

LIGHT-ABSORBING MATERIALS

This invention relates to light absorbing materials, useful for absorbing solar energy.

10 This application is related to application number 8110704 (publication number 2 081 876).

The collection of energy derived from solar radiation is an alluring prospect. One method contemplated for solar energy utilization is the
15 production of heat through absorption of solar energy by an absorbing, i.e. black, material, utilized in a solar collector. Collectors are typically fabricated by depositing an absorbing material on a substrate that is an efficient heat conductor. Solar energy is
20 directed onto the absorber by an optical system. The heat produced by absorption is conducted through the substrate and is either exchanged with a heat transfer medium or used directly.

A variety of materials have been proposed as
25 solar absorbers. (See C.M. Lambert, Solar Energy Materials, 1, 319 (1979).) Exemplary of these absorbing materials is electroplated black chrome (a complicated mixture of chrome and chrome oxides), an evaporated platinum-aluminum oxide mixture, and a dendritic
30 tungsten material (described in Solar Energy 17, 119 (1975), Solar Energy Materials 1, 105 (1979), and Applied Physics Letters, 26, 557 (1975), respectively). Although each of these exemplary materials has desirable properties, each also has some limitations.

35 The use of solar concentrators (the focusing of

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solar radiation onto an absorbing material) has been contemplated to increase the efficiency of heat production and to yield higher temperatures for directly driving chemical reactions. Below 300 degrees C, the chrome mixture and the dendritic tungsten typically are useful. However, at increased temperatures both materials degrade. The chrome/chrome oxide compositions undergo decomposition induced by temperatures above 300 degrees C. The tungsten materials are stable in an inert atmosphere above 300 degrees C, but seriously degenerate at these temperatures in the presence of an oxidizing medium such as air. Thus, although most of the newer absorbing materials appear useful for solar energy absorption of one sun, at higher sun densities--temperatures experienced when solar concentration is employed--they exhibit significant problems. The platinum/aluminum oxide composite exhibits better stability, but is generally not useful above approximately 500 degrees C.

Beside the difficulties associated with solar concentration, many of the absorbing materials, including those previously discussed, have acceptable absorption efficiencies but re-radiate a substantial portion of the absorbed energy. This re-radiation results in decreased solar conversion efficiency. Additionally, presently available materials, such as the evaporated platinum/aluminum oxide mixture, are expensive and severely limit the applications for which solar energy is economical.

A light-absorbing body according to the invention has a portion containing a multiplicity of voids that intersect the surface of the body or channels open to the surface of the body forming a reticulated structure, wherein the mean depth of the voids is at least $0.3\mu\text{m}$, from 20 to 80 percent of the volume of the said portion measured to the mean depth consists of voids or channels, the width of the voids or channels is less than $3\mu\text{m}$, and

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the wall direction over 75 percent of the wall length within any localized area defined by a square 10 μ m on side is within 20 degrees of the mean direction for the walls within the localized area.

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Materials embodying the invention may be made by placing sample materials on a sputterable substrate, i.e. a body containing material such as aluminium that undergoes sputtering, and introducing an etchant gas that forms low melting compounds with the material sputtered from the substrate and which also anisotropically etches the sample material. For example, when the sample material is silicon, an appropriate gas is CCl_2F_2 and an appropriate substrate is aluminum. Using a semiconductor sample such as GaAs, Ge, or silicon, materials that have high absorptivity in the solar range between about $0.2 \mu\text{m}$ to $2.0 \mu\text{m}$ and high reflectivity in the thermal infrared i.e. wavelengths longer than about $2.0 \mu\text{m}$, have been made. Since semiconductor grade material is not necessary, these materials are relatively inexpensive.

It is also possible to produce highly absorbing compositions from materials such as metals. However, these materials do radiate significantly in the infrared and thus, although quite useful, are generally not as efficient as the corresponding semiconductor materials.

Some embodiments of the invention will now be described by way of example with reference to the accompanying drawings of which:-

FIGS. 1-3 schematically illustrate materials according to the invention.

FIG. 4 shows micrographs of a material according to the invention; and

FIG. 5 is a graph of the reflectivity of the material of FIG. 4.

