



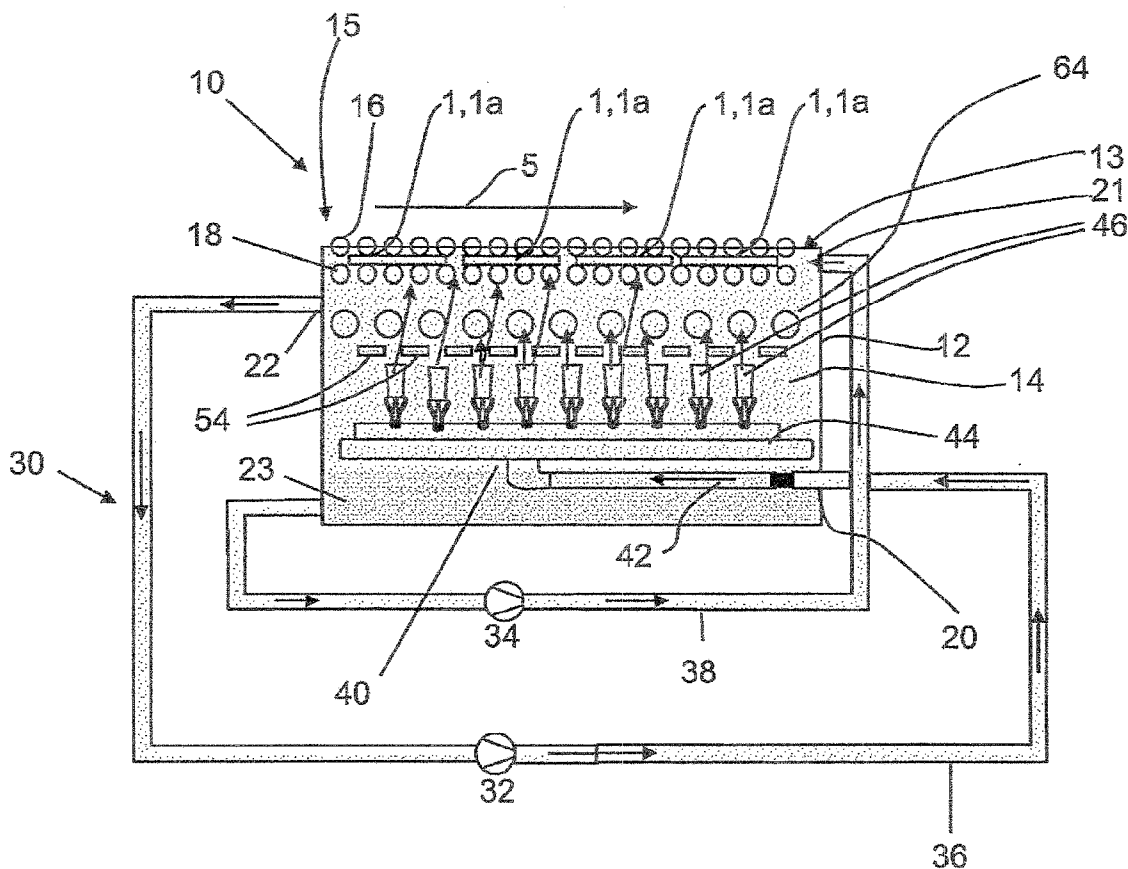
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(19) **United States**(12) **Patent Application Publication****Lippert et al.**(10) **Pub. No.: US 2011/0062028 A1**(43) **Pub. Date: Mar. 17, 2011**(54) **PROCESS AND APPARATUS FOR
ELECTROPLATING SUBSTRATES**(52) **U.S. Cl. 205/91; 204/298.02**(76) **Inventors:** **Lothar Lippert**, Limburg (DE);
Stefan Dauwe, Blankenbach (DE)(21) **Appl. No.: 12/883,551**(22) **Filed: Sep. 16, 2010**(30) **Foreign Application Priority Data**

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Publication Classification(51) **Int. Cl.**
C25D 5/18 (2006.01)
C25B 9/06 (2006.01)(57) **ABSTRACT**

An apparatus for electroplating one or more surfaces (2,3) on one or more substrates (1), especially solar cells (1a), is described. The apparatus includes an electrochemical coating bath (13), which has a coating tank (12) filled with an electrochemical coating liquid (14). The apparatus also includes a conveying device (15) for transporting the substrate through the coating bath (13), a light source circuit (60) with light sources (64) for irradiating the substrate (1) and an electrolytic cell rectifier circuit (50) for the substrate with anodes (54). The apparatus is characterized by a device for generating synchronous current pulses and light pulses, so that during a time interval between the current pulses the irradiating of the substrate or substrates is interrupted. A process for electrochemical plating of the surface of the substrate or substrates is also described.



