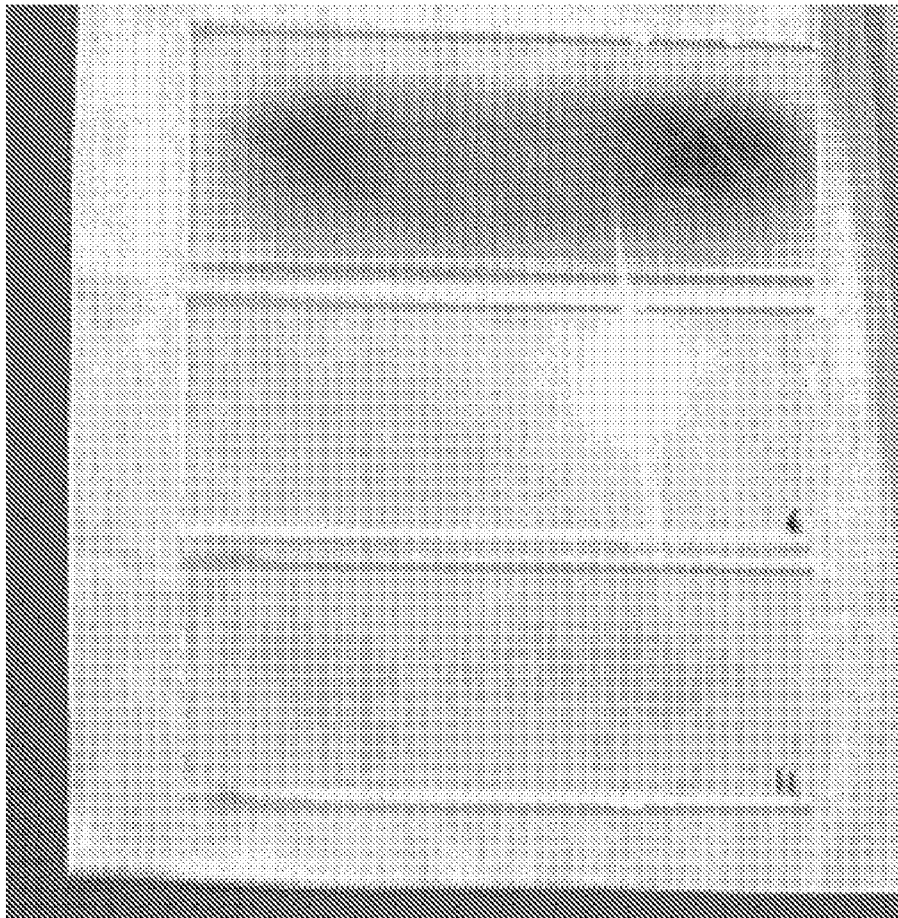




US 20090136739A1

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Ruuttu et al.(10) **Pub. No.: US 2009/0136739 A1**(43) **Pub. Date: May 28, 2009**(54) **COATING ON A PLASTIC SUBSTRATE AND A
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(52) **U.S. Cl.** **428/323**; 427/596; 427/597; 428/341;
428/335; 428/336(57) **ABSTRACT**

The invention relates in general level to a method for coating plastic products including large surface areas. The invention also relates to coated plastic 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 low production temperatures accomplishing the coating of plastic products, high coating production rate, excellent coating properties and overall low manufacturing costs.



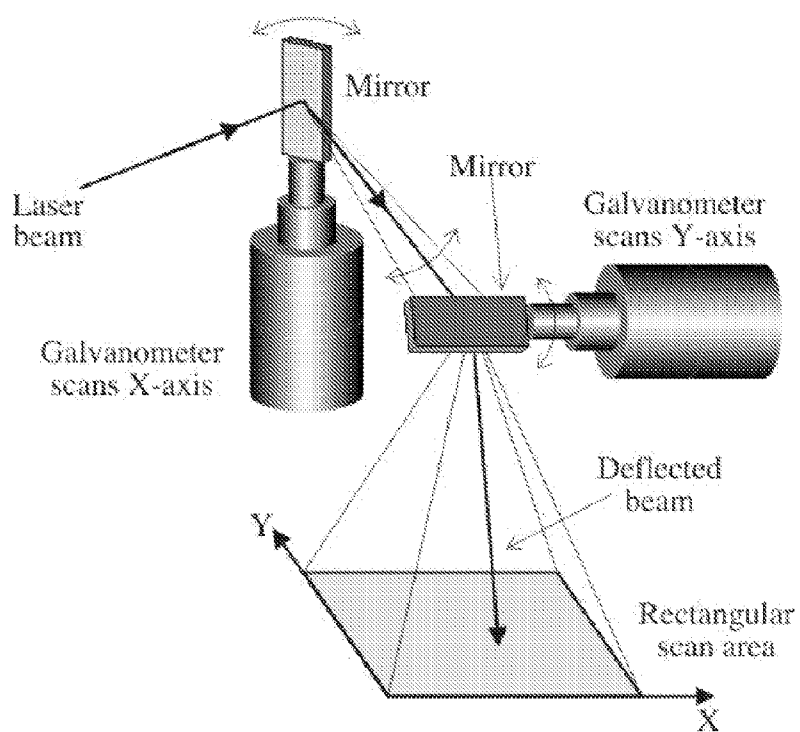


Figure 1

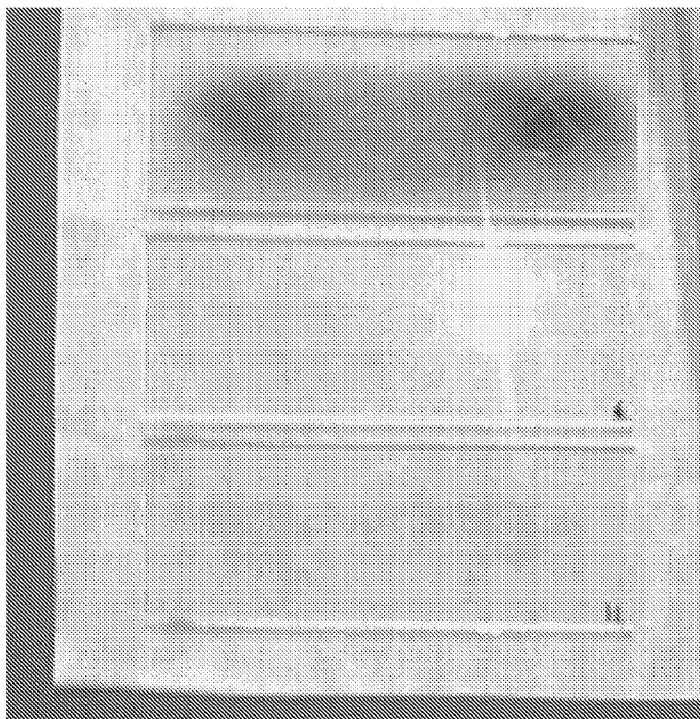
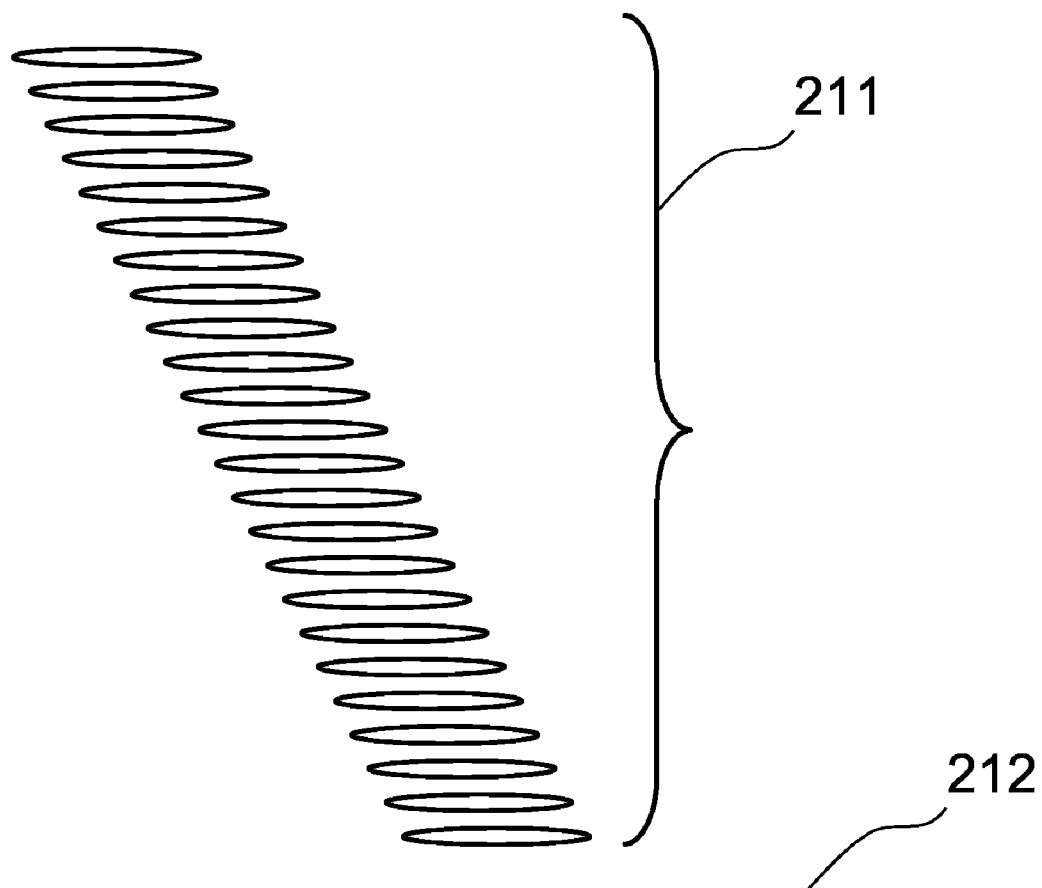


