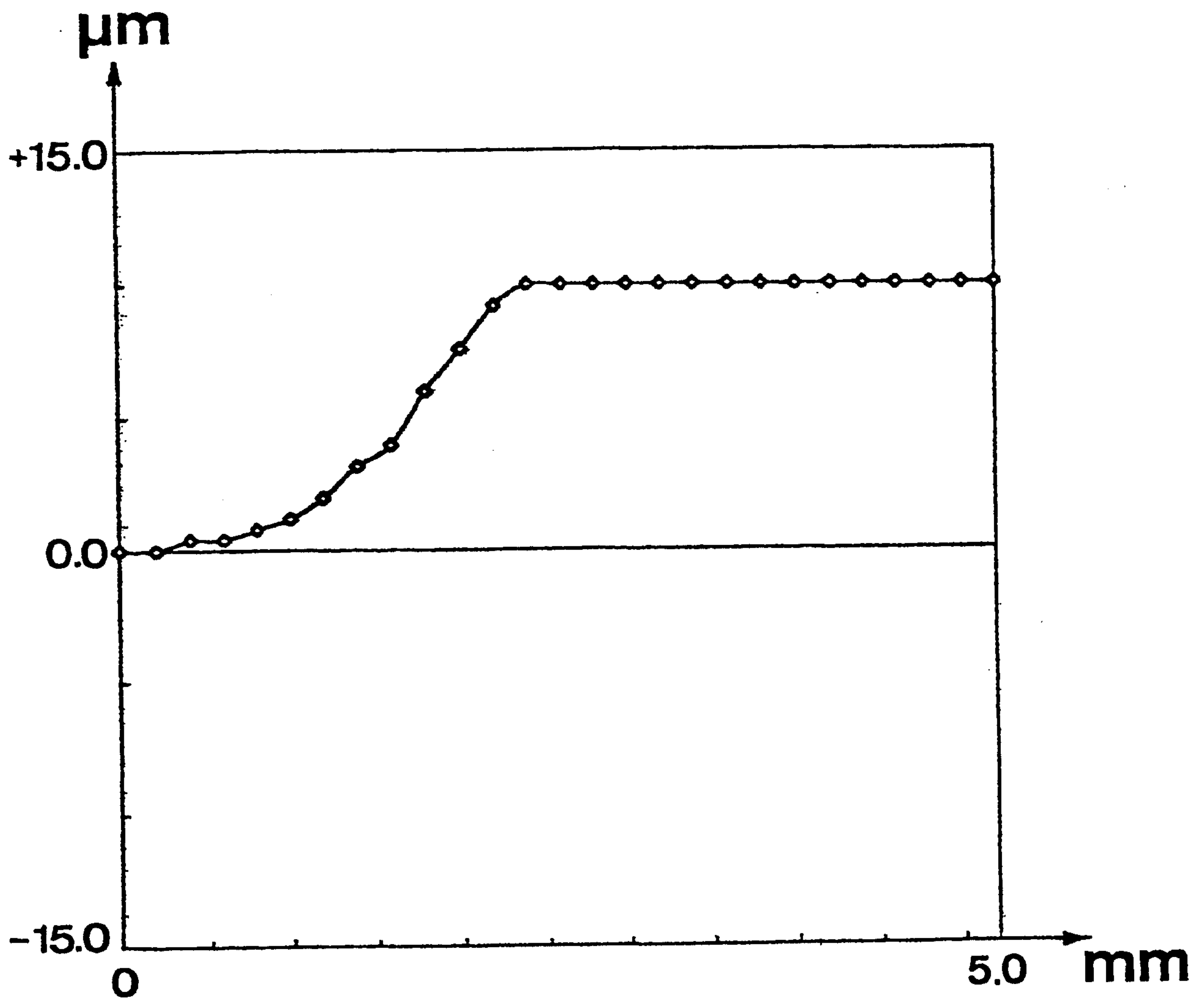


Fig. 1

