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(54) METHOD OF FORMING ANODIC TITANIUM OXIDE LAYERS HAVING DUAL-COLOR APPEARANCE AND ARTICLE HAVING THE SAME

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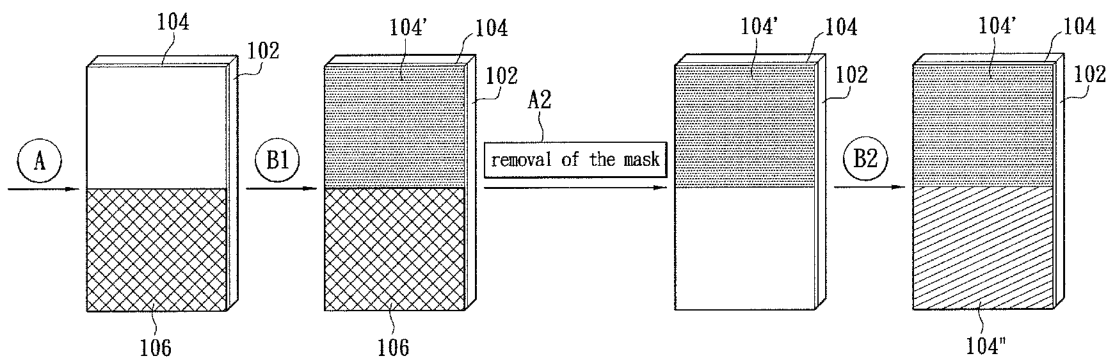
(57) **ABSTRACT**

A method of forming anodic titanium oxide layers having dual-color appearance includes the following steps: providing a cleaned substrate; depositing a titanium film on the substrate; forming a mask of a desired pattern covering a portion of the substrate; carrying out a first anodization by immersing the substrate in an electrolytic solution as anode; applying a first direct-current voltage to produce a first titanium oxide layer; removing the mask; carrying out a second anodization by immersing the substrate in the electrolytic solution as anode; applying a second direct-current voltage having a value smaller than that of the first voltage to produce a second titanium oxide layer; and cleaning the coated substrate. The instant disclosure also includes an article made by the above method.



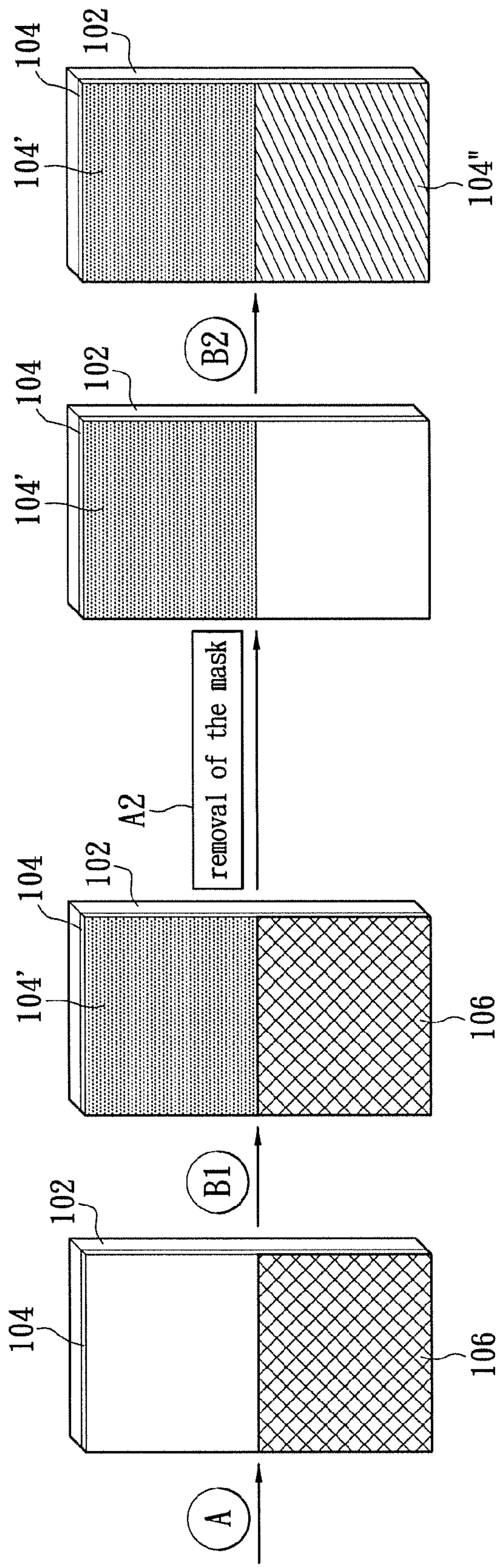

104
102
104'
104"
B2
104
102
104'
removal of the mask
A2
104
102
104'
106
B1
102
104
106
A

