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PROTECTIVE COATING MEANS FOR ARTICLES SUCH AS  
GOLD-PLATED JEWELRY AND WRISTWATCH COMPONENTS,  
AND METHOD OF FORMING SUCH COATING MEANS

This invention generally relates to the art of protecting articles that have exposed metallic surfaces which are susceptible to abrasion damage or corrosion, and has particular reference to protecting gold-plated articles of jewelry and exposed wristwatch components (such as bracelets and cases) with a transparent coating of one or more selected inert materials. The invention also provides methods for coating such articles and components with one or more overlying protective films that are transparent and composed of abrasion-resistant material.

As is well known, many articles of manufacture have metallic surfaces which on their accord become dull or tarnished in the environment in which the article is used. For example, hardware items such as building-identification plaques, handrails, doorknobs, decorative door-knockers, etc. that are composed of brass or a similar metal oxidize quite rapidly and abrade easily, and require constant polishing and waxing to maintain a brilliant pleasing appearance. Tarnishing is also an age old problem with articles such as flatware, trays, trophies, etc. that are made of silver or are silver plated.

While articles such as fine jewelry and the like that are made from solid gold or have gold-plated surfaces do not tarnish and thus do not present such a maintenance problem, they scratch easily and soon become unsightly

when subjected to the constant abrasion and "rubbing action" encountered during normal everyday use. Since gold is a relatively soft material, it also wears away quite rapidly when subjected to such conditions. If the article is of base metal and is gold-coated, this frequently exposes the base metal and creates an unsightly corroded appearance in the case of articles (such as chains, rings, lockets, watchbands, etc.) that are in direct contact with the person's body. These consequences thus present serious problems in the production and marketing of such items as gold-coated jewelry and gold-coated bracelets and casings for wristwatches. In order to compensate for the loss of gold that occurs during use by the customer, relatively thick gold coating is customarily used on high quality merchandise of this type to ensure that the article will retain its original pleasing appearance. However, in view of the extremely high cost of gold and the likelihood that it will become even more expensive in the future, the use of such heavy gold coating presents a serious economic problem in the watch and jewelry industries.

A practical and reliable means and method for protecting gold coated articles such as wristwatch components and the like from rapid wear and unsightly scratching (as well as corrosion if the gold coating has worn through) without materially changing its "natural" finish or appearance would, accordingly, not only be very desirable from a quality and marketing standpoint but would be very advantageous from a production and cost reduction standpoint. Such protective means would also be very useful in preventing skin reactions and similar problems that are sometimes encountered by certain individuals when they wear a ring, chain or similar article that is made from a particular metal or alloy.

The invention consists in a protectively coated article of jewelry such as a wristwatch component that is composed of a base metal and is coated with a sputter deposited layer comprising precious metal such as gold said

layer having a thickness substantially less than 100,000 Angstroms and is protected from scratches and abrasion damage, when the jewelry article is in use, by a thin adherent substantially transparent protective film comprising an inert non-metallic material that has:

a Knoop hardness in the range of from about 400 to about 2500 and is thus of sufficient hardness to be resistant to both scratches and abrasion,

a refractive index in the range of from about 1.4 to about 2.8,

said protective film having a thickness that is in the range of from about 15,000 to about 40,000 Angstroms and is also so correlated relative to the refractive index of the non-metallic inert material comprising said film that the film, in addition to being substantially transparent, is substantially devoid of discoloration due to optical interference effects that otherwise would be produced by incident light rays and thus alter the natural pleasing appearance of the underlying gold coated surface of the jewelry article,

said base metal and sputtered layer comprising gold having a thermal expansion coefficient greater than that of said protective film,

said protective coated article of jewelry including at least one material-layer which is physically in contact with and in between said protective film and said sputtered layer comprising gold,

said material-layer comprising a substantially transparent material having a thermal expansion coefficient greater than that of the protective material and less than that of said sputtered layer comprising gold,

said material-layer acting as a buffer means to reduce stresses caused by differences in thermal expansions of said protective film and said sputtered layer comprising gold.

The foregoing objectives are achieved herein by coating the surface of a metallic article of manufacture

with a thin substantially transparent and colorless film of a selected inert and non-metallic material which tenaciously adheres to the surface and has sufficient "hardness" to provide a very durable and abrasion-resistant protective finish and covering. In accordance with a preferred embodiment, the protective film is composed of a dielectric type material such as silicon dioxide, magnesium oxide, aluminum oxide, titanium dioxide, spinel, silicon nitride, silicon carbide and certain types of glasses that have the proper combination of hardness, transparency and thermal expansion characteristics. Other dielectric type materials which are substantially transparent in film thicknesses and are also suitable are tantalum oxide, niobium oxide, and germanium oxide. Certain types of glasses can also be used as a protective covering or as "buffer" layers between the protective films and the sputter coated substrates to compensate for differences in the thermal expansion characteristics of the substrate material and protective material.

