The invention provides an electrochemical treatment based surface modification device that comprises a solution tank, a cathode terminal, and an anode terminal. The solution tank is filled with an acidic solution which contains first valence metal ions. The first valence metal ions are partially reduced to second valence metal ions at the cathode terminal. The valence of the first valence metal ion is greater than that of the second valence metal ion. The anode terminal is provided an electrically conductive oxide, and the second valence metal ions move from the cathode terminal to the anode terminal to from a metal oxide. Wherein, the deposition and etching of the conductive oxide occur simultaneously on the surface of the anode.
ELECTROCHEMICAL TREATMENT BASED SURFACE MODIFICATION DEVICE

BACKGROUND OF THE INVENTION

[0001] Field of the Invention

[0002] This application claims priority of No. 101134076 filed in Taiwan R.O.C. on Nov. 19, 2012 under 35 USC 119, the entire content of which is hereby incorporated by reference.

[0003] The invention relates to a surface modification device, particularly to an electrochemical treatment based surface modification device.

[0004] Related Art

[0005] Tin-doped indium oxide (ITO), because of its excellent visible light transmittances and electric conductivities, has been the most widely used transparent conducting oxide (TCO) in optoelectronic applications. ITO however suffers from the disadvantages of poor heat stability, high cost, and worsening electric conductivity with increasing temperatures. More importantly, indium is an Earth-scarse element and thus lacks the long term supply stability. Consequently, there have been extensive and intensive research efforts to develop more stable, heat-durable, and cost-effective alternatives to replace ITO. Fluorine-doped tin oxide (FTO) is one of the few promising candidates. Although FTO is cheaper than ITO, FTO glass has to be thicker than ITO glass because of technical difficulties involved in manufacturing processes. However, thicker glass will present longer light paths so that light transmittances in the FTO glass will be lower. The applications of FTO glass in optoelectronics are thus limited by the relatively lower visible light transmittances.

[0006] Industry circle tries to improve the problem of lower visible light transmittances by using anti-reflection films (e.g., TiO₂, SiO₂, and PVA). Although anti-reflection films can increase visible light transmittances, they also decrease the electric conductivity at the same time.

SUMMARY OF THE INVENTION

[0007] An objective of the present invention is to provide a device for increasing light transmittance of conductive oxide films.

[0008] An objective of the present invention is to provide a device for cost saving.

[0009] An objective of the present invention is to provide a device for decreasing surface roughness of conductive oxide films.

[0010] The invention provides an electrochemical treatment based surface modification device that comprises a solution tank, a cathode terminal, and an anode terminal. The solution tank is filled with an acidic solution which contains first valence metal ions. The first valence metal ions are partially reduced to second valence metal ions at the cathode terminal. The valence of the first valence metal ion is greater than that of the second valence metal ion. The anode terminal is provided with an electrically conductive oxide, and the second valence metal ions move from the cathode terminal to the anode terminal to form a metal oxide. Whichever, the deposition and etching of the conductive oxide occur simultaneously on the surface of the anode terminal.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] FIG. 1 shows a schematic diagram illustrating an electrochemical treatment based surface modification device according to one embodiment of the invention.

[0012] FIG. 2 shows the cross-sectional and top view SEM images of the FTO layer before and after the electrochemical treatment.

[0013] FIG. 3A shows an evolution of surface morphology, layer thickness, and sheet resistance of the FTO layer.

[0014] FIG. 3B shows transmittance spectra of untreated and treated FTO samples at five different treatment temperatures. Insets are corresponding top view SEM images.

[0015] FIG. 4 shows XRD patterns of untreated and treated FTO samples. Inset is a local enlargement of the (110) diffraction peak.

[0016] FIG. 5 shows XRD pattern of corresponding deposits collected at cathode.

[0017] FIG. 6 shows XPS spectrum of FTO sample treated at 5V and 60°C for 30 min.

DETAILED DESCRIPTION OF THE INVENTION

[0018] Please refer to FIG. 1. FIG. 1 shows a schematic diagram illustrating an electrochemical treatment based surface modification device according to one embodiment of the invention. Surface modification device 10 comprises a solution tank 10a, a cathode terminal C, and an anode terminal A.