Figure 2

2 MHz



Laser spot scanning speed about 1 m/s

Figure 3

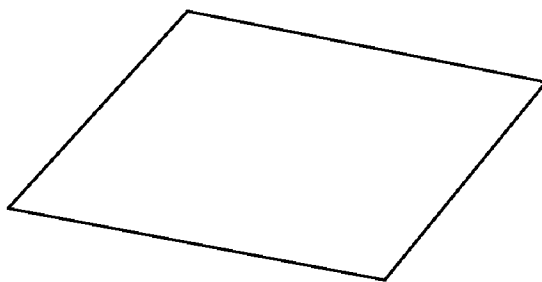


Figure 4

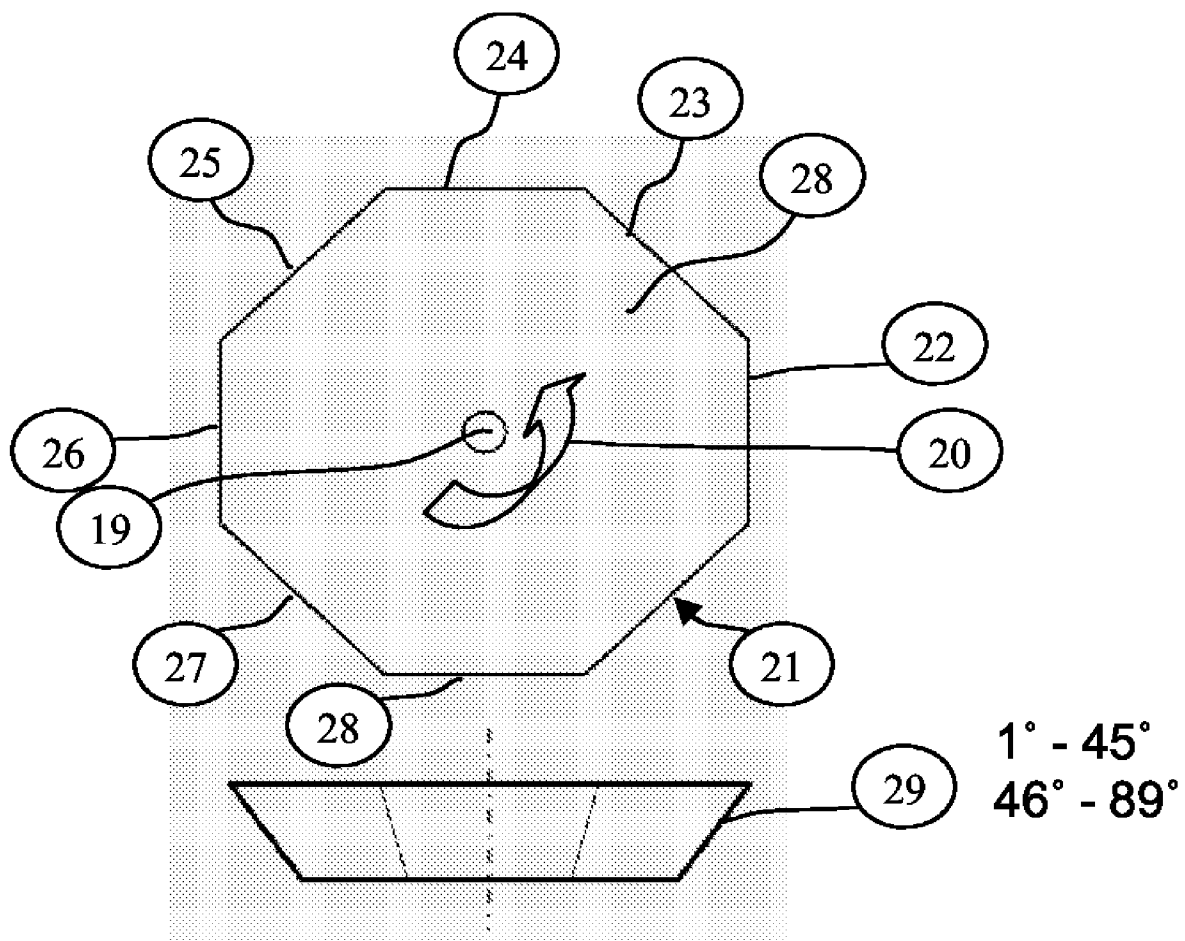


Figure 5

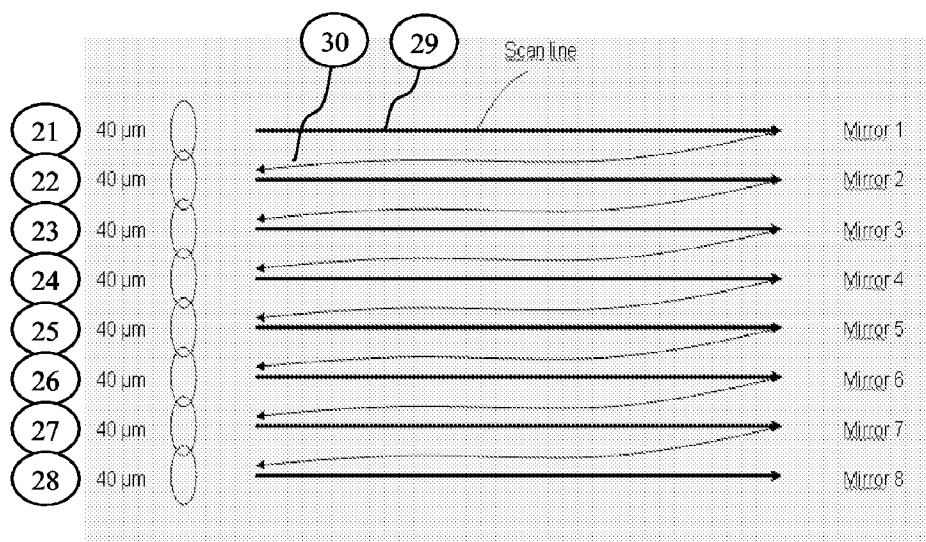


Figure 6

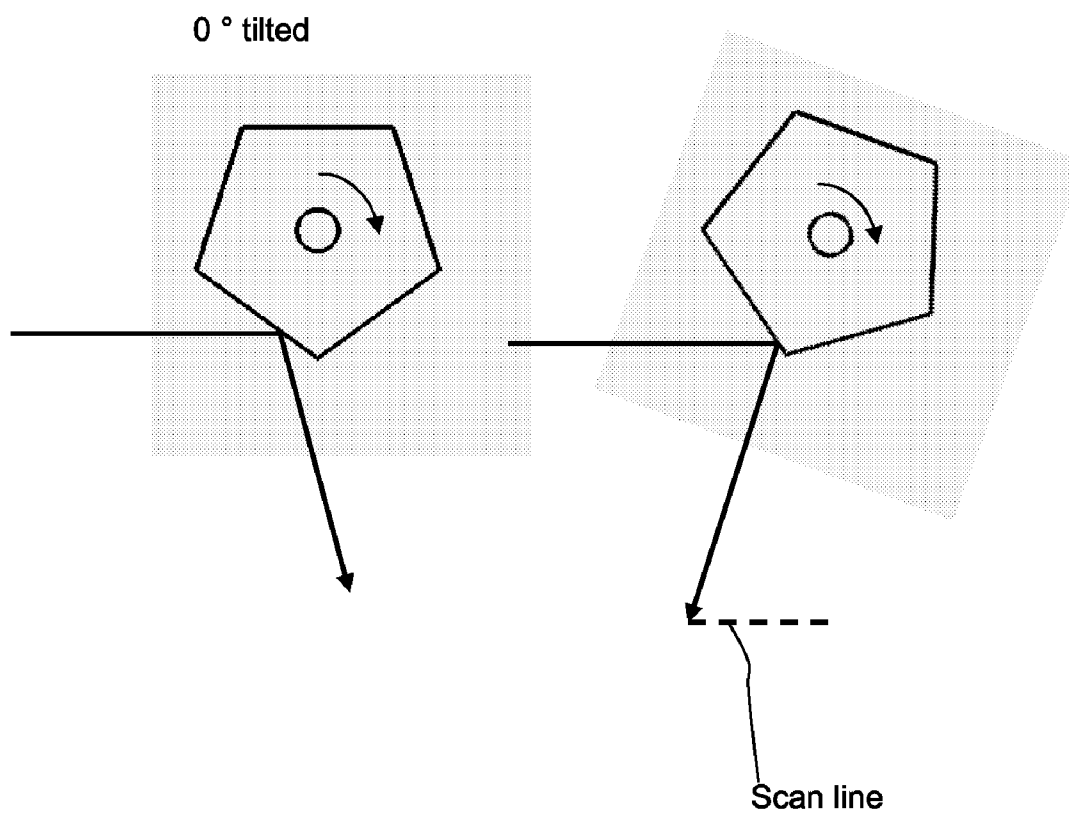


Figure 7

$> 0 < 45^\circ$ tilted

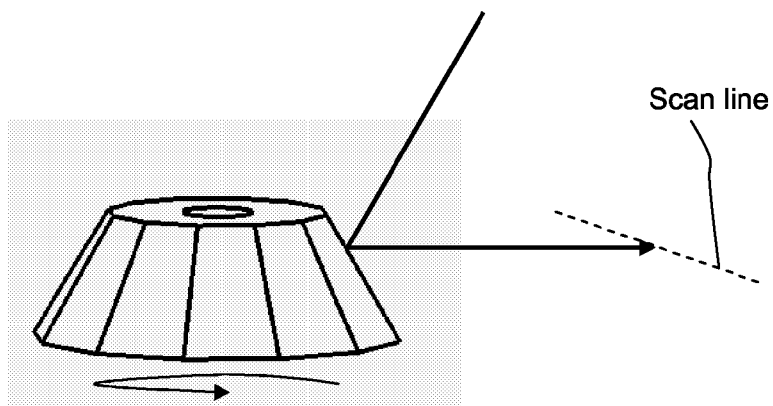


Figure 8

45° tilted

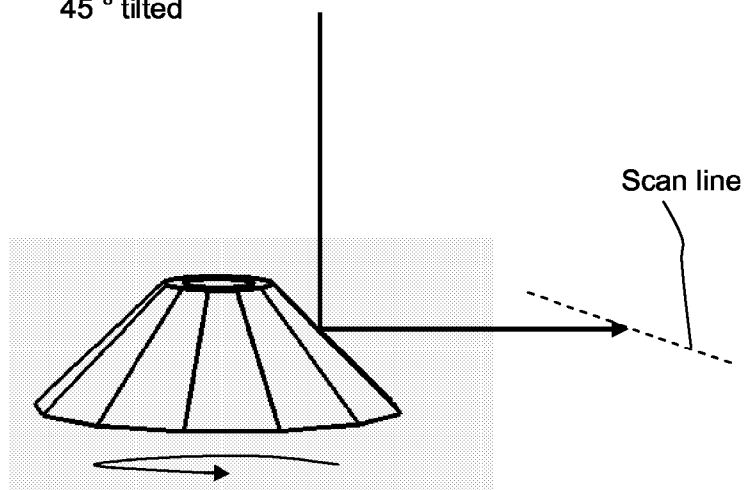


Figure 9

Sample tube

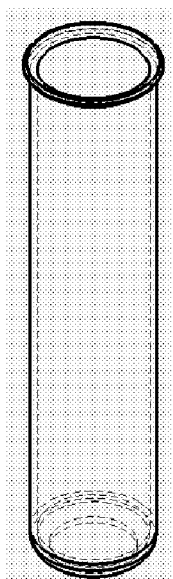
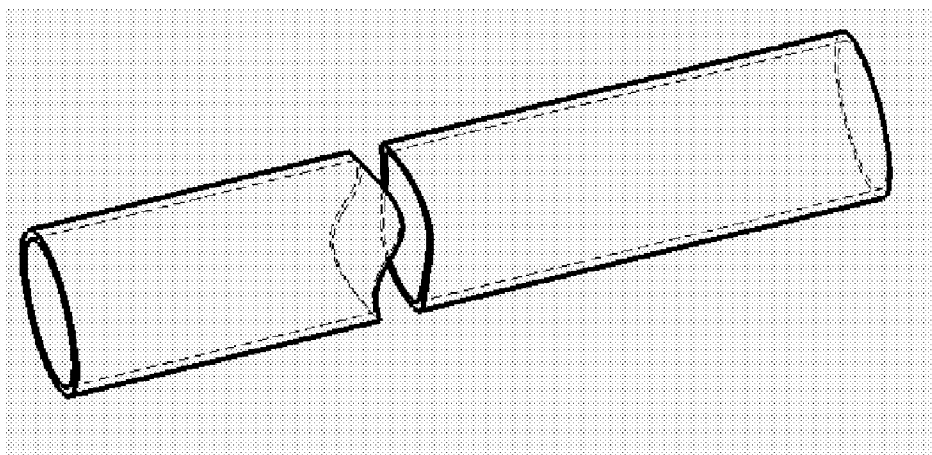


Figure 10



Plastic pipe

Figure 11

Plastic Drinking glass

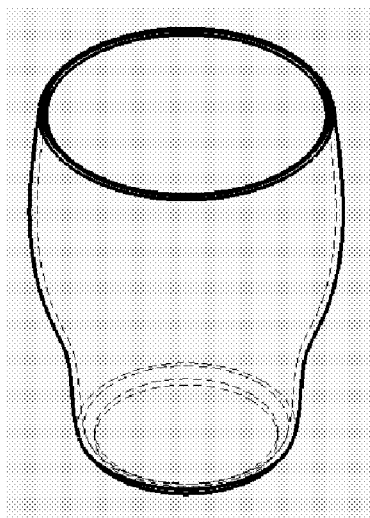
