# **Optical Materials for**

### ABSTRACT

The application of optical materials to solarenergy utilization is reviewed. It is shown that hundreds of square kilometers of optical materials will be required every year to have a significant input on the United State's energy economy. Most of these materials will have to be fabricated at a very low areal cost. Various high-volume, lowcost production processes applicable to solar-optical materials are presented. Major challenges to the optical technologist will be to control the optical properties of materials being fabricated at very high production rates and to develop new low-cost optical materials.

### INTRODUCTION

Solar energy may be utilized in a number of ways, both to generate and to conserve energy. These include: (1) architectural design and construction; (2) lowtemperature conversion for hot water, space heating, absorption air conditioning, and agricultural uses; (3) high-temperature conversion for electric-power generation and industrial processing; (4) photovoltaic conversion to electric power; and (5) photoelectrochemical conversion to chemical energy (oxygen and hydrogen). The costs associated with solar-energy utilization include: (1) collection, (2) accumulation, (3) conversion, (4) storage, and (5) conditioning for subsequent use. Any utilization scheme must make a systems analysis to determine both the feasibility and the economics of each stage.

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# Solar-Energy Applications

Historically, electrical-power generation capacity in the United States has increased at a rate of 7.5 per cent per year (to 1974). A projection of electrical energy requirements of the United States in the year 2000 shows that a one per cent impact on electrical-power generation will require on the order of 700 km<sup>2</sup> of collectors (assuming a 5 per cent solar-to-consumer efficiency).1 A 500 MW (peak) electric power plant (~ 100 MW average) will require about 13 km<sup>2</sup> of collectors (5 per cent efficiency) at a collector-totransmission cost of \$50-\$100/m<sup>2</sup>. A meaningful production for this type of collector would be at least 130 km<sup>2</sup> per year.<sup>1</sup>

Space heating accounts for 18 per cent of the energy consumption in the United States. Of this, threefifths is for residential heating. There are about  $6 \times 10^7$  dwelling units in the United States and this number is expected to double by the year 2000. Collectors for solar space heating require about onehalf of the dwelling area. To provide solar space heating for 10 per cent of these new dwellings will require approximately 1.9 x 10° m<sup>2</sup> (~ 1000 sq miles) of low-

The author is with Sandia Laboratories, Albuquerque, New Mexico 87115. temperature solar collectors. It is projected that the solar heating/ cooling industry could be worth \$2 billion a year by 1990 if the general public realizes the maximum potential energy obtainable through this use of solar energy.<sup>2</sup>

Figure 1 shows the solar spectrum external to the earth's atmosphere (AMO) after passing through two standard air masses (AM2). Note that 98 per cent of the AM2 energy is at wavelengths shorter than 2  $\mu$ m. Also shown is the spectral sensitivity of the normal human eye. The eye is sensitive to only 40 per cent of the AM2 radiation, with most of the remainder of the radiation being in the near infrared (solar infrared). Another important aspect of solar radiation is that there is both a direct and a diffuse component. The ratio of diffuse to total insolation will depend on the prevalent atmospheric conditions even on a clear day. Table 1<sup>3</sup> shows the variation in total and direct insolation for summer and winter for two areas of the United States. The insolation is shown both for a



Figure 1 Solar spectrum external to the earth's atmosphere (AMO) and after passing through two optical air masses (AM2). Spectral sensitivity of human eye. Radiation spectrum of a blackbody at several temperatures. Also shown is the transmission range for typical window glass.

#### **REFLECTOR - COLLECTOR SYSTEMS**



Figure 2 Focusing and nonfocusing photo-thermal collector configurations. The flat plate and Winston (compound parabolic concentrator) are nonfocusing collectors. The power-tower (heliostat) and parabolic trough collectors are focusing types.

horizontal surface and for a surface inclined to a 40° angle. Also shown are the ratios of diffuse to total insolation. Figure 1 also shows the thermal radiation spectra (thermal infrared) of a blackbody at several temperatures. Note that nearly all of the emitted radiation is at wavelengths greater than  $2 \mu m$ .