[0019] Solution tank 10a is filled with an acidic solution L. Acidic solution L has tetravalent tin ions (Sn⁴⁺). In the present embodiment, acidic solution L can be implemented by nitric acid. The source of Sn⁴⁺ can be implemented from stannic chloride (SnCl₂). There has 5V between cathode terminal C and anode terminal A.

[0020] In the present embodiment, cathode terminal C can be implemented by platinum (Pt). Anode terminal A provides a conductive oxide J, the conductive oxide J is implemented by fluorine-doped tin oxide (FTO).

[0021] Wherein, cathode terminal C has following reactions (1)–(4):

\[
\begin{align*}
\text{Sn}^{4+} + 2e^- & \rightarrow \text{Sn}^{2+} \\
\text{Sn}^{2+} + 2e^- & \rightarrow \text{Sn} \\
\text{Sn}^{4+} + 4e^- & \rightarrow \text{Sn} \\
2\text{H}^0 + 2e^- & \rightarrow \text{H}_2
\end{align*}
\]

(1) (2) (3) (4)

[0022] It should be noted that, as shown in reaction (1), Sn⁴⁺ are reduced to divalent tin ions (Sn²⁺) through partial reduction. We can know that the valence of Sn⁴⁺ is greater than valence of Sn²⁺. But the invention is not limited to the tin ion. It can be implemented by other metal ions.

[0023] Besides, as shown in reactions (2) and (3), Sn⁴⁺ and Sn²⁺ can also be reduced to Sn.

[0024] Moreover, anode terminal A has following reactions (5)–(8):

\[
\begin{align*}
2\text{H}_2\text{O} & \rightarrow \text{O}_2 + 4\text{H}^0 + 4e^- \\
2\text{Sn}^{4+} + \text{O}_2 + 4\text{H}_2\text{O} & \rightarrow 2\text{Sn}^{4+} + 4\text{H}^0 \\
\text{Sn(OH)}_3 + \text{Sn(OH)}_3 & \rightarrow 2\text{SnO}_2 + 4\text{H}_2\text{O} \\
\text{SnO}_2 + 4\text{H}^0 & \rightarrow \text{Sn}^{4+} + 2\text{H}_2\text{O}
\end{align*}
\]

(5) (6) (7) (8)

[0025] The detailed description for anode terminal A is as follows. Firstly, H₂O is oxidized to form O₂ and H⁺ (as shown
in reaction (5)). H⁺ will be reduced to H₂ at cathode terminal C (as shown in reaction (4)). The Sn⁺²⁺ is supplied through mass transfer from the partial reduction of Sn⁺⁺ at the cathode terminal C. Then, Sn⁺²⁺ reacts with H₂O and O₂ to first form Sn(OH)₄ (as shown in Reaction (6)), that further goes through a condensation reaction to form SnO₂ on the anode terminal A (FTO) surface (as shown in Reaction (7)).

**[0020]** It should be noted that, as shown in reaction (8), SnO₂ of FTO surface will react with H⁺⁺, wherein, H⁺⁺ are generated from reactions (5) or (6). On the other hand, the H⁺⁺ produced in the proximity of the anode terminal A surface from reactions (5) and (6) performed the etching of SnO₂. Consequently, deposition and etching of SnO₂ occurred simultaneously at the anode terminal A (FTO), the balance of which leading to the flattening of the FTO surface. Therefore, electrochemical reaction time in device 10 can be adjusted according to user’s demand.

**[0027]** Please refer to FIG. 2. FIG. 2 shows the cross-sectional and top view SEM images of the FTO layer before and after the electrochemical treatment. Here, untreated FTO glass (sheet resistance 6-8 Ω/sq, 2 mm×20 mm×20 mm) is used as the object for the flattening process. The electrochemical treatment is operated at 5V and 60°C for 30 minutes. The cathode terminal C and anode terminal A are kept 25 mm apart and the electrolyte is stirred at ambient condition.