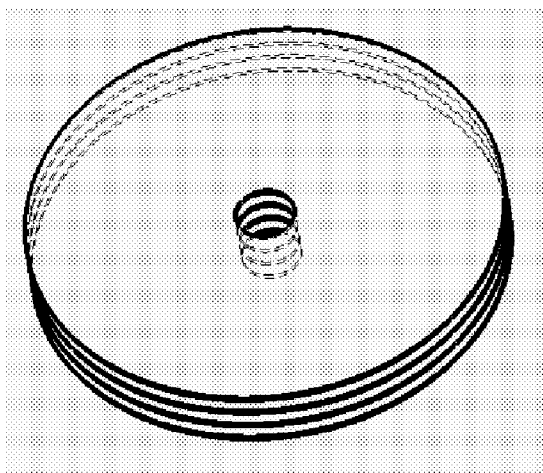


Figure 12



PlasticMaster discs

Figure 13

Plastic Mirror
surfaces

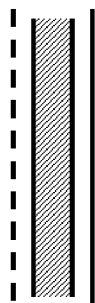
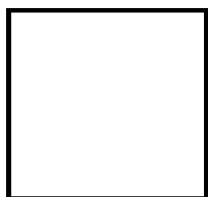


Figure 14a

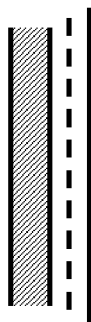


Figure 14b

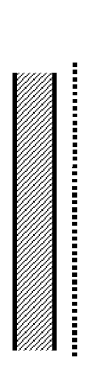


Figure 14c

Plastic shielding in airplane, train, or automobile

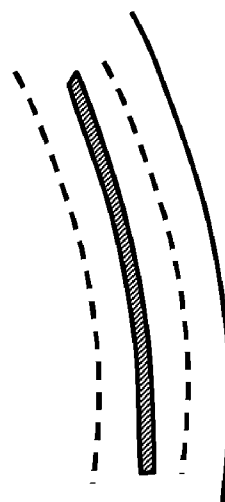
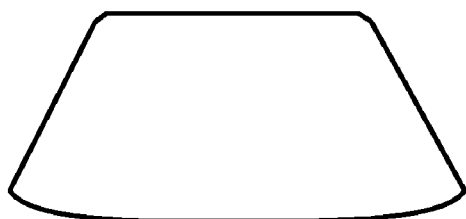


Figure 15

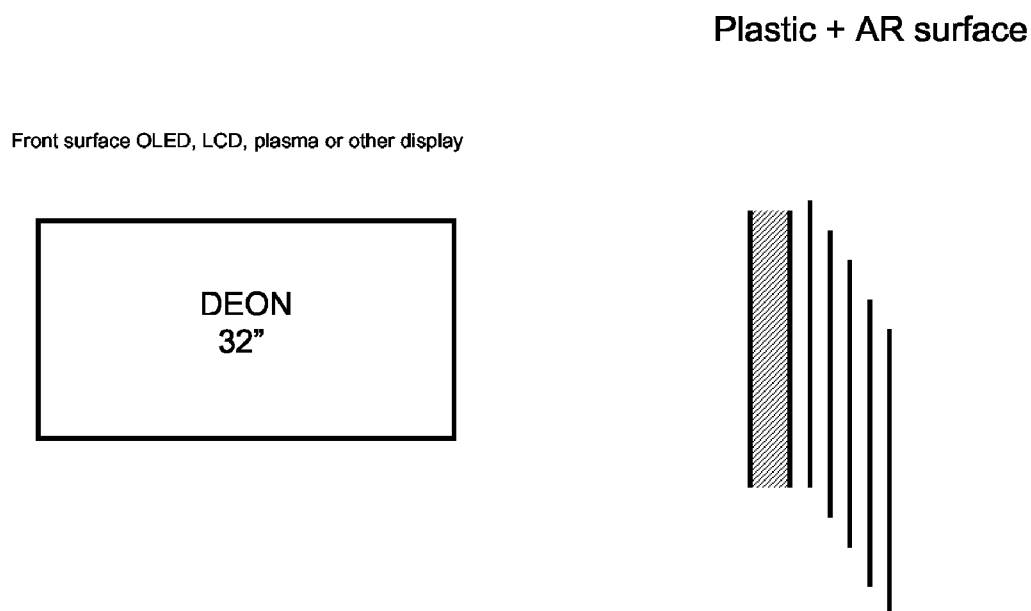
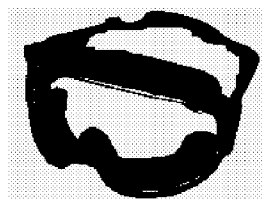
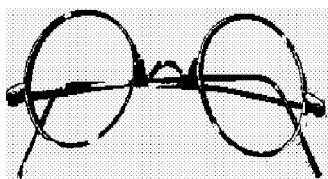


