SOLAR CELLS HAVING FILM FORMED INTEGRAL COVERS

This invention relates to solar cells having film formed integral covers formed from selected compositions and having a coefficient of expansion similar to that of the solar cell.

Solar cell covers have heretofore been provided for protecting solar cells from high energy particle radiation in space. Such solar cell covers have typically been comprised of thin sheets of fused silica which are cemented over the tops of the cells. In order to prevent degradation of the adhesive, it has been necessary to provide an ultra-violet light blocking filter on the cover. Covers having these capabilities are described in the United States Patent No. 4293732.

For space power systems there is a continuing need for lightweight solar cell arrays. As the requirements for power per satellite increase, there is an increasing need for lighter weight arrays. Although at the present time it is possible to manufacture relatively thin (i.e., a 2 mm solar cell having high performance), there does

not now exist a light weight cover with proven performance for protecting the light weight solar cell. Unless a new type solar cell cover is developed, future satellite programs may be faced with the prospect of cementing a 4 to 6 mm thick cover to a 2 mm thick cell in order to provide the required cell lifetime. Numerous attempts have heretofore been made to deposit covers directly to the surface of the solar cell. However, no cost effective manufacturing process has emerged which provides a real solution to the problem. There is, therefore, a need for a new and improved integral solar cell cover.

In one aspect the present invention provides a solar cell construction which comprises a solar cell and a film integral with the solar cell and covering the surface of the cell and formed from a composition comprising Al and/or Si with O and/or N, the composition having a coefficient of expansion similar to that of the solar cell.

In one embodiment the present invention provides a solar cell construction wherein the film is formed of a composition selected from SiO_2+Si_3N_4, SiO_2+Al_2O_3 or AlN+Si_3N_4 systems, the composition having a coefficient of expansion similar to that of the solar cell.

The term "Al-Si-O-N quaternary system" is used herein to refer to the compositions of Al and/or Si with O and/or N from which the solar cell cover is formed.

Our copending application No. 8012859 (publication No. 2048230) claims an apparatus and process for forming a mixed oxide and/or nitride and/or sulphide thin film on the surface of an article to be coated. This apparatus and process may be used to form the solar cells of the present invention.

At least in preferred embodiments, the invention claimed in our copending application comprises a contained plasma source in a cavity in which an RF field may be generated to ionise gas and form a plasma.

The article to be coated is placed outside the cavity which has an exit directed towards the article. Into the cavity is fed a gas comprising the non-metallic component of the thin film, for instance oxygen, nitrogen or a sulphur-containing compound. This gas is formed into a plasma and caused to exit from the cavity to impinge on the surface of the article to be coated.

A gas comprising the metallic or semi-metallic component of the thin film material, for instance a mixture of $AlCl_3$ and SiH_4, is either introduced into the cavity or directed out of a nozzle adjacent the article to be coated. In any event, the two gases react to form the thin film material which is deposited on the article.

The thickness of a solar cell cover formed by the

method of our copending application may be as little as 100 μm, and such a solar cell forms one embodiment of the invention.

The invention and above-discussed method and apparatus are further described below by way of example only and with reference to the accompanying drawings, in which:

Figure 1 is a schematic illustration of an apparatus incorporating the present invention and showing one method for forming an integral solar cell cover by deposition of silicon dioxide and aluminum oxide by a plasma-activated in-cavity oxidation of a silicon compound and an aluminum compound;

Figure 2 is a schematic illustration similar to Figure 1 showing the formation of an integral solar cell cover by deposition of silicon dioxide and aluminum oxide by external oxidation of a silicon compound and an aluminum compound in a plasma-activated oxygen discharge; and

Figure 3 is another schematic illustration similar to Figures 1 and 2 showing a method and apparatus for forming an integral solar cell cover by the deposition of silicon dioxide and aluminum oxide by evaporation of solid silicon dioxide in a plasma-activated in-cavity oxidation of an aluminum compound.