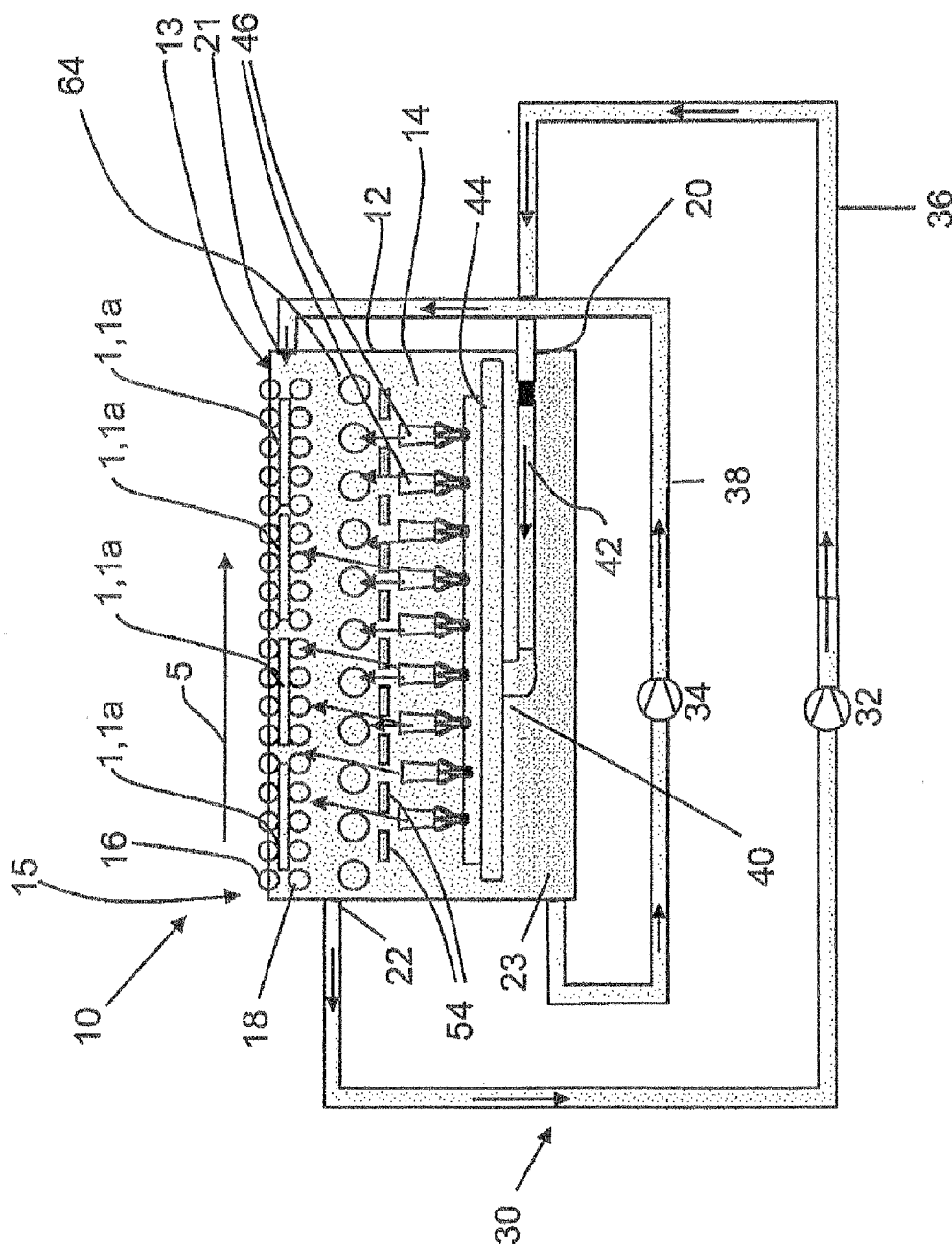
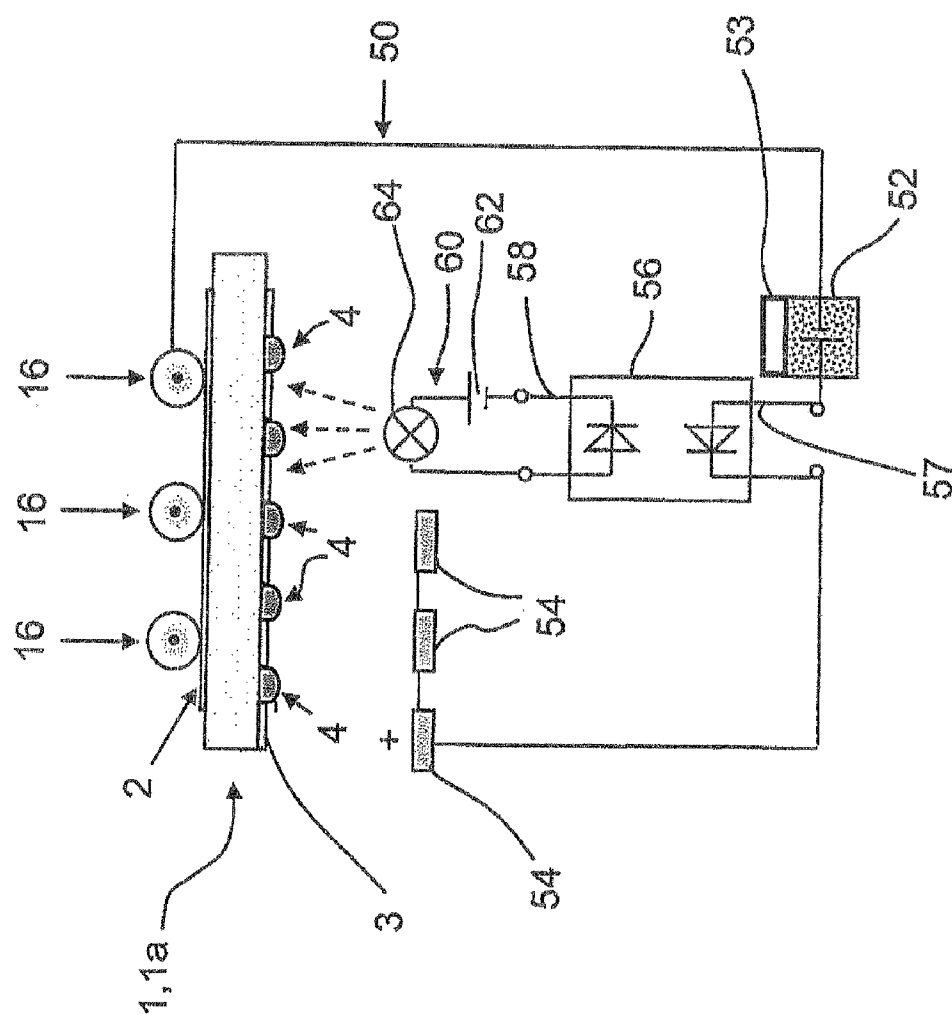


