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COATED GLASS PRODUCT**

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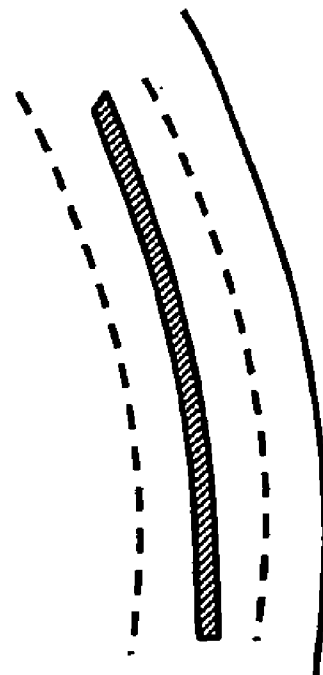
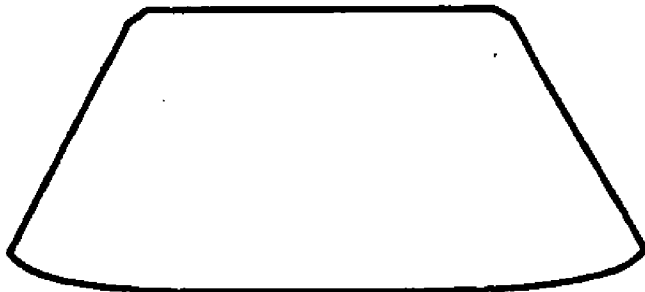
Feb. 23, 2006 (FI) 20060177

Feb. 23, 2006 (FI) 20060178

(57) **ABSTRACT**

The invention relates in general level to a method for coating glass products including large surface areas. The invention also relates to coated glass products manufactured by the method. The coating is carried out by employing ultra short pulsed laser deposition wherein pulsed laser beam is scanned with a rotating optical scanner including at least one mirror for reflecting the laser beam. The invention has several both industrially and qualitatively advantageous effects such as high coating production rate, excellent coating properties and overall low manufacturing costs.

Glass in airplane, train, or automobile



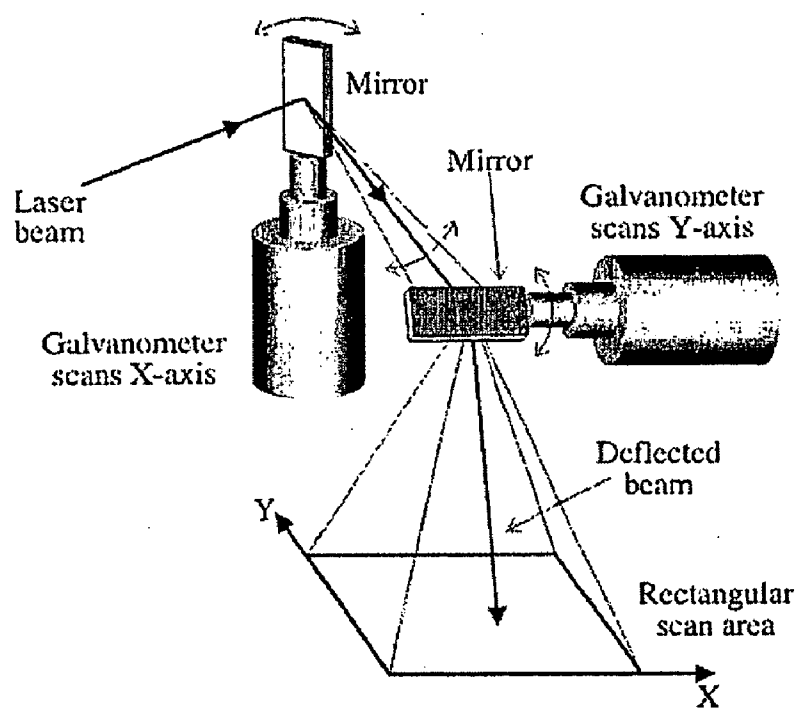


Figure 1

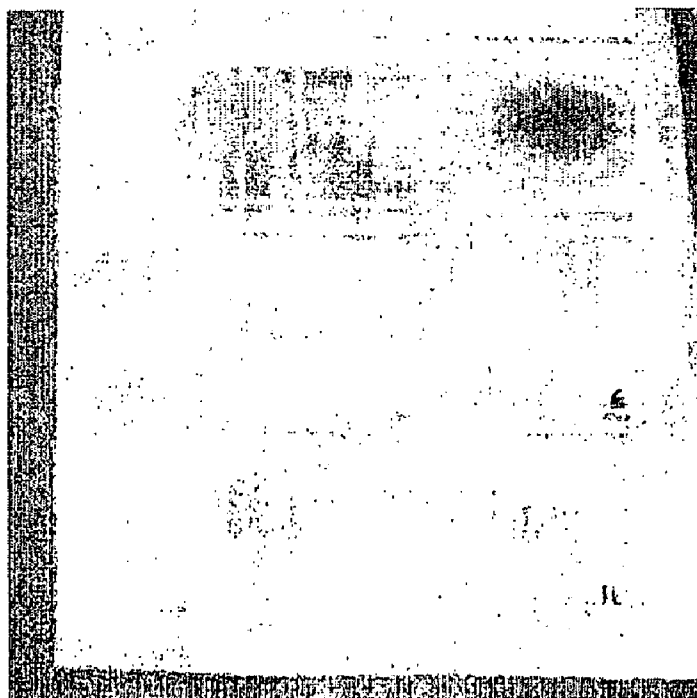
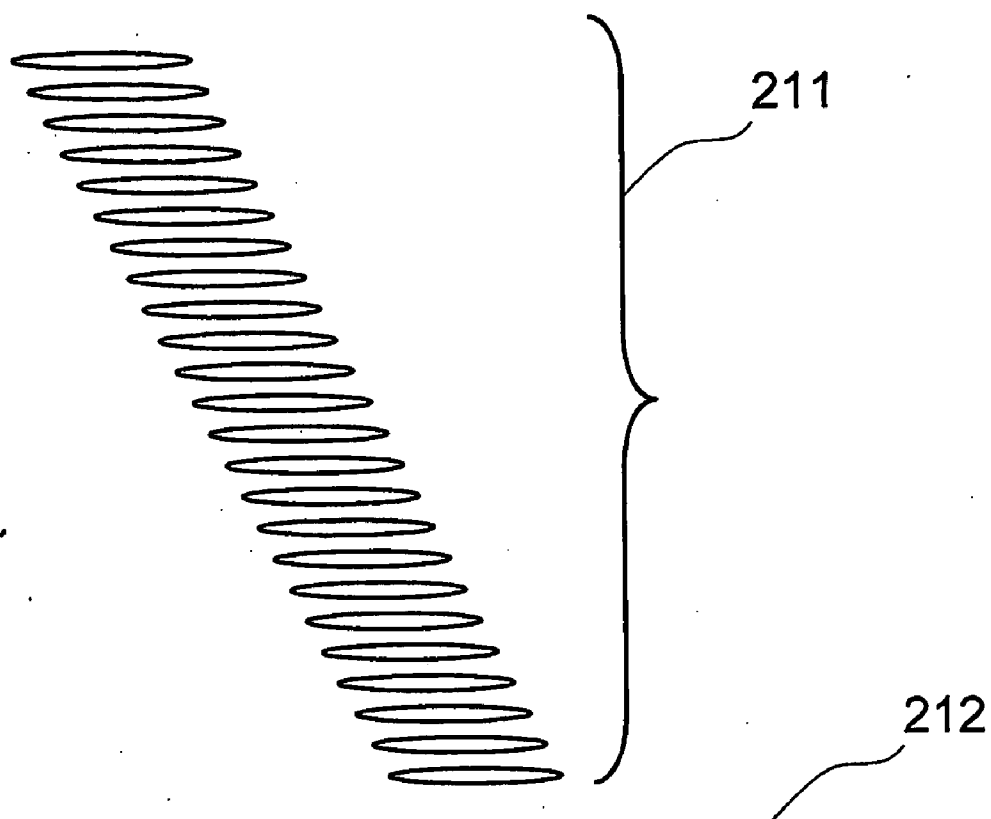