FIGS. 1-3 show a channeled material, i.e., a material containing
5 voids that intersect the surface of the material (FIGS 1 and 3) or
channels open to the surface forming a reticulated structure (FIG. 2).
In this description such voids or channels will be collectively
referred to indiscriminately as "voids" or "channels". The walls of
the voids in a localized area, i.e., in any area defined by a $10\mu\text{m}$ on
10 a side square, are either parallel to each other or no more than 20
degrees, preferably no more than 10 degrees, from the mean wall
direction where the wall direction is determined by an imaginary
tangent drawn at an intermediate point of the void wall. To determine
the intermediate points on a wall within a localized area, an
15 averaging procedure is used. (This procedure is done separately for
each localized area.) First a plane is drawn intersecting the surface
of the material in a portion where the voids emerge, 8 in FIG. 2, and
also intersecting the region of the material below the channeled
portion, 10. This intersection determines a curve, 11. A least
20 square fit straight line, 13, to this curve is then drawn. This
procedure is repeated for different intersecting planes to yield a
number of least-square-derived lines. The least square plane to this
series of lines within the localized area is then ascertained.
(Obviously, the larger the number of lines used for this least square
25 process the closer the fit. However, generally from ten to twenty
lines yield accuracy within experimental error.) The points at which
the plane thus determined cuts a wall of a void are the intermediate
points for purposes of the angle measurement. It might be noted that
this procedure in the case of a relatively flat material seems
30 cumbersome. However, the subject invention also encompasses the
presence of rough surfaces and curved surfaces such as spheres or
tubes where the

concepts of direction and distance are more complex and where this procedure is necessary to avoid ambiguities.

Some deviation from the angle requirement in some of the walls of the voids is obviously acceptable without substantially affecting the material absorption properties. Generally, it is sufficient for purposes of the invention if the desired wall direction requirement within any given localized area is substantially present, i.e., the wall direction is within the necessary 20 degree requirement over at least 75 percent of the wall length--the distance along the lines produced by connecting the defined intermediate points along the wall. (Although a random configuration of voids is preferred, symmetrical configurations are not precluded.) Examples of the general appearance for a discrete array, a reticulated structure, and a combination are shown in FIGS. 1, 2, and 3 respectively.

A substantial factor affecting absorption is the large change of refractive index at the absorbing material/atmosphere interface. To mitigate the losses due to the reflectivity produced by this large refractive index change, channels that decrease the size of this refractive index change are used. This decrease in refractive index change is most advantageously accomplished with channels that have cross-sectional dimensions smaller than the wavelength of the incident light. (It is understood that incident light is composed of a plurality of wavelengths at different intensities. For purposes of this invention, the wavelength for this spectrum is considered the light of shortest wavelength that composes at least 0.1 percent of the total intensity of the incident light.) Larger cross-sectional dimensions up to ten times greater still significantly increase absorption and are not precluded. For example for solar radiation (air mass 2) the most advantageous channel size is less than $0.3\mu\text{m}$, but channel sizes of less than $3\mu\text{m}$ preferably less than $1\mu\text{m}$ increase absorption and are contemplated within the invention. If the channel size criterion is

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satisfied, the incoming radiation encounters an average refractive index difference at the atmosphere/absorbing material interface which is smaller than would be experienced if the channels had not been present. (It should be noted that the refractive index of metals and materials such as semiconductors are different. Thus, the optimum channel cross-section and depth for these materials are somewhat different. However, channels within the given range yield excellent results and a controlled sample is used to determine the best values for a given material.)

The channel cross-sectional dimension--the channel size--for purposes of the invention is the size obtained by drawing a line at random along the least-squares-plane that determines the intermediate points on the walls of the voids in a localized area, measuring the distance along this line across each void, and calculating the mean value for these void distances.

The depth of the channels and the density of the channels also significantly affect the average refractive index difference and, thus, the extent of reflectivity. The mean channel depth should be approximately equivalent to or deeper than the wavelength of incident radiation. General channels deeper than $0.4\mu\text{m}$ preferably deeper than $0.8\mu\text{m}$ are desirable. However, channels deeper than $5\mu\text{m}$, although not precluded, are generally not advantageous since structural instability occurs. (The void depth is the vertical distance between the void bottom and the void opening measured perpendicular to the plane in a localized area defining the intermediate points.) It is also advantageous to have a large channel density so that the effective refractive index difference is smaller and, thus, the amount of reflected light is correspondingly smaller. Generally, channel densities, i.e., the fractional volume of voids in the total volume of the channeled region measured to the mean depth, in the range 20 percent to 80 percent are utilized. (Channel densities are given as fractional

volumes of the channeled region since it is possible to make a material where only a portion of the material is channeled.) If the channel density becomes too large the amount of material in a given area becomes undesirably low and, therefore, the amount of material available to absorb light is significantly diminished. For this reason, channel densities greater than 80 percent are usually not desirable.