FIG. 1

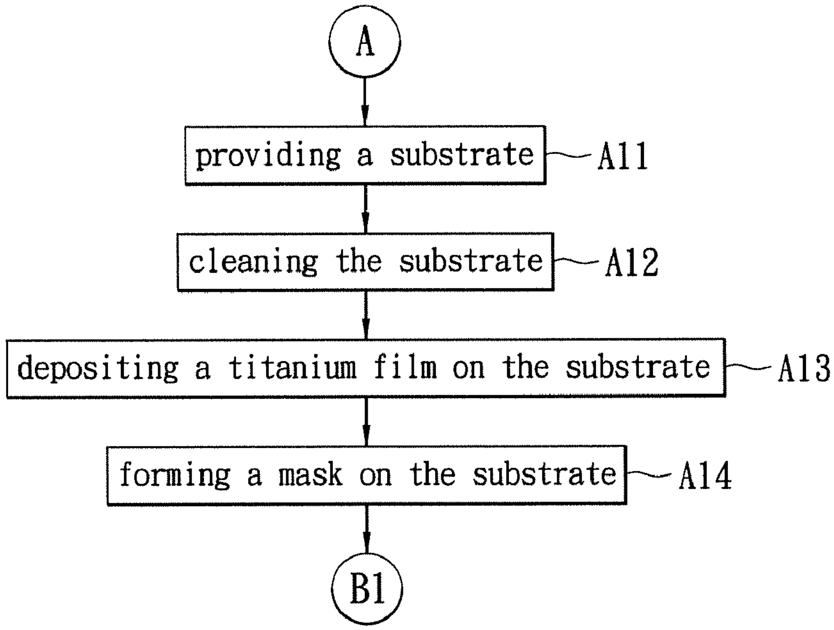

A
providing a substrate
A11
cleaning the substrate
A12
depositing a titanium film on the substrate
A13
forming a mask on the substrate
A14
B1

FIG. 2

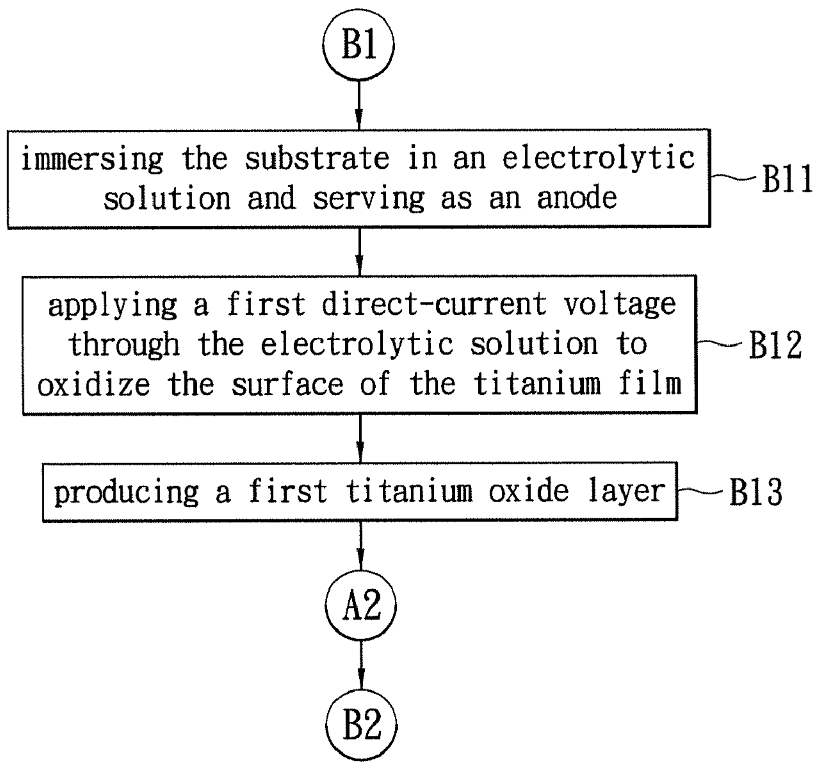

B1
immersing the substrate in an electrolytic solution and serving as an anode
B11
applying a first direct-current voltage through the electrolytic solution to oxidize the surface of the titanium film
B12
producing a first titanium oxide layer
B13
A2
B2