The protective film of selected inert material is preferably deposited by RF-sputtering techniques and the film thickness is controlled depending on its refractive index to prevent undesirable discoloration of the article by optical interference effects produced by incident light rays which enter the film. Such interference effects are exhibited by transparent films when the optical thickness (that is, the true thickness of the film multiplied by the refractive index of the film material) is comparable to the wavelength of light and thus falls within the range of from about 3,000 to 8,000 Angstroms (the visible portion of the spectrum). Since the refractive index for the various film materials is different, the optimum thickness range will also vary depending upon the particular material used to form the protective film.

Reference will now be made to the accompanying drawings, in which:

Figure 1 is a plan view of a gold-plated band or

bracelet for a wristwatch which has been protectively coated, the figure being given for facilitating description of the invention.

Fig. 2 is a fragmentary cross-sectional view, on a greatly enlarged scale, through a portion of the prior art watch bracelet shown in Fig. 1 and depicts the manner in which the thin plating of gold is protected by an overlying transparent film of inert abrasion-resistant material;

Fig. 3 is a similar cross-sectional view of a conventional prior art watch bracelet, on the same scale, and illustrates the much thicker gold plating commonly employed in the prior art for such watch components in the absence of the protective coating means of the present invention;

Fig. 4 is a similar cross-sectional view of an article wherein the substrate is provided with an adhesion-promoting primer layer before being coated with a sputtered layer of gold or the like and then protectively coated, this also being in accordance with the prior art;

Fig. 5 is a fragmentary cross-sectional view on an enlarged scale of an article in accordance with the invention, wherein a buffer or transition layer of a selected glass is employed between the transparent protective film and the coated surface of the substrate to compensate for the difference in the thermal expansion coefficients of the coated substrate and protective film; and

Fig. 6 is a similar view of an alternative embodiment in which two buffer or transition layers of different glasses are employed.

While the present invention can be used with advantage to protectively coat various kinds of articles having metallic surfaces that are subject to tarnishing or corrosion by the environment in which they are used as well as pieces of jewelry and the like that are coated with a layer of a precious metal of a type which gets easily scratched or rapidly worn away during normal use of the

jewelry, it is especially adapted for use in conjunction with gold-coated articles such as bracelets and cases for wristwatches and the like and it has accordingly been so illustrated and will be so described.

5           In order to facilitate an understanding of the present invention several prior art items will be described.

10           A typical exemplary watchband or bracelet 10 of the prior art is shown in Fig. 1 and consists of the usual intercoupled links L and a suitable latching member or clasp C. As illustrated in Fig. 2, such components are typically fabricated from a suitable base metal 12 (such as brass or stainless steel) which serves as a substrate for a plating 14 of gold, a gold alloy, or other precious metal  
15           that provides the desired attractive lustrous finish. As is customary in the gold-coating art, a thin layer 13 of nickel or other suitable metal is deposited on the substrate before the coating operation is performed, by electrode-position or other well known means. Such an  
20           initial layer is referred to as a "strike" in the art and is required to insure that the gold coating bonds properly to the substrate and that a smooth lustrous gold finish is produced if the substrate has a rough surface. Nickel  
25           "strikes" on brass substrates typically have a thickness in the order of 0.10 micron (1,000 Angstroms) or so. However, the thickness of such bonding layers is not critical and can be varied according to the gold coating requirements, the composition and condition of the base metal.

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The thickness of the gold coating 14 is drastically reduced and the coated surface of the watch bracelet 10 (or other article) is protected from scratching and abrasion by a film 16 of a selected inert non-metallic material that tenaciously adheres to the gold-coated surface of the substrate 12. In order to provide adequate long-term protection for the thin "soft" coating 14 of gold without altering its appearance, the protective film 16 must be formed from a material which is much "harder" than gold and is substantially transparent and substantially colorless in thin film form.

Some materials which meet all of these requirements and are thus suitable for use as protective films in accordance with the invention are silicon dioxide ( $\text{SiO}_2$ ), aluminum oxide ( $\text{Al}_2\text{O}_3$ ), titanium dioxide ( $\text{TiO}_2$ ), silicon nitride ( $\text{Si}_3\text{N}_4$ ), magnesium oxide ( $\text{MgO}$ ), spinel

( $\text{MgO} \cdot 3.5\text{Al}_2\text{O}_3$ ), Corning Glass No. 0080 (soda-lime glass), Corning Glass No. 7070, Corning Glass No. 7740 (PYREX glass), and Corning Glass No. 7059 (these are Trade ~~MARKS~~ MARKS and numbers).

