

ARTICLE EXHIBITING A GOLDEN COLOUR

This invention relates to articles exhibiting a golden colour. The articles may, for example, be spectacle frames, stationery, personal ornaments, accessories, etc.

5 It is known that nitrides such as titanium nitride or tantalum nitride exhibit a golden colour under certain conditions and they have been utilised as a substitute for expensive gold plating to provide the exterior of articles with a decorative appearance. It
10 is known to apply a coating of a nitride such as of titanium or tantalum on an article by sputtering, vapour deposition or ion plating, titanium metal or tantalum metal in a nitrogen atmosphere.

The colour tone of the nitride formed is greatly
15 dependent on the pressure of the gas in the nitrogen atmosphere when forming a nitride of, for example, titanium or tantalum. Particularly, the range of gas pressure to provide a golden colour is extremely limited. Accordingly, it has been necessary to control the partial pressure of the nitrogen gas with a high
20 accuracy in order to obtain a golden colour of high quality with good reproducibility. However, it is extremely difficult to adopt the process to industrial

mass production.

In view of the above, to obtain a beautiful golden colour with good reproducibility, it has been proposed in Japanese Patent Application No. 59(1984)-26664 that a hard layer of golden colour comprising titanium nitride or tantalum nitride is formed and then a coating of gold or gold alloy is formed on the layer. Although a beautiful golden colour can be obtained by this technique, this is due to the brightness of the gold coating on the surface of the titanium nitride or tantalum nitride layer. The gold coating is extremely thin in view of the cost of gold and accordingly it is easily abraded. However, since the layer of titanium nitride or tantalum nitride underlying the gold coating also exhibits a golden colour to some extent, if the gold coating is abraded, the abrasions are not particularly noticable. However, production is troublesome and cost is increased by the fact that gold is used.

The present invention seeks to provide an article exhibiting a golden colour at a reduced cost without using expensive gold. The present invention also seeks to provide an article exhibiting a golden colour with good reproducibility and by a process that is adapted to mass production.

According to the present invention, there is provided an article exhibiting a golden colour having formed on at least part of the surface thereof a composite film composed of either titanium nitride and tantalum nitride, in which case the amount of tantalum is 5 to 75% by weight, or zirconium nitride and tantalum nitride, in which case the amount of tantalum is 3 to 68% by weight.

Preferably the composite membrane is formed by vapour deposition, sputtering or ion plating.

Preferably the article is composed of a synthetic resin, metal or ceramic material, and a primer coating of nickel or chromium on which the composite film is formed.

The composite film may be formed in a nitrogen-containing atmosphere at a pressure in the range $(2.5-4.0) \times 10^{-2}$ Pa or in the range $(3.0-4.5) \times 10^{-2}$ Pa.

The invention is illustrated, merely by way of example, in the accompanying drawings, in which:-

Figure 1 is a graph showing the difference of colour tone for a composite film of an article according to the present invention of titanium nitride and tantalum nitride, a pure gold sputtered film and a conventional titanium nitride sputtered film;

Figure 2 is a graph showing the relationship

between the amount of tantalum constituting a factor for determining the tone of the composite film as described in Example 1 and the saturation C^* ;

Figure 3 is a graph showing the difference of colour tone for a composite film of an article according to the present invention of zirconium nitride and tantalum nitride, a pure gold sputtered film and a conventional zirconium nitride sputtered film; and

Figure 4 is a graph showing the relationship between the tantalum ingredient ratio constituting a factor for determining the colour tone of the composite film as described in Example 3 and saturation C^* .

Tantalum, when applied by reactive sputtering together with titanium or zirconium, acts as a buffer to the reaction system in which the titanium or zirconium react with nitrogen. Accordingly, upon forming a nitride of titanium or zirconium that actually exhibits a golden colour, the effect of fluctuation of the nitrogen partial pressure on the colour tone can be moderated.

Since an article according to the present invention exhibits a golden colour identical to that of gold itself stably with no substantial effect due to fluctuation of nitrogen partial pressure in the reaction atmosphere, the process is well suited to industrial

mass production at a reduced cost. In addition, the tone of the golden colour can be determined depending on the amount of tantalum in the composite film and this amount can be controlled extremely easily. Accordingly, it is possible to select the tone of the golden colour optionally over a wide range.

EXAMPLES

EXAMPLE 1

This example illustrates a composite film comprising a nitride of titanium and a nitride of tantalum.