FIG. 3

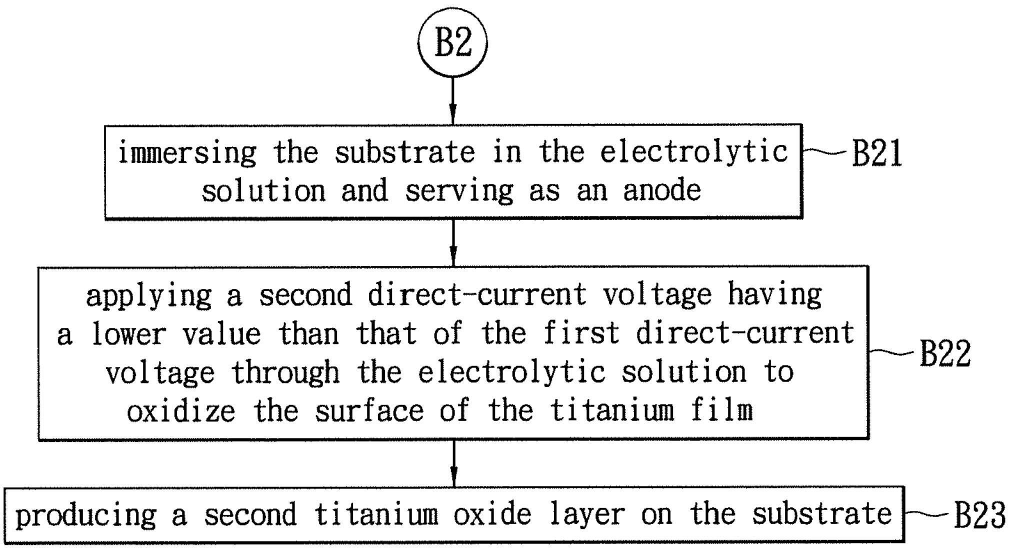

B2
immersing the substrate in the electrolytic solution and serving as an anode
B21
applying a second direct-current voltage having a lower value than that of the first direct-current voltage through the electrolytic solution to oxidize the surface of the titanium film
B22
producing a second titanium oxide layer on the substrate
B23

