

PATENT SPECIFICATION (11)

1 430 180



- (21) Application No. 36394/73 (22) Filed 31 July 1973 (19)
 (31) Convention Application No. 28 0 489 (32) Filed 14 Aug. 1972 in
 (33) United States of America (US)
 (44) Complete Specification published 31 March 1976
 (51) INT. CL.² C23C 13/12 H01J 37/02
 (52) Index at acceptance

C7F 1A 1V1 4N 4W 6B1C 6B1Y 6C 6D1A1 6D1B 6D2
 6E1B 6E2 6F1 6F2
 H1D 10 14A 14B 44 9L 9Y

- (72) Inventors JOSEPH EILERT BERG and
 RANDOLPH ERNEST BROWN, Jr.

(54) METHOD AND APPARATUS FOR DEPOSITING FILM ON A SUBSTRATE, AND PRODUCTS PRODUCED THEREBY

(71) We, PRECISION THIN FILM CORPORATION, a corporation organised under the laws of the State of California, United States of America, of 5525 Wilshire Boulevard, Los Angeles, California, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to film deposition methods and apparatus, particularly suitable for depositing a thin transparent hard film on a substrate.

With the increasing use of plastics and other non-glass lenses in eyeglasses and other items, it has become increasingly important to develop hardened surfaces on such relatively soft materials which surfaces resist scratching and abrasion. Various methods of developing such hardened surfaces have been employed, such as dipping of plastics lenses, the wiping on of a film, the use of harder plastics themselves, the provision of a laminated lens and similar approaches, but without success.

Similarly the surface properties of many materials and objects may be enhanced by the provision of an extremely thin surface coating of a suitable protective material. Razor blades, for example, may be made to last many times longer than at present with suitable protection of the fine cutting edge from corrosion.

In accordance with this invention, to deposit a film on a substrate molecular particles are emitted from a source of a selected material to be deposited, and are ionized and accelerated and directed towards a substrate by the use of a plurality of rings encircling the path of the emitted particles. The emitter, rings and substrate are maintained in a high vacuum.

In use predetermined electrical potentials

are maintained at the various elements of the structure employed in the apparatus. Either electrostatic or magnetic ion beam directing apparatus may be employed for beam control or some combination of the two systems may be utilized. An electrostatic field is required, however, to develop electron emission from ionizing elements positioned adjacent the path of the beam, so as to "super-ionize" the beam, thus permitting effective acceleration. The beam can be directed over a sufficient extent and controlled to such a degree as to permit bombardment of specimen substrate over a considerable area. Where the specimen substrate is non-conducting, provision may be made for the dissipation of surface charge carried to the substrate by the bombarding ions. Those ionized particles which do not impact the specimen materials may be caught on a collecting grid and removed from the system.

Material which has been successfully implanted in apparatus embodying the invention comprises minerals which are selected for their properties of hardness, elasticity, heat resistance and optical clarity. The materials may include trace amounts of minute impurities such as may be found in commercial grade materials. In one example these materials are implanted onto various types of plastics lenses with implantation occurring to a depth of approximately 10,000 Angstroms (1 micron) within the preferred range from several hundred Angstroms to a few microns and the process of implanting and depositing continuing until a film layer is built up to a preferred thickness of approximately 2 microns. The result is an eye-glass lens or other product which has the shatter-resistance of the plastics substrate under the surface film with abrasion-resistant properties equal to or better than those of glass.

In one particular arrangement embodying

the invention, an electron beam gun emitter is employed with a paste mixture of known minerals selected for their properties of hardness, elasticity, heat resistance and optical clarity, positioned in the electron beam gun target region. This electron beam gun is water-cooled, has a filament for emitting electrons and utilizes electromagnetic fields to cause the emitted electron beam to curve and bombard the target material. As a result, the target material and its molecules are bombarded off the surface as ionized molecular particles where they become accelerated by the field of the particle accelerator. A removable shutter is positioned in the region between the emitter and the accelerator to block or pass the beam as desired.

In one particular arrangement embodying the invention, the accelerating, directing and ionizing means comprises a series of spaced and insulated flat rings of varying diameters, increasing in the direction of beam traversal. Selected ones of these rings are fashioned as field-intensifying ionizing elements by silver soldering sharp needles with their points directed inward and generally equally spaced about the circumference of the rings. These sharp points serve as electron emitters for further ionizing particles as they pass through the rings. The accelerator structure is suspended from insulated wires extending to a support structure which also holds a target frame on which various lenses may be mounted. The collector screen extends over the specimen support brackets, physically and electrically separated therefrom, and is positioned across the divergent beam region so as to collect those particles that do not impact the specimens.

In operation of this embodiment, a bell jar type cover is placed over the entire structure and the region thus enclosed is evacuated to a high vacuum. The insulators and interconnecting conductors are arranged to develop various potentials at various elements of the structure. A DC power supply has been employed for developing these potentials with selected RF modulation of certain electrode elements being developed for an RF generator.