After placing an article made of ABS resin into a sputtering device and reducing the pressure to about $(1.0 - 2.0) \times 10^{-3}$ Pa, nitrogen gas was injected to a pressure of 3.0×10^{-2} Pa and then argon gas was added to increase the pressure of the gas mixture to 6.0×10^{-1} Pa. Shutters were disposed on both titanium metal and tantalum metal targets and reactive sputtering was conducted for 7 minutes at a high frequency output of 8 Watts/cm² while fully opening the shutter on the titanium metal target and opening the shutter to about one-third on the tantalum metal target. As a result, a composite film comprising titanium nitride and tantalum

nitride with the amount of tantalum being 45% by weight was coated on the ABS resin article to a thickness of 0.15 micron. In this case, since the coating was applied by means of sputtering, the temperature at which the film was formed could be controlled to be less than 70°C and thus deformation, etc. of the article did not take place.

The composite film thus formed exhibited a metallic appearance and a glossy and decorative golden colour. Further, the composite film had the same degree of hardness and close bondability as that of titanium nitride alone and showed improved corrosion resistance to that of titanium nitride alone since it had a more dense texture.

While the golden colour of the composite film is determined by the amount of tantalum, temperature and the partial pressure of the nitrogen gas during sputtering, since tantalum acts as a buffer in the reaction between nitrogen and titanium and also contributes to the reaction with nitrogen, the effect of fluctuation in the partial pressure of the nitrogen gas is reduced upon forming the titanium nitride which actually causes the golden colour and, as a result, the effect on the tone is decreased.

However, the partial pressure of nitrogen gas

under which the titanium nitride itself exhibits a golden colour is at least 2.5×10^{-2} Pa. Further, if the partial pressure goes higher than 4.0×10^{-2} Pa, the composite film itself becomes extremely fragile thereby causing an actual problem with respect to resistance to cracking. Accordingly, a suitable range for the partial pressure of the nitrogen gas is $(2.5-4.0) \times 10^{-2}$ Pa.

The graph of Figure 1 shows a difference of the colour tone for the composite film of titanium nitride and tantalum nitride of an article according to the present invention, a pure gold sputtered film and a conventional titanium nitride sputtered film. In this case, the tone is expressed by measuring L^* , a^* , b^* for each of the films by way of an L^* , a^* , b^* chromaticity diagram by using a light source C and a chromaticity meter and by plotting lightness L^* , saturation $C^* = \sqrt{(a^{*2} + b^{*2})}$, and hue $H^* = \tan^{-1}(b^*/a^*)$. It can be seen from the graph that the tone of the composite film of an article according to the present invention is excellent as compared with the conventional titanium nitride sputtered film both for lightness and saturation and it is approximately equal with the pure gold sputtered film for hue.

Further, the graph of Figure 2 was prepared by

plotting saturation C^* , tantalum amount (% by weight) and the sputtering temperature constituting the determining factors for the tone. In the graph, when the tones are classified under each of the conditions based on the saturation C^* , they can be divided into zones I to IV, in which the regions of the zones II and III are effective regions for obtaining decorative golden hard composite membranes and the amount of tantalum is 5 to 75% by weight within a sputtering temperature range of 50°C to 300°C .

Further, in the sputtering process described above, tantalum metal is more reactive with oxygen as compared with the titanium metal, has a gettering effect to oxygen as impurity gas in the vacuum atmosphere and can prevent undesired effects of oxygen on the colour tone.

EXAMPLE 2

This example illustrates a composite film of an article according to the present invention comprising a nitride of zirconium and a nitride of tantalum.

After placing an article made of ABS resin in a sputtering device and reducing the pressure to about $(1.0-2.0) \times 10^{-3}$ Pa, nitrogen gas was injected to a

pressure of 3.5×10^{-2} Pa and then argon gas was added to increase the pressure of the gas mixture to 6.0×10^{-1} Pa. Shutters were disposed on both of zirconium metal and tantalum metal targets and reactive sputtering was conducted for 7 minutes at a high frequency output of 6.3 Watts/cm² while fully opening the shutter on the zirconium metal target at 8 Watts/cm² and opening the shutter to about one-third on the tantalum metal target. As a result, a composite film comprising zirconium nitride and tantalum nitride with a tantalum amount of 36% by weight was coated on the ABS resin article to a thickness of 0.15 micron. In this case, since the coating was applied by means of sputtering, the temperature at which the composite film was formed could be controlled to be less than 70°C and thus deformation, etc. of the article did not take place.