A solar collector system typically consists of glazing to reduce convective heat loss, reflectors to give some degree of concentration, a receiving surface to absorb the

#### TABLE 1 AVERAGE TOTAL SOLAR INSOLATION

Test Area	Horiz Kwh	contal Flat Plate ′day/m² <sup>a</sup>	Flat Plate 40° Tilt Kwh/day/ m² <sup>a</sup>	Ratio of Diffuse to Total Insolation
Albuquerque, NM				,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,
Spring	5.23	(3.66 Direct)	6.33	0.3
Summer	7.25	(6.05)	7.37	0.2
Fall	5.44	(3.60)	6.68	0.3
Winter	3.09	(2.83)	5.84	0.1
Blue Hill, MA				
Spring	3.59	(1.87)	4.10	0.5
Summer	5.76	(3.73)	5.81	0.4
Fall	4.29	(3.14)	5.17	0.3
Winter	1.52	(0.98)	2.81	0.4

<sup>a</sup>1 Kwh/day/m<sup>2</sup> = 86 Ly/day (1 Langley = 1 cal/cm<sup>2</sup>).

From: E.C. Boes, "Solar Radiation Availability to Various Collector Geometries, A Preliminary Study," Sandia Laboratory Report SAND 76-0009, February 1, 1976.

solar radiation, insulation to reduce conductive heat losses, and a heat transfer medium such as air or water. Solar collectors may be either focusing or nonfocusing, and either may be concentrating or nonconcentrating.1 Figure 2 shows several types of collectors. The flatplate collector<sup>4</sup> is generally a nonfocusing, nonconcentrating collector, but the use of side reflectors (augmented flat plate) does give some concentration. The Winston reflector<sup>5</sup> (compound parabolic concentrator) is another nonfocusing (but concentrating) collector. The nonfocusing collectors will collect both the direct and diffuse (within limits) components of the incident radiation. A parabolic trough collector<sup>6</sup> focuses the direct component of the radiation on a receiver surface (line focus), as does the heliostat or power-tower collector<sup>7</sup> (point focus). These configurations generally track the sun by drive mechanisms. Table 2 summarizes the properties of several reflecting and refracting focusing collector systems.8

There are a number of applications of optical materials in solarenergy utilization and conservation. Some of these applications are summarized in Table 3.

#### **OPTICAL MATERIALS**

*Reflecting surfaces* may be used to reject the incident radiation or to

#### TABLE 2 SOLAR CONCENTRATORS

Туре	Concentration	Focal Zone
Multiple Heliostat	100-1000	Point
Parabolic Cylinder	r 10-50	Line
Compound Parab	olic	
Concentrator	3-10	Line
Reflecting Linear		
Fresnel	10-30	Line
<b>Reflecting Circula</b>	r	
Fresnel	50-1000	Point
Linear Fresnel		
Lens	3-50	Line
Circular Fresnel		
Lens	50-1000	Point

## TABLE 3 SOLAR ENERGY OPTICAL MATERIALS APPLICATIONS

Reflectors	Antireflection Surfaces	
Metals	Coatings	
Metallized Glass	Surface Treatments	
Metallized Polymers		
Solar-Transparent/IR Reflectors	Solar Transparent/IR Absorber	
Multilayer-Interference	Liquids	
Semiconductor Coatings	Glass	
Solar-Absorber/IR Transparent	Solar Cells	
Surface Effect	Heterojunction	
Semiconductor	Homojunction	
Interference	Schottky Barrier	