In one preferred arrangement embodying the invention, the electron beam gun emitter is maintained at the negative power supply voltage which is 10kv. The first, third and fifth rings of the accelerator structure (counting from the bottom nearest the electron beam gun emitter) are preferably maintained at neutral potential, although these may have their potentials controlled, if desired, to exert minor control on the particle beam. The second and fourth rings are the ionizing elements with the needles attached. These are maintained at a negative potential of -3,000 to -15,000 volts, modulated with an RF signal of 25 to 100 volts rms at 400 mega-

hertz. The sixth and final ring is maintained at a slight positive potential, although this is not critical and this ring may be left to float and assume the potential of the beam, if desired. The specimen support frame is maintained at a positive 4 to 10 kilovolts. This can also be modulated with an RF signal at an amplitude of 25 to 100 volts rms which serves to develop a controlled plasma that periodically discharges the plastics or other nonconducting material of the specimen substrate. The lenses or other products to be filmed are mounted in clips secured to the support frame. As an alternative to using a controlled plasma for discharging the substrate, isotope bodies may be mounted near the support frame for discharging the plastics substrate by radioactive bombardment. The collector screen is also maintained at a positive potential of from 4 to 10 kilovolts, thus providing a strong positive force drawing the negatively ionized beam particles toward the specimens being bombarded.

It has also been found possible to develop a beam which results in film deposition and implantation by reversing the polarity of potentials applied to the various elements of the structure. In any event, of course, the effectiveness of the ionizing elements is limited but the accelerating, beam shaping and directing, and collecting elements operate with positive ions essentially as described for negatively ionized particles.

In alternative embodiments of the invention, various types and configurations of accelerating and ionizing structures may be employed. One such structure utilizes a series of vertical vanes fixed to the various horizontal rings by insulator mounts. The vanes are preferably of stainless steel and fashioned with all surfaces made extremely smooth, as by electropolishing, except the inner edge which is sharpened to an extreme degree to provide electric field intensification. As explained previously, the succeeding rings increase in diameter and the vanes are angled along their inner sharp edges to match the gradient of ring inner diameter. The shape of such accelerating vanes influences the rate of acceleration of the beam particles. It may also be related to the shape of the specimen being coated. The shape of the beam may be varied by using rings which are elliptical or which present other shapes rather than circular.

Still another alternative arrangement of the accelerating ionizing structure may utilize the stacked rings as first described but with the ion emitting rings being fashioned with extremely sharp inner edges instead of having the needles mounted thereon as heretofore described. Still another embodiment may utilize a series of tubular rings with the accelerating rings being rounded and

polished while the electron emitter (ionizing) tubular elements are provided with a radially inward knife edge.

The potentials applied to the various elements of the accelerating structure may be stepped and varied as desired. A varying effect on the shape, density and velocity of the beam can be achieved by varying the potentials of the accelerating/ionizing structure as a function of distance from the emitter, for example.

Various arrangements and configurations of accelerating and beam directing elements may be employed to separate different particles in the beam so that bombardment of the specimens occurs only with the particles of desired size and velocity. Particular arrangements embodying the invention include structure for developing oriented magnetic fields which curve the desired particles along selected paths to the specimens while other particles that might have a deleterious effect upon the specimens being bombarded are directed along paths which impact shields or otherwise miss the specimens altogether.

The benefits provided by preferred apparatus and methods embodying the present invention are particularly useful in developing suitable low-cost lenses for eyeglasses and other applications from materials and fabrication processes formerly unsuitable. For example, it now becomes practical to form lenses by injection molding processes with the lenses in the final fabrication step being coated with films implanted by means of the present invention.

Moreover, arrangements embodying the present invention may be used for implanting films on substances and articles other than plastics lenses. For example, one or a plurality of beam ionizing and accelerating arrangements embodying the present invention may be used on a mass production basis to implant a film having the desired properties of hardness and resistance to abrasion on a thin sheet of plastics or other material suitable for lamination with other sheets of plastics, for example, to develop a desired combination of properties for an overall article. Such a laminated article may comprise an automobile windshield, for example, with the principal layer of the article being a thicker sheet of plastics having desirable properties of resistance to breakage with the outer surfaces being covered with thin laminations of plastics implanted with a film in accordance with the present invention. The resultant article develops, by virtue of the implanted film, the necessary properties of hardness and resistance to surface abrasion which are not provided by the inner sheet constituting the principal material of the article.

Mass production of such a film may be accomplished by feeding a thin sheet passing between respective storage rolls through an

evacuated chamber in which beam accelerating and ionizing structures embodying the present invention are located. It may also be possible to treat fabrics of various type in similar fashion. It has been found that the implantation of a particular material as a film has a beneficial result insofar as improvement of fire resistant or fire retardant properties is concerned. It is believed that the implantation of such a film tends to prevent oxidation by keeping air from reaching the combustible material underneath. It may be possible to treat fabrics in such fashion to develop fire retardant properties. Materials which are useful for this purpose comprise minerals which are non-combustible and which present a very small temperature coefficient of expansion, thus permitting the film to avoid rupture and remain intact as a protective coating over a considerable temperature range. Where multiple constituents of the protective film are present, they may be selected to compensate for their respective temperature coefficients so that the coefficient of expansion overall is approximately stabilized. Thus, the application of heat does not have the effect of fracturing the implanted film. As long as the implanted film, which itself is non-combustible, maintains its integrity, the oxidizable material underneath is prevented from combination with oxygen.