Figure 2

2 MHz



Laser spot scanning speed about 1 m/s

Figure 3

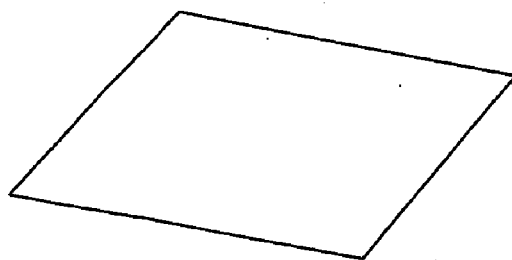


Figure 4

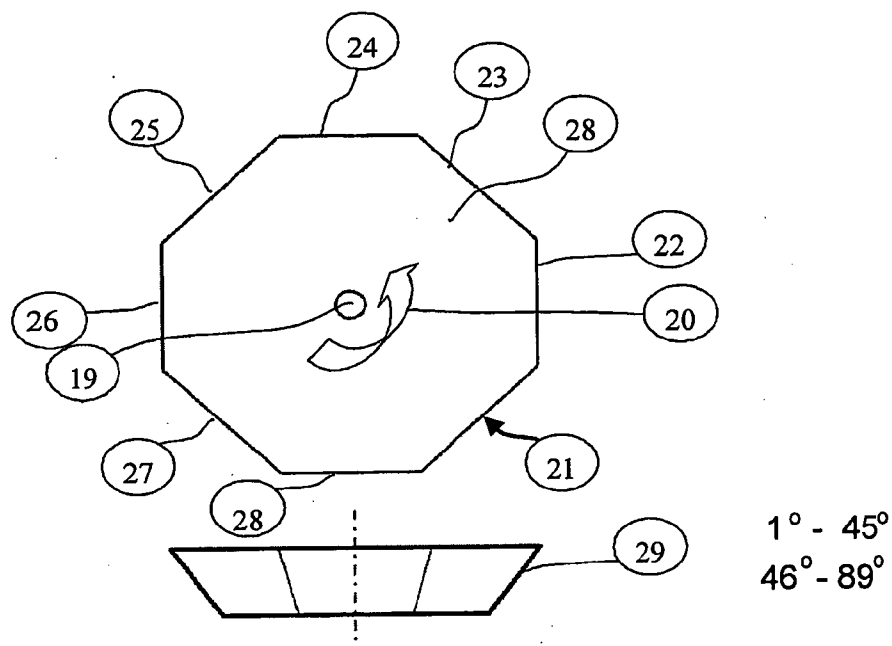


Figure 5

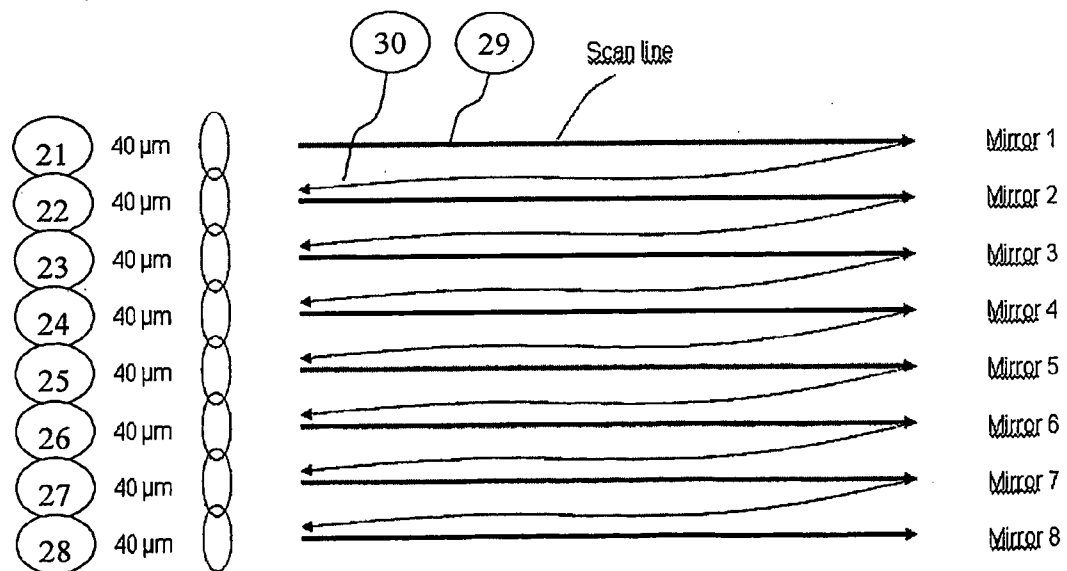


Figure 6

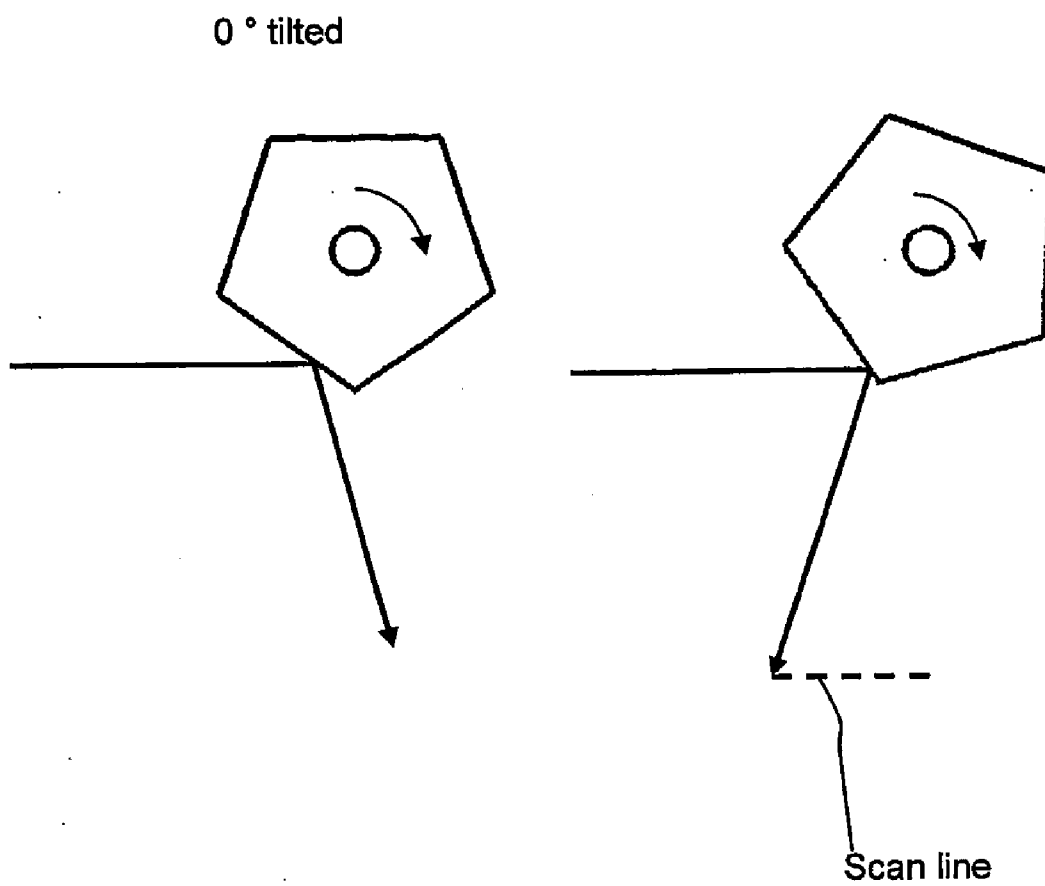


Figure 7

$> 0 < 45^\circ$ tilted

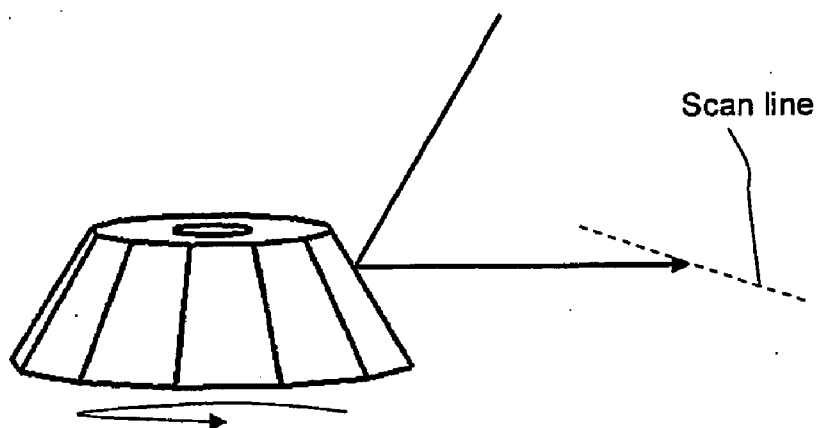


Figure 8

45° tilted

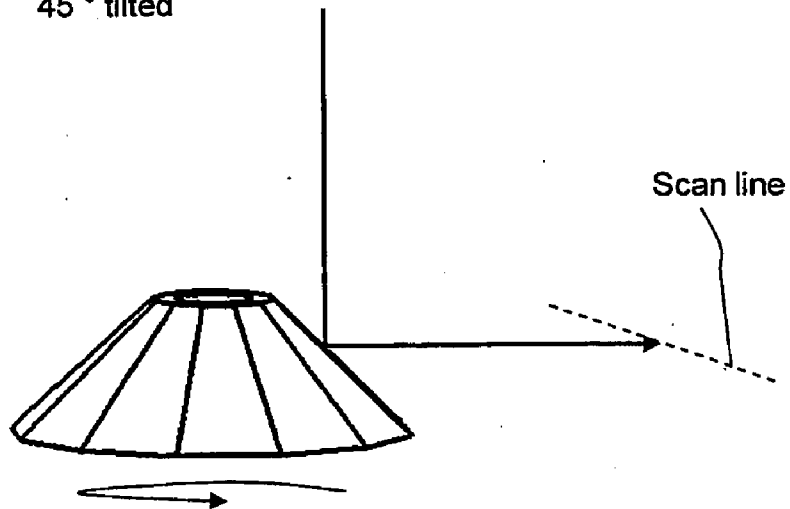


Figure 9

Sample tube

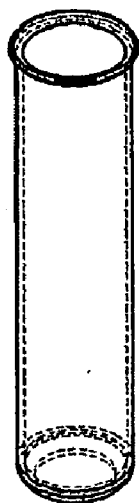
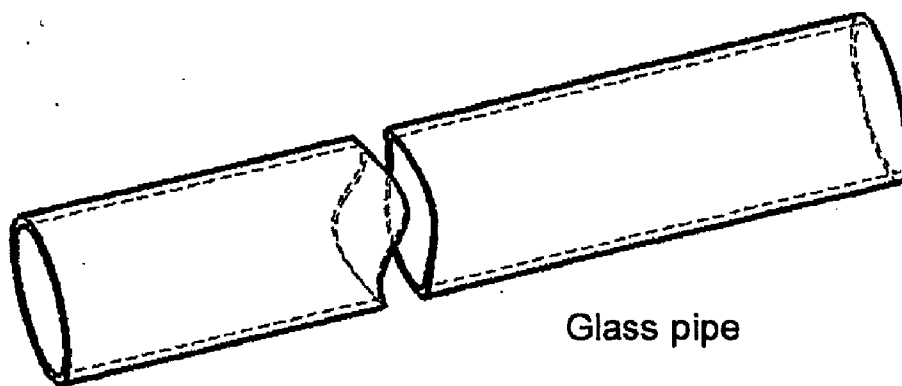


Figure 10



Glass pipe

Figure 11

Drinking glass

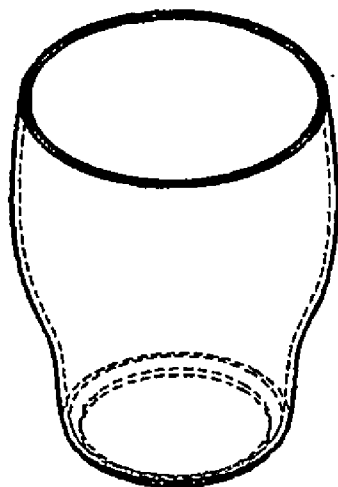
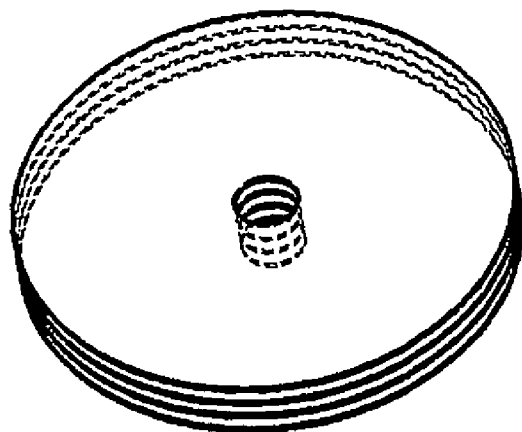
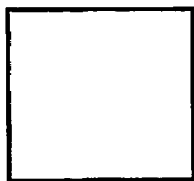


Figure 12



Master discs

Figure 13



Mirror surfaces

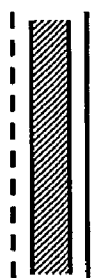


Figure 14a



Figure 14b

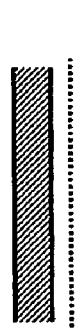


Figure 14c

Glass in airplane, train, or automobile

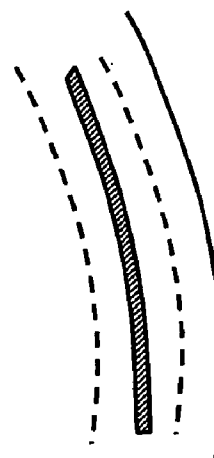
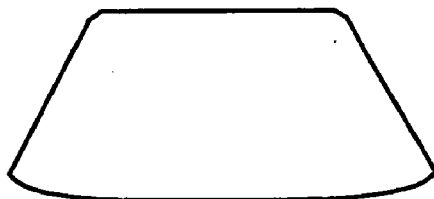


Figure 15

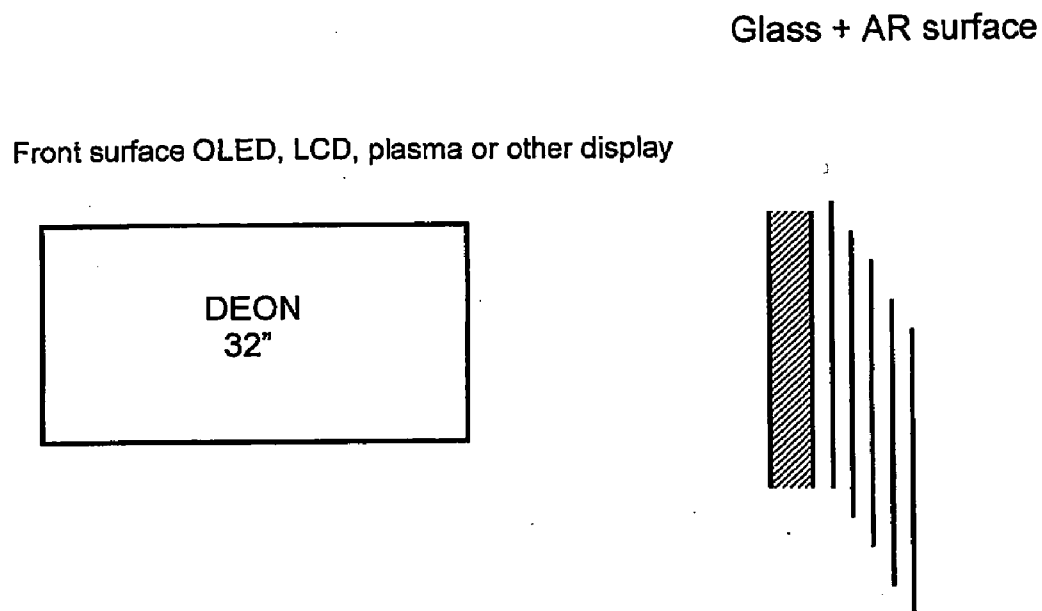
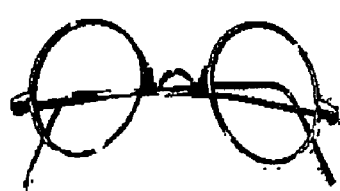