direct it to a desired location (solar reflectors). Since a highly reflecting surface is also a poor emitter at that wavelength (Kirchoff's law for opaque material), these surfaces may be used to reduce radiation and retain heat in a hot material. Figure 3 shows the reflectivity of various materials in the solar and near-infrared spectral regions.  $R_s$ is the average solar reflectivity. Silver and aluminum are good reflectors for both solar and infrared radiation. Materials such as nickel and molybdenum are poor solar reflectors but are useful for their low infrared emittance properties. Often an important property of the reflected radiation is its spatial dispersion. The amount of dispersion depends on the morphology of the reflecting surface. A white paint is a good reflector ( $R_s = 0.87$ ), but the reflected radiation is very diffuse; therefore, it is a poor reflector material for a focusing collector. Mirrors may be fabricated by shaping the optical material, such as a polished metal, or by applying the optical material to a shaped surface. The latter is the more common, and metal films may be deposited directly on shaped plastics or glass. Thin glass or

plastic sheets may be metallized and formed to shape. Metallization may be done by chemical reduction, vacuum deposition, sputter deposition, or spray pyrolysis.<sup>1</sup> Environmental protection is necessary on front surface mirrors and may be provided by laminated thin plastic sheets or deposited plastic or inorganic films. Partially reflecting metal films (usually aluminum, chromium, or gold) are in common use to reduce the transmitted radiation incident on windows. The films may be deposited directly on the window material<sup>9</sup> or may be deposited on a plastic film, which is then attached to the window. Usually there are deposited or laminated layers to provide environmental protection.

Antireflection surfaces are used to reduce reflection losses and thus increase solar transmission. Antireflection surfaces may be formed by surface treatments or by coating techniques. Surface leaching may change the near-surface composition,<sup>10</sup> thus forming a surface coating. Etching may be used to generate a surface morphology conducive to radiation trapping.11,12 Antireflection coatings may also be formed by controlling the properties and thicknesses of deposited films to give interference effects<sup>13</sup> or by generating a surface morphology on a deposited film conducive to radiation trapping.14,15

Solar transparent/infrared reflectors (windows) are useful in re-



Figure 3 Spectral reflectance of several metals and white paint.  $R_s$  is the integrated solar reflectance. Also shown is the AM2 solar spectrum.

taining heat in architectural applications by reflecting the thermal infrared. Semiconductor coatings may be used to transmit the visible and reflect the near infrared, if their energy gaps are such that they are transparent in the visible  $(E_{\rho} > 3 \text{ eV})$ , and they can be doped so as to have a large concentration of free carriers (~  $5 \times 10^{20}$ /cc). Figure 4 shows the spectral transmission properties of tin oxidecoated float glass. A typical sodalime window glass will have a solar transmittance of 0.85, and a 100°C blackbody reflectance of 14 per cent; the same glass with a 0.4- $\mu$ m thick coating of doped SnO<sub>2</sub> deposited by chemical spray pyrolysis<sup>16</sup> has a 100°C reflectance of 85 per cent and a solar transmittance of 75 per cent. Tin-oxide coatings can be deposited by spray pyrolvsis,<sup>17</sup> sputter deposition,<sup>18</sup> or glow discharge decomposition/reaction.<sup>19</sup> Other semiconductor coating materials of interest for infrared

reflectors include CaB<sub>6</sub>, CuC1, CuI, MnO, NiO, SiN, S, ZnO, ZnS, TiO<sub>2</sub>, Sb<sub>2</sub>P<sub>3</sub>, PbO, and Bi<sub>2</sub>O<sub>3</sub>.<sup>20</sup> Solar-transparent/ir-reflector coatings may also be obtained by using multilayer interference coatings (black mirrors).<sup>13</sup>

Solar transparent/ir absorbers are often used as windows to contain heat and reduce convective cooling. Glasses transmit the solar infrared but absorb the thermal infrared. Typical soda-lime window glass formed by the float-glass process has only 0.85 solar transmittance because of the iron-impurity absorption peak centered at 1.1  $\mu$ m. Iron-free window glass, such as ASG water white crystal #76, has a solar transmittance of 0.91 in 3.2mm thicknesses. Figure 4 shows the transmittance of a typical float glass. Attempts to make glass windows that absorb the solar infrared have not been very successful because thermal gradients generated in the glass give fracture