In the method which is utilized for forming a mixed oxide/nitride film from materials selected from the Al-Si-O-N quaternary system on articles such as solar cells by use of a plasma-activated source, the source is provided with a cavity and with means for generating a radio frequency field within the cavity. At least one of the constituents for the film is selected as a compound vapor. This compound vapor is chemically reacted with at least one other constituent to form the film with the temperature of the article preferably being maintained at a temperature of less than approximately 400°C or even below 150°C.

The apparatus 11 having a contained plasma source incorporating the present invention as shown in Figure 1 is similar to plasma activated sources such as those disclosed in United States Letters Patent 3,801,355 and 3,922,214. It is provided with a container 12 provided with a side wall 13 and top and bottom walls 14 and 16. Thus, as shown, the container 12 can be in the form of a closed end cylinder which forms a cylindrical cavity 17. The container or cylinder 12 is provided with a top opening 18 through which the plasma is discharged as

hereinafter described. It is also provided with a bottom hole 19 which is connected to piping 21 which is utilized for conducting selected gases into the cavity 17.

The container 12 is formed of material so that it will serve as a non-evaporating cavity, that is, it will not be evaporated by the plasma which is formed in the cavity. The material which is utilized is an insulating material which has relatively high melting and boiling points. By way of example, the container or cylinder 12 can be formed of a boron nitride which has very high melting and boiling points so that it is very difficult to evaporate the boron nitride from the wall or to deform the cavity shape. It has been found that fused quartz forms a relatively inexpensive satisfactory material for the formation of the cavity for low power plasmas.

Radio frequency energy is introduced into the cavity in a suitable manner such as by capacitive coupling or inductive coupling well known to those skilled in the art. Thus, there has been provided a helically wound induction coil 22 which surrounds the cylindrical container 12 and which is connected to a suitable source 23 of RF power. By way of example, the RF source 23 can have a power capability of 5 to 6 KW at a frequency of 13.6 MHz. By

providing a relatively low power, as for example a 1-1/2 KW from the RF generator to the coil 22, it is possible to operate the plasma generator shown in Figure 1 without causing evaporation of the silicon dioxide of which the cavity is formed whereby the silicon dioxide or fused silica cavity serves as a non-evaporative cavity.

A vacuum chamber 26 is formed by housing 27. The housing 27 is provided with an opening 28, not shown in Figure 1, which is connected to a suitable source of vacuum (not shown) for evacuating the chamber 26 and also for evacuating the cavity 17 provided within the container 12. The housing 27 can be such a size so that the entire container 12 can be mounted therein or alternatively the housing 27 can be mounted or associated with the container 12 in such a way that the chamber 26 is in communication with the cavity 17 through the opening 18 provided in the container 12.

Means (not shown) is provided within the housing 27 to permit the introduction of one or more solar cells 31 on which an integral solar cell cover is to be provided. Such solar cells 31 are of a conventional type and will not be described in detail.

In utilizing the apparatus which is shown in Figure 1 in order to provide a mixed oxide and/or

nitride thin film to form an integral solar cover for the solar cell 31, materials are selected from the Al-Si-O-N quaternary system. One or more constituents are introduced into the apparatus as a compound vapor and are chemically reacted to the required oxide or nitride within the plasma activated source or at the solar cell substrate while maintaining the solar cell substrate at a temperature which is below 400°C or even below 150°C. Thus, as shown in Figure 1, aluminum trichloride ($AlCl_3$) and silane (SiH_4) are introduced with oxygen (O_2) as a mixed gas through the piping 21 and introduced into the cavity 17. Operation of the RF power source 23 creates a radio frequency field within the cavity 17 to ionize the gas within the cavity to create a plasma. The plasma causes a chemical reaction to take place within the cavity so that the silane and the aluminum trichloride are oxidized. The silicon and the aluminum-containing products are in the vapor form and will pass with an oxygen plasma stream through the opening 18 into the chamber 26 so that they will strike the bottom side or surface of the solar cell cover 31. As the silicon and the aluminum-containing compound vapors in combination with the activated oxygen strike the solar cell or substrate, they will deposit a mixed