Figure 16



Goggles and visors

Eyeglassess, sunglasses

Figure 17

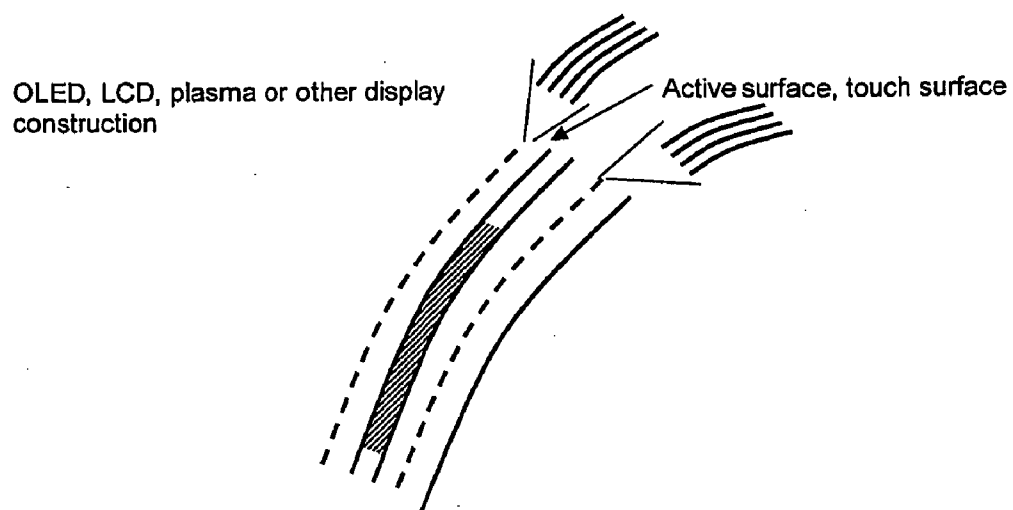


Figure 18

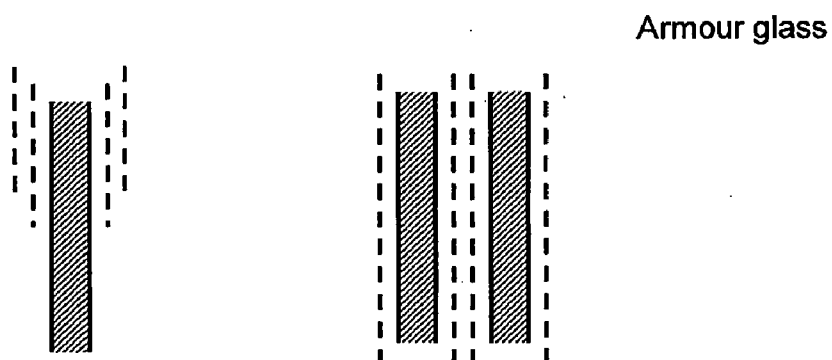
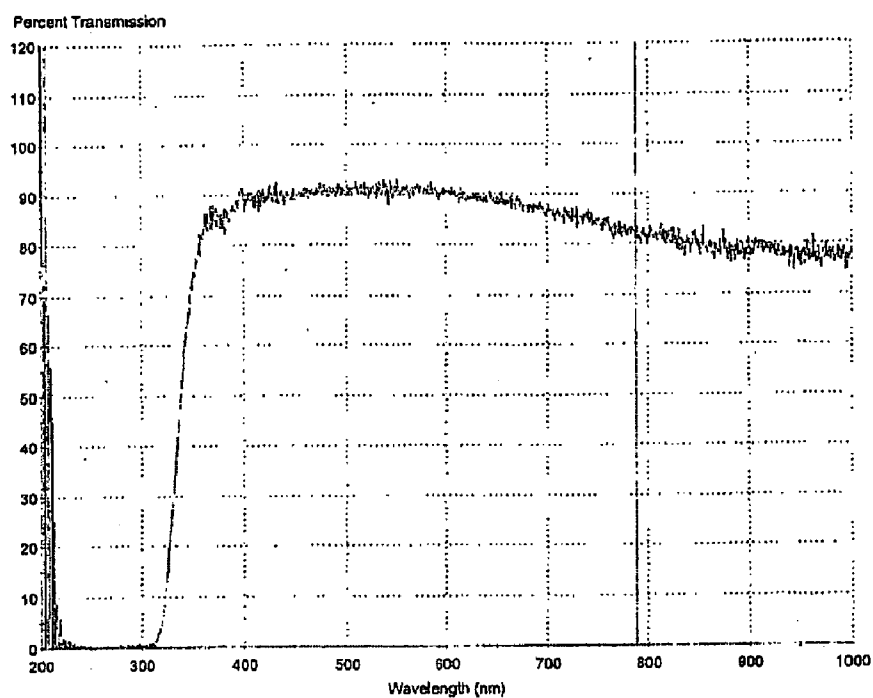
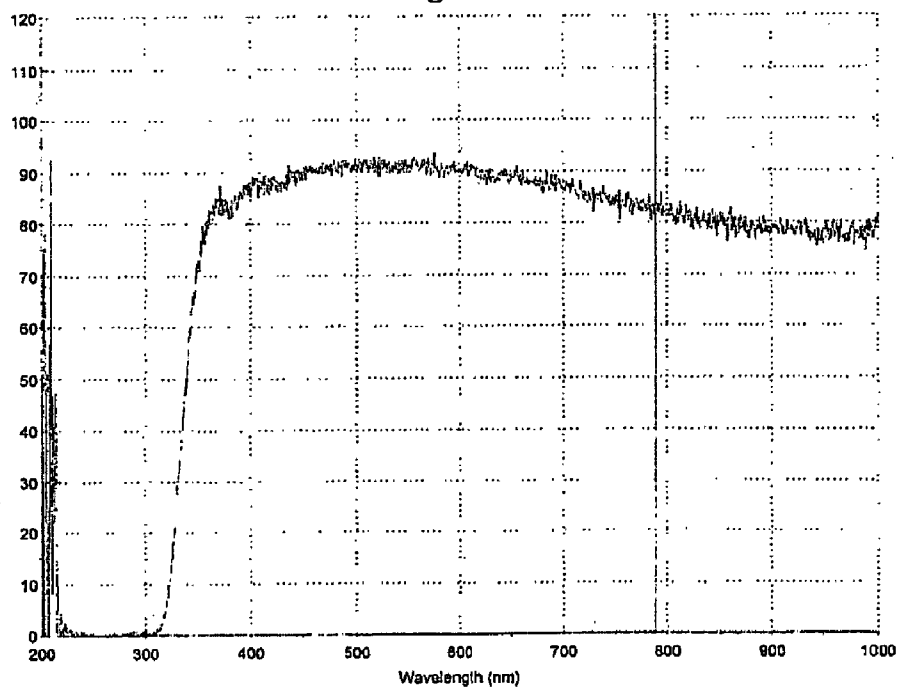
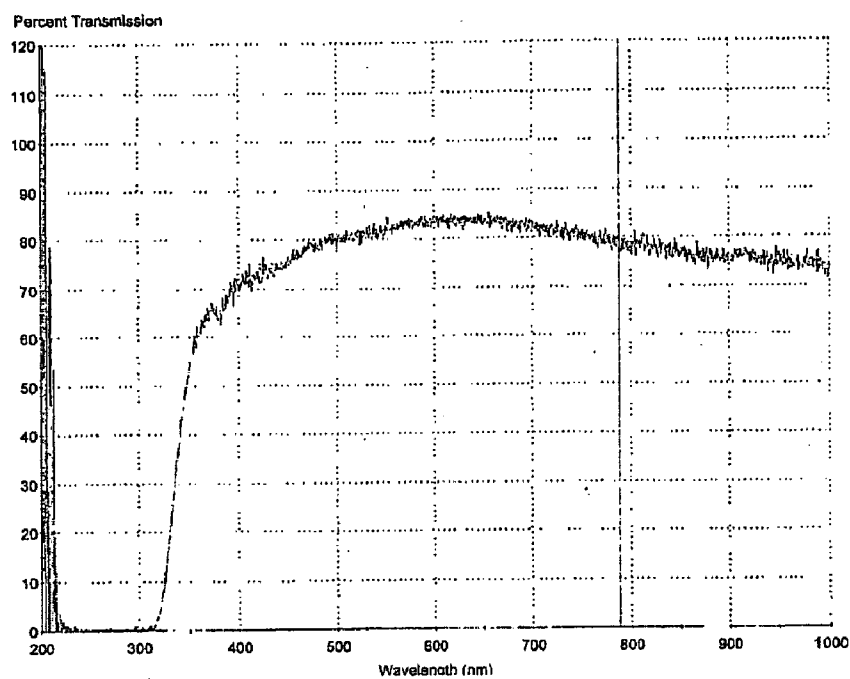


Figure 19



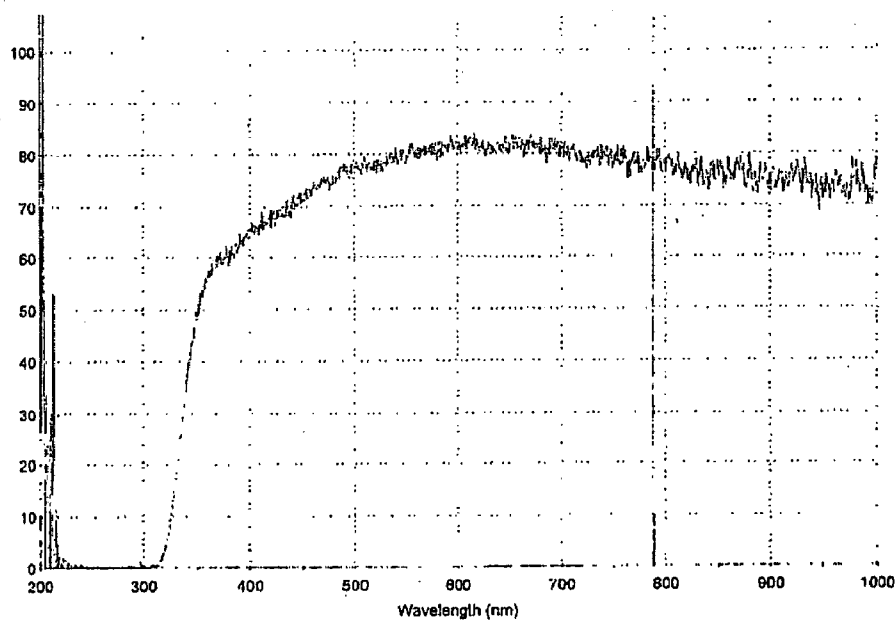
Reference glass, no ITO

Figure 20High transparency ITO
Resistivity $\sim 6 \times 10^{-3} \Omega\text{cm}$ **Figure 21**



Medium transparency ITO

Figure 22



Low transparency ITO
Resistivity $\sim 6 \times 10^{-3} \Omega\text{cm}$

Figure 23

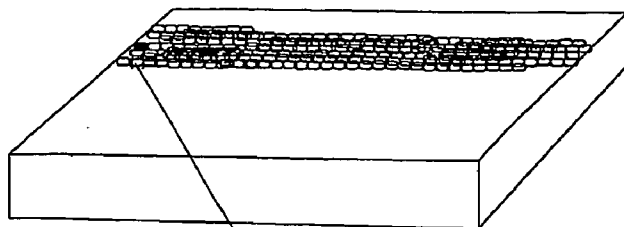


Figure 24a

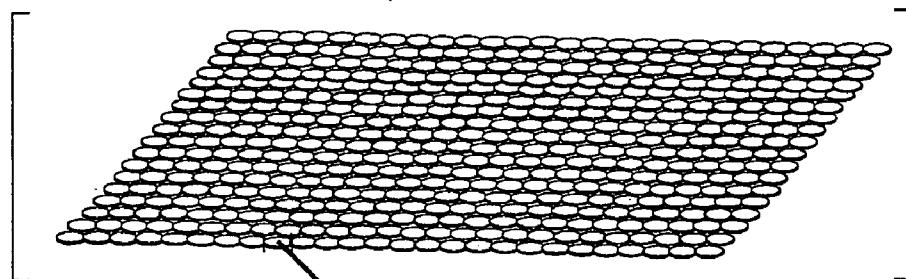


Figure 24b

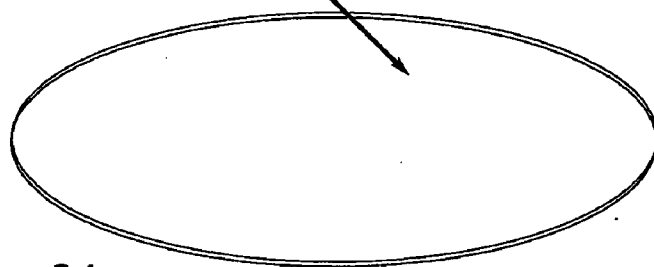


Figure 24c

$y = 50 - 200 \text{ nm}$,
for example 100 nm

$x = 1 \text{ } \mu\text{m} - 1000 \text{ } \mu\text{m}$,
for example $45 \text{ } \mu\text{m}$

