

Title: A method of producing a tin oxide coating

The invention is related to a method of producing a tin oxide coating.

Tin oxide is a semi-conducting transparent material with various beneficial properties such as a high reflectivity for infrared light, a high mechanical hardness, and a good environmental stability. These properties result in a variety of applications for tin oxide coatings. Tin oxide coatings are regularly applied as heating elements in aircraft windows. By applying a voltage difference over a tin oxide coating on such a window it becomes heated and any ice or fog on the window will evaporate. By the high reflectivity, tin oxide applied to windows reflect infrared radiation, and, hence, reflects heat as emitted by objects. This makes that the thermal insulation of a window with a tin oxide coating may be doubled, without significant loss of transparency. Tin oxide may also be applied as a protective and wear resistant coating on a glass container. Nowadays most of the glass bottles produced are coated with a 10-100 nanometer thin layer of tin oxide, allowing for a reduction of 20 % in weight of the bottle without compromising on the strength.

Tin oxide may also be doped. The application of a fluorine doped tin oxide coating improves amongst other properties the insulating properties of a glass window. Because of its excellent transparency and conductive properties, fluorine doped tin oxide layers are furthermore often used as a top electrode in for instance an amorphous silicon solar cell.

Other applications are to be found in displays, gas sensors, antistatic coatings on instrument panels and transparent electrodes in electro luminescent lamps.

The most common technique for depositing tin oxide coatings, especially on glass, is Chemical Vapour Deposition (CVD). The CVD process

has the advantage that it can be used in a continuous process for depositing uniform, homogeneous coatings on large areas, at often large deposition rates.

In the CVD process, chemically reacting gases are used to deposit a thin solid coating on a substrate. The chemically reacting gases, may comprise
5 a suitable tin compound and an oxidizing agent. For tin oxide-CVD, three different precursor recipes are used on an industrial scale.

Dimethyltin dichloride, having the disadvantage of being toxic, has been used with oxygen and/or a mixture of oxygen and water vapour as oxidizing agent.

10 Also monobutyltin trichloride has been used with oxygen and/or an oxygen and water vapour mixture as oxidizing agent.

By far the cheapest tin precursor however is Tin TetraChloride (TTC). With oxygen, the oxidizing rate of TTC is particularly low if occurring at all, and as such the combination of solely TTC and oxygen is hardly suitable
15 for industrial applicability.

With water vapour on the other hand, tin oxide formation occurs straight away. As soon as TTC and water react, a powdery deposit is left. To avoid an uncontrolled manner of the formation of this powdery deposit, one needs to either separate the TTC and water until deposition is desired.

20 Alternatively, one can provide conditions which inhibit the reaction between TTC and water. Such conditions may imply keeping the gas mixture of water and tin tetrachloride prior to deposition within a specified temperature range of 150°C -190 °C and at a ratio of 1 mol TTC to 5 mol of H₂O. However due to inaccuracy and/or failure of heating equipment, reaction may still occur at
25 places far from the substrate. It may also be difficult to keep the gas feed passages within the relatively small temperature range in which deposition does not take place. The powdery deposition leads to blockage of these passages. These deposition problems cause much downtime for cleaning of the CVD equipment, ultimately leading to an unfavourable cost effective
30 deposition process of tin oxide.

Another solution for the problem of deposition in unwanted areas is the supply in separate gas streams of tin tetrachloride and water vapour to the coating zone. The coating zone is defined as the zone in which deposition of the coating is desired. By providing tin tetrachloride and water vapour separate,
5 premature reaction of the tin salt with the water vapour, which causes solid deposits being formed in the interior of a vapour feed passage, is avoided. However once the tin tetrachloride and water vapour meet near the surface of the substrate, reaction will occur, and powder may be deposited with a detrimental effect on the quality of the tin oxide coating.

10 It is an object of the invention to provide a method for deposition of a tin oxide coating wherein the unwanted deposition outside the coating zone is avoided, or at least reduced.

The present inventors found that this aim is reached by a tin oxide coating process comprising two steps.

15 More in detail, the present invention relates to a method of producing a tin oxide coating comprising the steps of:

- providing a primary film of tin oxide on a substrate; and
- producing a tin oxide coating on said primary film by Chemical Vapour Deposition (CVD) comprising reaction of a substantially anhydrous gas
20 mixture comprising tin tetrachloride and oxygen and an alcohol.

Preferably, the alcohol comprises methanol.

Without wishing to be bound by any theory, it is believed that the primary film of tin oxide act as a catalyst in the CVD reaction of methanol and oxygen forming carbon dioxide and water. Subsequently, this water, present at
25 the tin dioxide surface, reacts with tin tetrachloride to form tin oxide and hydrogen chloride.