Figure 4 Spectral transmittance of 3.15-mm Herculite K float glass (PPG), tin oxide ( $\approx 2000 \text{ Å}$ ) deposited on float glass by spray pyrolysis, a 1-cm thick solution of 10 per cent Cu<sub>2</sub>SO<sub>4</sub> 5H<sub>3</sub>O, 50-µm Tedlar (duPont). Also shown are the AM2 spectrum, the sensitivity of the normal human eye, and the peak of the blackbody (BB) radiation for several temperatures.

problems. Many polymers transmit solar radiation and also portions of the thermal infrared. Degradation is a problem for many polymers that absorb the uv. Uv stabilizers lower the solar transmittance of polymers. Polymers suitable for solar application include FEP Teflon and Tedlar. Kapton, which is a high-temperature polymide, transmits well in the thermal ir but absorbs the blue portion of the solar. Figure 4 shows the solar- and ir-transmitting properties of Tedlar.

An interesting window application might be the use of visibly transparent infrared-absorbing fluid in a window, which could be circulated so that the thermal energy could be used for hot-water or absorption air conditioning. Figure 4 shows the absorption properties of a 1-cm thick, 10 per cent Cu<sub>2</sub>SO<sub>4</sub> water solution. The solution has a pale blue color in transmission but is very effective in absorbing the nearinfrared portion of the solar spectrum, which contains about 60 per cent of the solar energy. Wavelengths shorter than 5000 Å are 100 per cent transmitted.

Solar absorbing/ir transmitting materials may be used to give a selective absorbing surface. A selective solar absorber is one that strongly absorbs the incident solar radiation but does not emit in the infrared.<sup>1</sup> Selective absorber surfaces with the desired optical properties may be formed in a number of ways (see Reference 21 for an extensive literature review), but there are four optical effects that are utilized, usually in combination, to form such a surface:<sup>1</sup>

(1) Interference films use destructive interference effects<sup>13</sup> to absorb near the peak of the incident radiation. If multilayer films are used, this absorption peak may be made broad to cover the maximum of the solar spectrum. Figure 5 shows a multilayer interference coating (four layers) having a low solar reflectance, i.e., high solar absorptance ( $\alpha_s = 0.94$  at normal incidence) and a low infrared emittance  $[\varepsilon_{t,H}]$  $(305^{\circ}C) = 0.16/.^{22}$  Interference films may be formed by controlled deposited film thickness. Multilayer films may be formed by altering the film properties by changing process variables during deposition, as is done with 2-3 layer electrodeposited black nickel,<sup>1</sup> or by multiple depositions, as is done in the OCLI<sup>22</sup> or Ni/A1<sub>2</sub>O<sub>3</sub>-Mo-A1<sub>2</sub>O<sub>3</sub> (AMA)<sup>1</sup> coating. Optical effects in interference films are normally sensitive to the angle of incidence of incoming radiation since the effective film thickness changes with angle of incidence.

(2) Bulk selective absorbers are semiconductors such as the oxides or sulfides whose energy gap is such that they absorb the short wavelength radiation but are transparent in the infrared. Lead sulfide  $(E_g = 0.4 \text{ eV})$ , silicon  $(E_g = 1.1 \text{ eV})$ , germanium  $(E_g = 0.8 \text{ eV})$ , Cr<sub>2</sub>O<sub>3</sub>  $(E_g = 1.5 \text{ eV})$ , the mixed oxides of copper (CuO and Cu<sub>2</sub>O), and the mixed sulfides of nickel/ zinc are some of the semiconductor materials that are of interest.23 Because of their high index of refraction, smooth semiconductor surfaces show high reflectance losses, and antireflection coatings or surface radiation trapping<sup>14,15</sup> must be used to increase their absorptivity. If the energy gap is greater than 1 eV, the material will not absorb the near-infrared portion of the solar spectrum. Figure 6 shows the reflectance of a Cu<sub>2</sub>S ( $E_g = 1.8 \text{ eV}$ ) film, which is very black to the eye. The  $\alpha_s$ of this coating is only 0.79 since it does not absorb the near-infrared portion of the solar spectrum.<sup>24</sup> Coatings of semiconductor materials may be formed in a variety of ways, including chemical conversion, thermal oxidation, electroplating, and various physical vapor-deposition processes.<sup>21</sup>