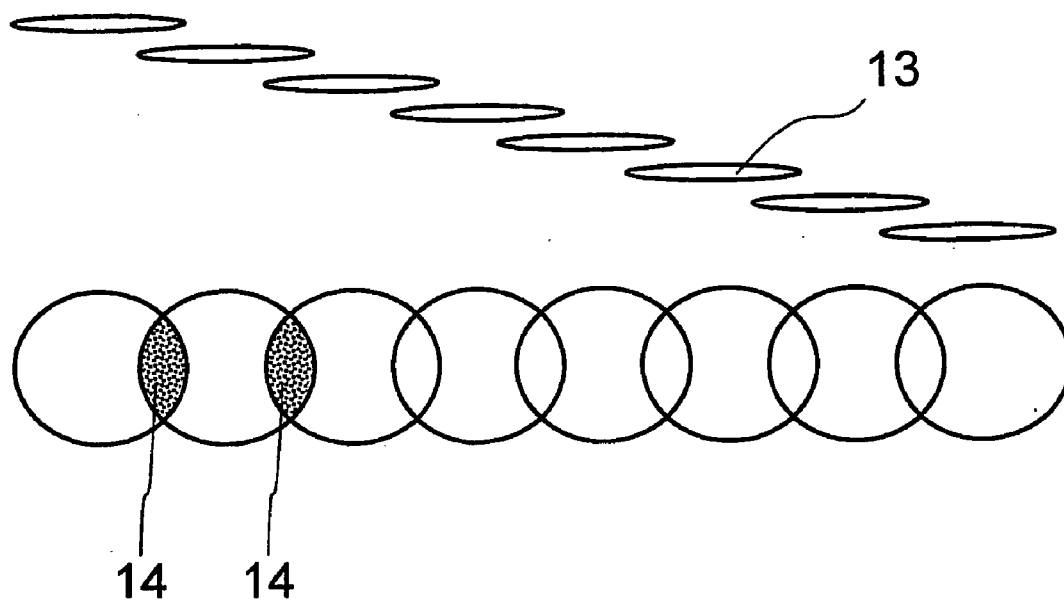


Figure 25a

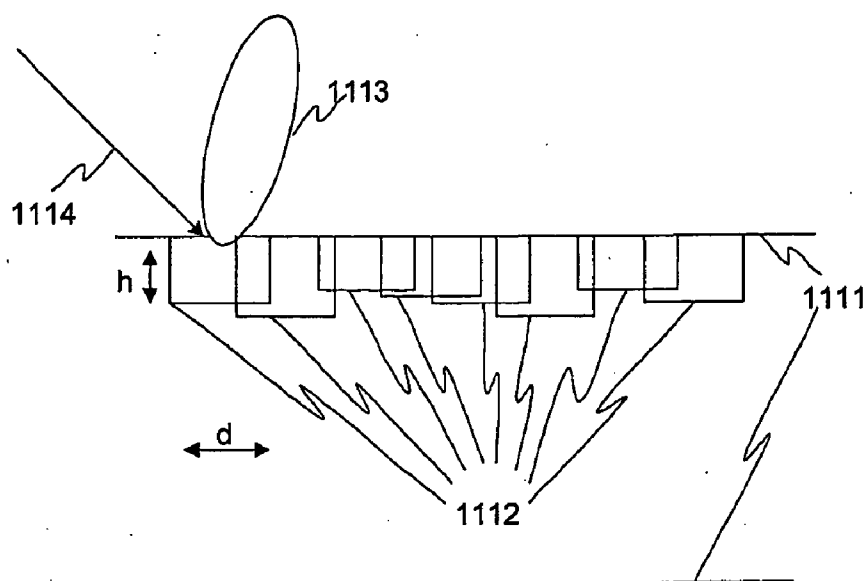


Figure 26a

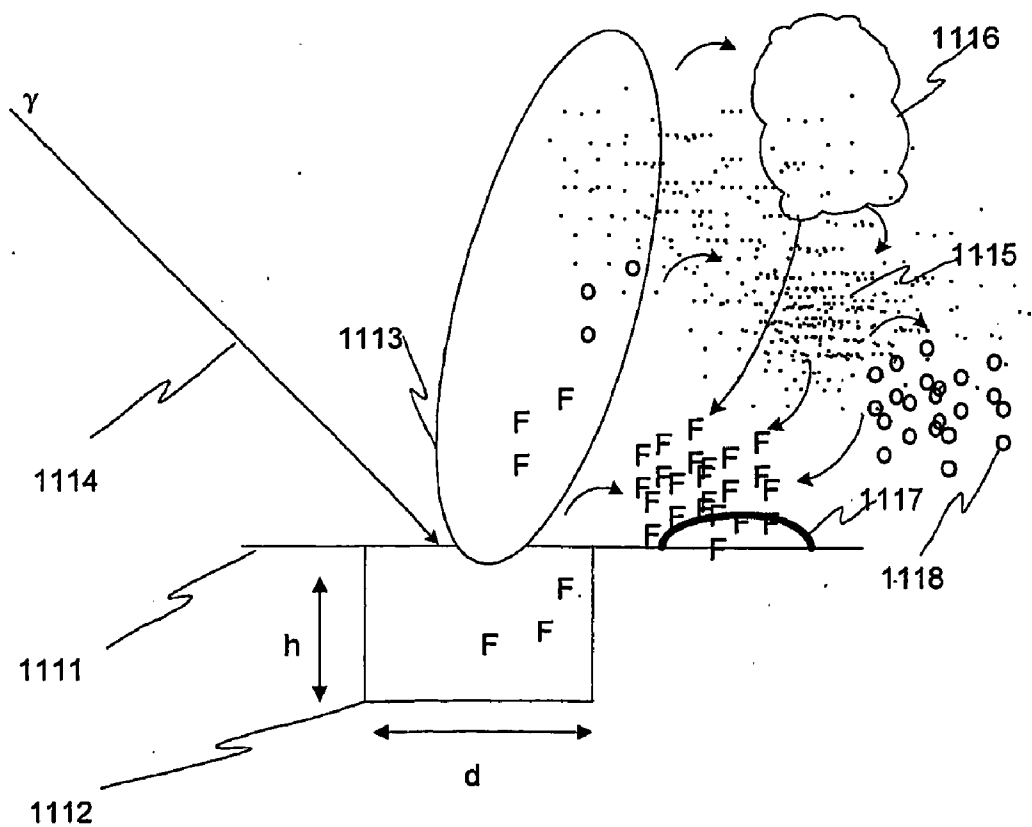


Figure 26b

COATING ON A GLASS SUBSTRATE AND A COATED GLASS PRODUCT

FIELD OF INVENTION

[0001] The invention relates generally to a method for coating glass products comprising large surface areas by ultra short pulsed laser ablation. The invention also relates to products manufactured by the method. The invention has many advantageous effects such as high coating production rate, excellent coating properties and low manufacturing costs.

BACKGROUND

Glass Products

[0002] Glass is a uniform material of arguable phase, usually produced when the viscous molten material cools very rapidly to below its glass transition temperature, without sufficient time for a regular crystal lattice form. The most familiar form of glass is the silica-based material used for household objects such as light bulbs and windows. Glass is biologically inactive material that can be formed into smooth and impervious surfaces. When in tension, glass is brittle and will break easily to sharp shards. When in compression, pure glass can withstand a great amount of force. The properties of glass are modified or changed mainly by the addition of other compounds or heat treatment.

[0003] Common glass contains about 70-72 weight % of silicon dioxide (SiO_2). Synthetic amorphous silica contains practically 100% silicon oxide being the raw material for the most expensive specialty glasses.

[0004] Glass has been used in architectural and building products since 11th century. Uses for glass in buildings include as a transparent material for windows, as internal glazed partitions and as architectural features. The present glass in buildings can be of a safety type, including wired, toughened and laminated glasses.

[0005] In addition to interior and exterior use, glass products can be found in wind screens of all kind of vehicles and ships, but also in chemical industries wherein both small and large-scale equipment is often built of glass. Additionally, glass products are commonly used in different optical devices such as lenses and protective shields of different electronic equipment both in consumer, scientific and military use. Glass is further commonly employed as disk material for various mastering systems.

[0006] Certain radiation stabilized glass-products can also be found on solar reflectors and solar cell cover glass.

[0007] As with other products also glass products comprising large surfaces and typically 3D-structures, most of the glass products remain uncoated even though their maintenance-cost, life-time and properties could be dramatically enhanced by for example introducing wear-resistant and scratch-free properties as well as inertness towards chemical conditions, by enhancing the thermal conductivity, resistivity, radiation protection, or by introducing the glass product with self-cleaning properties or—by introducing AR-functions (Anti-Reflective).

[0008] At present, the best quality optical lenses comprising rather small surfaces can be coated with for example poly-siloxanes and certain DLC-grades in order to increase the wear-resistance and to introduce scratch-free properties. The coatings are conducted in batch-wise processes in high-vacuum conditions and with long processing times.

[0009] If the polymers are not counted, the only existing large-scale industrial technology to treat glass products comprising large surfaces is the production of self-cleaning TiO_2 coating into glass by sputtering. Same function is also achieved by recent Hot-Aerosol-Layering-Operation (nHALO) and by ALD-techniques. In ALD-techniques, typical coating growth rate is less than one molecule layer per deposition cycle, the technique being thus inappropriate for other than high-end technical purposes such as IC-applications.

[0010] Same techniques can be applied to introduce some colorants to glass product. In such techniques, colour is not a surface coating, but a chemically and thermally stable surface zone modification.

Laser-Ablation

[0011] In the recent years, considerable development of the laser technology has provided means to produce very high-efficiency laser systems that are based on semi-conductor fibres, thus supporting advance in so called cold ablation methods.

[0012] At the priority date of the current application, solely fibrous diode-pumped semiconductor laser is competing with light-bulb pumped one, which both have the feature according to which the laser beam is lead first into a fibre, and then forwarded to the working target. These fibrous laser systems are the only ones to be applied in to the laser ablation applications in an industrial scale.

[0013] The recent fibres of the fibre lasers, as well as the consequent low radiation power seem to limit the materials to be used in the vaporization/ablation as the vaporization/ablation targets. Vaporizing/ablating aluminium can be facilitated by a small-pulsed power, whereas the more difficult substances to be vaporized/ablated as Copper, Tungsten, etc. need more pulsed power. The same applies into situation in which new compounds were in the interest to be brought up with the same conventional techniques. Examples to be mentioned are for instance manufacturing diamond directly from carbon (graphite) or alumina production straight from aluminium and oxygen via the appropriate reaction in the vapour-phase in post-laser-ablation conditions.

[0014] On one hand, one of the most significant obstacles to the forwarding progress of fibre-laser technology seems to be the fibre capability of the fibre to tolerate the high power laser pulses without break-up of the fibre or without diminished quality of the laser beam.

[0015] When employing novel cold-ablation, both qualitative and production rate related problems associated with coating, thin film production as well as cutting/grooving/carving etc. has been approached by focusing on increasing laser power and reducing the spot size of the laser beam on the target. However, most of the power increase was consumed to noise. The qualitative and production rate related problems were still remaining although some laser manufacturers resolved the laser power related problem. Representative samples for both coating/thin film as well as cutting/grooving/carving etc. could be produced only with low repetition rates, narrow scanning widths and with long working time beyond industrial feasibility as such, highlighted especially for large bodies.

[0016] If the energy content of a pulse is kept constant, the power of the pulse increases in the decrease of the pulse duration, the problem with significance increases with the decreasing laser-pulse duration. The problems are significant

even with the nano-second-pulse lasers, although they are not applied as such in cold ablation methods.

[0017] The pulse duration decrease further to femto or even to atto-second scale makes the problem almost irresolvable. For example, in a pico-second laser system with a pulse duration of 10-15 ps the pulse energy should be 5 μ J for a 10-30 μ m spot, when the total power of the laser is 100 W and the repetition rate 20 MHz. Such a fibre to tolerate such a pulse is not available at the priority date of the current application according to the knowledge of the writer at the very date.

[0018] The production rate is directly proportional to the repetition rate or repetition frequency. On one hand the known mirror-film scanners (galvano-scanners or back and forth wobbling type of scanners), which do their duty cycle in way characterized by their back and forth movement, the stopping of the mirror at the both ends of the duty cycle is somewhat problematic as well as the accelerating and decelerating related to the turning point and the related momentary stop, which all limit the utilizability of the mirror as scanner, but especially also to the scanning width. If the production rate were tried to be scaled up, by increasing the repetition rate, the acceleration and deceleration cause either a narrow scanning range, or uneven distribution of the radiation and thus the plasma at the target when radiation hit the target via accelerating and/or decelerating mirror.

[0019] If trying to increase the coating/thin film production rate by simply increasing the pulse repetition rate, the present above mentioned known scanners direct the pulses to overlapping spot of the target area already at the low pulse repetition rates in kHz-range, in an uncontrolled way. At worst, such an approach results in release of particles from the target material, instead of plasma but at least in particle formation into plasma. Once several successive laser pulses are directed into the same location of target surface, the cumulative effect seems to erode the target material unevenly and can lead to heating of the target material, the advantages of cold ablation being thus lost.

[0020] The same problems apply to nano-second range lasers, the problem being naturally even more severe because of the long lasting pulse with high energy. Here, the target material heating occurs always, the target material temperature being elevated to approximately 5000 K. Thus, even one single nano-second range pulse erodes the target material drastically, with aforesaid problems.

[0021] In the known techniques, the target may not only wear out unevenly but may also fragment easily and degrade the plasma quality. Thus, the surface to be coated with such plasma also suffers the detrimental effects of the plasma. The surface may comprise fragments, plasma may be not evenly distributed to form such a coating etc. which are problematic in accuracy demanding application, but may be not problematic, with paint or pigment for instance, provided that the defects keep below the detection limit of the very application.

[0022] The present methods wear out the target in a single use so that same target is not available for a further use from the same surface again. The problem has been tackled by utilising only a virgin surface of the target, by moving target material and/or the beam spot accordingly.

[0023] In machining or work-related applications the leftovers or the debris comprising some fragments also can make the cut-line uneven and thus inappropriate, as the case could for instance in flow-control drillings. Also the surface could be formed to have a random bumpy appearance caused by the

released fragments, which may be not appropriate in certain semiconductor manufacturing, for instance.

[0024] In addition, the mirror-film scanners moving back and forth generate inertial forces that load the structure itself, but also to the bearings to which the mirror is attached and/or which cause the mirror movement. Such inertia little by little may loosen the attachment of the mirror, especially if such mirror were working nearly at the extreme range of the possible operational settings, and may lead to roaming of the settings in long time scale, which may be seen from uneven repeatability of the product quality. Because of the stoppings, as well as the direction and the related velocity changes of the movement, such a mirror-film scanner has a very limited scanning width so to be used for ablation and plasma production. The effective duty cycle is relatively short compared to the whole cycle, although the operation is anyway quite slow. In the point of view of increasing the productivity of a system utilising mirror-film scanners, the plasma production rate is in prerequisite slow, scanning width narrow, operation unstable for long time period scales, but yield also a very high probability to get involved with unwanted particle emission in to the plasma, and consequently to the products that are involved with the plasma via the machinery and/or coating.

SUMMARY OF THE INVENTION

[0025] The maintenance cost for glass products is huge and steadily increasing and there is a great need for coating technologies for especially glass products comprising large surface areas. The product lifetime should be increased and the maintenance costs should be lowered, sustainable development being a prerequisite. The coating and especially uniform coating of large glass surfaces with one or several of the following properties: excellent optical properties, chemical and/or wear resistance, scratch-free surface, thermal resistance, coating adhesion, self-cleaning properties and properties derived from resistivity have remained an unsolved problem.

[0026] Neither recent high-technological coating methods, nor present coating techniques related to laser ablation either in nanosecond or cold ablation range (pico-, femto-second lasers) can provide any feasible method for industrial scale coating of glass products comprising larger surfaces. The present CVD- and PVD-coating technologies require high-vacuum conditions making the coating process batch wise, thus non-feasible for industrial scale coating of most of the present glass products. Moreover, the distance between the metal material to be coated and the coating material to be ablated is long, typically over 50 cm, making the coating chambers large and vacuum pumping periods time- and energy-consuming. Such high-volume vacuumed chambers are also easily contaminated with coating materials in the coating process itself, requiring continuous and time-consuming cleaning processes.

[0027] While trying to increase the coating production rate in present laser-assisted coating methods, various defects such as pinholes, increased surface roughness, decreased or disappearing optical properties, particulates on coating surface, particulates in surface structure affecting corrosion pathways, decreased surface uniformity, decreased adhesion, unsatisfactory surface thickness and tribological properties etc. take place.

[0028] The present coating methods also drastically restrict the materials employable for coating purposes in general and thus, limit the scope of different coated glass products avail-

able on market today. If applicable, then the target material surface is eroded in a manner that only the outmost layer of the target material can be employed for coating purposes. The rest of the material is either wasted or must be subjected to reprocessing before reuse.