This allows for the use of a gas mixture of tin tetrachloride which is substantially anhydrous and hence less reactive, preventing early deposition outside the coating zone. In other words, the gas mixture used for production
30 of a tin oxide coating on the primary film of tin oxide will not lead to blockage

of gas feed passages by powdery deposits and will not lead to a considerable deposition of material outside the coating zone in the reactor. As a consequence, the down time period of the CVD reactor is dramatically reduced, allowing for a more cost effective production process of tin oxide coatings on an industrial scale.

A further advantage is that the water is formed on the substrate with the primary film, where the water is needed for the subsequent formation of tin oxide.

It will be clear that with the term "a substantially anhydrous gas mixture" is meant a gas mixture to which water is not deliberately added, i.e. the feed stream is essentially not containing water. The amount of water vapour present in the gases of the gas mixture is sufficiently low to minimize or avoid completely formation of tin oxide outside the coating zone.

The primary film of tin oxide may be deposited on the substrate by an entirely different process and/or in an entirely different reactor. However, the deposition of the tin oxide coating and a deposition of the primary film of tin oxide may also be done in the same reactor. The primary film of tin oxide may under certain conditions even be found with the anhydrous gas mixture of TTC, oxygen and an alcohol. In that case the primary film of tin oxide may be formed by reaction of TTC and an aliquot of water which is for instance absorbed on the substrate surface. If no water (vapour) at all appears to be present in the reactor and/or on the substrate, the water supply only needs to be switched on for the very first stages of the deposition process, still enormously reducing deposition of material outside the coating zone as compared to the amount of deposit outside the coating zone in prior art methods.

In a more preferred embodiment of the present invention, the tin tetrachloride, oxygen and alcohol are pre-mixed before entering a CVD reactor. In this way, mixing of the gases, causing turbulence, can take place before the gas mixture is fed into the CVD reactor. The composition of the gas mixture

will then be homogeneous within the gas mixture by the time the gas mixture reaches the substrate where the deposition under the presumed catalysis by the tin oxide takes place. This allows for more controlled and homogeneous growth of the tin oxide coating on the primary film of tin oxide.

5 In a more detailed embodiment of the present invention the premixed tin tetrachloride, oxygen and alcohol is kept at a temperature within a range of -10 °C to 800 °C outside the CVD reactor.

 It is therefore not necessary to keep this pre-mixed gas mixture within a narrowly defined temperature range to avoid early deposition,
10 eliminating the risk that due to failure and/or inaccuracy of heating (control) equipment undesired deposition may still occur outside the coating zone. It may however still be advantageous, to keep the pre-mixed gas mixture within an elevated temperature range to avoid feeding a relatively cool gas mixture into the direction of the primary film of tin oxide at the substrate. Also at these
15 higher temperatures the gas mixture will not react and form the powdery deposit as long as, as is believed, there is no primary tin oxide present to aid the formation of water. As stated before, tin oxide deposition will predominantly take place in the coating zone in which the primary tin oxide film is placed. The method according to the invention provides a very easily
20 controlled, clean and convenient production process.

 The tin oxide film has a thickness of at least 0.5 nanometer. This means that at least a film comprising the unit cell of the crystal structure of tin oxide is present on the substrate. Preferably this film has a large coverage of the substrate. However, it is believed that tiny patches of uncovered
25 substrate will not prevent production of the tin oxide coating on the primary film of tin oxide. Those skilled in the art will easily find suitable coverage ranges. A thin film of tin oxide may even be formed by the reaction of TTC and water that is absorbed to the substrate surface. Also a few ppm of water vapour which is under practical conditions often initially present in a reactor

and/or a gas mixture may be enough to allow for formation of parts of a tin oxide film on the substrate.

In a more detailed embodiment of the invention, the tin oxide film in the coating zone is kept at a temperature within a range of 180°C-1000°C. This provides activation of the gases at the surface where the reactions occur. This wide temperature range also provides a part of a large parameter space in which the process may be fine-tuned to obtain highly desired specifications of the process and/or the tin oxide coating. Of course, when a heated premix of the used CVD gases is used, the temperature of the premix gases is preferably adapted to the temperature of the reaction zone.

According to a further detailed embodiment of the invention, the tin tetrachloride is present in a range varying from at least 0.1 mol % of a total gas mixture up to and including 20 mol % of the total gas mixture; oxygen is present in an amount of at least 0.1 mol % of the total gas mixture; and alcohol is present in an amount of at least 0.1 mol% of the total gas mixture. Also this enormous composition parameter space allows for optimizing the composition of the total gas mixture in order to achieve optimisation with respect to for instance growth rate, reactor geometry, desired tin oxide coating characteristics, cost- and/or energy efficiency. It may still be possible, if so desired, to supply each gas to the pre-mixing stage mixed with a diluent. Advantageously the diluent is a substantially inert gas, such as nitrogen.