5 The various properties of these materials which make them suitable for use as protective coatings pursuant to the invention are listed in Table I below. For comparison, electroplated gold has a Knoop hardness of about 130 and the thermal expansion coefficients for stainless steel  
10 and brass are  $173$  and  $169 \times 10^{-7}/^\circ\text{C}$ , respectively.

TABLE I

|    | Protective<br>Coating<br>Material | Hardness<br>(Knoop) | Refractive<br>Index (n) | Thermal Expansion<br>Coefficient<br>( $\times 10^{-7}/^\circ\text{C}$ ) |
|----|-----------------------------------|---------------------|-------------------------|-------------------------------------------------------------------------|
| 15 | $\text{SiO}_2$                    | 741                 | 1.46                    | 8                                                                       |
|    | $\text{Al}_2\text{O}_3$           | 1370                | 1.78                    | 73                                                                      |
|    | $\text{TiO}_2$                    | 879                 | 2.71                    | 96                                                                      |
|    | $\text{Si}_3\text{N}_4$           | 2500                | 1.87                    | 45                                                                      |
|    | MgO                               | 692                 | 1.69                    | 120                                                                     |
| 20 | Spinel                            | 1140                | 1.73                    | 59                                                                      |
|    | Corning Glass<br>No. 0080         | 400<br>(approx.)    | 1.512                   | 92                                                                      |
|    | Corning Glass<br>No. 7070         | 418<br>(approx.)    | 1.469                   | 32                                                                      |
| 25 | Corning Glass<br>No. 7740         | 418                 | 1.474                   | 33                                                                      |
|    | Corning Glass<br>No. 7059         | 424                 | 1.53                    | 46                                                                      |

30 The hardness data given in Table I is the Knoop microhardness for bulk materials and thus provides an indication of the abrasion resistance of the various

materials and their ability to protect the underlying plating of gold (or other precious metal).

Corning Glass No. 0080 is a soda-lime silicate type glass that is used in the electric lamp industry for lamp bulbs and the like. Such glasses typically contain 60 to 75% (by wt.)  $\text{SiO}_2$ , 5 to 18%  $\text{Na}_2\text{O}$ , 3 to 13%  $\text{CaO}$  or  $\text{MgO}$  (or a mixture thereof) and minor amounts of additional materials such as  $\text{Al}_2\text{O}_3$ , and  $\text{K}_2\text{O}$ . A specific example of a glass composition of this type is as follows: 73.6%  $\text{SiO}_2$ , 16%  $\text{Na}_2\text{O}$ , 3.6%  $\text{MgO}$ , 5.2%  $\text{CaO}$ , 1%  $\text{Al}_2\text{O}_3$  and 0.6%  $\text{K}_2\text{O}$ .

Corning Glass Nos. 7070 and 7740 are borosilicate type glasses that contain major amounts of  $\text{SiO}_2$  and  $\text{B}_2\text{O}_3$  and various minor constituents. Glass No. 7740 is marketed by Corning under the trade name "Pyrex" glass. A specific example of a No. 7740 type glass is as follows: 80.5% (by wt.)  $\text{SiO}_2$ , 12.9%  $\text{B}_2\text{O}_3$ , 2.2%  $\text{Al}_2\text{O}_3$ , and 0.4%  $\text{K}_2\text{O}$ .

A specific example of a No. 7070 type glass composition is as follows: 70% (by wt.)  $\text{SiO}_2$ , 28%  $\text{B}_2\text{O}_3$ , 1.2%  $\text{La}_2\text{O}_3$ , 1.1%  $\text{Al}_2\text{O}_3$ , 0.2%  $\text{K}_2\text{O}$  and 0.1%  $\text{CaO}$ .

Corning Glass No. 7059 is an aluminoborosilicate type glass which typically has the following composition; 50.2% (by wt.)  $\text{SiO}_2$ , 25.1%  $\text{BaO}$ , 13.0%  $\text{B}_2\text{O}_3$ , 10.7%  $\text{Al}_2\text{O}_3$  and 0.4%  $\text{Al}_2\text{O}_3$ .

Other dielectric type materials that are suitable for use as protective films in accordance with the invention are silicon carbide ( $\text{SiC}$ ) which has a Knoop hardness of 2500, tantalum oxide ( $\text{Ta}_2\text{O}_5$ ), niobium oxide ( $\text{Nb}_2\text{O}_5$ ) and germanium oxide ( $\text{GeO}_2$ ). Another glass which has also been found suitable is a high-lead-content solder glass which has a thermal expansion coefficient of  $117 \times 10^{-7}/^\circ\text{C}$  and typically contains 85% (by wt.)  $\text{BbO}$ , 7.5%  $\text{B}_2\text{O}_3$ , and 7.5%  $\text{SiO}_2$ .