FIG. 4

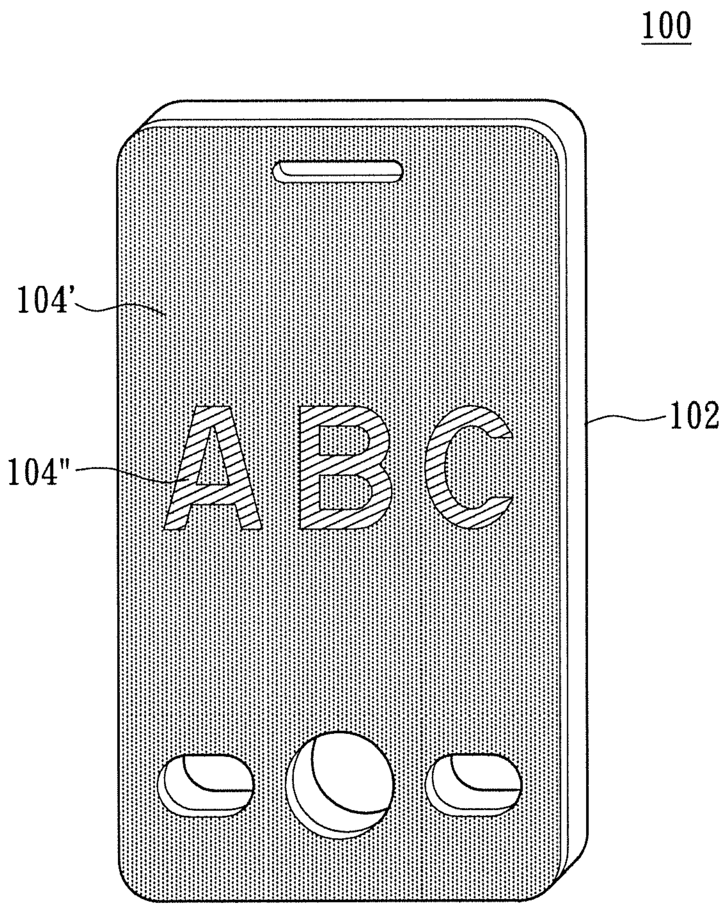

100
104'
104"
102
ABC

FIG. 5

METHOD OF FORMING ANODIC TITANIUM OXIDE LAYERS HAVING DUAL-COLOR APPEARANCE AND ARTICLE HAVING THE SAME

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] The instant disclosure relates to a method of forming anodic titanium oxide layers having dual-color appearance and an article having the same; more particularly, to a method of forming titanium oxide layers on a substrate, such that the substrate would have at least two different color finishes, and an article having the same.

[0003] 2. Description of Related Art

[0004] Portable electronic devices are very popular today, such as mobile phones, personal digital assistants (PDAs), laptops, etc. As the consumers begin to put more focus on the cosmetic appearances of these portable electronics, the housings of most portable electronics have shiny finishes for attractiveness. Especially for metal surfaces, which typically are specially processed to attain smoothness and shininess for visual attractiveness.

[0005] To apply color on surfaces of a housing, the existing technique involves anodizing to form a thin layer of titanium oxide on the metal surface for coloring. However, coloration done by such technique restricts the metal surfaces to a mono-colored state, unable to generate multi-color variations. Furthermore, the titanium oxide layer of different thicknesses formed by anodizing generates different colors, while its thickness depends on factors such as applied voltage. However, in practice, the process of forming multiple titanium oxide layers on a same housing to create different colorations thereon is quite challenging.

[0006] To form a different color on the housing, an alternative solution is to apply a plastic adhesive film to its metal surface. However, since the adhesive film covers the metal housing, the user is unable to sense the actual metallic color and touch feel.

[0007] Therefore, the challenge of producing at least two different colors on a metallic housing while maintaining the metallic touch feel is a main issue the manufacturers intend to resolve.

SUMMARY OF THE INVENTION

[0008] To address the aforementioned issues, the instant disclosure provides a method of forming anodic titanium oxide layers having dual-color appearance and an article having the same. The main objective is to resolve the issue of forming at least two metallic colors on a substrate, especially by anodizing, while maintaining metallic luster and its touch feel.

[0009] The method comprises the following steps: providing a substrate; cleaning the substrate; depositing a titanium film on the substrate; forming a mask of desired pattern over a portion of the substrate; taking the substrate having titanium film formed thereon as an anode and immersing into an electrolytic solution; applying a first direct-current voltage through the electrolytic solution to oxidize the surface of the titanium film and produce a first titanium oxide layer on the substrate; removing the mask; taking the substrate as an anode and immersing it again in the electrolytic solution; applying a second direct-current voltage having a smaller value than that of the first-direct voltage through the electrolytic solution, to oxidize the surface of the titanium film and produce a second titanium oxide layer on the substrate; and cleaning the substrate.

[0010] The instant disclosure also provides an article having anodic titanium oxide layers with dual-color appearance obtained by the above method. The product comprises a substrate and a titanium film formed thereon. The surface of the titanium film is oxidized in forming a first titanium oxide layer and a second titanium oxide layer thereon in a non-overlapping manner. The first titanium oxide layer shows a first color, while the second titanium oxide layer shows a second color.

[0011] For advantages, by first passing a high-voltage direct current for anodizing in forming the first titanium oxide layer having the first color, followed by passing a low-voltage direct current for anodizing in forming the second titanium oxide layer having the second color, the metal housing can be easily color-coated and maintain its metallic luster. The method does not produce dust contaminants and surface damages as would with sand blasting, nor requires adhesive film. For the above method, the process time is short, which is suitable for mass production. For example, each oxidation process only takes approximately one minute, while a particular color is being introduced on the surface of the housing. The color-forming oxidation process can be repeated with great accuracy by controlling the factors such as electroplating time, electrolytic solution, and voltage.

[0012] In order to further appreciate the characteristics and technical contents of the instant disclosure, references are hereunder made to the detailed descriptions and appended drawings in connection with the instant disclosure. However, the appended drawings are merely shown for exemplary purposes, rather than being used to restrict the scope of the instant disclosure.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] FIG. **1** is a step-by-step illustration of forming anodic titanium oxide layers having dual-color appearance of the instant disclosure.