The invention will now be described in more detail, by way of example, with reference to the accompanying drawings, in which:

Fig. 1 is a perspective view of a film depositing system;

Fig. 2 is a perspective view of particle bombardment apparatus embodying the invention within the vacuum chamber shown in Fig. 1, with the cover removed;

Fig. 3 is a perspective view of one particular arrangement of the ionizing and accelerating structure utilized in the apparatus of Fig. 2;

Fig. 4 is a plan view of another type of accelerator structure which may be utilized in the arrangement of Fig. 2;

Fig. 5 is a sectional view, taken along the line 5—5 of Fig. 4;

Fig. 6 is a schematic plan view of an accelerator structure for use in apparatus of Fig. 2;

Fig. 7A is a section taken along the line 7—7 of Fig. 6, showing details of another type of accelerator structure;

Fig. 7B is a sectional view taken along the line 7—7 of an alternative accelerator structure;

Fig. 8 illustrates a particular product produced by use of the apparatus of Fig. 2;

Fig. 9 is a combination schematic and block diagram of a further system embodying the invention;

Fig. 10 is a view of elements of a par-

tical product fashioned using the system of Fig. 9;

Fig. 11 is a view in section of another product;

5 Figs. 12, 13 and 14 are block diagrams illustrating various methods embodying the invention;

Fig. 15 is an elevational view, partially in section and broken away, of another arrangement embodying the invention for use in the system of Fig. 1; and

Fig. 16 is a similar view of yet another arrangement embodying the invention.

As is shown in Fig. 1, a complete film deposition system 10 may comprise a high voltage power supply 12, a high vacuum system 14 and an RF power supply 16. The vacuum system 14 comprises a bell jar housing or cover 18 having one or more viewing windows 19 and a vacuum control console 20. Suitable interconnections between the various components of the overall system are provided via cables 22 and 24.

Fig. 2 depicts a bombardment apparatus 25 mounted within the housing 18 of the vacuum system 14 of Fig. 1. The apparatus 15 is shown comprising upstanding frame support rods 30 mounted to a base plate ring 32 in position on the control console table 20. Recessed within the base plate ring 32 is an electron beam gun emitter 34, shown partially broken away in section, which, as represented in Fig. 2, may be water-cooled by means of tubes 36 and have a centrally 35 located target region 38 in which slug 40 of material to be evaporated is positioned. A filament (not shown) is positioned within the cavity 42. Suitable magnetic field generating coils are located within the structure adjacent the cavity 42. Various leads 44 are provided for carrying current to the filament and to the field generating coils. In operation of the electron beam gun emitter 34, electrons are emitted by the filament within the cavity 42 and directed outward and downward upon the target slug 40 under the influence of the generated electromagnetic field where they bombard and heat the slug 40 to cause emission of ionized molecular particles therefrom. A pivotable shutter 46, control- 45 lable from outside the vacuum housing, is provided to either block the cloud of emitted ionized particles or, alternatively when pivoted out of the way, to permit the ionized particles to respond to the field of the accelerating structure 48.

A specimen support or mounting frame 50 is shown mounted by means of insulators 52 atop the support rods 30. It is this frame 50 upon which the various articles, such as plastics lenses, may be secured for deposition of the film. A collector screen 54 is shown in position above the frame 50. It will be understood that the collector screen 54 is actually 65 mounted to the top of the housing 18 (Fig. 1)

but it is shown in position here as it is normally located when the housing 18 is in position, for a more complete understanding of the apparatus. The potential of the screen 54 may be determined by connections (not shown) to the inside of the housing 18.

The accelerating/ionizing structure 48 is suspended from the support rods 30 by means of wires 60 and insulator 62. The details of the accelerator/ionizer 48 are better shown in Fig. 3. It will be seen to comprise a plurality of flat rings, six in the illustrated example, increasing in both inner and outer diameter from bottom to top. The first, third and fifth rings 66 serve as guard rings and principally serve to isolate the field of the intermediate ionizing or emitting rings 68, although they may contribute to the electric field for particle acceleration and direction. An accelerating ring 70 is the uppermost ring in the structure 48. Although, six rings are shown in the structure, a greater or lesser number may be provided if desired. Adjacent rings are separated from one or another by means of insulators such as 72. The emitter rings 68 are provided with a plurality of needles 74 spaced generally equidistantly about the rings 68, and soldered thereto, as by silver solder. The points of the needles 74 are sharpened to a fine degree to provide electrical field intensification and point radially inward. Thus, the points of the needles 74 readily emit electrons under the influence of an electric field which serves to further ionize the molecular particles that are being acted upon by the accelerator structure 48 and drawn toward the specimen/collector region by the positive potentials applied thereto.

The potential of the various elements of the apparatus of Fig. 2 may be controlled by means of conductors and feedthrough insulators 80 extending through the base plate ring 32. Thus, a conductor 82 is connected to the specimen frame 50. A conductor 84 is connected to a lower wire 60 to control the potential of the accelerating ring 70. Conductors 86 extend to respective ones of the guard rings 66, while the potential of the emitter rings 68 is controlled by conductors 88. These are connected to the associated high voltage power supply 12 and RF power supply 16 (Fig. 1). Suitable voltages to be applied have been discussed above.

In one particular mode of operation of the apparatus, radioactive isotope blocks 90 may be utilized to discharge the build-up of surface charge on the specimens being filmed through radioactive bombardment. Such radioactive isotope blocks may also be suitably positioned at other points within the housing 18 in locations suitable for effectively discharging the specimens, if desired. Alternatively microwave RF energy may be 130

beamed at the specimens from suitable positioned slotted lossy wave-guide elements to produce a local plasma for discharging surface charge.