(3) *Mie scattering films* use finely divided particles to give forward scattering and multiple internal reflections to absorb radiation. The



Figure 5 Measured reflectance of a four-layer interference coating with a solar absorptance of 0.94. Also shown is the total hemispherical emittance as measured by an energy balance technique. (Sample prepared by Optical Coatings Laboratory, Inc.)

gold smokes are good examples of this effect. Low density-fine particle films also have effective indices of refraction lower than those of the bulk materials, and this decreases the reflective losses from such a surface. A problem with the smokes is their poor thermal-transport properties. If the particles are in a matrix, the thermal-transport properties are improved. Examples of such a system are tin particles in a MgF<sub>2</sub> matrix,<sup>21</sup> the semiconductor paints,  $^{21,24}$  and some of the electrodeposited systems where metal particles are co-deposited with an oxide matrix.<sup>21</sup>

(4) Radiation-trapping surfaces may be formed by controlling the surface morphology. If the surface discontinuities have dimensions on the order of the maximum wavelength to be absorbed, the surface may act as an assembly of cavity



Figure 6 Reflectance of a  $Cu_2S$  coating formed by chemical conversion of a copper surface in ammonia sulfide solution. Transmission samples prepared by pressing coating powder in a KBr pellet. Solar absorptance is only 0.79. Also shown is the reflectance of a very black commercial paint.



Figure 7 Total reflectance and total hemispherical emittance of a copper-surface argon sputter etched in a carbon atmosphere.  $a_s$  is given for an incidence angle of 0° (normal) and 70°. Inset shows morphology of surface.



Figure 8 Solar absorptance (AM2) as a function of incident angle for black chrome (ChromOnyx) deposited on surfaces with varying roughness. Black chrome on (1) Watts nickel (roughest), (2) sulfamate nickel (rough), and (3) bright nickel (smooth). Also shown is the total hemispherical emittance as a function of temperature. (ChromOnyx is a tradename of the Harshaw Chemical Company.)

absorbers for shorter wavelengths; but for longer wavelength radiation, the surface radiates as a flat surface. If the discontinuities on a surface having a low infrared emittance give a forward reflection, the surface may behave as a selective absorber by "trapping" the radiation by multiple reflection. Examples of such rough trapping surfaces are the copper oxide surface formed by chemical conversion of a copper surface,<sup>24</sup> vacuum deposition of lead sulfide,<sup>14</sup> gas evaporation of germanium,14 the chemical vapor deposition of metals,15 the chemical etching of silicon to form "black silicon,"12 and the sputter etching of copper to form a black surface.<sup>11</sup> Figure 7 shows the morphology and optical properties of a copper surface sputter-etched in a carbon atmosphere.11

The effect of electrodepositing coatings on a microscopically rough surfaces is shown in Figure 8, where a black chrome coating deposited on a rough surface results in about 5 per cent greater absorptivity than the same coating on a smooth surface.<sup>25</sup>



Figure 9 Total hemispherical emittance and solar absorptance of black chrome (ChromOnyx) on bright nickel as a function of thickness, i.e., charge passed (current density x time). Optimum value for a high  $\alpha_s$  but a rather low  $\varepsilon_{t,H}$  is shown. (Samples provided by Harshaw Chemical Company.)