The composite film thus formed exhibited a metallic appearance and a glossy and decorative golden colour. Further, the composite membrane had the same degree of hardness and close bondability as that of zirconium nitride alone and showed more excellent corrosion resistance than zirconium nitride alone since it had a more dense texture.

While the golden colour of the composite film is determined by the amount of tantalum, the

temperature and the partial pressure of the nitrogen gas, since tantalum acts as a buffer in the reaction between nitrogen and zirconium and also contributes to the reaction with nitrogen, the effect of fluctuation in the partial pressure of the nitrogen gas is reduced upon forming the zirconium nitride which actually causes the golden colour and the effect on tone is decreased as a result.

However, the partial pressure of nitrogen gas under which the zirconium nitride itself exhibits a golden colour is at least 3.0×10^{-2} Pa. Further, if the pressure goes higher than 4.5×10^{-2} Pa, the composite membrane itself becomes extremely fragile thereby causing an actual problem with respect to resistance to cracking. Accordingly, a suitable range for the partial pressure of the nitrogen gas is $(3.0-4.5) \times 10^{-2}$ Pa.

The graph of Figure 3 shows the difference in the colour tone for the composite film of zirconium nitride and tantalum nitride of an article according to the present invention, a pure gold sputtered film and a conventional zirconium nitride sputtered film in the same manner as in Figure 1. It can be seen from the graph that the tone of the composite film is excellent as compared with the conventional zirconium nitride

sputtered film both with respect to lightness and saturation. It can also be seen that it is approximately equal with respect to the hue of the pure gold sputtered film.

5 Further, the graph shown in Figure 4 was prepared by plotting the saturation C^* with respect to the amount of tantalum (% by weight) and the sputtering temperature constituting the determination factors for the tone. In the graph, when the colour tones are
10 classified under each of the conditions based on the saturation C^* , they can be divided into zones I to IV, in which the regions of zones II and III are effective regions for obtaining a decorative golden composite film and the amount of tantalum is 3 to 68% by weight within
15 a sputtering temperature range of 50°C to 300°C .

Further, in the sputtering process, the tantalum metal is more reactive with oxygen as compared with zirconium metal, has a gettering effect to oxygen as
impurity in the vacuum atmosphere and can prevent
20 undesired effects of oxygen on the tone.

Although the above examples employ a sputtering technique as an example, similar golden composite films can be formed also by means of vapour deposition and ion plating techniques. Both with vapour deposition and ion
25 plating, when an electron beam is employed as the

evaporation source, two electron guns and two crucibles are disposed in one device and vapour deposition or ion plating is conducted for titanium or zirconium independently at an appropriate evaporation rate in a nitrogen atmosphere to form the composite film. In the case of using one electron gun and crucible a composite material previously formulated to an appropriate ingredient ratio is placed in the crucible and evaporated.

The article on which the composite film is formed may be of, for example, resin, metal or ceramic material and a primer coating such as of nickel or chromium may be formed on the article by means of, for example, plating and, then the composite film described above may be formed thereover. Alternatively, it is also possible to apply a primer coating of metal such as chromium, nickel-chromium or nickel on the article by means of sputtering, vapour deposition or ion plating and, thereafter, applying the composite film.

The primer coating has the aim of improving the close bondability and/or, particularly in the case where the article is of metal, improving corrosion resistance.

CLAIMS

1. An article exhibiting a golden colour having formed on at least part of the surface thereof a composite film composed of either titanium nitride and tantalum nitride, in which case the amount of tantalum is 5 to 75% by weight, or zirconium nitride and tantalum nitride, in which case the amount of tantalum is 3 to 68% by weight.
2. An article as claimed in claim 1 in which the composite film is formed by vapour deposition, sputtering or ion plating.
3. An article as claimed in claim 1 or 2 composed of a synthetic resin, metal or ceramic material, and a primer coating of nickel or chromium on which the composite film is formed.
4. An article as claimed in any preceding claim in which the composite film is formed in a nitrogen-containing atmosphere at a pressure in the range $(2.5-4.0) \times 10^{-2}$ Pa or in the range $(3.0-4.5) \times 10^{-2}$ Pa.
5. An article exhibiting a golden colour substantially as herein described with reference to and as shown in the accompanying drawings.