5 Figs. 4 and 5 illustrate respectively plan and sectioned elevational views of one alternative type of accelerator/ionizing structure which may be substituted for that shown in Figs. 2 and 3. This structure, designated 48a, 10 comprises a plurality of rings 101, of which three are shown, electrically isolated from one another and from interconnecting vertical stainless steel vanes 102 by means of insulators 103. The vanes 102 are angled to 15 follow the contour of the inner diameters of the respective rings 101 and are sharpened to a fine razor edge along this portion of the vanes 102. The remainder of the structure is smoothed, as by electropolishing. Thus the 20 vanes 102 serve to emit electrons copiously along their sharpened inner edges under the influence of an electric field. Suitable connections (not shown) may be provided to control the potentials of the vanes 102 and 25 rings 101.

Fig. 6 is a schematic plan view of accelerating structure 48 and Figs. 7A and 7B are partial sectional elevations of alternative 30 arrangements for the structure 48. Fig. 7A illustrates a plurality of tubular rings of which the emitter rings 104 have been fashioned with an extended and sharpened inner edge. The remainder of the rings 106 are perfectly rounded and electropolished to 35 develop a smooth surface. The rings 104 under the influence of the applied electric field serve to discharge electrons inwardly from the sharpened inner edges.

Fig. 7B represents a structure similar to 40 that shown in Fig. 3, except that the needles 74 have been eliminated and the two emitter rings 68A have been provided with a sharply honed inner edge to accomplish the emission of electrons inwardly under the influence of the electric field. The remainder 45 of the rings 69 are smoother, as by electropolishing, as are the other surfaces and edges of the rings 68 apart from the sharpened inner edge thereof.

50 Other accelerator and ionizing structural configurations may be devised to accomplish the results achieved by the accelerator/ionizer structure 48 and alternative arrangements shown and described herein. In particular, the structure may be substituted or 55 modified by the inclusion of apparatus for generating magnetic fields, either in place of or in addition to the electric fields generated by certain of the elements herein shown in order to accomplish the desired result of 60 directing and shaping the particle beam to fit the particular specimen on which the film is being deposited.

Fig. 8 is a representation of a particular 65 lens 110 which has been specially coated in

the apparatus shown and described herein. Lens 110 on its left half 112 and the small circles 114 has been coated with an implanted film comprising principally minerals 70 such as those referred to hereinabove selected for their properties of hardness, elasticity, heat resistance, and optical clarity. Except for the small circular areas 114, the right half 116 is uncoated. This was accomplished 75 by first masking the right half 116 with a perforated foil layer before implanting the film. As a test, the lens 110 was then rubbed with various abrasive materials, including emery paper and steel wool. The coated 80 areas 112 and 114 were unmarked by these abrasive materials and the lens remains clear and transparent in these areas. Over the remainder of the right half 116, however, the lens was severely scratched to the point 85 where it was no longer transparent, as indicated by the stippling shown thereon. Similar experiments with soft lenses coated by other methods known in the art served to scratch and mar the lens face but did not affect the 90 films and filmed lenses produced by the present method.

Various other uses besides the coating of eye glass lenses and the like may be realized from the practice of the methods embodying the present invention. Figs. 9 and 10 illustrate another extensive area of use where the application of the present invention will be most important. Fig. 9 illustrates a continuous system utilizing a plurality of particle 95 bombardment units embodying the present invention arranged for a continuous film depositing process to implant a hard film on a cellulose plastics sheet. Facilities are known in the art for developing and maintaining a high vacuum chamber through which continuous materials may be fed for vacuum 100 processing. The combination schematic and block diagram of Fig. 9 is intended to represent such a system. It is shown comprising a large chamber 120 through which a plastics sheet 122 is fed between rolls 124 and 126 at opposite ends of the chamber. Successive vacuum barriers 128 are provided at each end of the chamber 120. The film may be fed through suitable sealing arrangements 115 130, here represented as rollers between which the sheet 122 passes in going between outside ambient pressure and the high vacuum inside the chamber 120. Air passages or ports 132 are provided to connect the various regions within the chamber 120 with a plenum chamber 134 which is maintained at a high vacuum by an associated vacuum system 138. Alternatively the reels 124, 126 may be positioned within the chamber 120, 125 in which case the need for the sealing elements for admitting the plastic 122 through the chamber walls is unnecessary. Within the chamber 120 and adjacent the sheet 122 which is supported on rollers or guides 136 130

is shown a plurality of units 15 (Fig. 2) mounted on a base 148. These units 15 are shown as being connected to a power supply unit 139 which may include both the high voltage power supply and RF generator supply used in the deposition system.

In operation of the system represented in Fig. 9, the sheet 122 is transferred from roll 124 to roll 126, passing through the vacuum chamber 120 and pass the ionized particle deposition units 15. One or more of the units 15 may be operated to implant the desired film on one or both sides of the sheet 122 so as to develop the film in the desired areas and to the desired thickness. If deposition on both sides of the sheet 122 is desired, it can easily be arranged, either by mounting additional units 15 on opposite sides of the sheet (possibly by using deflecting fields to develop the desired particle trajectories) or simply by doubling back the sheet 122 so that it traverses one or more of the units 15 with the opposite side of the sheet in position to be bombarded by the ionized particles therefrom.