**[0028]** In the present embodiment, under processing time 30 minutes and environment temperature 60°C, FTO surface will be the smoothest. It is because that nitrate ions (NO³⁻) in the cathode terminal C are reduced to NO ions, but NO ions will oxidize Sn⁺²⁺ to Sn⁺⁺ and impede the amount of Sn⁺²⁺ to deposit on anode terminal A when environment temperature is less than 60°C. Conversely, when environment temperature is greater than 60°C, cathode terminal C will generate relatively few NO³⁻, so that the deposition of Sn⁺²⁺ on anode terminal A will increase and make FTO surface rougher. Therefore, the present embodiment is based on 30 minutes and environment temperature 60°C of the electrochemical treatment.

**[0029]** By (a) and (b) in FIG. 2, evidently, the originally much rougher surface is replaced by a dense, smooth surface. From the top view SEM images, granular structure is evident for the untreated sample, whereas almost no structural features can be observed from the treated sample, indicating again the much improved surface flatness of the treated sample. As shown in (A) and (B) of FIG. 2, the layer thickness is increased from 640 nm to 755 nm by around 115 nm over a treatment period of 30 min at 5V, and the surface roughness is decreased from 15 to 5 nm as determined with an AFM. Presumably, thicker films exhibit lower light transmittances. The visible light transmittances of the treated sample, as discussed in a later section, however are increased by 6% (from 79 to 85% at 550 nm). Evidently, the gain in light transmittances through the suppression of light scattering at the FTO-air interface for the much flattened treated sample over-compensates the loss in transmittances from the thickness increase.

**[0030]** Please also refer to FIG. 3A. FIG. 3A shows an evolution of surface morphology, layer thickness, and sheet resistance of the FTO layer. Wherein, left axis shows sheet resistance of FTO and right axis shows thickness.

**[0031]** After the electrochemical treatment, FTO acquires the flattest surface, while the sheet resistance is only slightly increased from 7.7 Ω to 14 Ω. The thickness is increased from 640 nm to 755 nm under the environment temperature of 60°C. In the present embodiment, even though electrochemical treatment is controlled under environment temperature of 40°C, 50°C, or 70°C, the FTO surface is still rougher than that obtained from the environment temperature of 60°C.

**[0032]** Please also refer to FIG. 3B. FIG. 3B shows transmittance spectra of untreated and treated FTO samples at five different treatment temperatures. Insets are corresponding top view SEM images. Light transmittance of untreated FTO is about 75%. It can be increased to at least 85% after the electrochemical treatment. Therefore, the FTO film thickness increases after the electrochemical treatment; the sheet resistance is slightly increased, and the light transmittance of the FTO increases from 79% to 85%. Wherein, when the illumination wavelength is 550 nm, the increment of light transmittance is about 6%. This shows that although the thickness of the treated FTO is increased, FTO surface becomes relatively flat and avoids light scattering to increase light transmittances.

**[0033]** Then, please also refer to FIG. 4. FIG. 4 shows XRD patterns of untreated and treated FTO samples. Inset is a local enlargement of the (110) diffraction peak. Both patterns matched very well with that of SnO₂ of the tetragonal phase (JCPDS 77-0447). No extra diffraction peaks can be identified from both patterns, indicating that SnO₂ was the sole crystalline product at the anode after the treatment. If one examines the (110) diffraction peaks closely as enlarged in the inset, there can be observed left-shifts in 2θ of the fluorine-doped samples from that of the SnO₂. The left-shift in 2θ was caused by the F-doping, and was more pronounced for the untreated FTO sample because of its higher doping concentrations. Here, substitution of one O²⁻ by two F⁻ is necessary to maintain electroneutrality, and thus results in an increase in lattice parameters, giving left-shifts in 2θ.

**[0034]** Furthermore, inset is a local enlargement of the (110) diffraction peak. The fluoride ion doping can be proved by the inset of FIG. 4. Grain size of SnO₂ is enlarged when fluoride ions are doped into the crystal structure of SnO₂. According to Bragg’s law, 20 will shift to smaller angles when the grain size of SnO₂ becomes larger. As shown in FIG. 4, the maximum 20 shift level is observed for the untreated FTO, next is the treated FTO, and the lowermost peak is for the un-doped SnO₂. From the foregoing, the material deposition by the electrochemical treatment of the present invention is FTO crystals.