According to another embodiment of the present invention, hydrogen fluoride is present in the gas mixture in a range varying from at least 0.1 mol % of a total gas mixture up to and including 10 mol% of the total gas mixture. Incorporation of fluorine as a dopant in the tin oxide coating enhances, amongst other properties, the conductivity of the coating. This may be very advantageous for, for instance, use of a tin oxide coating on or as a top electrode of an amorphous silicon solar cell.

In a very advantageous embodiment of a method according to the invention, the tin oxide film is provided on a substrate selected from the group

consisting of glass, steel and aluminum. Each of these substrate materials may be provided with large surface areas.

Glass and steel are often provided in the shape of large but relatively thin plates. With the present invention it will be possible to deposit a tin oxide coating on the whole surface area without having to either take a number of precautions to avoid deposition of material outside the coating zone or discontinue the coating process due to blockage of for instance gas feed passages. Moreover, by carefully selecting the reaction conditions in combination with the controlled formation of tin oxide areas, the formed tin oxide areas can also be used as a kind of pattern.

Use of aluminum as a substrate allows for enormous batch sizes as aluminum may be coated with tin oxide whilst passing from roll to roll. Especially in the production of solar cells, this embodiment of the method according to the present invention would be very advantageous in terms of cost efficiency. Furthermore, using an aluminum sheet as a substrate allows for the production of a flexible top electrode of a solar cell.

The invention is further related to a use of film of tin oxide to allow CVD using anhydrous gas mixtures containing a tin precursor gas, oxygen and an alcohol. This additionally makes it possible to avoid or reduce the deposition of tin oxide by CVD in unwanted areas.

The present invention will now be further illustrated while referring to the following, non-limiting example.

EXAMPLE

Sample 1 is an uncoated glass substrate (reference sample). Sample 2 is a glass plate on which a primary film of tin oxide is deposited using tetramethyltin and oxygen. The thickness of the primary thin film of tin oxide is 347 nm.

Both samples are placed in an atmospheric pressure moving belt reactor (type Watkins Johnson WJ998). The samples are transported by the moving belt, with a speed of 6.4 cm/min, through a furnace regulated at 550 °C. Through a standard Watkins Johnson injector a gas mixture of TTC, methanol, oxygen
5 and nitrogen, with concentrations of 7.3 gram/hour, 0.15 sccm oxygen and 6.6 sccm nitrogen respectively. The mole fraction of TTC methanol is 1:5. The analysis of the coatings deposited on top of the samples as carried out by stepprofilometry reveals that on sample 1, the uncoated glass substrate, a tin oxide coating with a thickness of 68 nm has been deposited and that on sample
10 2, the glass plate within the primary film of tin oxide, a tin oxide coating with a thickness of 108 nm has been deposited.

Claims

1. A method of producing a tin oxide coating comprising the steps of:
 - providing a primary film of tin oxide on a substrate; and
 - producing a tin oxide coating on said primary film by Chemical Vapour Deposition (CVD) comprising reaction of a substantially anhydrous gas mixture comprising tin tetrachloride, oxygen and an alcohol.
2. A method according to claim 1, wherein said alcohol comprises methanol.
3. A method according to claim 1 or 2, wherein the tin tetrachloride, oxygen and alcohol are premixed before entering a CVD reactor.
4. A method according to claim 3, wherein the premixed tin tetrachloride, oxygen and alcohol is outside the CVD reactor kept at a temperature within a range of -10 °C to 600 °C.
5. A method according to anyone of the previous claims wherein said primary film has a thickness of at least 0.5 nm.
6. A method according to any one of the previous claims, wherein said primary film is kept at a temperature within a range of 180 °C – 1000 °C.
7. A method according to any one of the previous claims, wherein tin tetrachloride is present in a range varying from at least 0.1 mol % of a total gas mixture up to and including 20 mol% of the total gas mixture; oxygen is present in an amount of at least 0.1 mol% of the total gas mixture; and said alcohol is present in an amount of at least 0.1 mol% of the total gas mixture.
8. A method according to anyone of the previous claims, wherein hydrogen fluoride is present in the gas mixture in a range varying from at least 0.1 mol % of a total gas mixture up to and including 10 mol% of the total gas mixture.
9. A method according to anyone of the previous claims, wherein said primary film is provided on a substrate selected from the group consisting of glass, steel and aluminum.

10 Use of film of tin oxide to allow CVD using anhydrous gas mixtures containing a tin precursor gas, oxygen and an alcohol.