An outstanding benefit of implanting film on plastics sheet in this fashion is the opportunity which develops for fabricating a variety of articles which have heretofore been limited to fabrication from glass because of the need for surface protection by providing extreme resistance to abrasion. One such item is the automobile windshield. Such is represented in Fig. 10 as being formed of plastics sheet, preferably injection molded to a suitable thickness and shape, to which a sheet 142, cut from a sheet 122 which has been implanted with a hard film as described in connection with Fig. 9, may be bonded. In Fig. 10, only one sheet 142 is shown in conjunction with the base layer 140, although it will be understood that a sheet 142 may be provided on each side of the base layer 140.

Fig. 11 represents a cross-section of an article, such as the windshield of Fig. 10 or an injection-molded lens, for example, in which a base layer 150 is laminated between two layers 152. Each of the layers 152 is implated with a hardened film in the manner described hereinabove along its outer surface. Thus, the laminated structure will provide the desired combination of toughness and resilience that may correspond to the base layer 150 and still provide the resistance to abrasion along all surfaces that are subject to abrasive forces as is provided by the protective film implanted in the manner described herein. One method of producing such an article is illustrated in Fig. 12. The more generalized methods of operating apparatus as described in conjunction with Figs. 1—7 and 9 are illustrated in Fig. 13.

Thus far the deposition method has been described in the context of deposition of a

clear transparent film of a plastics substrate. However, it will be understood that other films may be deposited and that the substrate need not necessarily be plastics or, indeed, non-conducting. Various materials or compositions may be used as a source of the particles for deposition. One type of particular interest for sunglasses and windows for filtering the sun's rays is the deposition of a colored film. This may be accomplished by the inclusion of the oxides or other substances which impart the desired color to the film as deposited. Since the colors and tints achieved thereby have a tendency to fade, proportionally on exposure to ultraviolet light, it is desirable to implant a film of a deeper shade, color or tint that which is ultimately desired and thereafter by exposure to ultraviolet rays or a similar treatment fade the deposited film to the intended hue. With controlled rates of deposition of a colored film, the ultraviolet rays which are present in the plasma during the deposition process may develop the desired fading so that the ultimate level of tinting is already present when the deposition process is completed. Such methods are illustrated in Fig. 14.

An alternative arrangement for use in the system of Fig. 1 is illustrated in Fig. 15, which is a partial elevational view showing the details of particular features, partially in section and partially broken away. In Fig. 15, apparatus 150 is shown having many of its basic structural elements similar to the structure of the apparatus 15 of Fig. 2; where corresponding elements of structure are shown, the same reference numerals are employed. Thus, the apparatus 150 is shown comprising a base 32 mounted on a table 20, a combination accelerating and ionizing structure 48 suspended by wires 60 and insulators 62 from support members 30, a shutter 46 mounted for pivotal movement above the base 32, and a bell jar cover 18a corresponding to the bell jar 18 of the vacuum apparatus of Fig. 1.

In the configuration of Fig. 15, while the ionized particle beam is generated, accelerated and ionized in the same fashion as with the apparatus of Fig. 2, the beam is subsequently directed through a curved path to impact the mounted specimens. The purpose of directing the beam in such a fashion is to achieve a separation of particles of various sizes and weights, thus avoiding a deleterious effect on the specimen being coated which might be caused by the impacting of larger particles that are sputtered off the material which is the source of the film particles. It has been found that the impact upon the specimens being filmed of relatively large particles tends to produce pitting of the implanted film. As a consequence, the film is fractured or the larger particles are em-

bedded in the specimen and there is a tendency for absorption of moisture with a consequent lifting of film in the vicinity of the pits. In an extreme case the larger particles may develop undesirable surface irregularities. It has been found that the tendency to emit larger particles along with the smaller ones which are desired for the implanting process is diminished if the material comprising the source of the film is heated to a molten form before emission is initiated. However, applying this much heat to the system has an adverse effect in cases where the specimens are plastics or some other soft material since the heat tends to soften and melt the specimens and spoils the entire process.

A preferably arrangement for overcoming this problem is represented in Fig. 15 wherein the apparatus 150, in addition to comprising the elements already mentioned, includes means for establishing particularly oriented magnetic fields for directing the smaller particles to the specimens that are placed out of the path of the larger particles. This apparatus is shown additionally comprising a cylinder 164 containing magnetic field coils 165 for establishing a vertically directed magnetic field. The cylinder 164 is suspended from the support rods 30 by means of wires 160 and insulators 162. Above the cylinder 164 is shown a second magnetic field means 166 for establishing a magnetic field which is horizontally directed. Means 166 may comprise individual magnets 168 which may be in the form of permanent magnets or the magnets 168 may be the pole pieces of electromagnetic coil magnets. In one configuration, means 166 may be in the form of a generally flat plate mounted to the wall of the housing 18a on the far side thereof, with a corresponding magnetic field means of opposite magnetic polarity (not shown) on the near side of the beam path through the center of the housing 18a.