Figure 16



Goggles and visors

Eyeglassess, sunglasses

Figure 17

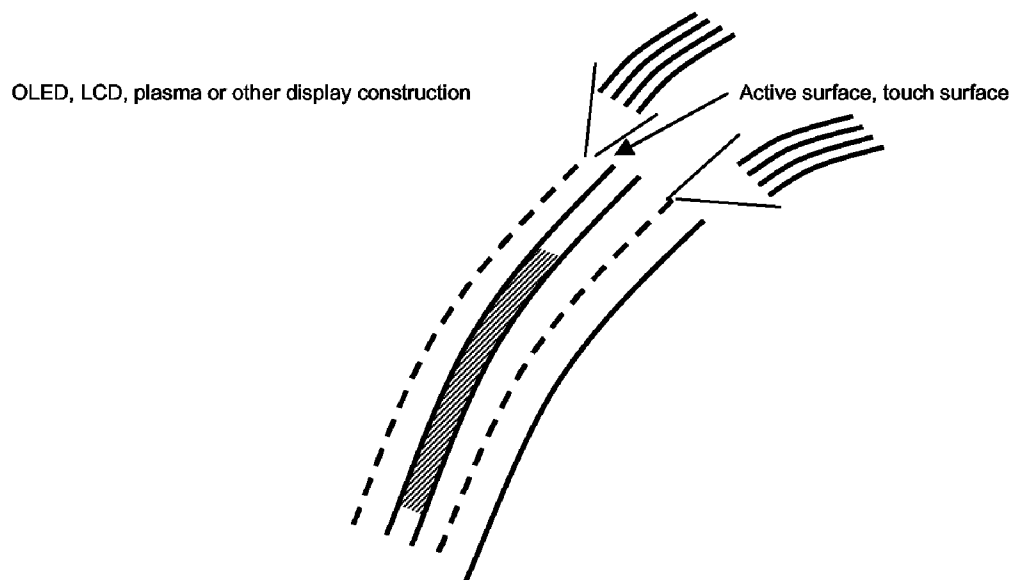


Figure 18

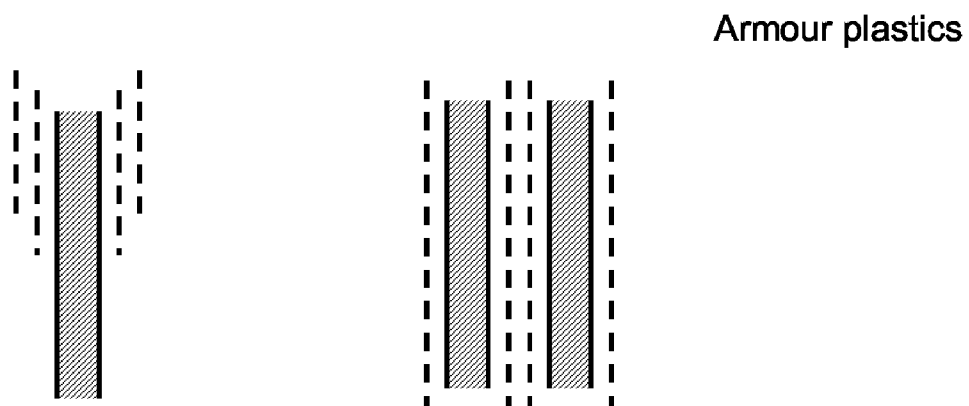
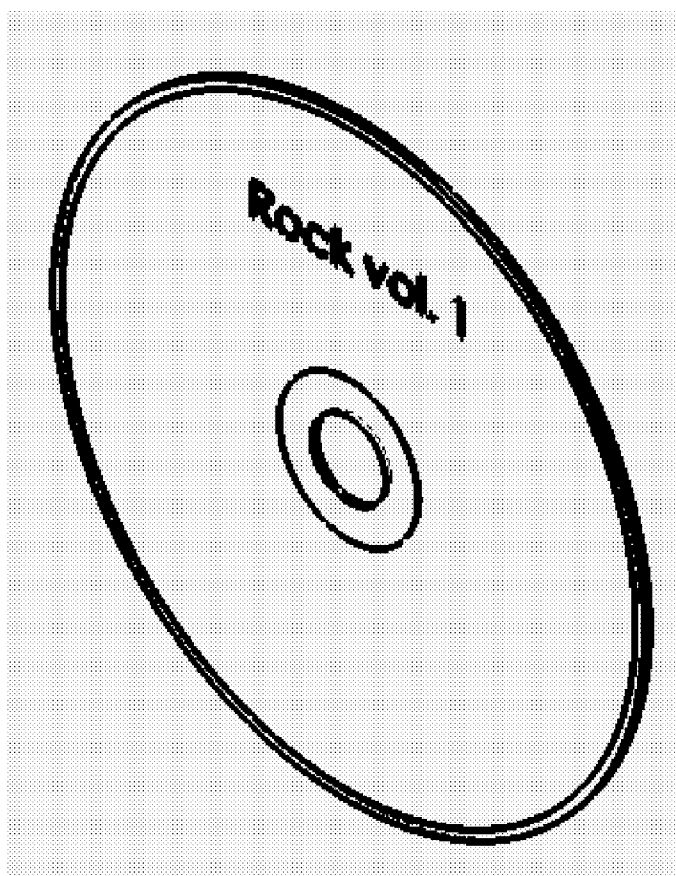


Figure 19



**Plastic
Disc**

Figure 20

plastic window

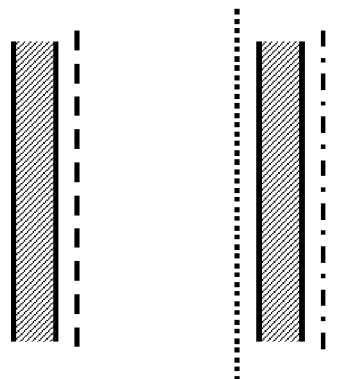
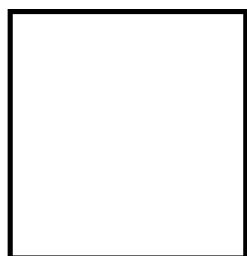