Any non-metallic material that is inert and has a refractive index in the range of from about 1.4 to about 2.8 and has a Knoop hardness of from about 400 to about 2,500, and has the ability to be deposited in thin adherent films that are of controlled thickness and is also

substantially transparent and colorless in such thicknesses can be used as material for the protective coating. An intervening layer (or layers) of other materials must be used as hereinafter disclosed to correct the mismatch of thermal expansions of the coating layer and the protective film. Various types of clear glass compositions (such as the aforesaid solder glass) that have thermal expansion coefficients which approximate that of stainless steel, for example, can also be used.

While the protective film 16 can be formed on the coated substrate 12 by various means including electron beam evaporation and chemical vapor-deposition techniques, deposition by RF-sputtering is preferred because sputtered films, in general, exhibit excellent adhesion, are dense and free from pinholes, provide satisfactory substrate coverage, and have the proper stoichiometry.

As is well known, transparent films will produce coloration due to optical interference or so-called "Newton ring" effects when the optical thickness (the product of the true or mechanical thickness and the refractive index) of the film is roughly of the same order of magnitude as the wavelength of light (from about 3,000 to 8,000 Angstroms). The film thickness range which enables incident light rays to produce such interference color effects thus depends upon the refractive index of the coating material and generally lies between 0.05 micron (500 Angstroms) and 1.5 microns (15,000 Angstroms) for the materials which are listed in Table I or referred to as being suitable. Hence, in order to avoid such undesirable discoloration of the gold-coated surface of the watchband 10 (or other article which is being protectively coated), the thickness of the protective film 16 must either be less than about 500 Angstroms or greater than about 15,000 Angstroms for these materials.

Since films with thicknesses less than 500 Angstroms would be too thin to provide adequate "long term" abrasion protection, protective films formed from the

aforementioned materials must have thicknesses that are greater than about 15,000 Angstroms. Protective films that are too thick, however, must also be avoided since they will tend to crack or peel away from the surface. Since the film thickness above which optical interference coloration effects are not discernible varies inversely with the refractive index of the film material, a thinner film of a high refractive index material can be employed. This is desirable from a manufacturing standpoint since shorter film-deposition times will be required and peeling will be inhibited. The following materials are preferred in this respect since they have high indices of refraction (shown in parenthesis): SiC (2.73), Nb<sub>2</sub>O<sub>5</sub> (2.24), Ta<sub>2</sub>O<sub>5</sub> (2.21), TiO<sub>2</sub> (2.71), GeO (2.1) and Si<sub>3</sub>N<sub>4</sub> (1.87). The refractive indices given in table 1 hereinbefore are only certain examples; the range of refractive indices is from 1.4 to 2.8.

The sputtering yield provides a relative indication of how easily a given material can be sputtered from a target and, hence, how rapidly a protective film of that material can be formed by sputter-deposition. This is an important consideration when coating in mass-production quantities is involved. In general, the ideal material for the protective coating from both a quality and manufacturing standpoint is thus a material which has high values of hardness, refractive index, and sputtering yield.

#### TEST DATA AND SPECIFIC EXAMPLES

Preliminary tests performed on small stainless-steel plates which were coated with a 2.5 microns (25,000 Angstroms) thick electroplated layer of 24 K gold have indicated that protective coatings of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub> and SiC which were formed by RF-sputtering exhibited excellent adhesion and protection of the substrates against abrasion. A portion of each of the gold-plated test plates was masked during deposition of the protective film to provide an uncoated "gold reference" surface for evaluation. Film adhesion was checked by a so-called "tape

test" which consisted of firmly pressing a piece of "Scotch" brand adhesive tape onto a film-coated portion of the test plate and then stripping the tape away. This is a very demanding test since any material which is not firmly bonded or securely anchored to the substrate will be lifted from its surface when the adhesive tape is stripped away. Abrasion resistance was determined by vigorously rubbing the coated and uncoated portions of the test plates with a pencil eraser and then with steel wool. The appearance of the coated portions of the plates was evaluated visually by noting any discoloration effects or undesirable altering of the natural color of the gold plating.

These preliminary tests verified that very thin films of the tested materials in a thickness range below what is required to avoid optical interference effects (that is, less than about 0.05 micron or 500 Angstroms) would not provide adequate "long term" abrasion protection of the gold-coated substrates. The sputtered films of SiC had a yellowish-brown tint and altered the natural gold color of the samples to a certain degree. Such films would, accordingly, be satisfactory only where a slight discoloration of the coated surface could be tolerated (or might even be desirable). Although the sputtered films of  $\text{TiO}_2$  were colorless and (due to their high refractive index) were devoid of any optical interference coloration even though they were only 1.5 microns or 15,000 Angstroms thick, the high refractive index of this material caused the film surface to have a high reflectivity which tended to mute the gold color of the substrate and slightly modify its appearance. The  $\text{Al}_2\text{O}_3$  sputtered very slowly and would thus probably not lend itself to mass production operations.