[0029] An aim of the current invention is to solve or at least to mitigate the problems of the known techniques.

[0030] A first object of this invention is to provide a new method how to solve a problem to coat a certain surface of a glass product by pulsed laser deposition that so that the uniform surface area to be coated comprises at least 0.2 dm^2 .

[0031] A second object of this invention is to provide new glass products being coated by pulsed laser deposition so that the coated uniform surface area comprises at least 0.2 dm^2 .

[0032] A third object of this invention is to provide at least a new method and/or related means to solve a problem how to provide available such fine plasma practically from any target to be used in coating of glass products, so that the target material do not form into the plasma any particulate fragments either at all, i.e. the plasma is pure plasma, or the fragments, if exist, are rare and at least smaller in size than the ablation depth to which the plasma is generated by ablation from said target.

[0033] A fourth object of the invention is to provide at least a new method and/or related means to solve how to coat the uniform surface area of a glass product with the high quality plasma without particulate fragments larger in size than the ablation depth to which the plasma is generated by ablation from said target, i.e. to coat substrates with pure plasma originating to practically any material.

[0034] A fifth object of this invention is to provide a good adhesion of the coating to the uniform surface area of a glass product by said pure plasma, so that wasting the kinetic energy to particulate fragments is suppressed by limiting the existence of the particulate fragments or their size smaller than said ablation depth. Simultaneously, the particulate fragments because of their lacking existence in significant manner, they do not form cool surfaces that could influence on the homogeneity of the plasma plume via nucleation and condensation related phenomena.

[0035] A sixth object of the invention is to provide at least a new method and/or related means to solve a problem how to provide a broad scanning width simultaneously with fine plasma quality and broad coating width even for large glass bodies in industrial manner.

[0036] A seventh object of the invention is to provide at least a new method and/or related means to solve a problem how to provide a high repetition rate to be used to provide industrial scale applications in accordance with the objects of the invention mentioned above.

[0037] An eighth object of the invention is to provide at least a new method and/or related means to solve a problem how to provide good quality plasma for coating of uniform glass surfaces to manufacture products according to the first to seven objects, but still save target material to be used in the coating phases producing same quality coatings/thin films where needed.

[0038] A further object of the invention is to use such method and means according previous objects to solve a problem how to cold-work and/or coat surfaces for coated products. The present invention is based on the surprising discovery that glass products comprising large surfaces can be coated with industrial production rates and excellent qualities regarding one or more of technical features such as opti-

cal transparency, chemical and/or wear resistance, scratch-free-properties, thermal resistance and/or conductivity, resistivity (electrical), coating adhesion, self-cleaning properties and possibly, tribological properties, particulate-free coatings, pinhole-free coatings and electronic conductivity by employing ultra short pulsed laser deposition in a manner wherein pulsed laser beam is scanned with a rotating optical scanner comprising at least one mirror for reflecting said laser beam. Moreover, the present method accomplishes the economical use of target materials, because they are ablated in a manner accomplishing the reuse of already subjected material with retained high coating results. The present invention further accomplishes the coating of glass products in low vacuum conditions with simultaneously high coating properties. Moreover, the required coating chamber volumes are dramatically smaller than in competing methods. Such features decrease dramatically the overall equipment cost and increase the coating production rate. In many preferable cases, the coating equipment can be fitted into production-line in online manner.

[0039] The coating deposition rates with 20 W USPLD-apparatus are $2 \text{ mm}^3/\text{min}$. While increasing the laser power to 80 W, the USPLD coating deposition rate is increased to $8 \text{ mm}^3/\text{min}$, accordingly. According to the invention, the increase in deposition rate can now be fully employed to high quality coating production.

[0040] In this patent application the term "coating" means forming material of any thickness on a substrate. Coating can thus also mean producing thin films with thickness of e.g. $<1 \text{ }\mu\text{m}$.

[0041] Various embodiments of the inventions are combinable in suitable part.

[0042] When read and understood the invention, the skilled men in the art may know many ways to modify the shown embodiments of the invention, however, without leaving the scope of the invention, which is not limited only to the shown embodiments which are shown as examples of the embodiments of the invention.

FIGURES

[0043] The described and other advantages of the invention will become apparent from the following detailed description and by referring to the drawings where:

[0044] FIG. 1. illustrates an exemplary galvano-scanner set-up comprising two galvano-scanners employed in state of the art cold ablation coating/thin-film production and in machining and other work-related applications. The number of galvano-scanners directing the laser beam varies but is typically limited to one single galvano-scanner,

[0045] FIG. 2. illustrates ITO-coating on polycarbonate sheet ($\sim 100 \text{ mm} \times 30 \text{ mm}$) produced by employing a prior art vibrating mirror (galvo-scanner), in different ITO thin-film thicknesses (30 nm, 60 nm and 90 nm),

[0046] FIG. 3. illustrates the situation wherein prior art galvanometric scanner is employed in scanning laser beam resulting in heavy overlapping of pulses with repetition rate of 2 Mhz.,

[0047] FIG. 4. illustrates an one possible embodiment of the invention in form of ITO-coated sheet of glass,

[0048] FIG. 5. illustrates one possible turbine scanner mirror employed in method according to the invention,

[0049] FIG. 6. illustrates the movement of the ablating beam achieved by each mirror in the example of FIG. 5,

[0050] FIG. 7. illustrates beam guidance through one possible rotating scanner to be employed according to the invention,

[0051] FIG. 8. illustrates beam guidance through one possible rotating scanner to be employed according to the invention,

[0052] FIG. 9. illustrates beam guidance through one possible rotating scanner to be employed according to the invention,

[0053] FIG. 10. illustrates one embodiment of coated product according to the invention,

[0054] FIG. 11. illustrates one embodiment of coated product according to the invention,

[0055] FIG. 12. illustrates one embodiment of coated product according to the invention,

[0056] FIG. 13. illustrates one embodiment of coated product according to the invention,

[0057] FIG. 14a. illustrates one embodiment of coated product according to the invention, having a plurality of different layers forming mirror structure, one layer being always comprised of glass,

[0058] FIG. 14b. illustrates one embodiment of coated product according to the invention, having a plurality of different layers forming mirror structure, one layer being always comprised of glass,

[0059] FIG. 14c. illustrates one embodiment of coated product according to the invention, having a plurality of different layers forming mirror structure, one layer being always comprised of glass,

[0060] FIG. 15. illustrates one embodiment of multi-coated product according to the invention,

[0061] FIG. 16. illustrates one embodiment of multi-coated product according to the invention,

[0062] FIG. 17. illustrates two embodiments of coated product according to the invention,

[0063] FIG. 18. illustrates one embodiment of multi-coated product according to the invention,

[0064] FIG. 19. illustrates two embodiments of multi-coated product according to the invention,

[0065] FIG. 20. illustrates transmission curve for uncoated glass plate,

[0066] FIG. 21. illustrates transmission curve for one side ITO-coated glass plate, possessing high transparency,

[0067] FIG. 22. illustrates transmission curve for one side ITO-coated glass plate, possessing medium transparency,

[0068] FIG. 23. illustrates transmission curve for one side ITO-coated glass plate, possessing low transparency,

[0069] FIG. 24a. illustrates an embodiment according to the invention, wherein target material ablated by scanning the laser beam with rotating scanner (turbine scanner),

[0070] FIG. 24b. illustrates an exemplary part of target material of FIG. 24a,

[0071] FIG. 24c. illustrates an exemplary ablated area of target material of FIG. 24b,

[0072] FIG. 25a. illustrates an exemplary way according to the invention to scan and ablate target material with turbine scanner (rotating scanner),

[0073] FIG. 26a. illustrates plasma-related problems of known techniques,

[0074] FIG. 26b. illustrates plasma-related problems of known techniques.

DETAILED DESCRIPTION OF EMBODIMENTS OF THE INVENTION

[0075] According to the invention there is provided a method for coating a certain surface of a glass product by laser ablation in which method the uniform surface area to be coated comprises at least 0.2 dm^2 and the coating is carried by employing ultra short pulsed laser deposition wherein pulsed laser beam is scanned with a rotating optical scanner comprising at least one mirror for reflecting said laser beam.

[0076] With glass products is hereby meant but not limited to glass products such as for construction as whole, in architectural and building products for interior and decorative use, for optics in both consumer, scientific and military use, vehicles such as cars, trucks, motorcycles and tractors, airplanes, ships, boats, trains, rails, tools, medical products, lenses and protective shieldings of mobile devices and displays, lightning, profiles, frames, component parts, process equipment, pipes and tanks for various industries such as chemical industries, power and energy industries, space ships, plain metal sheets, military solutions, ventilation, water pipes, as disk material for various mastering systems, solar reflectors and solar cell cover glass etc. The glass product must not be necessarily of glass as such. According to the invention, all the products comprising glass surfaces regardless whether their glass content is 100% or 0.1% can be coated with now presented method. Some of the possible embodiments of the invention are illustrated in FIGS. 4 and 10-19.

[0077] Ultra Short Laser Pulsed Deposition is often shortened USPLD. Said deposition is also called cold ablation, in which one of the characteristic features is that opposite for example to competing nanosecond lasers, practically no heat transfer takes place from the exposed target area to the surroundings of this area, the laser pulse energies being still enough to exceed ablation threshold of target material. The pulse lengths are typically under 50 ps, such as 5-30 ps. i.e. ultra short, the phenomena of cold ablation being reached with pico-second but also femto-second and atto-second pulsed lasers. The material evaporated from the target by laser ablation is deposited onto a substrate that can be held near room temperature. Still, the plasma temperature reaches 1.000.000 K on exposed target area. The plasma speed is superior, gaining even 100.000 m/s and thus, leading to better adhesion of coating/thin-film produced. In a more preferred embodiment of the invention, said uniform surface area comprises at least 0.5 dm^2 . In a still more preferred embodiment of the invention, said uniform surface area comprises at least 1.0 dm^2 . The invention accomplishes easily also the coating of products comprising uniform coated surface areas larger than 0.5 m^2 , such as 1 m^2 and over. As the process is especially beneficial for coating large surfaces with high quality plasma, it meets an underserved or unserved market of several different glass products.

[0078] In industrial applications, it is important to achieve high efficiency of laser treatment. In cold ablation, the intensity of laser pulses must exceed a predetermined threshold value in order to facilitate the cold ablation phenomenon. This threshold value depends on the target material. In order to achieve high treatment efficiency and thus, industrial productivity, the repetition rate of the pulses should be high, such as 1 MHz, preferably over 2 MHz and more preferably over 5 MHz. As mentioned earlier, it is advantageous not to direct

several pulses into same location of the target surface because this causes a cumulating effect in the target material, with particle deposition leading to bad quality plasma and thus, bad quality coatings and thin-films, undesirable eroding of the target material, possible target material heating etc. Therefore, to achieve a high efficiency of treatment, it is also necessary to have a high scanning speed of the laser beam. According to the invention, the velocity of the beam at the surface of the target should generally be more than 10 m/s to achieve efficient processing, and preferably more than 50 m/s and more preferably more than 100 m/s, even such speeds as 2000 m/s. However, in the optical scanners based on vibrating mirror the moment of inertia prevents achieving sufficiently high angular velocity of the mirror. The obtained laser beam at the target surface is therefore just a few m/s, FIG. 1 illustrating an example of such vibrating mirror employed in the present laser ablation methods, also called galvano-scanner.

[0079] As the present coating methods employing galvano-scanners can produce scanning widths at most 10 cm, preferably less, the present invention also accomplishes much more broader scanning widths such as 30 cm and even over 1 meter with simultaneously excellent coating properties and production rates.

[0080] According to one embodiment of the invention, rotating optical scanner is here meant scanners comprising at least one mirror for reflecting laser beam. Such a scanner and its applications are described in patent application FI20065867. According to another embodiment of the invention, rotating optical scanner comprises at least three mirrors for reflecting laser beam. In one embodiment of the invention, in the coating method employs a polygonal prism illustrated in FIG. 5. Here, a polygonal prism has faces **21**, **22**, **23**, **24**, **25**, **26**, **27** and **28**. Arrow **20** indicates that the prism can be rotated around its axis **19**, which is the symmetry axis of the prism. When the faces of the prism of the FIG. 5 are mirror faces, advantageously oblique in order to achieve scanning line, arranged such that each face in its turn will change, by means of reflection, the direction of radiation incident on the mirror surface as the prism is rotated around its axis, the prism is applicable in the method according to an embodiment of the invention, in its radiation transmission line, as part of a rotating scanner, i.e. turbine scanner. FIG. 5 shows 8 faces, but there may be considerably more faces than that, even dozens or hundreds of them. FIG. 5 also shows that the mirrors are at the same oblique angle to the axis, but especially in an embodiment including several mirrors, the said angle may vary in steps so that, by means of stepping within a certain range, a certain stepped shift on the work spot is achieved on the target, illustrated in FIG. 6, among other things. The different embodiments of invention are not to be limited into various turbine scanner mirror arrangements regarding for example the size, shape and number of laser beam reflecting mirrors.

[0081] The structure of the turbine scanner, FIG. 5, includes at least 2 mirrors, preferably more than 6 mirrors, e.g. 8 mirrors (**21** to **28**) positioned symmetrically around the central axis **19**. As the prism **21** in the turbine scanner rotates **20** around the central axis **19**, the mirrors direct the radiation, a laser beam, for instance, reflected from spot **29**, accurately onto the line-shaped area, always starting from one and the same direction (FIG. 6). The mirror structure of the turbine scanner may be non-tilted (FIG. 7) or tilted at a desired angle, e.g. FIGS. 8 and 9. The size and proportions of the turbine scanner can be freely chosen. In one advantageous embodi-

ment of the coating method it has a perimeter of 30 cm, diameter of 12 cm, and a height of 5 cm.