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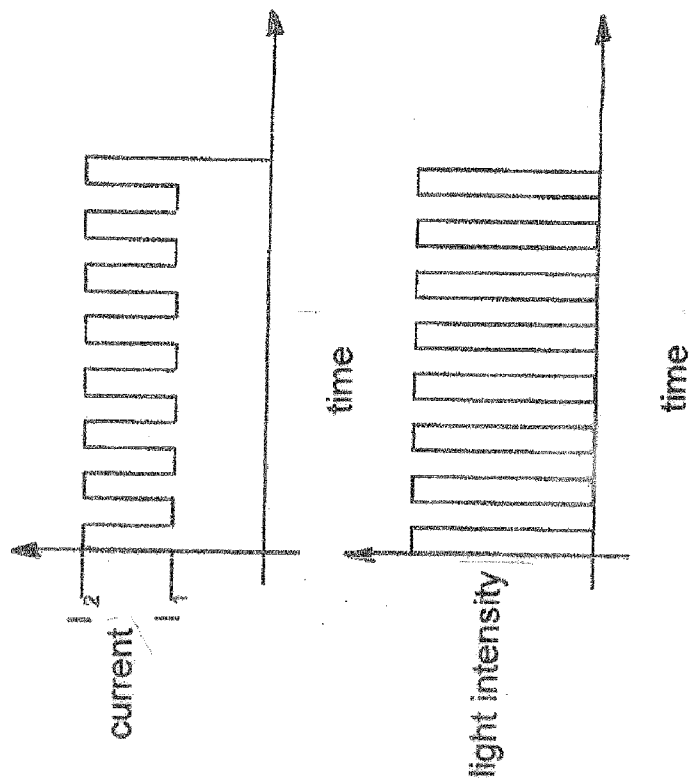