Experiments have indicated that the sputtering yield of  $\text{Si}_3\text{N}_4$  is comparable to that of  $\text{SiO}_2$  (0.13 molecule per ion at 1 kilovolt target voltage) and these two materials are thus good selections for protectively coating gold-coated substrates where coating times and costs are

critical factors.

Test data obtained with  $\text{SiO}_2$  films of varying thickness on gold-coated stainless steel sample plates have shown that protective films of this material that were approximately 1.4 microns or 14,000 Angstroms thick exhibited pale pink and green interference colors which indicated that the films were too thin. When films of  $\text{SiO}_2$  5 microns or 50,000 Angstroms thick were deposited on such gold-coated sample substrates, the coating cracked and flaked from the substrates due to high stresses present within the thick films.  $\text{SiO}_2$  films 3.4 microns (34,000 Angstroms) thick adheres well to the gold-coated substrates and also had excellent abrasion resistance, on the basis of the "eraser and steel wool" test. The color of the coated plates was indistinguishable from the original gold-coated substrate. Pursuant to these experimental data, the optimum thickness range for  $\text{SiO}_2$  protective films on gold-coated articles is accordingly within the range of about 1.5 to about 4 microns (that is, from about 15,000 to about 40,000 microns).

Similar tests conducted on gold-coated watch bracelets 10 of the type shown in Fig. 1 confirmed the foregoing early test data obtained on plate samples. These additional tests also revealed that cleanliness of the gold-coated substrates prior to deposition of the protective film is quite important. Some of the commercially available sample watchbands apparently had an organic film or coating on their surfaces which may have been applied by the manufacturer. This contamination produced undesirable brown stains when  $\text{SiO}_2$  protective films were applied and also caused flaking of the films. These coating problems were solved by subjecting the watchbands to a cleaning procedure which consisted of boiling the components in a suitable detergent, rinsing them in deionized water and methyl alcohol, and then drying them in air at around  $120^\circ\text{C}$ .

The additional series of tests also indicated

that the optimum thickness of  $\text{SiO}_2$  protective films was somewhat less for the gold-coated watchbands than for the gold-coated test blanks of metal. Films between about 2 and 3.5 microns thick tended to flake from the watchbands and no undesirable interference color effects were produced if the film thickness was greater than about 1.4 microns. The optimum thickness for protective films of  $\text{SiO}_2$  in the case of gold-coated watchbands of the kind shown in Fig. 1 is accordingly within the range of from about 1.5 to about 2 microns (that is, from about 15,000 to about 20,000 Angstroms).

The differences in the observed interference effects for  $\text{SiO}_2$  films deposited on the test blanks of gold-coated metal and on the gold-coated watchbands may have been due to the smooth surface finish of the test blanks and the fact that the watchbands had a textured surface finish.

A very important advantage afforded by the present invention from a cost standpoint is the fact that wrist-watch bracelets and other components for fine watches (as well as various articles of fine jewelry) can be provided with a much thinner coating of gold without detracting in any way from the quality or appearance of the components or articles since the natural appearance of the gold coating is preserved by the transparent film of protective material. This will be made clear hereinafter in connection with the description of Figs. 5 and 6 which relate the present invention.

As shown in Figs. 1 and 2, a prior art watchband 10 of high quality having a stainless steel substrate 12 which is provided with a nickel "strike" 13 about 1,000 Angstroms thick and then coated with a layer 14 of gold approximately 0.5 micron or 5,000 Angstroms thick (dimension "t1") can accordingly be made by protectively coating the thin layer of gold with a film 16 of  $\text{SiO}_2$  (or similar transparent material) that is approximately four times as thick as the gold coating - that is, a protective

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film of  $\text{SiO}_2$  approximately 2 microns or 20,000 Angstroms thick. The relative thicknesses of the gold coating, the bonding layer or "strike" and the protective film are substantially as shown in Fig. 2. Hence, the gold coating 14 is only one-fourth as thick as the protective film 16, and the nickel "strike" 13, in turn, is only one-fifth as thick as the gold coating.

If the article or substrate is such that it can be coated with a thinner layer of gold which still retains the natural appearance and color of solid gold, then gold coatings in the order or about 0.2 or 0.3 micron (about 2,000 or 3,000 Angstroms) can be used in combination with the protective film.

In contrast, conventional watch bracelets 11 (shown in Fig. 3) of good quality having similar substrates 18 of stainless steel which is primed by a nickel "strike" 19 about 1,000 Angstroms thick generally have a gold plating 20 that is approximately 10 microns or 100,000 Angstroms thick (dimension " $t_2$ ") -- that is, twenty times thicker than gold coating 14. Figs 2 and 3 are drawn to the same scale so that the relative thicknesses of the two gold coatings 14 and 20 is accurately shown and apparent from the drawing.