Above the magnetic field producing apparatus is an arrangement for suspending the specimens about the sides of the housing 18a. This mechanism is represented as a cylinder 170 having an extended upper lip adapted to be supported on a ring 172 by means of ball bearings 174 to permit rotation of the cylinder 170. A motor 176 with a drive roller 178 bearing against the cylinder 170 serves to drive the cylinder 170 in rotation within the housing 18a. Specimens in the form of lenses 180 are shown positioned on mounting racks 182 pivotally mounted in supports 184. The racks 182 are arranged to be pivoted through 180° at a particular point in the cycle of rotation of the cylinder 170 in order to rotate the lenses 180 relative to the cylinder 170 so that they may be coated on both opposite surfaces. As shown in Fig. 15, this pivoting mechanism comprises a block 186 having a

rod 188 extending to engage a trip lever 190 at the lower ends of the racks 182. Thus as each individual rack 182 passes the rod 188, the trip lever 190 is engaged by the rod 188 and caused to rotate so as to turn the lenses 180 around and expose the other side to bombardment on further rotation of the cylinder 170.

In the operation of the apparatus of Fig. 15, emitted particles are accelerated and ionized by means of the apparatus 48 as already described in connection with Fig. 2. As the particle beam passes through the apparatus 48, the larger particles pick up a lesser negative charge in proportion to their mass than do the smaller particles. In fact, the particles may have a positive charge upon emission which, in some instances, is not even neutralized by the emitted electrons during passage of the particles through the apparatus 48. As is known, the ballistic trajectory of a charge particle through a magnetic field may be dependent on the charge-to-mass ratio. Particles having a larger charge-to-mass ratio are deflected more by an orthogonal magnetic field than particles which have zero net charge or a smaller charge-to-mass ratio. Thus, the magnetic field directing and deflecting means of Fig. 15 serve to separate the particles which are larger than desired and those which are inadequately ionized from the particles of proper size and ionization to produce the desired film implantation on the lens specimens 180.

For apparatus such as is shown in Fig. 15, a collector and suitable surface charge discharging means may be positioned across the top underneath the dome of the housing 18a in the manner indicated in Fig. 2. Such a collector, in addition to being effective as an element establishing an electrostatic field, may also serve to collect and trap the charge particles of larger size or lesser charge-to-mass ratio which are not directed by means of the magnetic field of the magnetic field means 166 to the specimens 180. As an alternative to the arrangement as depicted in Fig. 15, the specimens may be mounted in the manner shown in Fig. 2 with magnetic field deflecting means such as a baffle being provided to cause the particles to follow a dog-leg curved path which ultimately directs the appropriate particles to the specimen while deflecting or trapping the undesired particles outside the region of the specimens being implanted.

As another alternative to the arrangement represented in Fig. 15 wherein the specimens are physically revolved by the cylinder 170 about the interior of the housing 18a during the film deposition process, the position of the specimens 180 may be fixed by holding the cylinder 170 stationary and the magnetic field of the magnetic field means 166 may be

rotated to cause the particle beam to sweep the specimen area. In such case, the magnetic field means 166 may itself comprise a cylindrical ring with the individual magnet field elements 168 being selectively magnetized by electromagnetic fields established by selective and successive energization of the respective electromagnetic coils to develop a horizontal magnetic field which rotates in controlled fashion in a plane generally orthogonal to the longitudinal axis of the apparatus 150. Such a swept field may selectively film any particular specimen as desired. At the same time it is effective in the manner already described at separating the desired particles from the undesired particles in order to provide an improved resultant filmed product. Also, if desired, the structure comprising the mounting racks 182 may be electrostatically charged so that these racks 182 serve additionally as a collector to attract the charged particles passing through the accelerating and ionizing structure 48 and the magnetic field means 164, 166.

Still another embodiment of the invention is represented in Fig. 16 which shows apparatus 200 such as may be employed in the system of Fig. 1. Apparatus 200 is similar to that shown in Fig. 2 with certain notable modifications. As shown in Fig. 16, the apparatus 200 comprises the vacuum chamber within a housing 18a having a table 20, a base 32, a particle emitter 34, a shutter 46 and the ionizing, accelerating and directing structure 48. The elements 34, 46, and 48 are positioned off-center within the vacuum chamber of the apparatus 200. Above the elements 34, 46 and 48, and aligned therewith, is a particle diverting and directing structure 202 suspended from support rods 204 by means of wires 206 and insulators 208. As shown in Fig. 16, the structure 202 includes a plurality of toroidal ring magnets 210 mounted within an outer housing or baffle 212. The respective ring magnetic 210 are successively positioned along the intended path of the selected ionized particles and so oriented as to direct the particles by means of an electromagnetic field from the vicinity of the apparatus 48 upward and sideways to establish a stream of ionized particles generally centrally located and symmetrically disposed about the longitudinal axis of the housing 18a. The baffle or shield 212 is so arranged as to prevent any line-of-sight path from the structure 48 to the specimens above the apparatus 200. In this arrangement, the upper portion of the apparatus may correspond to the upper part of Fig. 2 with the specimens symmetrically disposed across the upper end of the chamber 18a. In this arrangement, the particles which do not have the appropriate velocities and charge-to-mass ratio will not follow the same path through the apparatus 202 as do the

selected particles, but instead will tend to impact the baffle or shield comprising the housing 212 and thus be removed from the stream of ionized particles directed toward the specimens at the top of the apparatus.

Although Fig. 16 shows the diverting and directing apparatus 202 as including a plurality of ring magnets 210, it will be understood that this structure may be formed of a single solenoidal coil in place of the individual magnets 210. Alternatively a plurality of permanent magnets, suitably fixed in a series of rings, may be used as the magnets 210. Such an arrangement has the advantage of developing the desired particle-diverting field without the application of electrical power, thus reducing the power requirements of the apparatus 200 and avoiding the heat otherwise generated within the housing 18a by the electromagnet system.