It is advantageous to use a semiconductor material that has an optical absorption edge in the range 1 to $2\mu\text{m}$. (The optical absorption edge is the wavelength at which a sharp change in absorption occurs.) For crystalline semiconductor materials, this corresponds to a semiconductor having a bandgap in the range 1.2 to 0.6eV. These semiconductor materials advantageously have relatively low absorption cross-section for infrared radiation. Thus, the emission of infrared radiation is correspondingly low. However, light having an energy greater than the bandgap is efficiently absorbed. Through various decay processes within the semiconductor material the absorbed energy is transferred to states within the semiconductor material that induce heating in the material. Because the absorption of infrared radiation in these semiconductor materials is low, the emission of light at these frequencies is similarly low and thus heat is not dissipated by the emission of infrared light. Thus, the semiconductor material efficiently absorbs light, efficiently changes this light to heat energy, and does not dissipate this heat energy in the form of re-emitted infrared light.

The extent of absorption also depends on the thickness of the absorbing material. Generally for a semiconductor material with an appropriate bandgap, incident ultraviolet, visible and near-infrared radiation is absorbed within $1\mu\text{m}$ of the surface. Thicknesses significantly greater than this thickness as a result do not substantially increase absorption of usable radiation, but does increase the absorption (and thus emission) of

thermal infrared radiation. Therefore, it is advantageous to limit the thickness of the semiconductor material to less than $5\mu\text{m}$. Similarly, if a backing material for the absorbing material is used, it also affects thermal infrared emission. For example, if the backing has a metal surface, especially a highly polished metal surface, adjoining the absorbing material, infrared light will be efficiently reflected and equally effectively prevent re-emission. Thus, the backing material will not contribute to heat loss through re-emission.

Silicon is particularly advantageous for the structures of the subject invention. This material is abundant. Additionally, semiconductor grade material is not required and, therefore, it is possible to fabricate a relatively inexpensive absorber. Typical of other semiconductor materials exhibiting a high degree of absorption when having the previously specified channel are GaAs and Ge.

Materials such as small bandgap semiconductor materials with absorption edges longer than $2\mu\text{m}$, and metals, readily absorb in the infrared irrespective of their thickness. Therefore, their emission in the infrared is also substantial. As a result, these materials do not have the advantage of readily producing heat without substantial re-emission of infrared light. Nevertheless, metallic or small bandgap semiconductor materials having channels as described above exhibit relatively high absorptivity.

With materials having a discrete absorption spectrum which fall outside the metallic or semiconductor class the absorption of light falling within the discrete absorption spectrum is possible. The channels produced in these materials should be of the size previously discussed.

The channeled materials are advantageously produced by anisotropic etching, i.e., an etch process that removes material in the direction perpendicular to the surface at a rate of at least twice as fast as the

removal rate parallel to the surface, and that is capable of maintaining these rates to a depth of at least 0.4 μ m preferably to at least 0.8 μ m. (The removal rates are determined using an essentially flat control sample. A compendium of anisotropic etchants for a variety of materials is found in H.W. Lehmann and R. Widmer, Journal of Vacuum Science Technology, 15, 319 (1978).)

During the anisotropic etching the sample is masked in a pattern that produces the desired void dimensions and densities with a material whose entire thickness is not removed in the etching process.

In the preferred etching procedure, the etch mask is formed in situ during the etching process. This is accomplished, for example, by etching in an environment capable of producing sputtering, i.e., an environment which results in a measurable sputter yield, (see Handbook of Thin Film Technology, L.I. Maissel and R. Glang, McGraw Hill, N.Y. (1970) pages 3-15 for a suitable method of determining sputter yield), and placing the material to be etched, i.e. the sample material, on or in close proximity to a large area of sputterable substrate so that at least a portion of the substrate is exposed. (A sputterable substrate denotes a composition having a measurable sputter yield when used with the chosen anisotropic etching procedure.) In a preferred embodiment a reactive gas introduced in a plasma etching procedure is chosen to etch the sample material anisotropically and, at the same time, form compounds with the substrate material.

In practice, once the plasma is struck, etching begins on the sample and, at the same time, the plasma produces sputtering from the substrate surface. Some of the sputtered substrate is redeposited onto the sample. The sputterable substrate is chosen so that the redeposited material then reacts with the gases present to form a composition with low vapour pressure. (Alternatively, the sputtered material could react in the gas phase and condense on the surface of the sample or the sputtered

material alone could be inert to the environment but have appropriate properties to produce the desired results. The exact sequence is unimportant.) A low vapour pressure, e.g. of the order of 10^{-7} Torr, is required for the mask material thus formed to allow sufficient quantities of the composition to accumulate on the sample surface.