Figure 21

Plastic panel for exterior and interior use

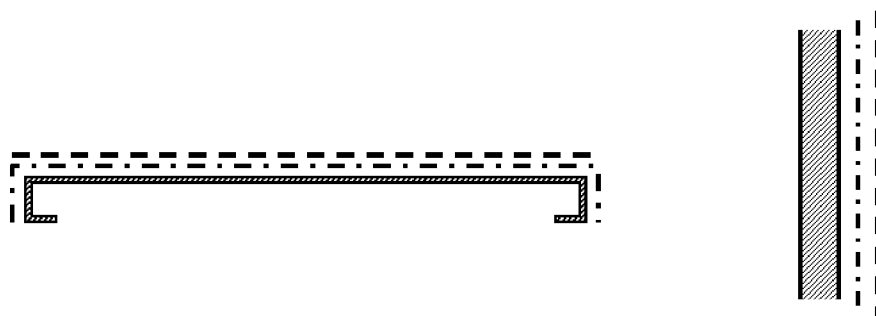


Figure 22

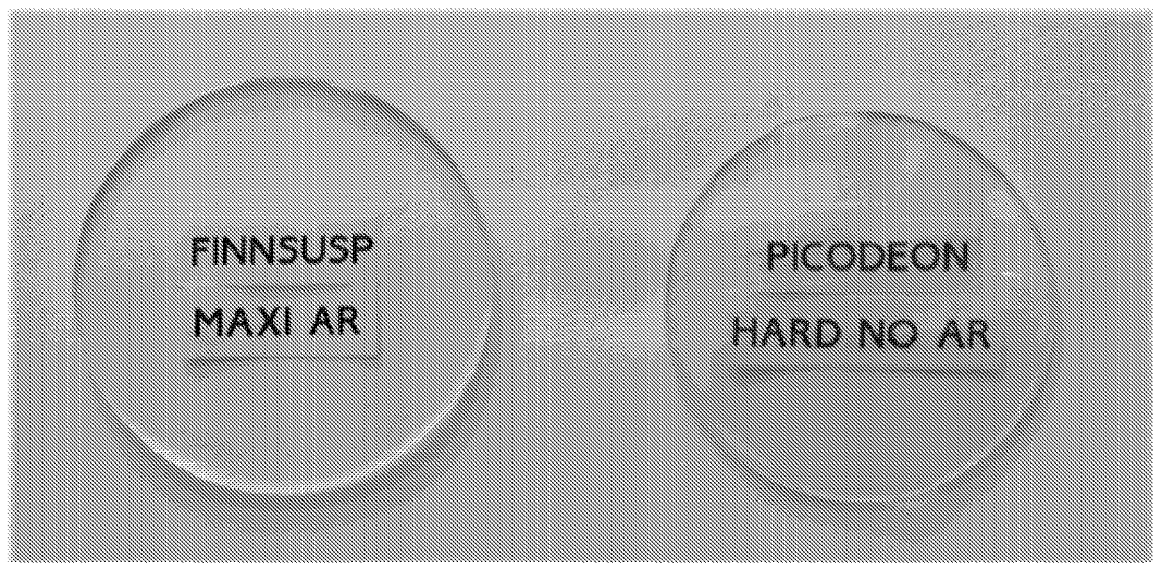


Figure 23

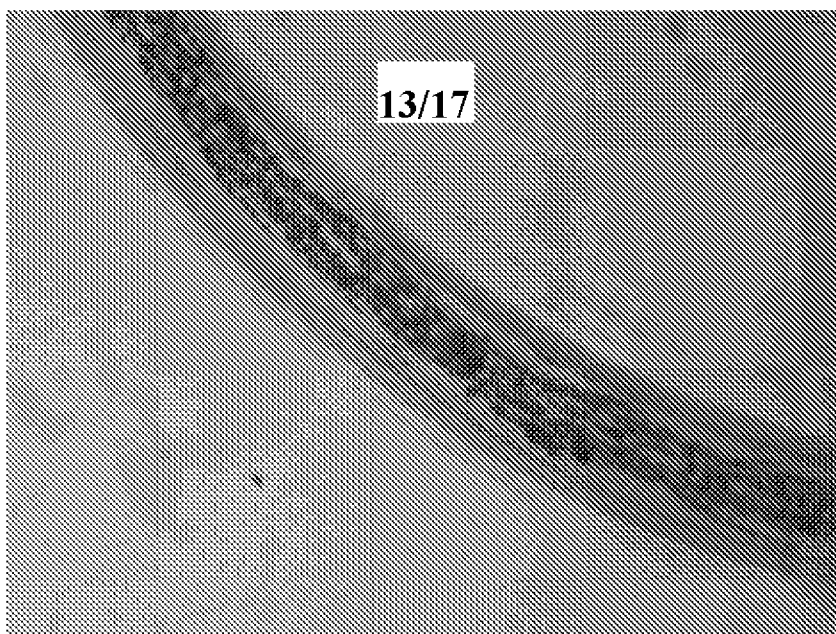


Figure 24



Figure 25

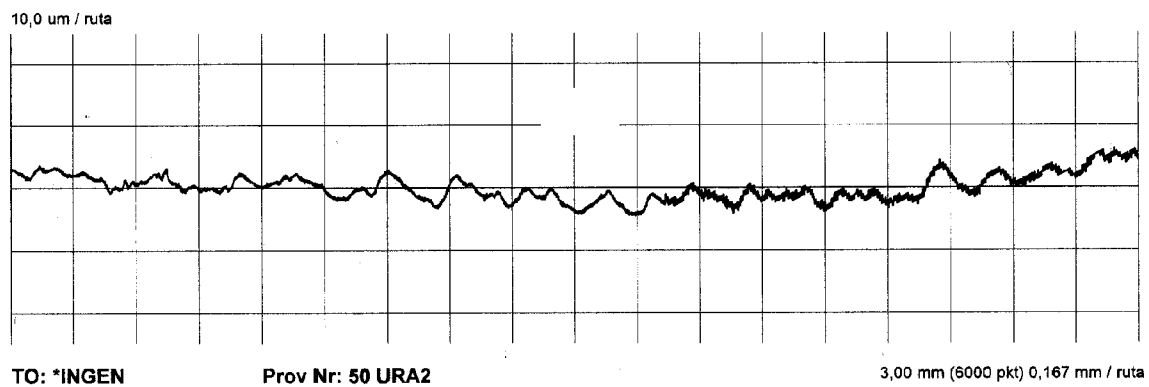


Figure 26

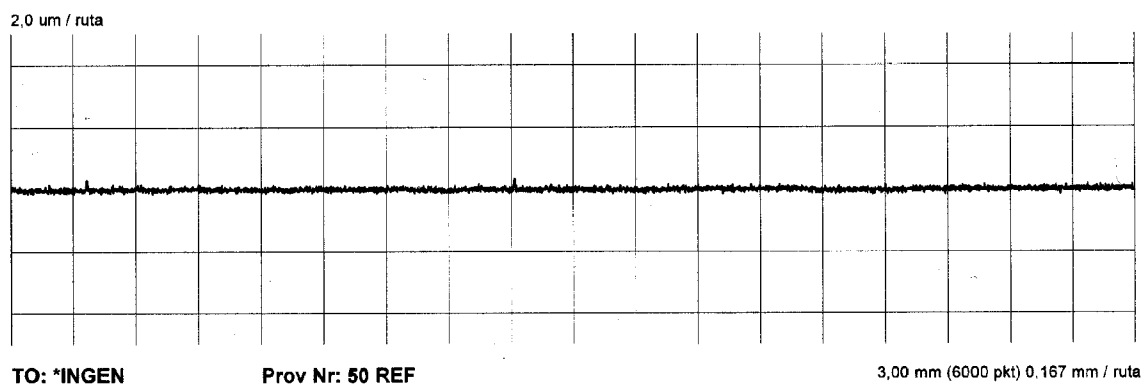


Figure 27

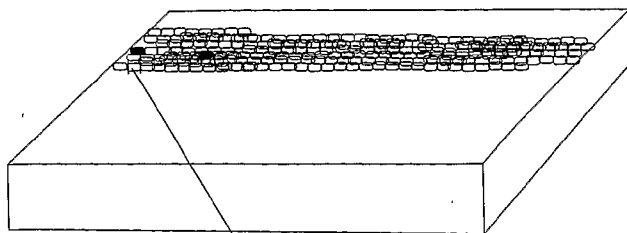


Figure 28a

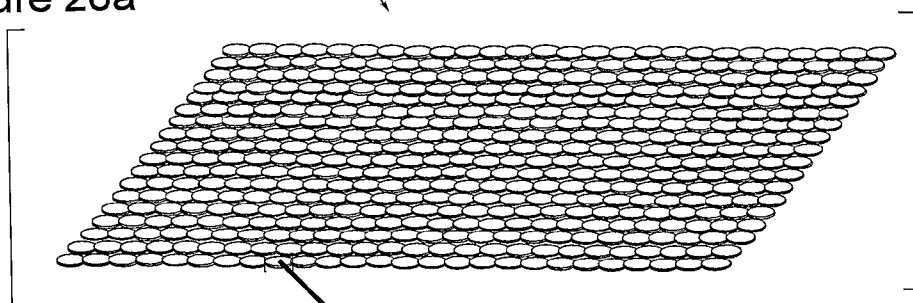


Figure 28b

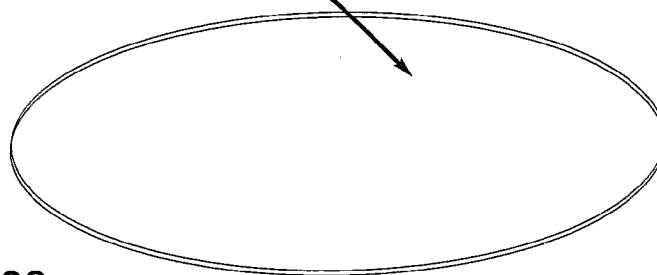


Figure 28c

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

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

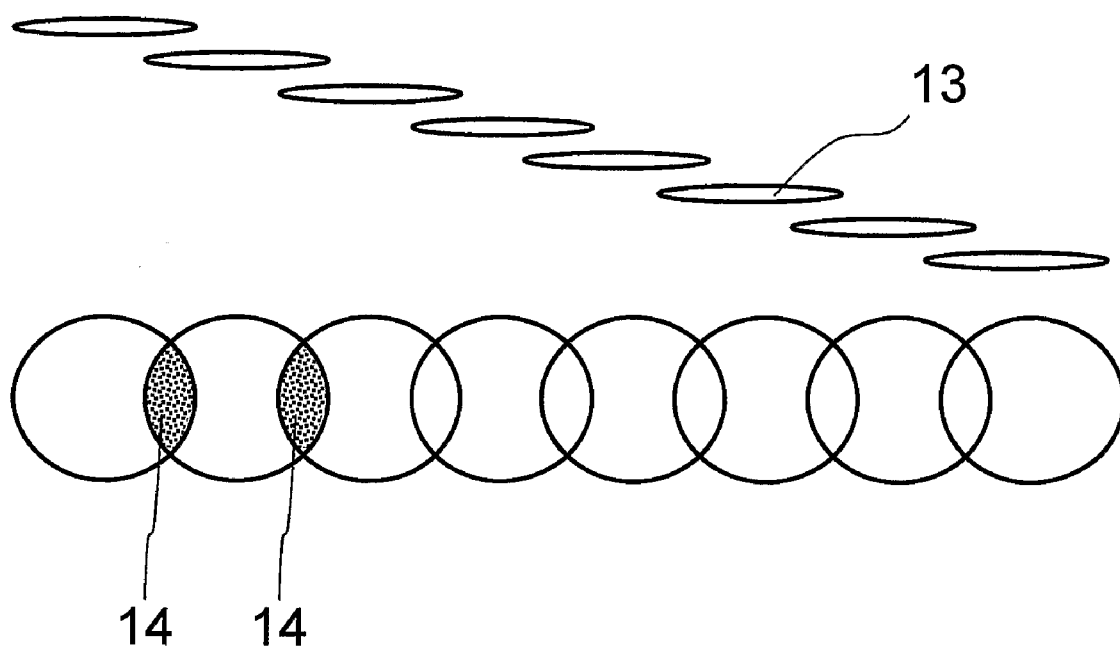


Figure 29a

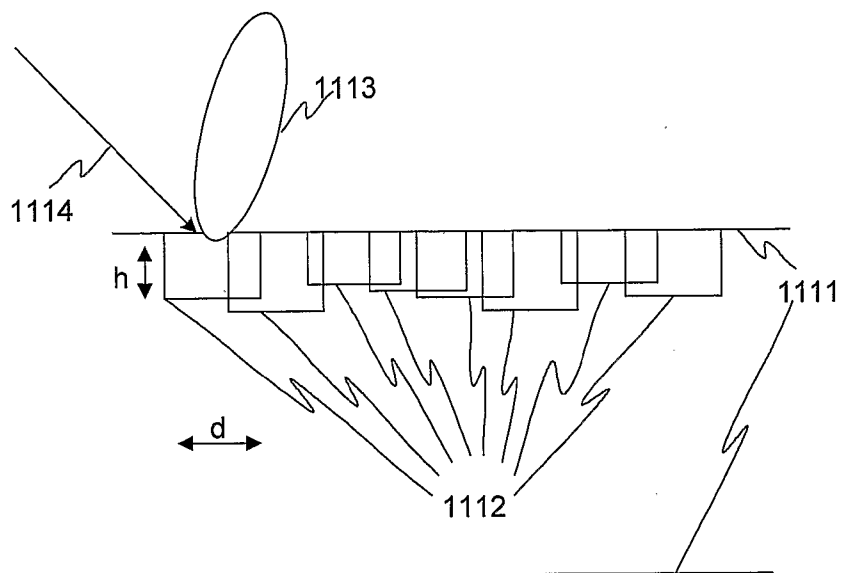


Figure 30a

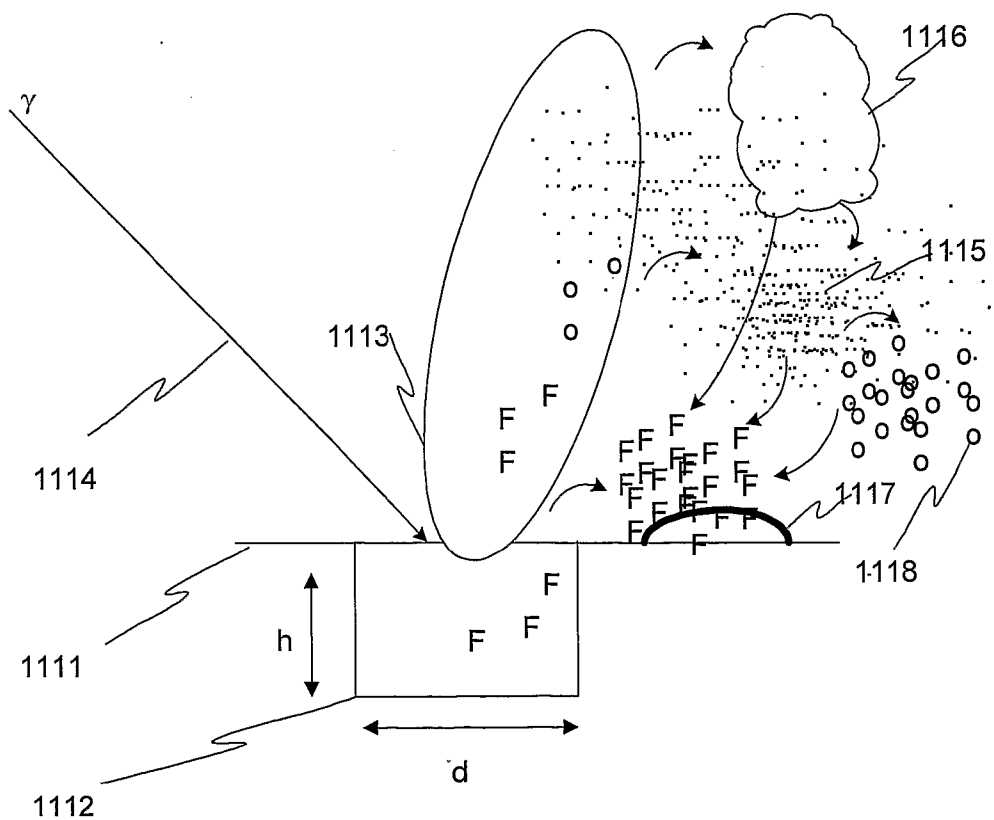


Figure 30b

COATING ON A PLASTIC SUBSTRATE AND A COATED PLASTIC PRODUCT

FIELD OF INVENTION

[0001] The invention relates generally to a method for coating plastic 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 low coating temperatures accomplishing coating of heat-sensitive plastic products, high coating production rate, excellent coating properties and low manufacturing costs.