Apparatus embodying the present invention may also be utilized to implant metal surfaces with desired compounds. Certain compounds may have the effect of changing the surface properties of the metallic article, similar to the hardening provided for plastics lenses and the like already described. In other circumstances, apparatus embodying the present invention may be utilized to implant surface films on selected portions of semiconductors in order to facilitate the fabrication of entire solid state circuits on single semiconductor chips.

It will of course be appreciated that the features of the various embodiments described can be used in combinations other than those illustrated.

WHAT WE CLAIM IS:—

1. Apparatus for depositing a film on a substrate, comprising an emitter of molecular particles of a selected material, means comprising a plurality of rings encircling the path of emitted particles for accelerating and directing the particles to a predetermined collector region remote from the emitter and including the substrate, and for ionizing the particles, and a device for maintaining a high vacuum within a space encompassing the emitter, the said means and the collector region.

2. Apparatus in accordance with claim 1, wherein the said means includes structure for injecting electrically charged particles into the path of the emitted molecular particles to add charge to the molecular particles.

3. Apparatus in accordance with claim 1 or 2, further including a mechanism for relieving the build-up of surface charge on the substrate during particle bombardment.

4. Apparatus in accordance with claim 3, wherein the substrate is mounted on a support frame in the collector region, and the said mechanism is arranged selectively to

rotated to cause the particle beam to sweep the specimen area. In such case, the magnetic field means 166 may itself comprise a cylindrical ring with the individual magnet field elements 168 being selectively magnetized by electromagnetic fields established by selective and successive energization of the respective electromagnetic coils to develop a horizontal magnetic field which rotates in controlled fashion in a plane generally orthogonal to the longitudinal axis of the apparatus 150. Such a swept field may selectively film any particular specimen as desired. At the same time it is effective in the manner already described at separating the desired particles from the undesired particles in order to provide an improved resultant filmed product. Also, if desired, the structure comprising the mounting racks 182 may be electrostatically charged so that these racks 182 serve additionally as a collector to attract the charged particles passing through the accelerating and ionizing structure 48 and the magnetic field means 164, 166.

Still another embodiment of the invention is represented in Fig. 16 which shows apparatus 200 such as may be employed in the system of Fig. 1. Apparatus 200 is similar to that shown in Fig. 2 with certain notable modifications. As shown in Fig. 16, the apparatus 200 comprises the vacuum chamber within a housing 18a having a table 20, a base 32, a particle emitter 34, a shutter 46 and the ionizing, accelerating and directing structure 48. The elements 34, 46, and 48 are positioned off-center within the vacuum chamber of the apparatus 200. Above the elements 34, 46 and 48, and aligned therewith, is a particle diverting and directing structure 202 suspended from support rods 204 by means of wires 206 and insulators 208. As shown in Fig. 16, the structure 202 includes a plurality of toroidal ring magnets 210 mounted within an outer housing or baffle 212. The respective ring magnetic 210 are successively positioned along the intended path of the selected ionized particles and so oriented as to direct the particles by means of an electromagnetic field from the vicinity of the apparatus 48 upward and sideways to establish a stream of ionized particles generally centrally located and symmetrically disposed about the longitudinal axis of the housing 18a. The baffle or shield 212 is so arranged as to prevent any line-of-sight path from the structure 48 to the specimens above the apparatus 200. In this arrangement, the upper portion of the apparatus may correspond to the upper part of Fig. 2 with the specimens symmetrically disposed across the upper end of the chamber 18a. In this arrangement, the particles which do not have the appropriate velocities and charge-to-mass ratio will not follow the same path through the apparatus 202 as do the

selected particles, but instead will tend to impact the baffle or shield comprising the housing 212 and thus be removed from the stream of ionized particles directed toward the specimens at the top of the apparatus.

Although Fig. 16 shows the diverting and directing apparatus 202 as including a plurality of ring magnets 210, it will be understood that this structure may be formed of a single solenoidal coil in place of the individual magnets 210. Alternatively a plurality of permanent magnets, suitably fixed in a series of rings, may be used as the magnets 210. Such an arrangement has the advantage of developing the desired particle-diverting field without the application of electrical power, thus reducing the power requirements of the apparatus 200 and avoiding the heat otherwise generated within the housing 18a by the electromagnet system.

Apparatus embodying the present invention may also be utilized to implant metal surfaces with desired compounds. Certain compounds may have the effect of changing the surface properties of the metallic article, similar to the hardening provided for plastics lenses and the like already described. In other circumstances, apparatus embodying the present invention may be utilized to implant surface films on selected portions of semiconductors in order to facilitate the fabrication of entire solid state circuits on single semiconductor chips.

It will of course be appreciated that the features of the various embodiments described can be used in combinations other than those illustrated.

WHAT WE CLAIM IS:—

1. Apparatus for depositing a film on a substrate, comprising an emitter of molecular particles of a selected material, means comprising a plurality of rings encircling the path of emitted particles for accelerating and directing the particles to a predetermined collector region remote from the emitter and including the substrate, and for ionizing the particles, and a device for maintaining a high vacuum within a space encompassing the emitter, the said means and the collector region.

2. Apparatus in accordance with claim 1, wherein the said means includes structure for injecting electrically charged particles into the path of the emitted molecular particles to add charge to the molecular particles.