The composition agglomerates on the surface of the sample and acts as a reactive etching mask. The agglomerations prevent etching of portions of the sample and result in the formation of channels. Exemplary of contemplated mask materials are compounds produced by the interaction of substrates such as aluminium, magnesium, and stainless steel with chlorine yielded by a chlorine-containing gas such as CCl_2F_2 .

The plasma should be produced under conditions which are conducive to the production of the desired mask on the sample material--that is in an atmosphere having particles with sufficient energy to induce sputtering. Generally plasmas produced using a power density in the range 0.2 to 2.5 watts/cm² are appropriate. The pressure of the etchant must be sufficient to produce anisotropic etching in the sample. Generally for isotropic etchants pressures in the range 2 to 40 μm Hg are utilized. Each etchant composition produces a species which actually induces the etching. For example, CCl_2F_2 produces chlorine and fluorine which etch silicon. It is possible to use the etchant composition alone, or in combination with other components. For example, it is possible to add inert gases, such as argon or helium, to stabilize a plasma, or to add a material to enhance production of the actual etching specie. Generally, the etching composition should be 5 to 100 percent of the total etchant.

The depth and channel dimension are controllable by varying the pressure of the etchant composition, the power density, and the etch time. The particular combination necessary to produce a desired channel depth and cross-sectional dimension in a given material is

determined by using a control sample. For example, when an aluminum substrate and a silicon sample are utilized, a total gas pressure in the range 5 to 40 μ m Hg, with an etchant composed of equal parts of O₂, Ar, and CCl₂F₂ produces a channel depth in the range 30 nanometres (300 Angstroms) to 2 μ m and cross-sectional dimension in the range 50 nanometres (500 Angstroms) to 500 nanometres (5000 Angstroms). At these pressures, a stable plasma is maintainable utilizing a power in the range 0.2W/cm² to 2.5W/cm². Although adequate etching is produced utilizing the etching composition, e.g., CCl₂F₂, alone, faster etching and more stable plasmas result when this etchant is combined with an inert gas such as Ar and with O₂. In a preferred embodiment, the use of oxygen with CCl₂F₂ at a ratio in the range 1:10 to 1:1 has been found to increase the degree of anisotropic etching somewhat and the addition of argon at a ratio of Ar to CCl₂F₂ in the range 1:10 to 1:1 produces a more stable plasma when CCl₂F₂ constitutes at least 8 percent of the total gas pressure.

The temperature of the sample at its surface also affects the channel dimensions. Generally, it is not possible to monitor this temperature. Nevertheless, the temperature is adjustable. For example, it is possible to insulate or heat sink the sample and affect the temperature. When heat sinking or insulation is utilized with a CCl₂F₂/Ar/O₂ mixture, cross-sectional dimensions were altered from about 200 nanometres (2000 Angstroms) for the former to about 400 nanometres (4000 Angstroms) for the latter under the same processing conditions. The effect of a particular temperature-control-measure is determined by a controlled sample.

In the preferred embodiment of the invention thin films on a supporting substrate are treated by the in situ formation of an etchant mask. However, thick samples, e.g., thicknesses greater than 2 μ m, are also suitable for treatment to produce the desired channels. Additionally, it is also possible to produce a suitable mask by

depositing the mask before the etch procedure is initiated. This is done, for example, on silicon by evaporating lead to a thickness in the range 50 nanometres (500 Angstroms) to 150 nanometres (1500 Angstroms) at temperatures in the range 25 degrees C to 100 degrees C.

The following example is illustrative of suitable parameters used in the production of highly absorbing materials:

10 Example

A silicon substrate measuring 2.54cm x 1.27cm x 0.051cm (1 inch x 0.5 inch x 0.020 inch) having one polished side with a local smoothness finer than 10 nanometres (100 Angstroms) was cleaned by immersing it in a hot water/detergent solution. The solution was ultrasonically agitated for approximately 10 minutes. The substrate was then removed from the detergent solution and sequentially rinsed in hot water followed by deionized water. The substrate was then scrubbed with a lint-free foam swab in deionized water. To remove the water, the substrate was treated in a vapour degreaser with isopropyl alcohol vapour.

The substrate was placed in an ion pumped vacuum station. The substrate was positioned approximately 12.7 cm (5 inches) above a multicrucible 3kW electron beam evaporation source. A layer of about 140 nanometres (1400 Angstroms) of tungsten was deposited on the substrate by energizing the crucible containing an approximately $1/3\text{cm}^3$ piece of tungsten. The thickness during the deposition was measured and monitored by using a standard quartz crystal film thickness measuring device. During the tungsten deposition, the vacuum pressure was maintained in the 10^{-6} Torr range by employing in addition to the ion pumps a titanium sublimation pump and a liquid nitrogen-cooled panel. The tungsten was deposited at a rate of about 1.2 nanometres (12 Angstroms) per second.