The thickness of the gold coatings employed on such fine watch components can be reduced by at least 95% (5,000 Angstroms versus 100,000 Angstroms) and up to 98% or so (2,000 Angstroms versus 100,000 Angstroms) with a corresponding reduction in the manufacturing cost of the watches. In view of the high cost of gold and other precious metals, the cost saving is very significant and constitutes an important competitive advantage, not only in the watch industry but in the manufacture of fine jewelry and similar articles that are composed of a base metal and provided with heavy coatings or platings of a precious metal to preserve their appearance.

Further tests on protective films for gold-coated articles such as watch bracelets have shown that an addi-

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tional reduction in their manufacturing cost can be realized by depositing the gold layer on the watch bracelets by sputtering techniques (rather than electroplating) so that both the gold-coating and protective-coating operations can be performed sequentially within the vacuum chamber of the RF-sputtering apparatus. Experiments confirmed that this could be achieved quite readily by providing one target of gold and another target of  $\text{SiO}_2$  (or other material from which the protective film is to be formed) within the vacuum chamber and then simply operating the sputtering apparatus in two different modes which selectively bombarded the targets to first deposit the required layer of sputtered gold onto the watchbands of base metal and then coat the resulting gold-coated surface with a film of sputtered  $\text{SiO}_2$ , the required thicknesses being obtained by properly controlling the target voltage, power input and the length of the sputtering operation in each mode.

A further advantage afforded by this method of sequentially-coating was the ability to sputter-coat the watchbands with a layer of 24K gold instead of the 14K gold conventionally used in the electroplating process. The sputtered-gold layers thus had a deeper and richer gold color (due to the higher gold content) compared to watchbands with gold-electroplated coatings--even though the sputtered-gold layers were much thinner and used less gold.

During the course of these experiments, it was also discovered that both the adherence and durability of the sputtered-gold coatings could be improved by depositing a very thin layer of titanium (Ti) on the stainless steel substrate before sputter-depositing the gold layer. The use of a sputtered film of Ti about 200 Angstroms thick permitted a layer of sputtered gold less than 0.5 micron thick (5,000 Angstroms) to pass the "tape test" for adhesion. Such a preliminary or "primer" layer of Ti accordingly enables sputtered gold layers approximately

0.25 or 0.3 micron thick (2,000 or 3,000 Angstroms) to be employed on substrates - thus providing a corresponding further reduction in coating and material cost without detracting from the appearance of the finished article as regards its natural gold "finish" and appearance.

A watch bracelet 10a (or other article) having a substrate 12a of a base metal (such as stainless steel or the like) that is provided with the composite sputtered coating is shown in Fig. 4. This bracelet is not in accordance with the invention but Fig. 4 is given to assist subsequent understanding of the invention. As will be noted, the substrate 12a has a thin primer layer 21 of titanium deposited on its surface to promote the adhesion of a layer 22 of sputtered gold which, in turn, is protected by a film 16a of  $\text{SiO}_2$  or other suitable material that is substantially transparent and does not noticeably alter the natural appearance or finish of the gold layer.

The film thickness of the adhesion-promoting primer-layer 21 of titanium is not especially critical and can be in the range of from about 50 to 400 Angstroms. Suitable thin films of other metals such as chromium nickel and Nichrome type alloys that have a similar adhesion-promoting effect can also be used. Nichrome <sup>TRADE MARK</sup> alloys are well known in the art and are composed of about 80% (by wt.) nickel and about 20% chromium.

The manufacture of the watch bracelet 10a or other article will also be facilitated if the primer layer 21 of titanium (or other metal) is sputter-deposited on the substrate 12a in sequential fashion with the overlying layers of gold and protective material in a common vacuum chamber of a properly modified and controlled RF-sputtering apparatus.

A form of composite protective coating for gold-coated watch components and similar articles, in accordance with the present invention, is shown in Fig. 5 and was developed to overcome an adherence problem encountered during trial runs using a production type sputtering system which operated at high deposition rates. When sputtering protective films of  $\text{SiO}_2$  onto gold-coated stainless steel

watchbands using such a system, it was discovered that the protective films sometimes flaked from the watchbands upon removal from the sputtering apparatus. While the exact cause of this problem is unknown, it is believed that it may be due to excessive heating of the watchbands produced by the high rate at which the sputtered material was deposited -- in combination with the subsequent cooling and a thermal expansion coefficient mismatch between the  $\text{SiO}_2$  film and stainless steel substrate which induced stresses in the films with resultant flaking.