[0082] In an embodiment of the invention it is advantageous that the mirrors **21** to **28** of the turbine scanner are preferably positioned at oblique angles to the central axis **19**, because then the laser beam is easily conducted into the scanner system.

[0083] In a turbine scanner according to be employed according to an embodiment of the invention (FIG. 5) the mirrors **21** to **28** can deviate from each other in such a manner that during one round of rotational movement there are scanned as many line-shaped areas (FIG. 6) **29** as there are mirrors **21** to **28**.

[0084] According to the invention, the surface to be coated can comprise whole or a part of the glass product surface.

[0085] In one preferred embodiment of the invention laser ablation is carried out under vacuum of 10^{-1} to 10^{-12} atmospheres. High vacuum conditions require quite long pumping times, and thus prolonged production times of coatings. With certain high end-products this is not so big problem, but with for example commodity products especially comprising larger surfaces this definitely is. If taking into account to for example novel wear- and scratch-free coatings, chemically inert coatings, tribological coatings, thermally resistant and/or thermally conductive coatings, resistive coatings, electrically conductive coatings and possibly simultaneously excellent transparencies, there simply aren't any coating methods available for said products, neither from technological point of view and/or from economical point of view.

[0086] Thus, in a more preferred embodiment of invention, the laser ablation is carried out under vacuum of 10^{-1} to 10^{-4} atmospheres. According to the invention, excellent coating/thin-film properties can be achieved already in low atmospheres, leading to dramatically decreased processing times and enhanced industrial applicability.

[0087] According to the invention it is also possible to conduct the coating in a manner wherein the distance between the target material and said uniform surface area to be coated is under 25 cm, preferably under 15 cm and most preferably under 10 cm. This accomplishes the development of coating chambers with drastically diminished volumes, making the overall price of coating production lines lower and decreasing further the time required for vacuum pumping.

[0088] In a preferred embodiment of the invention the ablated surface of said target material can be repeatedly ablated in order to produce defect-free coating. In case of most of the present coating technologies, the target material wears unevenly in a manner that the affected area cannot be reused for ablation and must thus be either discarded or sent for regeneration after certain use. The problem has been tackled by developing different techniques for feeding constantly new, non-ablated target surface for coating purposes by for example moving the target material in x/y-axis or by rotating a cylinder-formed target material. The present invention accomplishes simultaneously excellent coating properties and production rates as well as use of target material in a way wherein the good quality plasma retains its quality throughout the use of substantially whole piece of target material. Preferably, more than 50% of the single target material weight is consumed to production of good quality plasma according to the invention. With good quality plasma is meant plasma for producing defect-free coatings and thin-films, the high quality of plasma plume being maintained at

high pulse frequencies and deposition rates. Some of such properties are described here below.

[0089] According to one embodiment of the invention, the average surface roughness of produced coating on said uniform surface area is less than 100 nm as scanned from an area of 1 μm^2 with Atomic Force Microscope (AFM). More preferably, the average surface roughness is less than 30 nm. Most preferably, the average surface roughness is less than 10 nm.

[0090] With average surface roughness is here meant the average deviation from the centre line average curve fitted by a proper procedure, such as those available in AFM or profilometer. The surface roughness affects amongst the other the wear- and scratch-free properties, tribological properties as well as the transparency of coating on glass products coated according to the invention.

[0091] In a still preferable embodiment of the invention, the optical transmission of produced coating on said uniform surface area is no less than 88%, preferably no less than 90% and most preferably no less than 92%. It can even be higher than 98%. In some cases it can be beneficial to have limited optical transparency. Such examples include safety-screens, non-transparent windows, sun-glasses, protective screens for either sun-light or UV-light or other radiation.

[0092] In another embodiment of the invention, produced coating on said uniform surface area contains less than one pinhole per 1 mm^2 , preferably less than one pinhole per 1 cm^2 and most preferably no pinholes at said uniform surface area. Pinhole is a hole going through or substantially through the coating. Pinholes provide a platform for erosion of the originally coated material for example by chemical or environmental factors. Single pinhole in for instance coating of chemical reactor or tubing can lead to dramatically lowered life-time of said product.

[0093] Thus, in another preferred embodiment said uniform surface area is coated in a manner wherein the first 50% of said coating on said uniform surface area does not contain any particles having a diameter exceeding 1000 nm, preferably 100 nm and most preferably 30 nm. If the early stages of the coating manufacturing process produce micrometer size particles, such particles can cause open corrosion pathways in the next layers of produced coating. Moreover, due to irregular shape of particles, it is extremely difficult to seal the surface underneath such particles. Additionally, such particles increase surface roughness substantially. The present method allows even here increased lifetime and lowered maintenance cost of different glass products.

[0094] The glass product itself can comprise virtually whichever glass (silicate glass, quartz, lead glass etc), glass compound such as different glass composite materials or mixtures of these. According to one embodiment of the invention, said uniform surface area of glass product is coated with metal, metal oxide, metal nitride, metal carbide or mixtures of these. Non-limiting examples of metals include aluminum, molybdenum, titanium, zirconium, copper, yttrium, ruthenium, lead, magnesium, zinc, chromium, silver, gold, cobalt, tin, nickel, tantalum, gallium, rhodium, manganese, vanadium, platinum and virtually whichever metal.

[0095] When producing coatings according to invention which comprise both excellent optical, wear, and scratch-free properties, especially advantageous metal oxides are for example aluminum oxide and its different composites such as aluminum titan oxide (ATO). Due to its resistivity, high-optical transparencies possessing high-quality indium tin oxide (ITO) is especially preferred in applications wherein

the coating can be employed to warm-up the coated surface. It can also be employed in solar-control. Yttrium stabilized zirconium oxide is another example of different oxides possessing both excellent optical, wear-resistant and scratch-free properties. Some metals can be applied in solar cell applications. Here, the actual cells are many times grown on glass and the demand for reproducible, low-cost and high-quality coatings producing methods is increasing steadily. Here, the optical properties of metal-derived thin-films are somewhat different from those of bulk metals. In ultrathin films (<100 Å thick) variations make the concept of optical constants problematic, the quality and surface roughness of the coating (thin film) being thus critical technical features. Such coatings can easily be produced with the method of present invention.

[0096] As most of the pure metals, all the metals usually employed as mirrors (Al, Ag, Au, Cu, Rh and Pt) regardless their use are easily subjected to oxidation (Al), sulfide tarnishing (Ag) and mechanical scratching. Mirrors must therefore be coated with hard transparent protective layers. Thus, films of SiO, SiO₂ and Al₂O₃ are commonly used to protect evaporated Al mirrors, but usually at the cost of increasing absorbance. The problem can be tackled with present invention by producing hard coatings comprising better optical transparencies and heat conductivities. At present, various substrate film glue (e.g. Al₂O₃, SiO) are used to improve adhesion, but Ag film use in mirrors remains restricted. The adhesion of appropriate films can be enhanced by producing both now employed films and other enhanced carbon-based films such as diamond and carbon nitride with the method of present invention.

[0097] Dielectric materials employed in present optical coating applications include fluorides (e.g. MgF₂, CeF₃), oxides (e.g. Al₂O₃, TiO₂, SiO₂), sulfides (e.g. ZnS, CdS) and assorted compounds such as ZnSe and ZnTe. An essential common feature of dielectric optical materials in their very low absorption ($\alpha < 10^3/\text{cm}$) in some relevant portion of the spectrum; in this region they are essentially transparent (e.g. fluorides and oxides in the visible and infrared, chalcogenides in the infrared).

[0098] Dielectric coatings can be advantageously produced with the method of present invention.

[0099] Somewhere between dielectrics and metals is a class of materials called transparent conductors. According to electromagnetic theory, high conductivity and optical transparency are mutually exclusive properties since photons are strongly absorbed by the high density of charge carriers. Although there are materials that separately are far more conductive or transparent, the transparent conductors dealt with here exhibit a useful compromise of both desirable properties. Broadly speaking, transparent conducting films consist either of very thin metals or semiconducting oxides and/and most presently even nitrides such as indiumgalliumnitride in solar cell applications. The first widespread use of such films was to transparent electrical heaters in aircraft windshield de-icing during World War II. Today, they are somewhat used for automobile and airplane window defrosters, liquid crystal and gas-discharge displays, front electrodes for solar cells, antistatic coatings, heating stages for optical microscopes, IR-reflectors, photoconductors in television camera vidicons, and Pockel cells for laser Q-switches.

[0100] Metals that have conventionally been employed be as transparent conductors include Au, Pt, Rh, Ag, Cu, Fe and Ni. Simultaneous optimization of conductivity and transpar-

ency presents a considerable challenge in film deposition. At one extreme are discontinuous islands of considerable transparency but high resistivity; at the other are films that coalesce early and are continuous, possessing high conductivity but low transparency. For these reasons, the semi-conducting oxides such as SnO_2 , In_2O_3 , CdO , and, more commonly, their alloys (e.g. ITO), doped In_2O_3 (with Sn, Sb) and doped SnO_2 (with F, Cl, etc.) are used.

[0101] The prior art deposition systems include both chemical and physical methods. Hydrolysis of chlorides and pyrolysis of metalorganic compounds are examples of the former, reactive evaporation and sputtering in oxygen environment being examples of the latter. Optimum film properties require maintenance of tight stoichiometry. Since glass substrates, which are often heated close to the softening temperature in prior art technologies, are commonly used, care must be taken to prevent stresses and warpage of the final product. The present method of invention solves the problems associated with softening temperature (cold ablation) but yields also said films in high quality and economically feasible manner.

[0102] For the most part, η in fluoride and oxide films has a value less than 2 at the reference wavelength of 0.55 μm . For many applications, however, it is important to have films with higher refractive index in the visible range. To meet these needs, materials like ZnS and XnSe are typically employed. High transmittance is an essential requirement in optical films, and as an arbitrary criterion only materials with an absorption constant less than $\alpha=10^3/\text{cm}$ are entered in the following list: NaF(c), LiF(c), CaF_2 (c), Na_3AlF_6 (c), AlF_3 (a), MgF_2 (c), ThF_4 (a), LaF_3 (c), CeF_3 (c), SiO_2 (a), Al_2O_3 (a), MgO (c), Y_2O_3 (a), La_2O_3 (a), CeO_2 (c), ZrO_2 (a), SiO (a), ZnO (c), TiO_2 , ZnS (c), CdS (c), ZnSe (c), PbTe , Si (a), Ge (a); (c)=crystalline; (a)=amorphous.

[0103] In practice, however, only films with significantly lower absorption can be tolerated. For example, in laser AR coatings losses must be kept to less than 0.01%, corresponding to $k \approx 4 \times 10^{-5}$ or $\alpha=10/\text{cm}$ at $\lambda=5500 \text{ \AA}$.

[0104] The present method of invention solves the problems associated with difficulties to yield films with higher refractive index in the visible range and accomplishes the production of said films in high quality and economically feasible manner. Moreover, it is now possible to produce above listed materials and compounds in crystalline form, enhancing further the film properties.

[0105] If certain metal oxides such as titan oxide and zinc oxide are applied on surface thicknesses providing UV-activity of produced coating, the coating can possess self-cleaning properties. Such properties are highly desired in order to accomplish the use and decrease the maintenance cost of several metal products in both interior and exterior use.

[0106] The metal oxide coatings can be produced by either ablating metal or metals in active oxygen atmosphere or by ablating oxide-materials. Even in latter possibility, it is possible to enhance the coating quality and/or production rate by conducting the ablation in reactive oxygen. When producing nitrides it is according to the invention possible to use nitrogen atmosphere or liquid ammonia in order to enhance the coating quality. A representative example of invention is production of carbon nitride films (C_3N_4).

[0107] According another embodiment of the invention, said uniform surface area of glass product is coated with carbon material comprising over 90 atomic-% of carbon, with more than 70% of sp^3 -bonding. Such materials include for

example amorphous diamond, nano-crystalline diamond or even pseudo-monocrystalline diamond. Various diamond coatings give the glass product excellent tribological, wear- and scratch-free properties but increase also the heat-conductivity and -resistance.

[0108] Diamond-coatings on glass can be used with special preference in protective eye-ware, in electronic device displays, in protecting glass equipment applied in hazardous conditions, and if of high quality, i.e. crystalline form, is semiconductor applications, in solar cells, in diode pumps for instance for laser applications etc.

[0109] In a still another embodiment of the invention, said uniform surface area of glass product is coated with material comprising carbon, nitrogen and/or boron in different ratios. Such materials include boron carbon nitride, carbon nitride (both C_2N_2 and C_3N_4), boron nitride, boron carbide or phases of different hybridizations of B—N, B—C and C—N phases. Said materials are diamond-like materials having low densities, are extremely wear-resistant, and are generally chemically inert. For example carbon nitrides can be employed to protect glass products against corrosive conditions, as coatings for medical devices, battery electrodes, humidity and gas sensors, semiconductor applications, in solar cells, tools, etc.

[0110] According to one embodiment of the invention certain uniform surface area of glass product is coated with organic polymer material. Such materials include but are not limited to chitosan and its derivatives, polysiloxanes, and different organic polymers.

[0111] By coating a glass product with chitosan there are promising perspectives to produce a new class of glass products for marine and other water environments as well as new glass products for both interior and exterior use.

[0112] Here, polysiloxanes are especially advantageous for manufacturing products with relatively high wear-resistance and scratch-free properties with simultaneously excellent optical transparencies.