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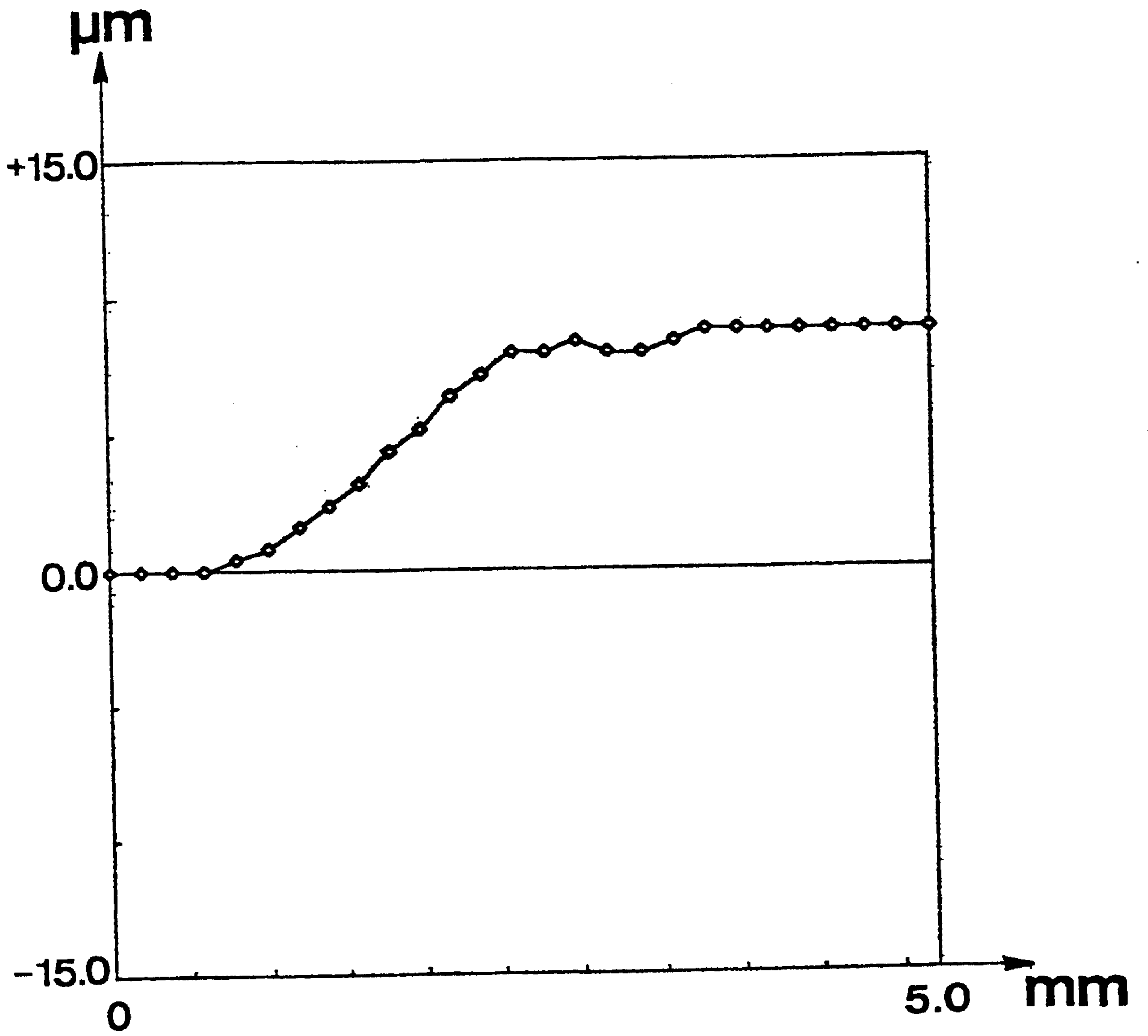