Fig 5

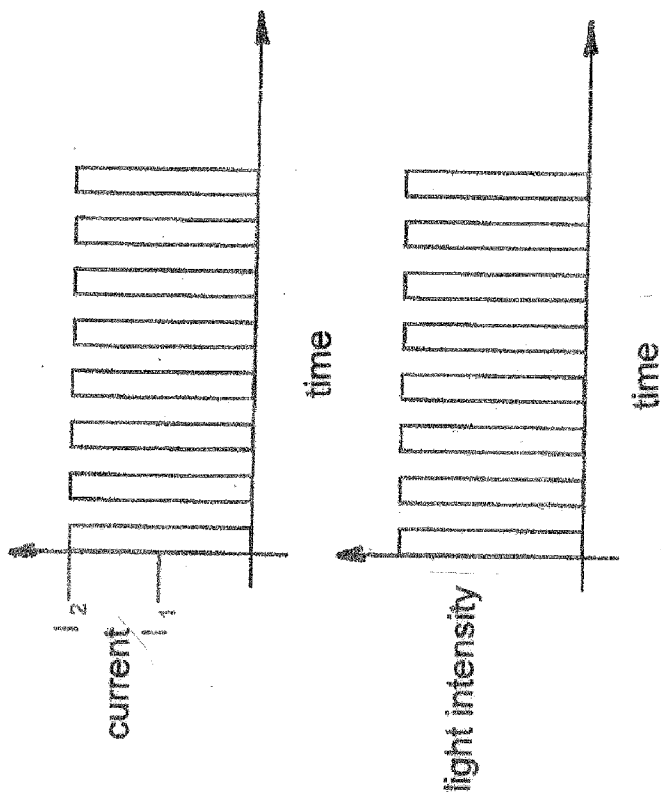


Fig 4

PROCESS AND APPARATUS FOR ELECTROPLATING SUBSTRATES

CROSS-REFERENCE

[0001] The subject matter described and claimed herein below is also described in German Patent Application No. 10 2009 029 551.8, filed on Sep. 17, 2009 in Germany. This German Patent Application provides the basis for a claim of priority of invention for the invention described and claimed herein below under 35 U.S.C. 119 (a)-(d).

BACKGROUND OF THE INVENTION

[0002] 1. The Field of the Invention

[0003] The present invention relates to a process for electroplating at least one surface of at least one substrate, especially solar cells, in which the substrate is moved through an electrolyte coating liquid, is irradiated with light and an electroplating current is applied to the substrate by means of an electrolytic cell rectifier circuit.

[0004] It also relates to an apparatus for performing the process, comprising an electrochemical coating bath, which comprises a coating tank filled with an electrochemical coating liquid, a conveying device for transporting the substrate through the coating bath, a light source circuit with at least one light source for irradiating the substrate and an electrolytic cell rectifier circuit for the substrate with an anode.

[0005] 2. The Description of the Related Art

[0006] DE 10 2007 038 120 A1 describes a type of coating apparatus, in which solar cells are conveyed through a coating tank, which contains a coating bath, by means of conveying rollers. Different types of light sources, e.g. LEDs, whose wavelengths are adjusted or set according to the respective coating liquid, are arranged on the underside of the tank.

[0007] The coating can be exclusively light induced, but also can be current assisted. The irradiation with the light sources generates a voltage in the cell, which induces a current flow. This current flow initiates a deposition of metal from the coating bath on the front side of the solar cell. The solar cell is the cathode in the electroplating current circuit, which is characterized as an electrolytic cell rectifier circuit. However the combined light- and current-generated coating process produces no significant increase of throughput.

[0008] DE 42 25 961 A1 teaches that operating with constant direct voltage in an electroplating circuit is harmful. The object to be coated is located in substantially the same electric field on its path through the coating bath. The plating speed, i.e. the speed with which the deposited metal layer is built up on the substrate, is however comparatively small. That means that the length of the electrochemical plating apparatus for a given speed of movement of the object must be very great.

[0009] In order to achieve a greater plating speed the electrochemical circuit, i.e. the electrolytic cell rectifier circuit, is operated with a pulsed current, as proposed in DE 42 25 961 A1. It has been said that the plating speed can then be increased many times with these measures. The current-free time intervals between the current pulses are compensated for by increasing the current applied during the current pulse.

SUMMARY OF THE INVENTION

[0010] It is an object of the present invention to increase the throughput of the substrate through the coating apparatus as well as the speed of the coating process.

[0011] According to a first aspect of the invention the apparatus for electroplating a substrate according to the invention comprises an electrochemical coating bath, which has a coating tank filled with the electrochemical coating liquid; a conveying device for transporting the substrate through the coating bath; a light source circuit with at least one light source for irradiating the substrate; an electrolytic cell rectifier circuit for the substrate with an anode and means for producing synchronous current pulses and light pulses, so that during a time interval between the current pulses the irradiating is interrupted.

[0012] According to a second aspect of the invention the process for electroplating the substrate according to the invention comprises:

[0013] a) moving the substrate through an electrolytic coating liquid;

[0014] b) during the moving of the substrate irradiating the substrate with light;

[0015] c) during the irradiating passing an electroplating current through the substrate by means of an electrolytic cell rectifier circuit; and

[0016] d) pulsing the electrical current and the light synchronously, so that during a time interval between current pulses the irradiating is interrupted.

[0017] The apparatus for the invention is particularly characterized by means for producing synchronous current pulses and light pulses, so that the irradiation is interrupted between the current pulses.

[0018] It has been shown that the throughput can be increased when the process not only uses current pulses but also light pulses synchronized with the current pulses. Synchronous pulses means that the light pulse is always applied to the substrate when the current pulses is applied. The pulse interval between the current pulses always coincides with the pulse interval between the light pulses. In order to interrupt the irradiation of the substrate surface to be coated, for example the light source can be shut off. Also it is possible to mask the light source during the pause interval. LEDs are the preferred light sources.