[0014] FIG. **2** is a flowchart showing the steps of a preparation process A of the instant disclosure.

[0015] FIG. **3** is a flowchart showing the steps of a first anodizing B**1** of the instant disclosure.

[0016] FIG. **4** is a flowchart showing the steps of a second anodizing B**2** of the instant disclosure.

[0017] FIG. **5** is a perspective view showing the use of instant disclosure for a housing of the electronic device.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENT

[0018] Please refer to FIG. **1**, which shows a step-by-step illustration of the method in forming anodic titanium oxide layers having dual-color appearance of the instant disclosure. The present method can be broken into a preparation process A, a first anodizing B**1**, removal of the mask A**2**, and a second anodizing B**2**. Each different stage is explained in details hereinbelow.

[0019] [Preparation Process A]

[0020] Please refer to FIGS. **1** and **2**, with FIG. **2** showing a flowchart listing the steps of the preparation process A of the instant disclosure. In step **A11**, a substrate **102** is provided. The substrate **102** is mainly made of metallic material and can be a metal housing, such as aluminum, aluminum alloy, stainless steel, or magnesium alloy housing. The substrate **102** may also be a non-metallic housing as well.

[0021] Then, for step A**12** regarding the metal housing, the substrate **102** may first be cleaned prior to anodic treatment. Generally speaking, the cleaning process includes degreasing, acid washing (pickling), rinsing (water), and drying. Degreasing is performed to remove oil and grease off the surface of the substrate **102**, which can be done by immersing the substrate **102** in a solvent bath. Acid washing, or pickling, is used to remove rust or oxidation layer from metal surfaces. Different pickle liquors, which contain strong acids, are used for different metals. For example, common steel can be treated with hydrochloric acid or sulfuric acid. If necessary, a corrosion inhibitor can be added to decrease the corrosion rate of the metal. For stainless steel, mixed acid of nitric acid and hydrofluoric acid is used. Low concentrations of nitric acid can be used to treat aluminum and its alloy. Rinsing is then performed to remove any debris left on the surface of the substrate **102** after acid washing, followed by drying the substrate **102** itself.

[0022] Next, in step A**13**, a titanium film **104** is deposited on the substrate **102**. The deposition technique may be physical vapor deposition (PVD), such as vacuum sputtering or evaporative deposition. The thickness of the titanium film may be 0.5 to 1.5 micrometers. The aforementioned coating technique can be used for substrate made of different metallic material or even for non-metallic substrate.

[0023] Then, in step A**14**, a mask **106** of desired pattern is formed on the substrate **102**. The masked portion of the substrate **102** is reserved for second anodizing, while the first anodizing B**1** is being conducted. The preparation process A has thus been completed up to this point, before advancing to the process of applying first coloration through anodizing.

[0024] The aforementioned mask **106** can be a tape, preferably a peelable mask. The peelable mask has a low cost, is easy to use, and does not leave any mark behind. Using the peelable mask, the mask **106** can be formed on the substrate **102** by the screen printing technique in a particular pattern. Often used to protect certain parts of a printed circuit board, the peelable mask is a strippable coating formed by a dried liquid-based protective ink after being transferred onto the substrate **102**.

[0025] [First Anodizing B**1**]

[0026] Please refer to FIGS. **1** and **3**, with FIG. **3** being a flowchart showing the steps of the first anodizing B**1**. For a first step B**11**, the substrate **102** having the titanium film **104** thereon is immersed in an electrolytic solution and serves as an anode. For the instant disclosure, the electrolytic solution must be acidic, such as sulfuric acid, sodium phosphate, chromic acid, etc. For example, a sample electrolytic solution can include sulfuric acid in an amount between approximately 0.1% and 10% by volume. The preceding example is only for explaining purpose. Since different electrolytic solutions differ chemically, the oxide coatings to be grown would have different characteristics as well. For example, the oxide coating obtained through the sulfuric acid solution has excellent corrosion and wear resistances.