BACKGROUND

Plastic Products

[0002] Plastic covers a range of synthetic or semisynthetic polymerization products. They are composed of organic condensation or addition polymers and may contain other substances to improve performance or economics. There are few natural polymers generally considered to be "plastics". Plastics can be formed into objects of films and even fibers. Their name is derived from the fact that they are malleable, having property of plasticity. In other words, they are very versatile in processing offering a very broad scope of product design. That is one of the main reasons why the plastics have gained so much use after their invention. The plastic products are lightweight, and often they possess good break-resistance and non-splitting features. Additionally, several plastic grades such as polycarbonates can be prepared to be transparent.

[0003] Plastics can be classified in many ways, but most commonly by their polymer backbone (polyvinyl chloride, polyethylene, polyethyl methacrylate, and other acrylics, silicones, polyurethanes etc. Other classifications include thermoplastic thermoset, elastomer, engineering plastics, addition or condensation or polyaddition, and glass transition of temperature. Some plastics are partially crystalline and partially amorphous in molecular structure, giving the both a melting point (the temperature at which the attractive intermolecular forces are overcome) and one or more glass transitions (temperatures above which the extent of localized molecular is substantially increased). So-called semi-crystalline plastics include polyethylene, polypropylene, poly(vinyl chloride), polyamides (nylons), polyesters and some polyurethanes. Many plastics are completely amorphous, such as polystyrene and its copolymers, poly(methyl methacrylate), and all the thermosets.

[0004] Some of the problems associated with plastics are their heat sensitivity, their poor wear and mechanical properties and easy decomposition due to chemical and radiation-based interactions (such as natural UV-radiation) *Reymuuta???*

[0005] Such problems have been tackled by introducing some special plastics such as PEEK (Polyetheretherketones). PEEK possesses extraordinary mechanical properties, the Young's modulus being 3.6 GPa and tensile strength of 170 Mpa, melts at around 350° C. and is "highly resistant to thermal degradation".

[0006] The second approach to tackle these problems is to introduce different coatings on plastics. Most of the CVD- and PVD-based methods require elevated process temperatures being thus not employable to coat plastics. Hence if

coated, most of the plastics are coated with different lacquers being generally not able to give properties required from present products.

Laser-Ablation

[0007] 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.

[0008] 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.

[0009] 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.

[0010] 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.

[0011] 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.

[0012] 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.

[0013] 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.

[0014] 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.

[0015] 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.

[0016] 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.

[0017] 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.

[0018] 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.

[0019] In machining or work-related applications the left-overs 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.

[0020] 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

[0021] The maintenance cost for plastic products is huge and steadily increasing and there is a great need for coating technologies for especially plastic 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 plastic surfaces with one or several of the following properties: excellent optical properties, chemical and/or wear resistance, thermal resistance, resistivity, coating adhesion, self-cleaning properties and possibly, tribological properties has remained an unsolved problem. Partly, this is because of heat sensitive nature of plastic product itself partly because the overall lack of methods to solve previously mentioned coating problems, regardless the substrate to be coated.

[0022] There is also an increasing demand for various bendable electronics. Plastics possess several excellent properties to be employed as a scaffold for such devices, but the techniques to manufacture such complex devices on plastics, especially on industrial scale remain non-existing.

[0023] 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 plastic products, especially 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 metal products. Moreover, the distance between the plastic 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.

[0024] 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, inadequate resistivity (electrical), unsatisfactory surface thickness and tribological properties etc. take place.

[0025] The present coating methods also drastically restrict the materials employable for coating purposes in general and thus, limit the scope of different coated metal products available on market today. If applicable, 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. An aim of the current invention is to solve or at least to mitigate the problems of the known techniques.

[0026] A first object of this invention is to provide a new method how to solve a problem to coat a certain surface of a plastic product by pulsed laser deposition that so that the uniform surface area to be coated comprises at least 0.2 dm^2 . A second object of this invention is to provide new plastic products being coated by pulsed laser deposition so that the coated uniform surface area comprises at least 0.2 dm^2 . 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 plastic 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.

[0027] 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 plastic 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.

[0028] A fifth object of this invention is to provide a good adhesion of the coating to the uniform surface area of a plastic 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.

[0029] 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 plastic bodies in industrial manner.

[0030] 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.

[0031] 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 fine plasma for coating of uniform plastic 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.

[0032] 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.

[0033] The present invention is based on the surprising discovery that plastic products comprising large surfaces can be coated with industrial production rates and excellent qualities regarding one or more of technical features such as optical transparency, chemical and/or wear resistance, scratch-free properties, thermal resistance and/or conductivity, coating adhesion, self-cleaning properties and possibly, tri-

bological 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. Normally, plastic products are especially difficult to coat due to their extreme heat-sensitivity.

[0034] 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 plastic 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.

[0035] 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.

[0036] 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. $<1 \text{ }\mu\text{m}$.

[0037] Various embodiments of the inventions are combinable in suitable part.

[0038] 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

[0039] The described and other advantages of the invention will become apparent from the following detailed description and by referring to the drawings where:

[0040] 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,

[0041] 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).

[0042] 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.

[0043] FIG. 4 illustrates one polycarbonate sheet coated comprising wear-resistant coating according to the invention

[0044] FIG. 5 illustrates one possible turbine scanner mirror employed in method according to the invention,

[0045] FIG. 6 illustrates the movement of the ablating beam achieved by each mirror in the example of FIG. 5,

[0046] FIG. 7 illustrates beam guidance through one possible rotating scanner to be employed according to the invention,

[0047] FIG. 8 illustrates beam guidance through one possible rotating scanner to be employed according to the invention,

[0048] FIG. 9 illustrates beam guidance through one possible rotating scanner to be employed according to the invention,

[0049] FIG. 10 illustrates one embodiment of coated product according to the invention,

[0050] FIG. 11 illustrates one embodiment of coated product according to the invention,

[0051] FIG. 12 illustrates one embodiment of coated product according to the invention,

[0052] FIG. 13 illustrates one embodiment of coated product according to the invention,

[0053] 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 plastic,

[0054] 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 plastic,

[0055] 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 plastic,

[0056] FIG. 15 illustrates one embodiment of multi-coated product according to the invention,

[0057] FIG. 16 illustrates one embodiment of multi-coated product according to the invention,

[0058] FIG. 17 illustrates two embodiments of coated product according to the invention,

[0059] FIG. 18 illustrates one embodiment of multi-coated product according to the invention,

[0060] FIG. 19 illustrates two embodiments of multi-coated product according to the invention,

[0061] FIG. 20 illustrates one embodiment of coated product according to the invention,

[0062] FIG. 21 illustrates two embodiments of coated product according to the invention,

[0063] FIG. 22 illustrates one embodiment of multi-coated product according to the invention,

[0064] FIG. 23 illustrates one embodiment of coated product according to the invention and one state of the art product,

[0065] FIG. 24 illustrates optical micrograph of wear track on commercial coated pycarbonate plate,

[0066] FIG. 25 illustrates comparable optical micrograph of wear track on coated pycarbonate plate according to the invention, with identical wear track to that of FIG. 24,

[0067] FIG. 26 illustrates the surface profile of the wear track of commercial PC-plate after wear testing,

[0068] FIG. 27 illustrates the surface profile of the wear track of YAG-coating according to the invention,

[0069] FIG. 28a illustrates an embodiment according to the invention, wherein target material ablated by scanning the laser beam with rotating scanner (turbine scanner).

[0070] FIG. 28b illustrates an exemplary part of target material of FIG. 28a.

[0071] FIG. 28c illustrates an exemplary ablated area of target material of FIG. 28b.

[0072] FIG. 29a illustrates an exemplary way according to the invention to scan and ablate target material with turbine scanner (rotating scanner).

[0073] FIG. 30a illustrates plasma-related problems of known techniques.

[0074] FIG. 30b 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 plastic product by laser ablation in which method the uniform surface area to be coated comprises at least 0.2 dm² 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 plastic products is hereby meant but not limited to metal products such as for construction as whole, interior and decorative use, for certain limitations to machinery, vehicles such as cars, trucks, motorcycles and tractors, airplanes, ships, boats, trains, rails, tools, medical products, housings of electronic devices, power plugs, car rear and front lamps, canteen trays, thermos flasks, tea strainers, hairdryer and binocular housings, milking cans, film cassettes, switch relays, fishing rod reels, traffic-light housings and lenses, lenses of mobile devices and cameras, 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, bearings, piston parts, pumps, compressor plate valves, cable insulation applications, in applications comprising ultra-high vacuum conditions, screws, water pipes, drills and their parts etc. The plastic product must not be necessarily of plastic as such. According to the invention, all the products comprising plastic surfaces regardless whether their metal 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 10-22.

[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 cold ablation being reached with pico-second, femto-second and atto-second pulsed lasers. The material evaporated from the target by laser ablation is deposited onto a substrate that is 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, better prospective for adequate adhesion of coating/thin-film produced.

[0078] In another preferred embodiment of the invention, said uniform surface area comprises at least 0.5 dm². In a still preferred embodiment of the invention, said uniform surface area comprises at least 1.0 dm². The invention accomplishes easily also the coating of products comprising uniform coated surface areas larger than 0.5 m², such as 1 m² 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 plastic products.

[0079] 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, also called galvano-scanner.

[0080] 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.

[0081] 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.

[0082] 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 embodiment of the coating method it has a perimeter of 30 cm, diameter of 12 cm, and a height of 5 cm.

[0083] 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.

[0084] 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.

[0085] According to the invention, the surface to be coated can comprise whole or a part of the plastic product surface.

[0086] In one especially preferred embodiment of invention, thin plastic sheets for various use as in construction or interior finishing, the whole sheet is coated in order to gain the preferred effect or effects of coating. One such representative product according to invention comprising a copper thin sheet of 1200 mm×1500 mm with thickness of 1 mm and coated first with CuO₂ and finished with a protective coating of transparent ATO (aluminumtitanoxide) is illustrated in FIG. 4. CuO₂ gives the interior effect, ATO giving wear resistance as well as preventing the leakage of harmful copper compound into nature. ATO can be replaced with for example aluminum oxide, yttrium stabilized zirconium oxide, yttrium aluminum oxide, titanium dioxide and various carbon based coatings.

[0087] 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, resistive coatings, tribological coatings, thermally resistant and/or thermally conductive 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.

[0088] Thus, in a specially 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.

[0089] According to the invention it is 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.

[0090] 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 here 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.

[0091] 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. 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 metal products coated according to the invention.