[0019] The plating speed could be still further increased many times with the synchronous light pulses in comparison to the constant irradiation according to DE 10 2007 038 120 A1.

[0020] Preferably the means for synchronous production of current pulses and light pulses comprises at least one pulse generator in the electrolytic cell rectifier circuit and/or in the light source circuit.

[0021] The electrolytic cell rectifier circuit and/or the light source circuit are preferably connected to the pulse generator.

[0022] A pulse generator can be provided to which both circuits are connected. Also an individual pulse generator can be provided in each circuit. The individual pulse generators in each circuit would be connected together for production of synchronous pulses.

[0023] Preferably the light source circuit is coupled by means of an optocoupler with the electrolytic cell rectifier circuit. Because of the galvanic separation of the input and the output the coupling provided by the optocoupler has the advantage that interfering effects from one circuit will not be transmitted to the other circuit. The coupling of the circuits by means of an optocoupler thus provides the advantage of a greater stability and uniformity of the generated pulses.

[0024] According to another embodiment of the apparatus according to the invention the light source circuit and/or the

electrolytic cell rectifier circuit have at least one control device, which can control the light intensity of the light source and/or the strength of or current applied during the current pulses according to the widths of the current pulses and/or the light pulses. The morphology of the deposited metal layers can be influenced by means of the at least one control device via the respective heights of the light pulses and the current pulses. Graduated metal layers with optimized properties can be deposited. Another possibility consists of simultaneous variation of the heights of the light pulses and the current pulses, whereby the height of the current pulses is decreased and the height of the light pulses is simultaneously increased during the electrochemical plating process.

[0025] In order to further increase the plating speed and thus the throughput, means for producing a coating liquid flow are provided. Since the at least one substrate is moved through the resting coating liquid, a flow is already present at the at least one surface of the at least one substrate. When the means for producing a coating liquid flow is operated, an additional flow over the at least one surface of the at least one substrate in addition to the flow due to the substrate motion is thus provided.

[0026] Indeed when the current density is increased, e.g. by increasing the height of the current pulses, the throughput is indeed increased, because the coating thickness to be attained is reached sooner. However the current density cannot be arbitrarily increased, because the so-called limiting current density must be considered. The term "limiting current density" means the current density at which the free metal ion concentration at the cathode surface to be coated, approaches zero.

[0027] When the limiting current density is exceeded, gaseous hydrogen is produced because of depletion of the metal ions in the electrolyte, which produces, among other things, pores in the previously deposited metal layer, with the consequence that the morphology of the metal layer is impaired, which can lead to pulverization of the metal layer.

[0028] It has been shown that the higher the flow speed of the coating liquid at the surface of the cathode area of the at least one substrate, the higher the limiting current density.

[0029] According to the first embodiment the means for producing the flow of the coating liquid comprises at least one nozzle for conducting the coating liquid. Because of the use of the at least one nozzle the coating liquid flow is advantageously a turbulent flow, which is preferably so large that it prevails or reinforces the flow caused by the transport of the substrate through the coating liquid at the surface to be coated.

[0030] Preferably the at least one nozzle is arranged in the coating bath opposite to the surface to be coated.

[0031] The at least one nozzle is preferably oriented perpendicular to the at least one surface of the at least one substrate to be coated. Because of that a flow of coating liquid is directed to the at least one surface of the at least one substrate so that whirls or eddies in the flow are produced at the substrate. These eddies or whirls at the surface of the substrate should have a speed which is greater than the relative speed of the coating liquid caused by the transport of the substrate.

[0032] Preferably the nozzles are arranged between the anodes of the electrolytic cell rectifier circuit. The liquid fed from the nozzles can then flow unhindered to the surface to be coated and the flow is not impaired by the presence of the anodes.

[0033] The nozzles are preferably Venturi nozzles, with which a high outlet speed of the coating liquid can be attained.

[0034] According to a second embodiment the means for producing the flow speed of the coating liquid is a circulating device.

[0035] This circulating device is preferably a countercurrent flow device. The countercurrent device produces a flow which is in a direction that is opposite to the transport direction of the substrate in the coating bath. The inlet of the coating tank is preferably arranged at the outlet of the transport device and the outlet of the coating tank is preferably arranged at the inlet of the transport device. The coating liquid is preferably pumped in a direction that is opposite to the transport direction of the substrate. Preferably the inlet and outlet of the counter-current flow device are at the same height as the transport device, i.e. arranged at the height of the substrate to be transported, so that the counter flow is not hindered by the other structures in the coating bath.

[0036] The device with the nozzles can similarly be used alone as the circulating device. It is however preferred to provide both devices in combination with each other.