3. Apparatus in accordance with claim 1 or 2, further including a mechanism for relieving the build-up of surface charge on the substrate during particle bombardment.

4. Apparatus in accordance with claim 3, wherein the substrate is mounted on a support frame in the collector region, and the said mechanism is arranged selectively to





* C L N S *

1,430,180

9

apply an RF modulated signal to the support frame to relieve surface charge build-up.

5. Apparatus in accordance with claim 3, wherein the surface charge relieving mechanism comprises at least one radioactive isotope element positioned to irradiate the substrate.

6. Apparatus in accordance with any of claims 1 to 5, wherein the said means comprises a plurality of electric field-intensifying electrodes.

7. Apparatus in accordance with claim 6, wherein the field-intensifying electrodes comprise a plurality of sharpened elements arrayed adjacent the path of the particles.

8. Apparatus in accordance with claim 6 or 7, wherein the field-intensifying electrodes comprise a plurality of sharp-pointed needles affixed to at least one of the rings and substantially equally spaced about the rings with the points directed inwardly and located generally equidistant from the centre of the rings.

9. Apparatus in accordance with claim 8, including guard rings disposed on opposite sides of the ring(s) to which the needles are affixed, all of the rings being spaced apart and arrayed in the direction of travel of said particles.

10. Apparatus in accordance with claim 6, wherein the field-intensifying electrodes comprise a plurality of vanes extending along the direction of travel of the particles through the rings and substantially equally circumferentially spaced.

11. Apparatus in accordance with any of claims 1 to 10 wherein the said means further include a collector element in the form of a screen positioned in the collector region beyond the substrate in the direction of travel of the particles.

12. Apparatus in accordance with any of claims 1 to 11, further including apparatus for selectively blocking particle emission from the source region.

13. Apparatus in accordance with any of claims 1 to 12, comprising a plurality of emitters and particle directing elements arranged in sets, and apparatus for transferring the substrate in the form of a continuous strip past each set in sequence to implant the film on at least one side of the strip.

14. Apparatus in accordance with claim 13, wherein the sets and the path of the strip therethrough are arranged to implant the films on opposite sides of the strip.

15. Apparatus in accordance with any of claims 1 to 14, further comprising magnetic field elements for diverting at least selected ones of the particles from a straight line path in order to impact specimens of the substrate positioned outside the straight line path.

16. Apparatus in accordance with claim 15, wherein the magnetic field elements are

arranged to separate certain of the particles from others of the particles and direct the selected particles to impact the specimens.

17. Apparatus in accordance with claim 15 or 16, wherein the magnetic field elements comprise a plurality of ring magnets positioned to divert the selected particles over a predetermined curved path and direct them toward the specimens.

18. Apparatus in accordance with claim 17, further including a baffle for trapping those particles which are not selectively directed toward the specimens.

19. A method of depositing a film on a substrate comprising the steps of emitting molecular particles in a vacuum from a source of material to be deposited, ionizing the particles after emission from the source of material, and accelerating and directing the particles to a specimen remote from the source material to implant a film on the specimen to a selected depth of penetration and thickness, the ionizing and the accelerating and directing of the particles being effected at least in part by means of a plurality of rings encircling the path of emitted particles.

20. A method in accordance with claim 19, further including the step of removing charge from the specimen as it is built up thereon by the impact of charge particles.

21. A method in accordance with claim 19 or 20, wherein the source of material contains a tinting substance, and further including the step of exposing the specimen to ultraviolet radiation to develop the desired tint in the film.

22. A method in accordance with claim 19, 20 or 21, further including the step of selecting constituents having compensating coefficients of expansion with temperature for the source material in order to develop a low coefficient of expansion with temperature for the implanted film.

23. A fabrication method including a method in accordance with any of claims 19 to 22, wherein the substrate is relatively thin, flexible plastics sheet, and further including the steps of adhesively affixing a portion of the sheet to one side of a relatively thick sheet of plastics having the desired physical properties of the finished device except that of hardness so that the film is along the outer surface of the two sheets in combination, and shaping the two sheets in combination to the desired dimensions of the device.

24. A method in accordance with claim 23, further including the step of adhesively affixing another portion of the relatively thin sheet to the second side of the relatively thick sheet with the film along the outer surface of the sheets in combination.

25. A product having at least a portion thereof implanted with a film by a method in

70

75

80

85

90

95

100

105

110

115

120

125

130

accordance with any of claims 19 to 22, the implantation occurring to a depth of from several hundred angstroms to several microns.

5 26. A product in accordance with claim 25, wherein the product is an eyeglass lens comprising a plastics substrate and a transparent film deposited thereon.

10 27. A product comprising a sheet of relatively tough material having a relatively soft surface by itself laminated between a pair of flexible sheets, each having a hardened film on its outer surface implanted by a method in accordance with any of claims
15 19 to 22.

28. Apparatus for depositing a film on a substrate, constructed substantially as herein described and shown in any of the various embodiments illustrated in the accompanying drawings.

29. A method of depositing a film on a substrate, substantially as herein described with reference to the accompanying drawings.

REDDIE & GROSE,
Agents for the Applicants,
6, Bream's Buildings,
London, EC4A 1HN.

Printed for Her Majesty's Stationery Office by Burgess & Son (Abingdon), Ltd.—1976.
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY,
from which copies may be obtained.