[0113] According to still another embodiment of invention said uniform surface area is coated with inorganic material. Such materials include but are not limited to for instance stone, glass and ceramic derived materials.

[0114] In one especially preferred embodiment of the invention, different glass sheets and 3D-glass structures such as a small ash-tray made of glass were coated by ablating a target material comprising pink agate resulting in colored but opaque coating result.

[0115] According to one embodiment of invention, said uniform surface of the glass product is coated with only one single coating. According to another embodiment of the invention, said uniform surface of the glass product is coated with multilayered coating. Several coatings can be produced in for different reasons. One reason might be to enhance the adhesion of certain coatings to glass product surface by manufacturing a first set of coating having better adhesion to glass surface and possessing such properties that the following coating layer has better adhesion to said layer than to glass surface itself. Additionally, the multilayered coating can possess several functions not achievable without said structure. The present invention accomplishes the production of several coatings in one single coating chamber or in the adjacent chambers.

[0116] The present invention further accomplishes the production of composite coatings to glass product surface by ablating simultaneously one composite material target or two or more target materials comprising one or more substances.

[0117] According to invention the thickness of said coating on uniform surface of glass product is between 20 nm and 20 μm , preferably between 100 nm and 5 μm . The coating thicknesses must not be limited to those, because the present invention accomplishes the preparation of molecular scale coatings on the other hand, very thick coatings such as 100 μm and over, on the other hand.

[0118] The present invention further accomplishes the preparation of 3D-structures employing the glass component as a scaffold for growing said 3D-structure.

[0119] According to the invention there is also provided a glass product comprising a certain surface being coated by laser ablation wherein the coated uniform surface area comprises at least 0.2 dm^2 and that the coating has been carried by employing ultra short pulsed laser deposition wherein pulsed laser beam is scanned with a rotating optical scanner comprising at least one mirror for reflecting said laser beam. The benefits received with these products are described in more detail in the previous description of the method.

[0120] In a more preferred embodiment of the invention said uniform surface area comprises at least 0.5 dm^2 . In a still more preferable embodiment of the invention said uniform surface area comprises at least 1.0 dm^2 . The invention accomplishes easily also the products comprising uniform coated surface areas larger than 0.5 m^2 , such as 1 m^2 and over.

[0121] According to one embodiment of the invention the average surface roughness of produced coating on said uniform surface area is less than 100 nm as scanned from an area of 1 μm^2 with Atomic Force Microscope (AFM). Preferably, the uniform surface roughness is less than 50 nm and most preferably it is under 25 nm.

[0122] According to another embodiment of the invention the optical transmission of produced coating on said uniform surface area is no less than 88%, preferably no less than 90% and most preferably no less than 92%. In some cases the optical transmission can exceed 98%.

[0123] According to still another embodiment of the invention said produced coating on said uniform surface area contains less than one pinhole per 1 mm^2 , preferably less than one pinhole per 1 cm^2 and most preferably no pinholes at said uniform surface area.

[0124] According to still another embodiment of the invention said uniform surface area is coated in a manner wherein the first 50% of said coating on said uniform surface area does not contain any particles having a diameter exceeding 1000 nm, preferably 100 nm and most preferably 30 nm.

[0125] The glass product according to the invention can comprise virtually whichever glass, glass composite materials. As mentioned earlier, the definition of glass product in this connection must be understood in a manner, wherein the product comprises a certain glass surface, which has been coated according to now invented method. The glass content of the product scaffold (uncoated product) can thus vary everywhere between 0.1 to 100%.

[0126] According to one embodiment of the invention said uniform surface area of glass product is coated with metal, metal oxide, metal nitride, metal carbide or mixtures of these. The possible metals were described earlier in description of now invented coating method.

[0127] According to another embodiment of the invention said uniform surface area of glass product is coated with carbon material comprising over 90 atomic-% of carbon, with

more than 70% of sp^3 -bonding. The possible carbon materials were described earlier in description of now invented coating method.

[0128] According to still another embodiment of the invention said uniform surface area of glass product is coated with material comprising carbon, nitrogen and/or boron in different ratios. Such materials were described earlier in description of now invented coating method.

[0129] According to still another embodiment of the invention said uniform surface area of glass product is coated with organic polymer material. Such materials were described earlier in more detail in description of now invented coating method.

[0130] According one embodiment of the invention said uniform surface area is coated with inorganic material. Such materials were described earlier in more detail in description of now invented coating method.

[0131] According to another preferred embodiment of the invention said uniform surface of glass product is coated with multilayered coating. According to another preferred embodiment of the invention said uniform surface of glass product is coated with single coating layer.

[0132] According to one preferred embodiment of the invention the thickness of said coating on uniform surface of glass product is between 20 nm and 20 μm , preferably between 100 nm and 5 μm . The invention accomplishes also coated glass products comprising one or several atomic layer coatings and thick coatings such as exceeding 100 μm , for example 1 mm. The present invention further accomplishes the 3D-structures prepared by employing the glass component as a scaffold for growing said 3D-structure.

EXAMPLES

Example to Demonstrate Known Art Problems— Laser Technology

[0133] FIG. 2 represents the ITO-coating on polycarbonate sheet ($\sim 100 \text{ mm} \times 30 \text{ mm}$) produced by employing a prior art optical scanner, namely vibrating mirror (galvo-scanner), in different ITO thin-film thicknesses (30 nm, 60 nm and 90 nm). Although the ITO-coating is not deposited on metal substrate, the picture clearly demonstrates some of the problems associated with employing vibrating mirror as an optical scanner especially in ultra short pulsed laser deposition (USPLD) but also in laser assisted coatings in general. As a vibrating mirror changes its direction of angular movement at its end positions, and due to moment inertia, the angular velocity of the mirror is not constant near to its end positions. Due to vibrating movement, the mirror continuously brakes up and stops before speeding up again, causing thus irregular treatment of the target material at the edges of the scanned area. As it can be seen from FIG. 2, this in turn results in low quality plasma comprising particles especially in the edges of the scanned area and finally, in low quality and seemingly uneven coating result. Although not made on glass substrate, this example clearly demonstrates some of the drawbacks associated with present USPLD method employing conventional scanners. The coating parameters have been selected in order to demonstrate the uneven distribution of ablated material due to the nature of employed scanner. If selecting the

parameters appropriately, the film quality can be enhanced, problems becoming invisible but not excluded.

Example to Demonstrate Known Art Problems—Laser Technology

[0134] Conventionally galvanometric scanners are used to scan a laser beam with a typical maximum speed of about 2-3 m/s, in practice about 1 m/s. This means that even 40-60 pulses are overlapping with a repetition rate of 2 MHz (FIG. 3).

Example to Demonstrate Known Art Problems—Laser Technology

[0135] Plasma related quality problems are demonstrated in FIGS. 26a and 26b, which indicate plasma generation according to known techniques. A laser pulse $\square$ 1114 hits a target surface 1111. As the pulse is a long pulse, the depth h and the beam diameter d are of the same magnitude, as the heat of the pulse 1114 also heat the surface at the hit spot area, but also beneath the surface 1111 in deeper than the depth h. The structure experiences thermal shock and tensions are building, which while breaking, produce fragments illustrated F. As the plasma may be in the example quite poor in quality, there appears to be also molecules and clusters of them indicate by the small dots 1115, as in the relation to the reference by the numeral 1115 for the nuclei or clusters of similar structures, as formed from the gases 1116 demonstrated in the FIG. 26b. The letter "o"s demonstrate particles that can form and grow from the gases and/or via agglomeration. The released fragments may also grow by condensation and/or agglomeration, which is indicated by the curved arrows from the dots to Fs and from the os to the Fs. Curved arrows indicate also phase transitions from plasma 1113 to gas 1116 and further to particles 1115 and increased particles 1117 in size. As the ablation plume in FIG. 26b can comprise fragments F as well as particles built of the vapours and gases, because of the bad plasma production, the plasma is not continuous as plasma region, and thus variation of the quality may be met within a single pulse plume. Because of defects in composition and/or structure beneath the deepness h as well as the resulting variations of the deepness (FIG. 26a), the target surface 1111 in FIG. 26b is not any more available for a further ablations, and the target is wasted, although there were some material available.

Example of Invention—1

[0136] FIG. 24a demonstrates a target material ablated with pico-second-range pulsed laser employing rotating scanner with speed accomplishing the ablation of target material with slight overlapping of adjacent pulses, avoiding the problems associated with prior art galvano-scanners. FIG. 24b shows enlarged picture of one part of the ablated material, clearly demonstrating the smooth and controlled ablation of material on both x- and y-axis and thus, generation of high quality, particle-free plasma and further, high quality thin-films and coatings. FIG. 24c demonstrates one example of possible x- and y-dimensions of one single ablation spot achieved by one or few pulses. Here, it can be clearly seen, that the invention accomplishes the ablation of material in a manner wherein the width of the ablated spot is always much bigger than the depth of the ablated spot area. Theoretically, the possible particles (if they would be generated) could now have a maximum size of the spot depth. The rotating scanner now accomplishes the

production of good quality, particle free plasma with great production rate, with simultaneously large scanning width, especially beneficial for substrates comprising large surface areas to be coated. Furthermore, the FIGS. 24a, 24b and 24c clearly demonstrate that opposite to present techniques, the already ablated target material area can be ablated for new generation of high class plasma—reducing thus radically the overall coating/thin-film producing cost.

Example of Invention—2

[0137] FIG. 25a demonstrates an example wherein coating is carried out by employing a pico-second USPLD-laser and scanning the laser pulses with turbine scanner. Here, the scanning speed is 30 m/s, the laser spot-width being 30 μ m. In this example, there is an $\frac{1}{3}$ overlapping between the adjacent pulses.

Examples of Invention—Coated Products

[0138] The following samples were grown on various glass substrates by employing ultra short pulsed laser deposition (USPLD) with a picosecond-range laser (X-lase, 20-80 W) at 1064 nm. Substrate temperature varied from room temperature to 400° C. and target temperature in the, range of room temperature to 700° C. Both oxide, sintered graphite, sintered graphitic $C_3N_4H_x$ (Carbodeon Ltd Oy) and various metal targets were employed. When employing oxygen atmosphere, the oxygen pressure varied in the range of 10^{-4} to 10^{-1} mbar. When employing nitrogen atmosphere, the nitrogen pressure varied in the range of 10^{-4} to 10^{-4} mbar. The employed scanner was a rotating mirror scanner accomplishing tunable velocity of the beam at the surface of the target between 1 m/s to 350 m/s. The employed repetition rates varied between 1 to 30 MHz, clearly demonstrating the importance of both the scanner and high repetition rates when producing high quality coatings in industrial manner. Deposited films were characterized by confocal microscope, FTIR and Raman spectroscopy, AFM, optical transmission measurements, ESEM and in some cases, electrical measurements (University of Kuopio, Finland; ORC, Tampere, Finland and Corelase Oy, Tampere Finland). Electrical resistivity of the samples varied in the range of $2-40 \times 10^{-3} \Omega$ cm and was quite sensitive to deposition parameters which were not completely optimized in order to obtain lowest resistivities. The resistivities obtained are quite comparable to those reported for ITO-films prepared by sputtering method (typically $2-6 \times 10^{-3} \Omega$ cm).

[0139] The employed spot sizes varied between 20 to 80 μ m. The wear tests were carried out by employing pin on disk-method (University of Kuopio, Finland), the tests being carried out at room temperature 22 C and 50% (AD-coatings) or 25% (others) relative humidity (without lubrication) with loads in the range 10-125 g using a hardened steel ball (AISI 420), 6 mm in diameter, as a pin. For AD-coatings the rotation speed was 300-600 rpm and for lenses 1 rpm. All the coatings possessed excellent wear properties as well as adhesions.

Example 1

[0140] A disc of single crystal SiO_2 was coated by ablating sintered carbon with pulse repetition rate of 4 MHz, pulse energy 2.5 μ J, pulse length 20 ps and the distance between the target material and surface to be coated was 8 mm. The vacuum level was 10^{-5} atmospheres during the coating process. The process resulted in a uniform pale-brown, transpar-

ent coating. The coating thickness was 150 nm and the average surface roughness was determined to be 20 nm as scanned from an area of $1\ \mu\text{m}^2$ with Atomic Force Microscope (AFM). No pinholes or detectable particles were found on any measured area.

Example 2

[0141] Several glass sheets with surface area $100\ \text{mm} \times 150\ \text{mm}$ and thickness of $\sim 3\ \text{mm}$ was coated by ablating ITO ($\text{In}_2\text{O}_3:\text{SnO}_2$; 9:1; Sigma technology, China) with repetition rate of 4 MHz, pulse energy 2-10 μJ , pulse length 20 ps and the distance between the target material and surface to be coated was varied between 30 mm and 50 mm. The vacuum level was 10^{-5} atmospheres during the coating process. The process resulted in a uniform, transparent coating. The coating thickness was 150 nm and the average surface roughness was determined to be 0.3 nm as scanned from an area of $1\ \mu\text{m}^2$ with Atomic Force Microscope (AFM). No pinholes were found on any measured area. Electrical resistivity of the samples varied in the range of $2\text{--}40 \times 10^{-3}\ \Omega\text{cm}$. Examples of transmission curves of reference glass (uncoated), high-transparency ITO comprising resistivity of $\sim 6 \times 10^{-3}\ \Omega\text{cm}$, medium transparency ITO as well as low transparency ITO with resistivity of $2 \times 10^{-3}\ \Omega\text{cm}$ are illustrated in FIGS. 20, 21, 22 and 23 respectively.