[0037] The process for electroplating at least one surface of the at least one substrate is characterized in that the electroplating current and the light are synchronously pulsed, wherein the irradiation with the light is interrupted in the time interval between the current pulses.

[0038] The respective widths of the light pulses and the current pulses advantageously amount to from 0.1 ms to 10000 ms. Preferred pulse widths are 1 ms to 1000 ms, particularly 1 ms to 100 ms.

[0039] The pulse widths are preferably selected to be equal to the time interval between the pulses.

[0040] The current pulses and/or the light pulses are preferably rectangular pulses.

[0041] The heights and the widths of the light pulses and/or the current pulses can be varied. The variation of the pulses permits deposition of e.g. graded metal layers with optimized properties. In this way individual plating programs may be realized by means of the control device or control devices.

[0042] It has been shown that it is preferable to reduce the pulse heights of the light pulses when the pulse widths are increased. Thus for example if the light intensity is 10% of the maximum light intensity when the pulse width is 100 ms, the light intensity can be 20% of the maximum with a pulse width 1 ms and 80% with a pulse width of 0.5 ms.

[0043] To improve the throughput a direct current can be applied in the interval between the current pulses, whose strength I_1 is less than or equal to $0.5 \times I_2$ wherein I_2 is the pulse height of or current applied during the current pulses. However the value I_1 of the current during the time interval between the current pulses is preferably low enough so that the required regeneration of the electrolytic coating liquid and/or the metal concentration at the cathode surface to be coated is not impaired.

[0044] The coating liquid is preferably put into a counter flow opposite to the feed direction of the at least one substrate in the vicinity of the at least one surface of the at least one substrate to be coated.

[0045] In addition to this counter flow or even independently of this counter flow a turbulent flow of this coating

liquid can be produced at least in the vicinity of the at least one surface of the at least one substrate to be coated.

BRIEF DESCRIPTION OF THE DRAWING

[0046] The objects, features and advantages of the invention will now be illustrated in more detail with the aid of the following description of the preferred embodiments, with reference to the accompanying figures in which:

[0047] FIG. 1 is a vertical cross-sectional view through a coating tank according to the invention;

[0048] FIG. 2 is a circuit diagram for and a diagrammatic view of one embodiment of an arrangement of the light sources;

[0049] FIG. 3 is a circuit diagram for and a diagrammatic view of another embodiment of an arrangement of the light sources; and

[0050] FIGS. 4 and 5 are respective graphical illustrations of the correlation between current and light intensity pulses in the process according to the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0051] An apparatus 10 for coating substrates 1 is illustrated in FIG. 1. Solar cells 1a are used as substrates in the present example. The apparatus 10 includes a coating tank 12, which comprises a coating bath 13, which contains an electrolytic coating liquid 14.

[0052] A conveying device 15, which comprises upper conveying rollers 16 and lower conveying rollers 18, is provided in the upper part of the coating tank 12. The solar cells 1a are held between the upper and lower conveying rollers 16, 18 and conveyed in the direction of the arrow 5. Since the coating tank 12 is filled with the coating liquid 14, the solar cells 1a are completely within the coating bath 13.

[0053] A circulation device 30 for producing a flow in the coating bath 13, which has a first liquid conductor 36, is provided. The coating tank 12 has a first outlet 22 below the conveying device 15, to which the first liquid conductor 36 is connected. The coating liquid 14 is pumped from the coating tank 12 via the first outlet 22 and fed back into the coating tank 12 through a first inlet 20, which is arranged in the bottom region of the coating tank 12, by means of a first pump 32 arranged in this first liquid conductor 36.

[0054] An inlet flow system 40 with an inlet pipe 42 in the interior of the coating tank 12 is connected at one end to the first liquid conductor 36. At the other end of the inlet pipe 42 a horizontally oriented distributor pipe 44 is connected, in which a plurality of Venturi nozzles 46 are provided. These Venturi nozzles 46 are oriented vertically and thus arranged perpendicular to the solar cells 1a.

[0055] The input coating liquid flows with a high speed from these Venturi nozzles 46 and thus impinges substantially perpendicularly on the facing or front side 3 of the solar cells 1a to be coated from below (see FIG. 2).

[0056] So that this flow of coating liquid is not disturbed by parts or components of the apparatus, these Venturi nozzles 46 are arranged between the anodes 54 of the direct current circuit 50 (see FIG. 2). Light sources 64, which are LED light strips, are arranged above the anodes 54. The arrangement of light strips is only illustrated schematically. Especially this leads to turbulent flow on the surface 3 of the solar cells 1a, so

that the coating liquid 14 can regenerate rapidly in the vicinity of the surface 3 to be coated during the interval between the pulses.