film of silicon dioxide (SiO_2) and aluminum oxide (Al_2O_3) with the oxygen plasma aiding and ensuring that the materials which are deposited upon the solar cell are fully reacted, or in other words, are in fully oxidized conditions at the time of deposition. The pressure differential (the pressure in the chamber 26 is less than in the cavity 17) makes possible a sustained plasma reaction in the high pressure region within the source while maintaining substantially collision free paths for the molecules in the vapor stream to the substrate.

When the materials for the combination of chemical reactions are selected such that premature thermal decomposition and solid product deposition will not occur within the cavity nor within the gas supply piping 21, the length of time that the apparatus can operate in a steady state condition would be substantially unlimited. Therefore, it is possible to run such apparatus continuously or for long periods of time which particularly lends itself to continuous operations such as roll coating.

Although the apparatus has been described in conjunction with the providing of integral covers on silicon solar cells, the same apparatus can be utilized for placing covers on gallium arsenide (GaAs) in solar cells. In order to prevent degradation of the

solar cells or the substrates, deposition temperatures will be such that the substrate temperatures may be maintained below 400°C or even 150°C. If desired, various deposition parameters can be varied such as the ratio of the reactant gases, the total reactant gas pressure and the RF power. It is desirable to match closely as possible the thermal expansion of the cover to the thermal expansion of the substrate. In changing from a silicon substrate to a gallium arsenide substrate, it will be necessary to modify the reactant gas ratio to favor the deposition of a mixture which has a higher coefficient of thermal expansion. For example, in the aluminum oxide (Al_2O_3) and silicon dioxide (SiO_2) film, matching to a gallium arsenide substrate will result from an increase in the $AlCl_3$:SiH_4 ratio to promote the deposition of a more aluminum-rich glass.

During the deposition of such materials and as they are modified to match the semiconductor substrates thermomechanically, it is desirable to deposit simultaneously on witness plates to verify that the cover layer transparency has been maintained.

The integral solar cell covers can be deposited to the desired thickness, for example, in the order of several mm or even thicker, to provide the desired radiation protection.

It should be appreciated that although the apparatus and method have been described in conjunction with Figure 1, that the materials used could be introduced in a vapor form. It also should be appreciated that it would be possible to form an aerosol of the liquid and to form a gas in the plasma within the cavity. Alternately, a liquid or powder compound could be introduced into the cavity and evaporated at the relatively low power limits of the source without evaporating the container forming the cavity.

Another apparatus for thin-film coating is shown in Figure 2 in which the apparatus is very similar to that shown in Figure 1 with the exception that certain portions as, for example, the vacuum chamber have not been shown. In this embodiment of the invention, oxygen and gas or an oxygen containing gas mixture is introduced through the piping 21 into the cavity 17 wherein an oxygen plasma is formed and discharged through the top opening 18 so the oxygen comes into contact with the bottom side of the solar cell 31. At the same time one or more of the constituents selected in connection with Figure 1 are introduced as reactive gases through an auxiliary nozzle (not shown) which is located outside of the cavity 17 but within the housing forming a vacuum chamber and

adjacent the surface of the substrate or solar cell which is to be covered. The oxygen plasma which is generated within the source then chemically reacts with the vapors at or near the surface of the substrate causing them to decompose or to oxidize to form a mixed film of the materials in the same manner as hereinbefore described in conjunction with Figure 1 to provide a cover on the solar cell 31.

It should be appreciated that, as well as oxygen, nitrogen can be used as the active species to form nitrides within the scope of the present invention. It also should be appreciated that in place of silane in the method shown in conjunction with Figure 1, it may be desirable to utilize a different material because of the tendency of silane, which is very reactive with oxygen, to form SiO_2 powder within the cavity which could possibly close up the top opening 18. To avoid such a problem, it is only necessary to select a less reactive silicon compound such as tetraethylorthosilicate (TEOS) $(C_2H_5O)_4Si$.