Fig. 2

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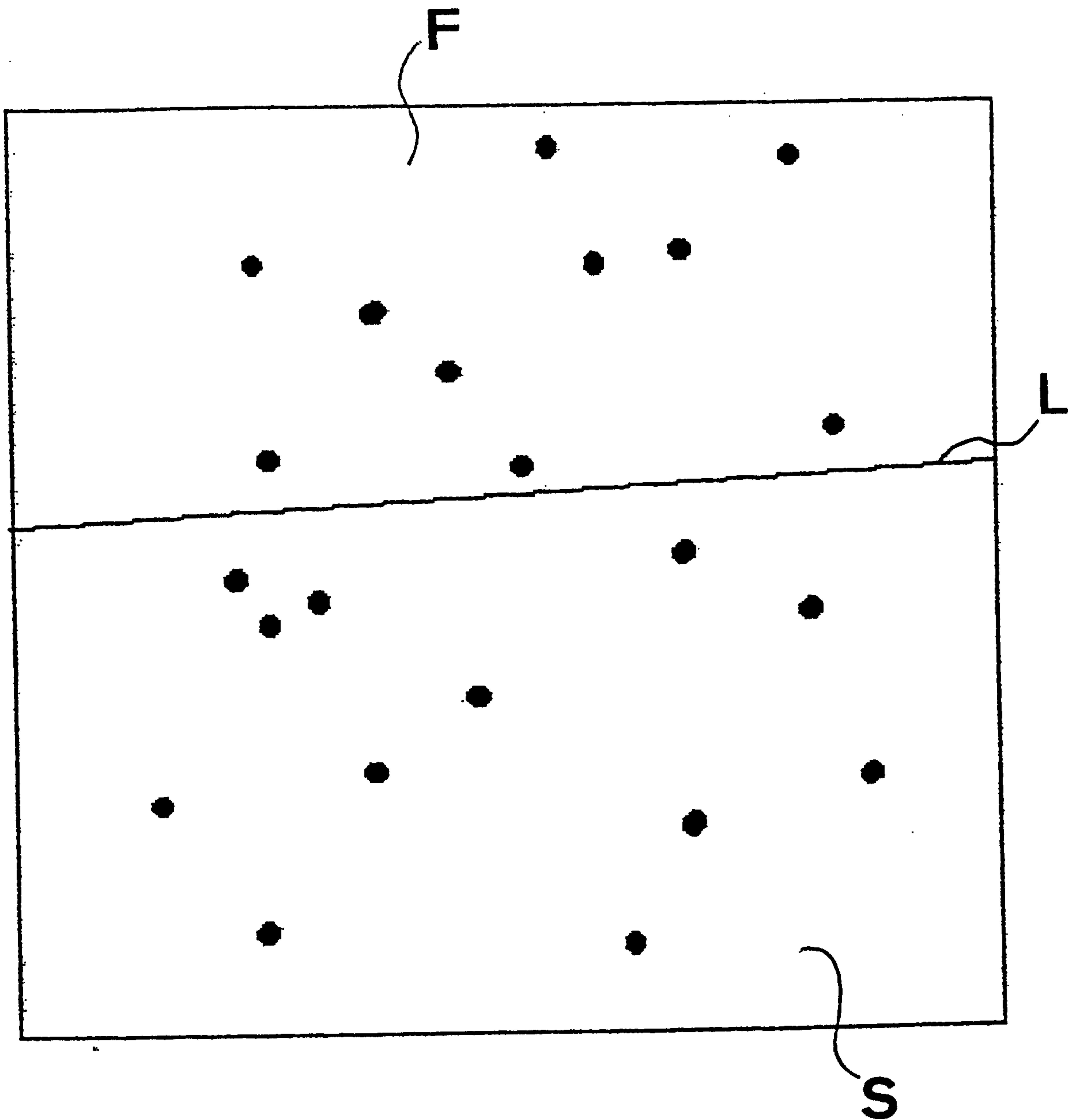