[0027] Next, for step B**12**, a first direct-current voltage is applied through the solution to oxidize the surface of the titanium film **104**. The value of the first direct-current voltage is greater than a second direct-current voltage to be applied later in the second anodizing B**2**. Preferably, the first direct-current voltage is above 30 volts to oxidize the surface of the titanium film **104**, where the first direct current may be a constant current. After a short period, approximately one minute, as shown in step B**13**, a first titanium oxide layer **104'** is formed on the substrate **102**. If the voltage is high enough, the thickness of the first titanium oxide layer **104'** can be increased to top 300 nanometers. Thereby, the surface hardness of the titanium coating can be increased against wear, such as for a housing of the electronic device. Through the formation of the first titanium oxide layer **104'**, a first color is applied on the substrate **102**. The color is produced by the reflection of light at and through the formed oxide layer, which is transparent and electrically insulated. More specifically, the color is produced by the interference of first reflected light wave from the upper surface of the titanium oxide layer with the second reflected light wave from the lower surface of the titanium oxide layer, where the interaction of light waves produces the phenomenon called interference coloring. Oxide layers having different thicknesses can produce different light interferences of various colors. Notably, the nanopores formed on the titanium oxide due to the acid in the electrolytic solution do not require sealing.

[0028] Next, the substrate **102** is removed from the electrolytic solution. If necessary, the substrate **102** can be cleaned with water and dried. The drying process is conducive in removing the peelable mask. Then, the mask removal process A**2** is proceeded to remove the mask **106** for exposing portion of the substrate **102** not oxidized. The substrate **102** is now ready to undergo the second anodizing B**2** in forming a second color.

[0029] [Second Anodizing B**2**]

[0030] Please refer to FIG. **4**, which is a flowchart showing the steps of second anodizing of the instant disclosure, in conjunction with FIG. **1**. In step B**21**, the substrate **102** having a first color is again immersed in the electrolytic solution and serves as an anode. The electrolytic solution used during the first anodizing B**1** may be used again for the present step. Next, for step B**22**, the second direct-current voltage having a smaller value than that of the first direct-current voltage is applied through the electrolytic solution to oxidize the surface of the titanium film **104**. For example, the first direct-current voltage may be 35 volts, and the second direct-current voltage can be 15 volts. The recommended minimum difference is in the 2- to 5-volt range. After a period of time, approximately one minute, as indicated by step B**23**, a second titanium oxide layer **104"** is formed on the substrate **102**. Visually, the formation of the second titanium oxide layer **104"** by the second direct-current voltage does not cause any significant negative impact on the cosmetic effect of the earlier formed first titanium oxide layer **104'**. In other words, the first color formed by the first titanium oxide layer **104'** is not affected by the second color formed by the second titanium oxide layer **104"**.

[0031] During anodizing, if the composition and concentration of the electrolytic solution changes within a tolerated range, only the sizes of the nanopores would be affected, while the thicknesses and colors of the oxide layers remain basically unaffected. The overriding factor in determining the thicknesses of the oxide layers is current density, which is typically voltage-controlled. As voltage increases, a thicker coating is produced. Combines with the light interference effect as previously mentioned, the change in coating thickness produces different coloration on the substrate **102**.

[0032] The instant disclosure also discovered that if lower voltage is applied before higher voltage for anodizing, the produced oxide layers and colorations are unstable. Conversely, if the surface of the substrate first undergoes high voltage process in the first anodizing and followed by low voltage process in the second anodizing, the earlier formed oxide layer by the high voltage process can remain stable with minimal color change over time.

[0033] To illustrate the above argument, an example is given hereinbelow. The first direct-current voltage is 35 volts, and the second direct-current voltage is 15 volts, with sulfuric acid being the electrolytic solution. The measured lab values based on the CIE (Int'l Commission on Illumination) are as follows:

[0034] [After the First Anodizing]

[0035] The lab values of the first color are: 75.25, −9.72, −7.03

[0036] [After the Second Anodizing]

[0037] The lab values of the first color are: 72.01, −9.43, −4.34

[0038] The lab values of the second color are: 26.23, 26.75, 12.98

[0039] The above lab results show the first color is not significantly affected after the second anodizing. However, if the setting is reversed, such that the first direct-current voltage for the first anodizing is 15 volts and the second direct-current voltage for the second anodizing is 35 volts, the corresponding lab results show the first color is significantly affected by the second anodizing where the first color suffers significant change.

[0040] Lastly, the substrate **102** is thoroughly cleaned. The cleaning step can include water rinsing and drying, where the drying temperature may be approximately in the 120- to 150-° C. range.