It was found that this problem could be solved by using an additional transparent layer of a suitable material between the  $\text{SiO}_2$  film and the gold-coated stainless steel substrate, which additional layer is composed of a material that has a thermal expansion coefficient between that of  $\text{SiO}_2$  ( $8 \times 10^{-7}/^\circ\text{C}$ ) and that of stainless steel ( $173 \times 10^{-7}/^\circ\text{C}$ ). The additional layer thus serves as a buffer or "transition" layer that compensates for the expansion mismatch between the substrate and protective  $\text{SiO}_2$  film without interfering with the ability of the film to protect and preserve the natural appearance of the gold coating.

The soda-lime silicate type glass marketed by the Corning Glass Company under the trade designation Corning Glass No. 0080 (listed in Table I) is a material particularly suitable for use as such a buffer layer since it has a thermal expansion coefficient of  $92 \times 10^{-7}/^\circ\text{C}$  (about midway between that of stainless steel and  $\text{SiO}_2$ ) and is transparent and colorless in the thicknesses required. This glass composition also has an index of refraction of 1.512 and a Knoop hardness of about 400 as indicated in the Table. However, any of the glasses listed in Table I (as well as the aforementioned solder glass) can be used as a buffer material since they all have thermal expansion coefficients that are much higher than that of  $\text{SiO}_2$ . Since materials such as  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  have high coefficients of thermal expansion, they are also especially suitable for use as a buffer material.

Tests have shown that stainless steel watchbands provided with a sputtered gold layer approximately 5,000 Angstroms thick can be provided with a sputtered composite transparent protective coating that exhibits excellent  
5   adhesion and durability and consists of a layer of Corning No. 7059 Glass about 1.5 microns thick (15,000 Angstroms) that was covered by a film of  $\text{SiO}_2$  approximately 0.5 micron (5,000 Angstrom) thick. The relative thicknesses of the  
10   transition or buffer layer of glass and the  $\text{SiO}_2$  film are not critical and can vary considerably from the stated values. For example, the film thicknesses of the  $\text{SiO}_2$  can be within the range of from about 0.2 micron to about 2 microns (2,000 to 20,000 Angstroms) and the buffer layer of  
15   glass can be from about 1 to 4 microns thick (10,000 to 40,000 Angstroms). However, the combined thicknesses of the protective film and buffer layer must be sufficient to prevent the occurrence of optical interference effects and undesired coloration of the gold-coated surface of the article.

20       As illustrated in Fig. 5, a watchband 10b or other article consists of a substrate 12b of stainless steel (or other base metal), a "strike" or bonding layer 13b of nickel or the like, a thin coating 14b of gold (or other precious metal) that is protectively shielded from  
25   scratching and other damage by a substantially transparent and colorless composite coating which consists of the buffer layer 24 of a selected glass and a much thinner layer 25 of  $\text{SiO}_2$  or other suitable abrasion-resistant material.

30       ALTERNATIVE MULTIPLE "BUFFER-LAYER" EMBODIMENT (FIG. 6)

The invention is not limited to the use of a single layer of a buffer material to correct the mismatch of the thermal expansion and contraction characteristics of the gold-coated substrate and the protective film but  
35   includes within its scope the use of two or more buffer layers for this purpose. A multiple buffer-layer embodiment 10c is shown in Fig. 6.

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As illustrated, this embodiment comprises a substrate 12c of a base metal, the usual very thin "strike" or bonding layer 13c of nickel or the like, a gold coating 14c of reduced thickness, two buffer layers 26, 27 of two different substantially transparent colorless materials that have thermal expansion coefficients which provide a "two-step" transition from the high expansion coefficient of the plated substrate 12c to the much lower expansion of the transparent protective film 28.

In the case of a stainless steel gold-coated substrate and a protective film of  $\text{SiO}_2$ , a first buffer layer of soda-lime silicate glass (No. 0080 glass) and a second buffer layer of Corning No. 7059 Glass would be a good combination of buffer materials since they would provide a "balanced" transition from 173 to 92 to 46 to 8 (in terms of the expansion coefficients of the respective materials, starting with the substrate).

The thickness of the buffer layers is not critical but they obviously should be thin enough to maintain the composite coating below about 40,000 Angstroms or so. They may be of equal thickness (as shown in Fig. 6) or their relative thickness can be varied and correlated with the expansion coefficients of the particular materials to provide an optimum "gradation" of stress forces at the interface of the substrate and protective film. However, in Fig. 6 the total thickness of the illustrated composite coating (that is, buffer layers 26, 27 and the protective film 28) is the same as the thickness of the composite coating used in the single-buffer layer embodiment shown in Fig. 5. This is preferred since it would reduce the sputter-coating times to a minimum.

#### SPECIFIC EXAMPLE OF SPUTTER-COATING PROCESS

Following is a specific example of the manner in which the substantially transparent abrasion-resistant films or coatings of the present invention are applied to articles of substrates by sputter-deposition using experimental apparatus.