It also should be appreciated that apparatus can be utilized for generating a plasma using an inert gas such as argon or helium with the principal disadvantage being a slower process because of the

coupling geometry in the gas flow. When an inert gas plasma is utilized, the reactive agents are supplied in vapor form. In both of the types of the apparatus shown in Figures 1 and 2, it can be seen that a non-evaporating type cavity is utilized.

In another apparatus which is shown in Figure 3, vapor is formed from silicon dioxide powder introduced into the plasma. Higher power is provided in the formation of the plasma within the cavity to cause evaporating of the SiO_2. In addition, auxiliary gasses are supplied through the piping into the cavity 17, thus as shown, oxygen and aluminum trichloride are introduced and gas is formed in the cavity which is combined with the evaporating of the solid SiO_2, so that there is provided in the cavity oxidation of the aluminum compound to provide the aluminum oxide (Al_2O_3) and the SiO_2 which passes through the opening 18 with the oxygen plasma to impinge upon the bottom surface of the solar cell 31 to form a mixture of the silicon dioxide and the aluminum oxide in the manner hereinbefore described.

In the apparatus shown in Figures 1, 2 and 3, the RF coils have been shown surrounding the container 12 formed in the cavity 17. It should be appreciated that if desired, RF coils can be provided at a different location, as for example, below the container

12. When this is the case, a flux concentrator (not shown) well known to those skilled in the art can be utilized for transferring flux to the level of the cavity to form the plasma hereinbefore described.

From the foregoing it can be seen that it has been possible to deposit integral solar cell covers whose composition falls in the Al-Si-O-N quaternary system. Normally, the coating compositions are selected on the basis of optical transmittance and thermo-mechanical compatibility with the substrate. A table of the coefficients of expansion are set forth below:

TABLE I

Material	Coeff. of Thermal Exp. ppm/°C
Si	4.2
SiO_2 (fused silica)	0.5
Al_2O_3	8.0
Si_3N_4	2.69
AlN	4.89

A composition can be selected from the SiO_2 + Si_3N_4, SiO_2 + Al_2O_3 or AlN + Si_3N_4 systems. Starting materials employed can include hydrides or organometallics (e.g., triethylaluminum). The plasma-activated source, as hereinbefore described,

is employed to deposit these selected materials to provide mixed films which are fully reacted at high rates. As hereinbefore pointed out, to obtain the desired film composition, one or more of the constituents is introduced into the apparatus as a compound vapor and chemically reacted to the required oxide or nitride either within the solar cell or at the solar cell substrate. The solar cell substrate can be readily maintained at a temperature below 400°C so that its performance will not be degraded by the application of the integral solar cell cover. Because low temperatures can be maintained on the substrate, the method apparatus particularly lends itself to continuous roll coating on sheet material which cannot withstand high temperatures.

The method and apparatus hereinbefore described have a number of advantages in the formation of thin film coatings. In general, low deposition temperatures can be utilized to permit coating on substrates such as plastics which cannot withstand high heat, as for example, coating temperatures more than approximately 100-150°C. The rate of coating with the present method and apparatus is significantly higher than that which can be obtained by sputtering. The plasma source can be used continuously by the use of a non-evaporating cavity or by supplying powdered material to the cavity.

* C L M S *

CLAIMS:

1. A solar cell construction which comprises a solar cell and a film integral with the solar cell and covering the surface of the cell and formed from a composition comprising Al and/or Si with O and/or N, the composition having a coefficient of expansion similar to that of the solar cell.

2. A solar cell construction as claimed in Claim 1 wherein the film is formed of a composition selected from SiO_2+Si_3N_4, SiO_2+Al_2O_3 or AlN+Si_3N_4 systems.

3. A solar cell construction as claimed in Claim 1 substantially as hereinbefore described.

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