Fig. 3

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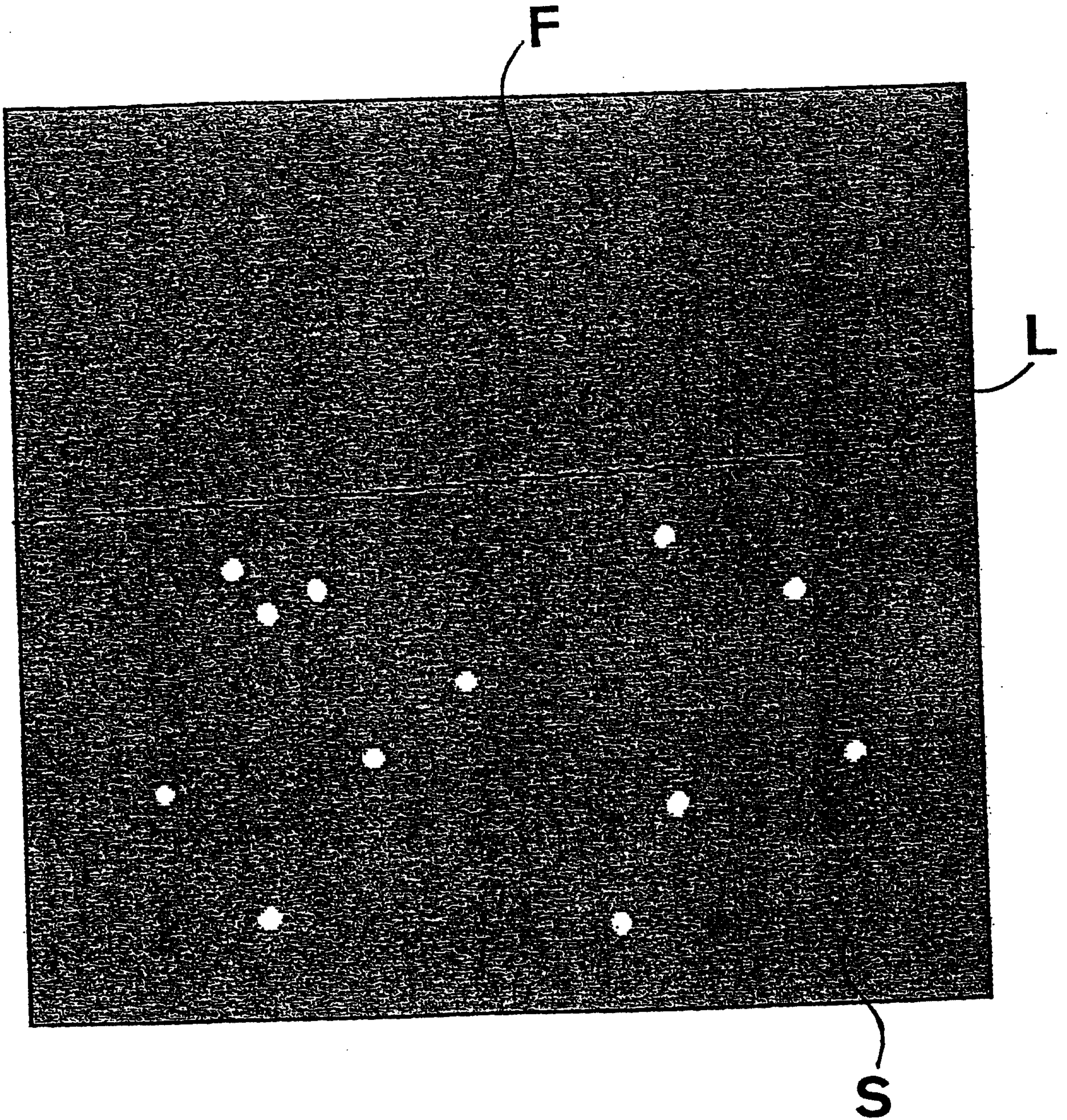


Fig. 4

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