Following the tungsten deposition a layer of silicon about $2.2\mu\text{m}$ thick was deposited in a similar manner

at a rate of about 2 nanometres (20 Angstroms) per second. In this case, however, the entire thickness of the film was deposited in three layers with a waiting period of at least one-half hour between evaporations. This was
5 done to prevent overheating of the substrate and the vacuum system fixtures. The pressure in the vacuum system varied from about 1×10^{-8} to 4×10^{-7} Torr during the silicon deposition. After cooling to about 40
10 degrees C the silicon coated substrate was removed from the deposition system for subsequent etching.

The reactive ion etching process was done using a conventional diode sputtering system. The system used an oil diffusion pump with an optically dense water-cooled baffle. The plasma was generated by a 13.56 MHz rf
15 generator connected to two parallel, water-cooled electrodes 12.7cm (5 inches) in diameter. The rf matching network on the sputtering system was tuned to supply all of the power to the electrode on which the samples were to be etched. The electrode on which the samples were
20 etched was covered with a 12.7cm (5 inch) diameter aluminum plate which was thermally connected to the water-cooled electrode. The second electrode was of fused quartz.

The flow of the reactive gases through the sputtering systems was controlled using both pressure and
25 flow-ratio servo systems. A capacitance manometer was used to monitor the pressure. The signal from this manometer was used to adjust the flow of CCl_2F_2 . (This may be designated as the main gas). The flow of the other two gases O_2 and Ar was controlled by a flow/ratio controller.
30 By this means, either the flow of the secondary gases or the ratio of their flow to the main gas flow could be held constant. The flow rate of all the gases was monitored using a thermal mass flowmeter with a 100 standard cubic centimetre per minute (SCCM) full scale sensitivity. The
35 gases were mixed in an external manifold before entering the station. The manifold was heated to approximately 48 degrees C to reduce adsorption of gases on the walls.

38 The cleaned silicon sample was placed in the

centre of the aluminum plate with the deposited silicon upward and the system was pumped down to a pressure of less than $1\mu\text{m}$. Argon, CCl_2F_2 , and oxygen were fed into the chamber at equal rates of 3.7 SCCM using the flow control system described above. (It should be noted that equal rates are not equivalent to equal mole fraction and that relative pumping speeds of gases determine the actual mole fraction in the plasma). The total pressure in the chamber was controlled to be $20\mu\text{m}$. The rf power was turned on to 70W total giving a self bias of -540V on the aluminum plate. The power was applied for a total of 9 minutes.

The surface of the Si film, as observed by use of a scanning electron microscope, has a columnar etch pattern. (Electron micrographs are shown in FIG. 4, a micrograph at 45 degrees indicated 30 and a micrograph of a cleaved edge taken at an angle of 70 degrees indicated by 31). The voids on the silicon have channel dimensions of about 100 nanometres (1000 Angstroms). The vertical depth was about 500 nanometres (5000 Angstroms).

The appearance of this absorbing film to the unaided eye is dark black. The specular reflectivity was measured using a commercial reflectivity attachment with a dual beam spectrophotometer. From this measured reflectance, FIG. 5, the absorptance over the visible spectrum, i.e., the wavelength range of $0.4\mu\text{m}$ to $0.7\mu\text{m}$ is greater than 99.5 percent. The solar absorptance, i.e., the weighted average of the films' absorptivity over the solar spectrum is greater than 85 percent.

CLAIMS

1. A light-absorbing body having a portion containing a multiplicity of voids that intersect the surface of the body or channels open to the surface of the body forming a reticulated structure, wherein the mean depth of the voids is at least $0.3\mu\text{m}$, from 20 to 80 percent of the volume of the said portion measured to the mean depth consists of voids or channels, the width of the voids or channels is less than $3\mu\text{m}$, and the wall direction over 75 percent of the wall length within any localized area defined by a square $10\mu\text{m}$ on side is within 20 degrees of the mean direction for the walls within the localized area.

2. A body as claimed in claim 1, wherein at least the said portion of the body is of a material which comprises a semiconductor.

3. A body as claimed in claim 2, wherein said material comprises silicon, germanium or gallium arsenide.

4. A body as claimed in any of the preceding claims wherein the wall direction is within 10 degrees of the mean wall direction.

5. A body as claimed in any of the preceding claims wherein the width of the voids or channels is less than $1\mu\text{m}$.

6. A body as claimed in any of the preceding claims in intimate contact with a metal surface.

7. A light absorbing body substantially as herein described with reference to FIG. 4 and 5 of the accompanying drawings.