[0057] In order to produce a flow opposite to the conveying direction 5 within the coating bath the coating tank 12 has a second outlet 23 in its left lower region. A second liquid conductor 38 is connected to this second outlet 23. A second pump 34 is provided in the second liquid conductor 38. This conductor 38 opens into a second inlet 21 in the upper right region of the coating tank 12. The second inlet 21 is located in the vicinity of the solar cells 1a, so that a horizontal flow in a direction opposite to the conveying direction 5 is produced between the second inlet 21 and the first outlet 22.

[0058] The apparatus 10 for example can be equipped without the second liquid conductor 38. Another embodiment of the apparatus can be designed without the inlet flow system 40 with and without the second liquid conductor 38. In the embodiment without the second liquid conductor 38 the first liquid conductor 36 is preferably connected to the second inlet 21 to the coating tank 12.

[0059] A solar cell 1a is illustrated in the detailed cross-sectional view that is part of FIG. 2. It has a metallization on its back side 2 and strips 4 comprising a suitable paste for formation of contact fingers on its front side 3. Screen printing paste is advantageously used for formation of the electrode structures. Metal is deposited from the electrochemical coating liquid only in the vicinity of this screen printing paste during the electrochemical deposition.

[0060] The upper conveying rollers 16 contact the metallized rear side 2 of the solar cells 1a and can be used for application of an electrochemical current. For this purpose an electrolytic cell rectifier circuit 50 is provided, which connects the upper transport rollers 16 with the anodes 54, which are preferably silver anodes. A first voltage source 52 and a pulse generator 53 are provided in the electrolytic cell rectifier circuit 50. Current pulses are applied to the solar cells 1a and the anodes 54 by means of the pulse generator 53.

[0061] Furthermore a light source 64, e.g. a LED, is shown in FIGS. 2 and 3 and represents a plurality of light sources for irradiation of the surface 3 of the substrate to be coated. This light source 64 is connected in a light source circuit 60, which has a second voltage source 62.

[0062] Both circuits 50 and 60 are coupled with each other by means of an optocoupler 56. The input 57 of the optocoupler 56 is connected to the electrolytic cell rectifier circuit 50 and the outlet 58 of the optocoupler is connected to the light source circuit 60.

[0063] The optocoupler 56 is switched in such way that the light source 64 is turned on at the same time that a current pulse is generated, so that the light pulse is produced simultaneously with the current pulse. During the time interval between the current pulses the light source 64 is turned off.

[0064] In FIG. 3 an additional embodiment of the apparatus according to the invention is illustrated, in which no optocoupler 56 is provided. Instead of the optocoupler 56 the light source circuit 50 is connected directly to the pulse generator 53, which thus produces the pulse for both circuits 50 and 60.

[0065] Optionally a second control device 66 can be provided in the light source circuit 60. The control device 66 can control the light pulse strength for example according to the length of the pulse, i.e. the pulse width.

[0066] Similarly a control device 59 can be provided, with which current pulses having different pulse widths and height can be generated. A completely automatic electroplating pro-

gram with individual coating steps may be provided by means of both control devices 59, 60. This is of special advantage in order to form graduated layers on which specific electrode structures are formed by the paste 4.

[0067] Two diagrams of the current pulses and the light pulses are illustrated in FIG. 4. The light pulses and the current pulses are of equal length. Respective time intervals are provided between the current pulses and the light pulses, which are of the same length as the pulse widths. The light pulses and the current pulses are completely synchronized. The light intensity is zero between the pulses in the time interval. In order to achieve this the light source can be turned off or masked during the time interval.

[0068] Another embodiment of the process according to the invention is illustrated in FIG. 5, in which a direct current, with a value I_1 , is applied during the time interval between the current pulses. The current, I_1 , amounts to 50% of the current I_2 , which is applied to the substrate during the current pulses. The current pulse in the embodiment of FIG. 5 is the same height as that shown in FIG. 4.

PARTS LIST

[0069]	1 substrate
[0070]	1a solar cell
[0071]	2 rear side
[0072]	3 front side
[0073]	4 paste
[0074]	5 conveying direction
[0075]	10 apparatus
[0076]	12 coating tank
[0077]	14 electrolytic coating liquid
[0078]	15 conveying device
[0079]	16 upper conveying rollers
[0080]	18 lower conveying rollers
[0081]	20 first inlet
[0082]	21 second inlet
[0083]	22 first outlet
[0084]	23 second outlet
[0085]	30 circulating device
[0086]	32 first pump
[0087]	34 second pump
[0088]	36 first liquid conductor
[0089]	38 second liquid conductor
[0090]	40 inlet flow system
[0091]	42 inlet pipe
[0092]	44 distributor pipe
[0093]	46 Venturi nozzle
[0094]	50 electrolytic cell rectifier circuit
[0095]	52 first voltage source
[0096]	53 pulse generator
[0097]	54 anode
[0098]	56 optocoupler
[0099]	57 input of the optocoupler
[0100]	58 output of the optocoupler
[0101]	59 first control device
[0102]	60 light source circuit
[0103]	62 second voltage source
[0104]	64 light source, LED
[0105]	66 second control device

[0106] While the invention has been illustrated and described as embodied in a process and apparatus for electroplating substrates, it is not intended to be limited to the

details shown, since various modifications and changes may be made without departing in any way from the spirit of the present invention.