**[0035]** Please refer to FIG. 5. FIG. 5 shows XRD pattern of corresponding deposits collected at cathode terminal C. FIG. 5 is to verify that the deposited product on the surface of cathode terminal C during the electrochemical treatment is Sn. FIG. 5 shows the XRD pattern of the cathode after electrochemical treatment at 5V and 60°C for 30 min. Expectedly, the product obtained at the cathode is Sn (JCPDS 89-0898) from the reduction of Sn⁺²⁺ and Sn⁺⁺.

**[0036]** Then, please refer to FIG. 6. FIG. 6 shows the XPS spectrum of the FTO sample treated at 5V and 60°C for 30 min.

**[0037]** To further confirm the chemical composition of the deposit at the anode, the surface elemental composition of the treated sample prepared at 5V and 60°C for 30 minutes is determined with XPS. The newly deposited layer is 165 nm in thickness, which is able to well shield the base FTO layer from being sampled by the XPS measurement. FIG. 6 shows the XPS of the treated FTO sample, which displays an evident spin-orbit doublet at 486.8 (3d₁₀₂) and 495.3 eV (3d₁₃₂) for
the confirmation of the oxidation state of Sn\textsuperscript{4+} for the smooth dense layer, proving the formation of SnO\textsubscript{2} as the product.

[0038] While the present invention has been described by the way of examples and in terms of preferred embodiments, it is to be understood that the present invention is not limited thereto. To the contrary, it is intended to cover various modifications. Therefore, the scope of the appended claims should be accorded the broadest interpretation so as to encompass all such modifications.

[0039] In conclusion, a novel, facile, one-step Sn\textsuperscript{4+}-based anodic deposition process is developed, by which flattening and thus transmittance enhancements of the FTO layer are achieved for commercial FTO glass. The unique design of the indirect and in-situ supply of Sn\textsuperscript{2+} from the starting Sn\textsuperscript{4+} through partial reductions for the anodic deposition of SnO\textsubscript{2} and the use of HNO\textsubscript{3} for controlled SnO\textsubscript{2} deposition rates at the anode is critical for the slow and balanced SnO\textsubscript{2} deposition and etching to create the significantly flattened dense film. Consequently, utilizing the present electrochemical treatment on FTO surfaces will make FTO smoother and increase light transmittances. FTO can replace the FTO as a transparent conductive material.

What is claimed is:

1. An electrochemical treatment based surface modification device comprising:
   a solution tank filling with an acidic solution, which is comprised first valence metal ions;
   a cathode terminal, at which the first valence metal ions are reduced to a second valence metal ions through partial reduction; and
   an anode terminal at which a conductive oxide is provided and the second valence metal ions move from the cathode terminal to the anode terminal to form a metal oxide;

wherein, the deposition and etching of the conductive oxide occur simultaneously on the surface of the anode terminal.

2. The device according to claim 1, wherein the first valence metal ions or the second valence metal ions are reduced to a metal on the cathode terminal.

3. The device according to claim 1, wherein the first valence metal ions are tetravalent metal ions and the second valence metal ions are divalent metal ions.

4. The device according to claim 3, wherein hydrogen ions and oxygen are formed from oxidation of water on the anode terminal.

5. The device according to claim 4, wherein the metal hydroxide is synthesized from the second valence metal ions and water.

6. The device according to claim 5, wherein the metal hydroxide converts to the metal oxide on the anode terminal through condensation reaction.

7. The device according to claim 6, wherein the metal oxide on the anode terminal is etched, and the tetravalent metal ions and fluorine ions are released from the anode terminal.

8. The device according to claim 7, wherein metal Sn is formed from reduction of tetravalent metal ions on cathode terminal, and some parts of tetravalent metal ions are deposited with fluorine ions on the anode terminal.

9. The device according to claim 8, wherein the metal oxide is fluorine-doped tin oxide (FTO).

10. The device according to claim 1, wherein the acidic solution is nitric acid.

* * * * *