The articles of substrates are loaded into an RF-sputtering apparatus along with a suitable target of the selected coating material, a 6-inch diameter target of  $\text{SiO}_2$  for example. The sputtering chamber is then evacuated to a pressure of about  $5 \times 10^{-7}$  Torr and filled with approximately  $1.4 \times 10^{-2}$  Torr of a mixture of 90% argon and 10% oxygen which serves as the sputtering gas. An RF target voltage of 750 volts is then applied to the target so that the power input is around 200 watts. The sputtering apparatus was operated for approximately 10 hours under these conditions and films of  $\text{SiO}_2$  having a thickness of from 1.5 to 2.0 microns (15,000 to 20,000 Angstroms) were deposited on the substrate. If a production type magnetron RF-sputtering apparatus were used, the time required to deposit  $\text{SiO}_2$  films of such thicknesses could be reduced to approximately 1 or 2 hours.

As will be appreciated by those skilled in the art, the operating parameters of the sputtering apparatus can be adjusted in accordance with the sputtering yields etc., of the various coating materials so that films of the thicknesses required for each of the described embodiments can be readily and efficiently deposited.

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CLAIMS:

1. A protectively coated article of jewelry such as a wristwatch component that is composed of a base metal and is coated with a sputter deposited layer comprising precious metal such as gold, said layer having a thickness substantially less than 100,000 Angstroms and is protected from scratches and abrasion damage, when the jewelry article is in use, by a thin adherent substantially transparent protective film comprising an inert non-metallic material that has;
  - a Knoop hardness in the range of from about 400 to about 2500 and is thus of sufficient hardness to be resistant to both scratches and abrasion;
  - a refractive index in the range of from about 1.4 to about 2.8,
  - said protective film having a thickness that is in the range of from about 15,000 to about 40,000 Angstroms and is also so correlated relative to the refractive index of the non-metallic inert material comprising said film that the film, in addition to being substantially transparent, is substantially devoid of discoloration due to optical interference effects that otherwise would be produced by incident light rays and thus alter the natural pleasing appearance of the underlying gold coated surface of the jewelry article,
  - said base metal and sputtered layer comprising gold having a thermal expansion coefficient greater than that of said protective film,
  - said protective coated article of jewelry including at least one material-layer which is physically in contact with and in between said protective film and said sputtered layer comprising gold,
  - said material-layer comprising a substantially transparent material having a thermal expansion coefficient greater than that of the protective material and less than that of said sputtered layer comprising gold,
  - said material-layer acting as a buffer means to



reduce stresses caused by differences in thermal expansions of said protective film and said sputtered layer comprising gold.

5        2. The protectively-coated article as in Claim 1 wherein the material comprising said film is a dielectric type material selected from the group consisting essentially of  $\text{SiO}_2$ ,  $\text{SiC}$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{GeO}_2$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{Nb}_2\text{O}_5$ , and spinel.

10       3. The protectively-coated article as in Claim 1 wherein the material constituting said film comprises a glass from the group consisting of soda-lime silicate, borosilicate, aluminino borosilicate and lead solder type glasses.

15       4. The protectively-coated article as in Claim 2 or 3 wherein the protective film comprises a sputter-deposited layer of said dielectric type materials or said glasses respectively.

20       5. The protectively-coated article as in Claim 1 wherein the protective material comprises  $\text{SiO}_2$ , having a film thickness in the range of the from about 15,000 Angstroms to about 20,000 Angstroms.

25       6. The protectively-coated article as in Claim 1 wherein said buffer means comprises a plurality of layers of stress-reducing material with the material in each layer having a different thermal expansion coefficient.

30       7. The protectively-coated article as in Claim 6 wherein said buffer means comprises two layers of stress-reducing glass-like materials that provide a graded transition from the thermal expansion characteristic of the coated substrate to that of the protective film.

35       8. The protectively-coated article as in Claim 6 wherein the thickness of the buffer means is greater than that of the protective film and is sufficient, in conjunction with the film thickness, to prevent undesirable coloration of the coated article by optical interference effects from incident light rays.

9. The protectively-coated article as in Claim 8

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wherein a layer of an adhesion-enhancing material is disposed between the base metal substrate and the coating of precious metal, said adhesion-enhancing layer having a thickness that is less than that of the precious-metal coating.

10. The protectively-coated article as in claim 9 wherein the coating of precious metal comprises a layer of gold and said adhesion-enhancing layer comprises a bonding layer of nickel.

11. The protectively-coated article as in claim 9 wherein;

the coating of precious metal comprises a sputtered layer of gold or a gold alloy, and

the adhesion-enhancing layer comprises a primer layer of one of titanium, chromium, nickel or a nickel chrome alloy.

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