[0092] 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.

[0093] 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, medical implant, space ship, different parts of different vehicles and their plastic mechanical parts or further, in metallic construction protected by said plastic coating, or interior structure leads easily to dramatically lowered life-time of said product.

[0094] 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 plastic products.

[0095] The plastic product itself can comprise virtually whichever plastic, plastic compound such as composite materials or mixtures of these. Preferable plastic grades include such as polyethylene (PE), polystyrene (PS), polyvinylchloride (PVC), polycarbonate (PC), polytetrafluoroethylene (Teflon), polyimide (PI, Kapton), Mylar, PEEK, cellulose-derived plastics, polyamides etc. In one embodiment of the invention, the polymer material is also subjected to lithography. In such applications it is preferable to use polymers withstanding temperatures up to 100° C. Additionally, said plastic product can comprise virtually whichever 3D-structure.

[0096] Due to huge volumes of plastic products, one especially preferred embodiment of the invention is to coat plastic product already in its sheet form, and here, preferably in a coating station integrated into plastic sheet (or 3D-product) production line. In such an approach, the uncoated plastic product is not contaminated with any substances/dirt/reaction and unnecessary surface treatment steps to remove such possible contaminants prior coating are avoided. The same applies for both large sheets such as polycarbonate sheets but also for smaller plastic products such as lenses of mobile devices.

[0097] According to one embodiment of the invention, said uniform surface area of plastic product is coated with metal, metal oxide, metal nitride, metal carbide or mixtures of these. Non-limiting examples of metals include aluminum, molybdenum, titan, zirconium, copper, yttrium, magnesium, lead, zinc, ruthenium, chromium, rhodium, silver, gold, cobalt, tin, nickel, tantalum, gallium, manganese, vanadium, platinum and virtually whichever metal.

[0098] 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 plastic 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.

[0099] 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_2 , SiO_2 and Al_2O_3 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. Al_2O_3 , 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.

[0100] Dielectric materials employed in present optical coating applications include fluorides (e.g. MgF_2 , CeF_3), oxides (e.g. Al_2O_3 , TiO_2 , SiO_2), 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).

[0101] Dielectric coatings can now be advantageously produced on plastics with the method of present invention.

[0102] 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 semi-conducting oxides and/or 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.

[0103] Metals that have conventionally been employed be as transparent conductors include Au, Pt, Rh, Ag, Cu, Fe and Ni. Simultaneous optimization of conductivity and transparency 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.

[0104] 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—none of the systems being beneficial for plastics. Optimum film properties require maintenance of tight stoichiometry. The prior art techniques employ commonly glass substrates and in such techniques the glass body is commonly heated up close to the softening temperature. In that system, care must be taken to prevent stresses and warpage of the final product. Such system can not be employed at all to heat sensitive plastic bodies. Thus, the present method of invention also solves the problems associ-

ated with softening temperature with glass products and yields said films in high quality and economically feasible manner.

[0105] For the most part, n in fluoride and oxide films has a value less than 2 at the reference wavelength of $0.55 \mu\text{m}$. 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.

[0106] 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 $k = 4 \times 10^{-5}$ or $\alpha = 10/\text{cm}$ at $\lambda = 5500 \text{ \AA}$.

[0107] The present method of invention solves the problems associated 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.

[0108] 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.

[0109] 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 (C_3N_4 films).

[0110] 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.

[0111] 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).

[0112] According another embodiment of the invention, said uniform surface area of plastic 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 plastic product excellent tribological, wear- and scratch-free properties but increase also the heat-conductivity and -resistance.

[0113] Diamond-coatings on plastics 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.

[0114] In a still another embodiment of the invention, said uniform surface area of plastic 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 metal products against corrosive conditions, as coatings for medical devices and implants, battery electrodes, humidity and gas sensors, semiconductor applications, protecting computer hard disks, in solar cells, tools, etc.

[0115] According to one embodiment of the invention certain uniform surface area of plastic product is coated with organic polymer material. Such materials include but are not limited to chitosan and its derivatives, polysiloxanes, and different organic polymers.

[0116] By coating metal product with chitosan there are promising perspectives to produce a new class of plastic products for marine and other water environments as well as new plastic products for both interior and exterior use.

[0117] Here, polysiloxanes are especially advantageous for manufacturing products with relatively high wear-resistance and scratch-free properties with simultaneously excellent optical transparencies.

[0118] 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 and ceramic derived materials.

[0119] In an especially preferred embodiment of the invention, different plastic sheets and 3D-metal structures were coated by ablating a target material comprising pink agate resulting in colored but opaque coating result.

[0120] According to one embodiment of invention, said uniform surface of the plastic product is coated with only one single coating. According to another embodiment of the invention, said uniform surface of the plastic 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 plastic product surface by manufacturing a first set of coating having better adhesion to plastic surface and possessing such properties that the following coating layer has better adhesion to said layer than to plastic 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.

[0121] The present invention further accomplishes the production of composite coatings to plastic product surface by ablating simultaneously one composite material target or two or more target materials comprising one or more substances.

[0122] According to invention the thickness of said coating on uniform surface of plastic 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.

[0123] The present invention further accomplishes the preparation of 3D-structures employing the plastic component as a scaffold for growing said 3D-structure.

[0124] According to the invention there is also provided a plastic product comprising a certain surface being coated by laser ablation wherein the coated uniform surface area comprises at least 0.2 dm² 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.

[0125] In a more preferred embodiment of the invention said uniform surface area comprises at least 0.5 dm². In a still more preferable embodiment of the invention said uniform surface area comprises at least 1.0 dm². The invention accomplishes easily also the products comprising uniform coated surface areas larger than 0.5 m², such as 1 m² and over.

[0126] 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 μm² with Atomic Force Microscope (AFM). Preferably, the uniform surface roughness is less than 50 nm and most preferably it is under 25 nm. 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%.

[0127] According to still another embodiment of the invention said produced coating on said uniform surface area contains less than one pinhole per 1 mm², preferably less than one pinhole per 1 cm² and most preferably no pinholes at said uniform surface area.

[0128] 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.

[0129] The plastic product according to the invention can comprise virtually whichever plastic, plastic compound such as composite materials or mixtures of these. As mentioned earlier, the definition of plastic product in this connection must be understood in a manner, wherein the product comprises a certain plastic surface, which has been coated according to now invented method. The plastic content of the product scaffold (uncoated product) can thus vary everywhere between 0.1 to 100%.

[0130] According to one embodiment of the invention said uniform surface area of plastic 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.

[0131] According to another embodiment of the invention said uniform surface area of plastic product is coated with carbon material comprising over 90 atomic-% of carbon, with more than 70% of sp³-bonding. The possible carbon materials were described earlier in description of now invented coating method.

[0132] According to still another embodiment of the invention said uniform surface area of plastic 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.

[0133] According to still another embodiment of the invention said uniform surface area of plastic product is coated with organic polymer material. Such materials were described earlier in more detail in description of now invented coating method.

[0134] 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.

[0135] According to another preferred embodiment of the invention said uniform surface of plastic product is coated with multilayered coating. According to another preferred embodiment of the invention said uniform surface of plastic product is coated with single coating layer.

[0136] According to one preferred embodiment of the invention the thickness of said coating on uniform surface of plastic product is between 20 nm and 20 μ m, preferably between 100 nm and 5 μ m. The invention accomplishes also coated plastic products comprising one or several atomic layer coatings and thick coatings such as exceeding 100 μ m, for example 1 mm. The present invention further accomplishes the 3D-structures prepared by employing the plastic component as a scaffold for growing said 3D-structure.

EXAMPLES

Example to Demonstrate Known Art Problems—Laser Technology

[0137] FIG. 2 represents the ITO-coating on polycarbonate sheet (~100 mm×30 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 (US-PLD) 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.

[0138] 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

[0139] 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

[0140] Plasma related quality problems are demonstrated in FIGS. 30a and 30b, 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. 30b. 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. 30b 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. 30a), the target surface 1111 in FIG. 30b is not any more available for a further ablations, and the target is wasted, although there were some material available.

Example of Invention—1

[0141] FIG. 28a 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. 28b 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. 28c 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. 28a, 28b and 28c 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

[0142] FIG. 29a 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 μm . In this example, there is an $\frac{1}{2}$ overlapping between the adjacent pulses.

Examples of Invention—Coated Products

[0143] The following samples were grown on various plastic substrates by employing ultra short pulsed laser deposition (USPLD) with a picosecond-range laser (X-lase, 20-80 W) at 1064 nm. Substrate temperature was varied in the range of 50-120° C. and target temperature in the range of room temperature to 700° C. The utilized spot size varied between 20 μm to 70 μm , being in most of the coating runs 40 μm . Both oxide, sintered graphite, sintered graphitic $\text{C}_3\text{N}_4\text{H}_x$ (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^{-1} mbar. The plastic samples were preferably oven-dried prior coating procedure. 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). The employed spot sizes varied between 20 to 80 μm . 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. No macroparticles due to deposition were observed on imaged areas. In some applications the existence of pinholes would not be a critical issue.

Example 1

[0144] A sheet of polycarbonate comprising 100 mm×200 mm was coated by ablating sintered carbon with pulse repetition rate of 4 MHz, pulse energy 2.5 μJ , 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, transparent 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 μm^2 with Atomic Force Microscope (AFM). No pinholes or detectable particles were found on any measured area.

Example 2

[0145] Several lacquer coated plastic lenses (Finnsusp, Finland) was coated by ablating aluminum titan oxide (ATO)

with pulse repetition rate of 4 MHz, pulse energy 5 μJ , pulse length 20 ps and the distance between the target material and surface to be coated was 25 mm. The vacuum level was 10^{-5} atmospheres during the coating process. The process resulted in a uniform, transparent coating. The coating thicknesses varied between 100 to 600 nm and the average surface roughness was determined to be under 10 nm as scanned from an area of 1 μm^2 with Atomic Force Microscope (AFM). No pinholes or detectable particles were found on any measured area.

[0146] Here, the wear resistance was tested by using a pin-on-disk testing with varying loads 10-100 g and test runs lasting 250-1000 rounds. Comparison of coated lens to commercial lenses was done by comparing the prepared coating (FIG. 23, right side) to two commercial French lenses (Commercial A and B) and MaxiAR coated lens by Finnsusp Ltd (Commercial C, FIG. 23, lens on left side). Lenses A and B were damaged in test runs easily even with low loads and short runs. On the contrary, the lens C (Finnsusp comparative sample) was significantly more wear resistant and withstands high loads without significant damage to the surface although the uttermost this surface layers were slightly worn. The transparency was not altered unless the coating damaged fully.