Example 3

[0142] One ITO-coated glass piece of example 2 was coated by ablating aluminum titanoxide with repetition rate of 1 Mhz, pulse energy 12 μJ , pulse length 20 ps and the distance between the target material and surface to be coated was 30 mm. The vacuum level was 10^{-5} atmospheres during the coating process. The process resulted in a uniform, transparent coating. The ATO coating thickness was measured to 500 nm and the average surface roughness was determined to be 10 nm as scanned from an area of $1\ \mu\text{m}^2$ with Atomic Force Microscope (AFM). No pinholes were found on any measured area. The oxide coated final product possessed remarkably better wear resistance and scratch-free properties as compared to non-coated glass material. The adhesion of the multilayered structure was good.

Example 4

[0143] One ITO-coated glass piece of example 2 was coated by ablating yttrium stabilized zirconium oxide with repetition rate of 1 Mhz, pulse energy 10 μJ , pulse length 20 ps and the distance between the target material and surface to be coated was 10 mm. The vacuum level was 10^{-5} atmospheres during the coating process. The process resulted in a uniform, transparent coating. The YAG coating thickness was measured to 300 nm and the average surface roughness was determined to be 2 nm as scanned from an area of $1\ \mu\text{m}^2$ with Atomic Force Microscope (AFM). No pinholes were found on any measured area. The oxide coated final product possessed remarkably better wear resistance and scratch-free properties as compared to non-coated glass material. The adhesion of the multilayered structure was good.

Example 5

[0144] A glass sheet with surface area $100\ \text{mm} \times 150\ \text{mm}$ and thickness of $\sim 3\ \text{mm}$ was coated by ablating indium-tin metal target (9:1) in active oxygen atmosphere the oxygen pressure varying in the range of 10^{-4} to 10^{-4} mbar. The

employed repetition rate was 4 MHz, pulse energy 5 μJ , pulse length 20 ps and the distance between the target material and surface to be coated was 35 mm. The vacuum level was 10^{-5} atmospheres before the reactive gas feed. The process resulted in a uniform, transparent ITO-coating. The coating thickness was 150 nm and the average surface roughness was determined to be below 1 nm as scanned from an area of $1\ \mu\text{m}^2$ with Atomic Force Microscope (AFM). No pinholes were found on measured area of ITO-coating. Electrical resistivity of the sample was $2.2 \times 10^{-3}\ \Omega\text{cm}$.

Example 6

[0145] A drinking glass according to FIG. 12 was coated by ablating pink agate (crushed and sintered) with pulse repetition rate of 30 MHz and the distance between the target material to be coated was 2 cm. The glass was pre-heated into approximately $120^\circ\ \text{C}$. The vacuum level was 10^{-4} atmospheres during the coating process. The processes resulted in pink agate coloured, opaque coatings with thickness of 150 nm. The average surface roughness was determined to lower than 2 nm as scanned from an area of $1\ \mu\text{m}^2$ with Atomic Force Microscope (AFM). No pinholes were found on any measured area of agate coating.

Example 8

[0146] A glass sheet with surface area comprising $500\ \text{mm} \times 600\ \text{mm}$ was coated by ablating cold-pressed chitosan with pulse repetition rate of 10 MHz, pulse energy 5 μJ , pulse length 20 ps and the distance between the target material and surface to be coated was 20 mm. The glass-material was pre-heated into approximately $120^\circ\ \text{C}$. The vacuum level was 10^{-5} atmospheres during the coating process. The process resulted in partially opaque coating possessing coating thickness of 260 nm. The average surface roughness was determined to be lower than 4 nm as scanned from an area of $1\ \mu\text{m}^2$ with Atomic Force Microscope (AFM). No pinholes were found on any measured area of polymer coating.

Example 9

[0147] A glass sheet with surface area comprising $300\ \text{mm} \times 300\ \text{mm}$ was coated by ablating vanadium metal in active oxygen atmosphere the oxygen pressure varying in the range of 10^{-4} to 10^{-1} mbar. The pulse repetition rate of 25 MHz, pulse energy 5 μJ , pulse length 20 ps, the distance between the target material and surface to be coated being adjusted to 30 mm. The glass-material was pre-heated into approximately $120^\circ\ \text{C}$. The vacuum level was kept at 10^{-5} atmospheres before the actual coating process. The process resulted transparent coating possessing coating thickness of 10 nm. The average surface roughness was determined to be 0.14 nm as scanned from an area of $1\ \mu\text{m}^2$ with Atomic Force Microscope (AFM). No pinholes were found on any measured area of vanadiumoxide coating.

Example 10

[0148] A glass sheet with surface area comprising $300\ \text{mm} \times 300\ \text{mm}$ was coated by ablating copper metal target. The pulse repetition rate of 17 MHz, pulse energy 4.5 μJ , pulse length 20 ps, the distance between the target material and surface to be coated being adjusted to 70 mm. The glass-material was pre-heated into approximately $120^\circ\ \text{C}$. The vacuum level was 10^{-5} atmospheres during the coating process. The short process resulted transparent coating possess-

ing coating thickness of 3 nm. The average surface roughness was determined to be 0.14 nm as scanned from an area of $1 \mu\text{m}^2$ with Atomic Force Microscope (AFM). No pinholes were found on any measured area of copper coating. The copper coating seemed to be easily oxidized.

Example 11

[0149] The procedure of example 10 was repeated and the copper coated glass sheet was subjected to another coating process without opening the vacuumed coating chamber between the following coating steps. The next coating layer was produced by ablating yttrium stabilized zirconium oxide with pulse repetition rate of 5 MHz and pulse length of 19 ps. The vacuum level was kept constantly at 10^{-5} atmospheres during the coating process, without any vacuum drops between the following coating procedures. The process resulted transparent YAG-coating possessing coating thickness of 180 nm. The average surface roughness was determined to be 0.14 nm as scanned from an area of $1 \mu\text{m}^2$ with Atomic Force Microscope (AFM). No pinholes were found on any measured area of YAG-coating.

Example 12

[0150] A laboratory glass tube according to FIG. 10 was coated by ablating sintered, graphitic carbon nitride ($\text{C}_3\text{N}_4\text{Hx}$, Carbodeon Ltd Oy) target material. The pulse repetition rate of was 2 MHz, pulse energy 5 μJ , pulse length 20 ps, and the distance between the target material and surface to be coated was adjusted to 15 mm. The glass-material was pre-heated into approximately 120°C . The vacuum level was 10^{-5} atmospheres during the coating process. The process resulted in C_3N_4 -coating possessing coating thickness of 19 nm. The average surface roughness was determined to be 0.14 nm as scanned from an area of $1 \mu\text{m}^2$ with Atomic Force Microscope (AFM). No pinholes were found on any measured area of copper coating. The copper coating seemed to be easily oxidized.

Example 13

[0151] A glass sheet with surface area $100 \text{ mm} \times 150 \text{ mm}$ and thickness of $\sim 3 \text{ mm}$ was coated by ablating gallium nitride target (GaN). The employed repetition rate was 4 MHz, pulse energy 6 μJ , pulse length 20 ps and the distance between the target material and surface to be coated was 60 mm. The vacuum level was kept at 10^{-5} atmospheres. The process resulted in a uniform, transparent GaN -coating. The coating thickness was 20 nm and the average surface roughness was determined to be under 1 nm as scanned from an area of $1 \mu\text{m}^2$ with Atomic Force Microscope (AFM). No pinholes were found on any measured area.

Example 14

[0152] The gallium nitride coated glass sheet of example 13 was coated with ITO by ablating ITO ($\text{In}_2\text{O}_3:\text{SnO}_2$; 9:1; Sigma technology, China) with repetition rate of 4 MHz, pulse energy 6 μJ , pulse length 20 ps and the distance between the target material and surface to be coated was adjusted to 50 mm. The vacuum level was 10^{-5} atmospheres during the coating process. The process resulted in a uniform, transparent ITO-coating. The coating thickness was 150 nm and the average surface roughness was determined to be 0.3 nm as

scanned from an area of $1 \mu\text{m}^2$ with Atomic Force Microscope (AFM). No pinholes were found on any measured area.

Example 15

[0153] The gallium nitride and ITO-coated glass sheet of example 14 was coated with aluminum oxide (Al_2O_3) by ablating metallic aluminum fed as foil in active oxygen atmosphere the oxygen pressure varying in the range of 10^{-4} to 10^{-1} mbar. with repetition rate of 4 MHz, pulse energy 4.5 μJ , pulse length 20 ps and the distance between the target material and surface to be coated adjusted to 50 mm. The vacuum level was 10^{-5} atmospheres before the actual coating process. The process resulted in a uniform, transparent aluminumoxide-coating. The coating thickness was 300 nm and the average surface roughness was determined to be under 8 nm as scanned from an area of $1 \mu\text{m}^2$ with Atomic Force Microscope (AFM). No pinholes were found on any measured area.

Example 16

[0154] A glass sheet with surface area comprising $300 \text{ mm} \times 300 \text{ mm}$ was coated by ablating titan in active oxygen atmosphere the oxygen pressure varying in the range of 10^{-4} to 10^{-1} mbar. The pulse repetition rate of 25 MHz, pulse energy 5 μJ , pulse length 20 ps, the distance between the target material and surface to be coated being adjusted to 30 mm. The glass-material was pre-heated into approximately 120°C . The vacuum level was kept at 10^{-5} atmospheres before the actual coating process. The process resulted transparent coating possessing coating thickness of 20 nm. The average surface roughness was determined to be 0.14 nm as scanned from an area of $1 \mu\text{m}^2$ with Atomic Force Microscope (AFM). No pinholes were found on any measured area of titan oxide coating. The coated glass object was subjected to organic dirt after which it was subjected to light and certain humidity. The coating possessed self-cleaning properties.

Example 17

[0155] A glass sheet with surface area comprising $300 \text{ mm} \times 300 \text{ mm}$ was coated with aluminum oxide (Al_2O_3) by ablating metallic aluminum fed as foil in active oxygen atmosphere the oxygen pressure varying in the range of 10^{-4} to 10^{-1} mbar. with repetition rate of 48 MHz, pulse energy 4.5 μJ , pulse length 20 ps and the distance between the target material and surface to be coated adjusted to 25 mm. The vacuum level was 10^{-5} atmospheres before the actual coating process. The process resulted in an uniform aluminium oxide-coating. The coating thickness was 2100 nm and the average surface roughness was determined to be under 2 nm as scanned from an area of $1 \mu\text{m}^2$ with Atomic Force Microscope (AFM). No pinholes were found on any measured area.

1-33. (canceled)

34. A method for coating a certain surface of a glass product by laser ablation, characterized in that the uniform surface area to be coated comprises at least 0.2 dm^2 and the coating is carried by employing ultra short pulsed laser deposition wherein pulsed laser beam is scanned with a rotating optical scanner comprising at least one mirror for reflecting said laser beam.

35. A method according to claim 34, characterized in that said uniform surface area comprises at least 0.5 dm^2 , preferably at least 1.0 dm^2 .

36. A method according to claim **34**, characterized in that the employed pulse frequency of said laser deposition is at least 1 MHz.

37. A method according to claim **34**, characterized in that the average surface roughness of produced coating on said uniform surface area is less than 100 nm as scanned from an area of 1 μm^2 with Atomic Force Microscope (AFM).

38. A method according to claim **34**, characterized in that said uniform surface area of glass product is coated with material comprising at least one of following materials or a mixture of these:

metal, metal oxide, metal nitride and/or metal carbide; or carbon, nitrogen and/or boron; or carbon material comprising over 90 atomic-% of carbon, with more than 76% of sp^3 -bonding; or organic polymer material; or inorganic material.

39. A method according to claim **34**, characterized in that said uniform surface of glass product is coated with multilayered coating.

40. A method according to claim **34**, characterized in that the thickness of said coating on uniform surface of glass product is between 20 nm and 20 μm , preferably between 100 nm and 5 μm .

41. A glass product comprising a certain surface being coated by laser ablation, characterized in that the coated uniform surface area comprises at least 0.2 dm^2 and that the coating has been carried by employing ultra short pulsed laser deposition wherein pulsed laser beam is scanned with a rotating optical scanner comprising at least one mirror for reflecting said laser beam.

42. A glass product according to claim **41**, characterized in that said uniform surface area comprises at least 0.5 dm^2 , preferably at least 1.0 dm^2 .

43. A glass product according to claim **41**, characterized in that the average surface roughness of produced coating on

said uniform surface area is less than 100 nm as scanned from an area of 1 μm^2 with Atomic Force Microscope (AFM).

44. A glass product according to claim **41**, characterized in that the optical transmission of produced coating on said uniform surface area is no less than 88%, preferably no less than 90% and most preferably no less than 92%.

45. A glass product according to claim **41**, characterized in that the said produced coating on said uniform surface area contains less than one pinhole per 1 mm^2 , preferably less than one pinhole per 1 cm^2 and most preferably no pinholes at said uniform surface area.

46. A glass product according to claim **41**, characterized in that said uniform surface area is coated in a manner wherein the first 50% of said coating on said uniform surface area does not contain any particles having a diameter exceeding 1000 nm, preferably 100 nm and most preferably 30 nm.

47. A glass product according to claim **41**, characterized in that said uniform surface area of glass product is coated with material comprising at least one of following materials or a mixture of these:

metal, metal oxide, metal nitride and/or metal carbide; or carbon, nitrogen and/or boron; or carbon material comprising over 90 atomic-% of carbon, with more than 70% of sp^3 -bonding; or organic polymer material; or inorganic material.

48. A method according to claim **41**, characterized in that said uniform surface of glass product is coated with multilayered coating.

49. A glass product according to claim **41**, characterized in that the thickness of said coating on uniform surface of glass product is between 20 nm and 20 μm , preferably between 100 nm and 5 μm .

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