[0041] Based on the above method of the instant disclosure, an article having anodic titanium oxide layers with dual-color appearance can be fabricated. Moreover, by using the peelable mask and the screen printing technique, different cosmetic designs can be formed on the metal substrate, such as letters, decorative patterns, etc. As shown in FIG. **5**, a housing **100** of an electronic device is illustrated. The first color of the first titanium oxide layer **104'** on the substrate **102** serves as the background color. A decorative pattern made up by the letters “A”, “B”, and “C”, which is created by the peelable mask, is shown by the second color of the second titanium oxide layer **104"** without affecting the first color.

[0042] Based on the method of forming anodic titanium oxide layers having dual-color appearance and the article having the same of the instant disclosure, the associated advantages and attributes are as follows. By using the deposition technique to deposit the titanium film, such as vacuum sputtering for the housing of the electronic device, up to thousands of housings can be processed simultaneously, with titanium coating being more cost-effective than using pure titanium substrate. Furthermore, by first forming the first titanium oxide layer having the first color through high-voltage anodizing, followed by forming the second titanium oxide layer having the second color through low-voltage anodizing, the metal housing can be easily processed to display its colorations with metallic touch feel. Moreover, the second titanium oxide layer formed by the low-voltage anodizing would not induce any negative impact on the color of the first titanium oxide layer formed earlier in the process.

[0043] Other attributes of the instant disclosure include short fabrication time, which is suitable for mass production. Special colorations can be formed on the surfaces of the housing. By adjusting the electroplating time, the electrolytic solution, and voltage, the colorization of the substrate can be accurately controlled with excellent repeatability. The yield rate can be improved significantly.

[0044] The descriptions illustrated supra set forth simply the preferred embodiment of the instant disclosure; however, the characteristics of the instant disclosure are by no means restricted thereto. All changes, alternations, or modifications conveniently considered by those skilled in the art are deemed to be encompassed within the scope of the instant disclosure delineated by the following claims.

What is claimed is:

1. A method of forming anodic titanium oxide layers having dual-color appearance, comprising the steps of:
- a. providing a substrate;
- b. cleaning the substrate;
- c. depositing a titanium film on the substrate;
- d. forming a mask of desired pattern over a portion of the substrate;
- e. carrying out a first anodization process by immersing the substrate in an electrolytic solution as an anode;
- f. applying a first direct-current voltage through the electrolytic solution to produce a first titanium oxide layer on the substrate;
- g. removing the mask;
- h. carrying out a second anodization process by immersing the substrate in the electrolytic solution as an anode;
- i. applying a second direct-current voltage having a value smaller than that of the first voltage to produce a second titanium oxide layer on the substrate; and
- j. cleaning the substrate.

2. The method of forming anodic titanium oxide layers having dual-color appearance of claim **1**, wherein the substrate is a metallic housing.

3. The method of forming anodic titanium oxide layers having dual-color appearance of claim **1**, wherein the thickness of the titanium film is in the range of 0.5 to 1.5 micrometers.

4. The method of forming anodic titanium oxide layers having dual-color appearance of claim **1**, wherein the cleaning step before depositing the titanium film includes degreasing, acid washing (pickling), rinsing (water), and drying in sequence.

5. The method of forming anodic titanium oxide layers having dual-color appearance of claim **1**, wherein the voltage of the first direct current is at least 30 volts.

6. The method of forming anodic titanium oxide layers having dual-color appearance of claim **1**, wherein the difference between the voltages of the first direct current and the second direct current is at least 2 volts.

7. The method of forming anodic titanium oxide layers having dual-color appearance of claim **1**, wherein the mask may be a peelable mask formed on the substrate by the screen printing technique.

8. An article having titanium oxide layers with dual-color appearance, fabricated by the method of forming anodic titanium oxide layers having dual-color appearance of claim **1**, comprising:

a substrate; and

a titanium film formed on the surface of the substrate,

wherein the surface of the titanium film includes a first titanium oxide layer region showing a first color and a second titanium oxide layer region showing a second color, the second titanium oxide layer region being formed on a masked area.

9. The article having titanium oxide layers with dual-color appearance of claim **8**, wherein the substrate is a metallic housing.

10. The article having titanium oxide layers with dual-color appearance of claim **8**, wherein the thickness of the titanium film is in the range of 0.5 to 1.5 micrometers.

11. The article having titanium oxide layers with dual-color appearance of claim **8**, wherein the thickness of the first titanium oxide layer is greater than 300 nanometers.

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