[0147] The wear resistance of ATO-coated lens was best, the comparison of wear resistance between the samples being presented as maximum load without damages for 1000 rounds in table 1 below:

TABLE 1

Test lens	Max Load Without Failure @1000 rounds
Comm. A	<15 g
Comm. B	<15 g
Comm. C	25-50-75 g
Picodeon Ltd	≥ 100 g

Example 3

[0148] Several sheets of polycarbonate comprising 300 mm×200 mm One was coated by ablating yttrium stabilized zirconium oxide with repetition rate of 2 Mhz, pulse energy 5 μJ , pulse length 20 ps and the distance between the target material and surface to be coated was 45 mm. The vacuum level was 10^{-5} atmospheres during the coating process. The process resulted in a uniform, transparent coating. The coating thickness was measured from 100 nm even to 1 μm and the average surface roughness was determined to be below 3 nm as scanned from an area of 1 μm^2 with Atomic Force Microscope (AFM). No pinholes were found on any measured area.

[0149] The oxide coated final product possessed remarkably better wear resistance and scratch-free properties as compared to commercial polycarbonate sheet. The surface profiles of the wear track for a commercial PC-plate after wear testing are presented in FIG. 26 (commercial product) and FIG. 27, the optical micrographs of the wear tracks being represented in FIGS. 24 and 25, respectively. The figures clearly demonstrate the difference in favor to yttrium stabilized zirconium oxide-coated pc-plate. Please, note also the different vertical scales of FIGS. 26 and 27. The adhesion of the coating structure was good.

Example 4

[0150] A sheet of polycarbonate comprising 300 mm×250 mm was coated by ablating titan oxide in oxygen atmosphere

with pulse repetition rate of 2 MHz, pulse energy 4 μJ , pulse length 10 ps and the distance between the target material and surface to be coated was 45 mm. The vacuum level was 10^{-2} atmospheres during the coating process. The process resulted in transparent coating possessing coating thickness of 20 nm. The average surface roughness was determined to be 2 nm as scanned from an area of $1\text{ }\mu\text{m}^2$ with Atomic Force Microscope (AFM). No pinholes were found on any measured area of titan oxide-coating. The coated object was subjected to organic dirt after which it was subjected to light and certain humidity. The coating possessed self-cleaning properties.

Example 5

[0151] A sheet of polycarbonate comprising 300 mm $\times$ 250 mm was coated by ablating titanium with pulse repetition rate of 12 MHz, pulse energy 5 μJ , pulse length 20 ps and the distance between the target material and surface to be coated was 60 mm. The vacuum level was 10^{-4} atmospheres during the coating process. The process resulted in metallic titan coating possessing coating thickness of 50 nm. The average surface roughness was determined to be 0.14 nm as scanned from an area of $1\text{ }\mu\text{m}^2$ with Atomic Force Microscope (AFM). No pinholes were found on any measured area of titanium-coating.

Example 6

[0152] A sheet of polycarbonate comprising 300 mm $\times$ 250 mm was coated by ablating pink agate (crushed and sintered) with pulse repetition rate of 15 MHz and the distance between the target material to be coated was 3 cm. The vacuum level was 10^{-5} atmospheres during the coating process. The processes resulted in pink agate coloured, opaque coatings comprising thickness of 100 nm. The average surface roughness was determined to be under 3 nm as scanned from an area of $1\text{ }\mu\text{m}^2$ with Atomic Force Microscope (AFM). No pinholes were found on any measured area of agate coating.

Example 7

[0153] A sheet of polycarbonate comprising 300 mm $\times$ 250 mm was coated by ablating cold-pressed chitosan with pulse repetition rate of 2.5 MHz, pulse energy 5 μJ , pulse length 19 ps and the distance between the target material and surface to be coated was 25 mm. The vacuum level was 10^{-7} atmospheres during the coating process. The process resulted in partially opaque coating possessing coating thickness of 280 nm. The average surface roughness was determined to be 10 nm as scanned from an area of $1\text{ }\mu\text{m}^2$ with Atomic Force Microscope (AFM). No pinholes were found on any measured area of chitosan-polymer coating.

Example 8

[0154] A sheet of polycarbonate comprising 10 mm $\times$ 25 mm was coated by ablating hot-pressed $\text{C}_3\text{N}_4\text{H}_x$ with pulse repetition rate of 1 MHz, pulse energy 5 μJ , pulse length 20 ps and the distance between the target material and surface to be coated was 65 mm. Nitrogen pressure varied in the range of 10^{-4} to 10^{-1} mbar. The coating thickness was measured to 100 nm. The average surface roughness was determined to be under 3 nm as scanned from an area of $1\text{ }\mu\text{m}^2$ with Atomic

Force Microscope (AFM). No pinholes were found on any measured area of carbon nitride coating.

Example 9

[0155] A sheet of polycarbonate comprising 100 mm $\times$ 250 mm was coated by ablating ITO in oxide form (90 wt. % In_2O_3 ; 10 wt. % SnO_2) with pulse repetition rate of 22 MHz, pulse energy 5 μJ , pulse length 20 ps and the distance between the target material and surface to be coated was 12 cm. Oxygen pressure varied in the range of 10^{-4} to 10^{-1} mbar. The process resulted in a uniform, transparent coating. The coating thickness was measured to 220 nm and the average surface roughness was determined to be under 3 nm as scanned from an area of $1\text{ }\mu\text{m}^2$ with Atomic Force Microscope (AFM). No pinholes were found on any measured area of ITO coating. Electrical resistivity of the sample was measured to $2.2\times 10^{-3}\text{ }\Omega\text{cm}$.

Example 10

[0156] A sheet of acryl plastics comprising 100 mm $\times$ 100 mm was coated by ablating ITO from a metal target (90 wt. % In; 10 wt. % Sn) with pulse repetition rate of 16 MHz, pulse energy 5 μJ , pulse length 20 ps and the distance between the target material and surface to be coated was 6 cm. Oxygen pressure varied in the range of 10^{-4} to 10^{-1} mbar. The process resulted in a uniform, transparent coating. The coating thickness was 40 nm and the average surface roughness was determined to be under 2 nm as scanned from an area of $1\text{ }\mu\text{m}^2$ with Atomic Force Microscope (AFM). No pinholes were found on any measured area of the ITO coating.

Example 11

[0157] A sheet of acryl plastics comprising 100 mm $\times$ 100 mm was coated by ablating aluminum oxide with pulse repetition rate of 4 MHz, pulse energy 5 μJ , pulse length 20 ps and the distance between the target material and surface to be coated was 2 cm and the vacuum level was 10^{-3} atmospheres during the coating process. The process resulted in a uniform, transparent coating. The coating thickness was 800 nm and the average surface roughness was determined to be under 3 nm as scanned from an area of $1\text{ }\mu\text{m}^2$ with Atomic Force Microscope (AFM). No pinholes were found on any measured area of the aluminumoxide coating.

Example 12

[0158] The ITO-coated sample of example 10 was coated by ablating aluminumoxide with same conditions as in previous sample 11. The process resulted in a uniform, transparent coating. The aluminumoxide coating thickness was again 800 nm and the average surface roughness was determined to be under 3 nm as scanned from an area of $1\text{ }\mu\text{m}^2$ with Atomic Force Microscope (AFM). No pinholes were found on any measured area of the aluminum oxide coating.

Example 17

[0159] A polycarbonate sheet with surface area comprising 300 mm $\times$ 300 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 12 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 of aluminum oxide coating was 500 nm and the average surface roughness was determined to be below 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.

Example 18

[0160] Sheets of mylar and polyethylene comprising 100 mm×250 mm were coated by ablating ITO in oxide form (90 wt. % In_2O_3 ; 10 wt. % SnO_2) with pulse repetition rate of 15 MHz, pulse energy 5 μJ , pulse length 20 ps and the distance between the target material and surface to be coated was 50 mm. Oxygen pressure varied in the range of 10^{-4} to 10^{-1} mbar. The process resulted in uniform, transparent coatings. The coating thicknesses were measured to 150 nm and 180 nm and the average surface roughness was determined to be under 3 nm as scanned from an area of $1 \mu\text{m}^2$ with Atomic Force Microscope (AFM) in both of the samples. No pinholes were found on any measured area of ITO coatings.

[0161] Electrical resistivity of both of the samples was measured to $2.4 \times 10^{-3} \Omega\text{cm}$.

Example 19

[0162] Sheets of polyvinylchloride, polyimide, polystyrene and acryl comprising surfaces of 50 mm×450 mm were coated by ablating yttrium aluminumoxide (ATO) with pulse repetition rate of 4 MHz, pulse energy 5 μJ , pulse length 20 ps, the distance between the target material and surface to be coated being kept at 5 cm. The vacuum level was 10^{-2} atmospheres during the coating processes. The process resulted in a uniform, transparent coating. The coating thickness was 440 nm, 440 nm, 450 nm and 460 nm respectively, and the average surface roughness were determined to be under 3 nm as scanned from an area of $1 \mu\text{m}^2$ with Atomic Force Microscope (AFM) in all of the samples. No pinholes were found on any measured area of the ATO-coatings.

1-33. (canceled)

34. A method for coating a certain surface of a plastic 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 $1 \mu\text{m}^2$ with Atomic Force Microscope (AFM).

38. A method according to claim 34, characterized in that said uniform surface area of plastic 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.

39. A method according to claim 34, characterized in that said uniform surface of plastic 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 plastic product is between 20 nm and $20 \mu\text{m}$, preferably between 100 nm and $5 \mu\text{m}$.

41. A plastic 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 plastic 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 plastic 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 $1 \mu\text{m}^2$ with Atomic Force Microscope (AFM).

44. A plastic 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 plastic 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 plastic 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 plastic product according to claim 41, characterized in that said uniform surface area of plastic 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 plastic product according to claim 41, characterized in that said uniform surface of plastic product is coated with multilayered coating.

49. A plastic product according to claim 41, characterized in that the thickness of said coating on uniform surface of plastic product is between 20 nm and $20 \mu\text{m}$, preferably between 100 nm and $5 \mu\text{m}$.

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