[0107] Without further analysis, the foregoing will so fully reveal the gist of the present invention that others can, by applying current knowledge, readily adapt it for various applications without omitting features that, from the standpoint of prior art, fairly constitute essential characteristics of the generic or specific aspects of this invention.

[0108] What is claimed is new and is set forth in the following appended claims.

We claim:

1. An apparatus for electroplating at least one surface (2,3) of at least one substrate (1), said apparatus comprising an electrochemical coating bath (13), which has a coating tank (12) filled with an electrochemical coating liquid (14); a conveying device (15) for transporting the at least one substrate through the coating bath; a light source circuit (60) with at least one light source (64) for irradiating the at least one substrate (1); an electrolytic cell rectifier circuit (50) for the at least one substrate with anodes (54); and means for producing synchronous current pulses and light pulses, so that during a time interval between said current pulses the irradiating with the at least one light source is interrupted.
2. The apparatus as defined in claim 1, wherein the means for producing synchronous current pulses and light pulses comprises at least one pulse generator (53) in the electrolytic cell rectifier circuit (50) and/or in the light source circuit (60).
3. The apparatus as defined in claim 2, wherein said electrolytic cell rectifier circuit (50) and said light source circuit (60) are electrically connected to said at least one pulse generator (53).
4. The apparatus as defined in claim 1, wherein the light source circuit (60) is coupled with the electrolytic cell rectifier circuit (50) by an optical coupler (56).
5. The apparatus as defined in claim 1, wherein the light source circuit (60) and/or the electrolytic cell rectifier circuit (50) has at least one control device (59, 66), which controls a light intensity of the at least one light source (64) and/or amplitudes of the current pulses in accordance with respective widths of the current pulses.
6. The apparatus as defined in claim 1, further comprising means for producing a flow of the electrochemical coating liquid (14).
7. The apparatus as defined in claim 6, wherein said means for producing the flow of the electrochemical coating liquid (14) comprises at least one nozzle for conducting the electrochemical coating liquid (14).
8. The apparatus as defined in claim 7, wherein the at least one nozzle is arranged in the coating bath (13) opposite to the at least one surface (2,3) of the at least one substrate (1) to be coated.
9. The apparatus as defined in claim 7, wherein the at least one nozzle in the coating bath (13) is oriented in a direction perpendicular to the at least one surface (2,3) of the at least one substrate (1) to be coated.
10. The apparatus as defined in claim 7, wherein the at least one nozzle is arranged between the anodes (54) of the electrolytic cell rectifier circuit (50).
11. The apparatus as defined in claim 7, wherein the at least one nozzle is at least one Venturi nozzle (46).

12. The apparatus as defined in claim 6, wherein said means for producing the flow of the electrochemical bath liquid (14) comprises a circulating device (30).

13. The apparatus as defined in claim 12, wherein said circulating device (30) is a countercurrent flow device.

14. A process for electroplating at least one surface of at least one substrate, said process comprising the steps of:

- a) moving the at least one substrate through an electrolytic coating liquid;
- b) during the moving of the at least one substrate irradiating the at least one substrate with light;
- c) during the irradiating applying an electric current to the at least one substrate by means of an electrolytic cell rectifier circuit; and
- d) pulsing the electrical current and the light synchronously, so that during a time interval between current pulses the irradiating is interrupted.

15. The process as defined in claim 14, wherein pulse widths of light pulses produced by the pulsing of the light and of the current pulse are each from 0.1 ms to 10,000 ms.

16. The process as defined in claim 14, wherein said time interval between the current pulses is equal to a pulse width of said current pulses.

17. The process as defined in claim 15, wherein the current pulses and the light pulses are rectangular-shaped pulses.

18. The process as defined in claim 15, wherein the light pulses and the current pulses have respective pulse widths and/or respective amplitudes and said respective pulse widths and/or said respective amplitudes are varied during the process.

19. The process as defined in claim 15, wherein the more the amplitudes of the light pulses are reduced, the greater are the pulse widths of the light pulses.

20. The process as defined in claim 14, further comprising applying a direct current (I_1) to the at least one substrate during said time interval between the current pulses that is less than or equal to one half of a current (I_2) applied during the current pulses.

21. The process as defined in claim 14, wherein the electrochemical bath liquid flows in a direction that is opposite to a conveying direction (5) of the at least one substrate at least in the vicinity of the at least one surface of the at least one substrate to be coated.

22. The process as defined in claim 21, further comprising a turbulent flow of the electrochemical bath liquid at least in the vicinity of the at least one surface of the at least one substrate to be coated.

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