Generally, it is found that a coating system with the best solarabsorbing properties utilizes several of these effects. Examples of this are the control of the coating thickness to minimize "volume emittance" and to obtain destructive interference of radiation reflected at the interface, control of the surface morphology to increase radiation trapping, and the inclusion of fine particles in the matrix to take advantage of the Mie effect. One selective solar-absorber coating, which has the desired optical and stability properties, is an electrodeposited black chrome (ChromOnyx).25 This material consists of a variable composition Cr-Cr<sub>2</sub>O<sub>3</sub> coating about 1800 Å  $(0.18 \ \mu m)$  thick. The coating has a high chromium content near the interface (Cr/O Auger peak height ratio 1:1) decreasing continuously to the surface (Cr/O Auger peak height 1/10).<sup>21</sup> These coatings exhibit no interference structures in the reflectance spectra. To achieve a high solar absorptance,  $\alpha_s$ , and a low thermal emittance,  $\varepsilon_t$  H, the thickness must be carefully controlled. Figure 9 shows  $\alpha_s$  and  $\varepsilon_{t,H}$ of ChromOnyx as a function of plating time at various current densities. Note that the emittance is linearly proportional to the product of the current density and time (thickness). In order to keep the emittance low, the thickness must be carefully controlled.

There are a number of ways to fabricate selective solar-absorbing coatings, and the preparation techniques and properties of some of the most interesting coating systems are summarized in Table 4. Each of these coating techniques requires specialized processing, and at the present time none of this processing is available on a low-cost, massproduction basis. What would be especially desirable for lowtemperature collectors would be a simple, low-cost coating technique, such as a paint or chemical treatment, which could be incorporated into an assembly line.26

TABLE 4 SOLAR SELECTIVE PHOTOTHERMAL ABSORBERS

Material	Deposition Technique	a <sub>s</sub>	$\epsilon_{t,H}^{(^{\circ}\mathrm{C})}$
	Low Temperature (<150°C)		
Cu <sub>x</sub> O <sub>y</sub>	Chemical Conversion	>0.91	0.16 (<100)
Steel (Fe₃O₄)	Chemical Conversion	0.90	0.07 (90)
Multilayer (OCLI)	Vacuum Deposited	0.94	0.13 (122)
Cr <sub>x</sub> O <sub>y</sub>	Electrodeposited	>0.96	0.10 (100)
	High Temperature (>300°C)		
Cr <sub>x</sub> O <sub>v</sub>	Electrodeposited	>0.95	0.2 (350)
WC + Co	Plasma Sprayed	0.95	0.4 (600)
Cr <sub>2</sub> O <sub>3</sub>	Paint	0.98	>0.9 (900)
Multilayer (OCLI)	Vacuum Deposited	0.94	0.16 (305)

Receiver Designs. Figure 10 shows conceptual receiver configurations that could be used, along with the required optical properties of the materials involved. Whenever a material is transparent to the infrared, the surface underneath must have a low infrared emittance (high infrared reflectance). In the "fluid receiver" every component must have a low infrared emittance, and the solar radiation is absorbed in the working fluid itself. Such a fluid might be composed of silicon particles in a mineral-oil fluid. The container might be a material, such as sodium chloride. which is transparent in both the solar and the infrared.

In the "container receiver," the solar energy is absorbed in the container walls and the heat is conducted to the working fluid. The container material must have a high solar absorptance and a low infrared emittance. Silicon ( $E_{\rho} =$ 1.11 eV) is such a material, and several glassy semiconductor materials such as SeTe (1.31 eV).  $As_4Se_3Te_3$  (1.31 eV),  $Ge_5Se_3Te_7$ (1.36 eV), GeSeTe (1.58 eV), GeAsTe (1.32 eV), and As (1.39 eV), might be used. If the container material is transparent to the thermal infrared, the heattransfer fluid must have a low infrared emittance. Neither the fluid collector nor the container



Figure 10 Conceptual design of various solar receivers. Table indicates the ideal optical properties of the various parts of the receiver.

collector is feasible at present because of the difficulty and expense in fabricating the necessary materials. Since nonperfect materials exhibit a "volume emittance," thick material will have appreciable emittance and thin layers may not.

The "coating receiver" is the most interesting solar receiver. In this design, a coating with a low surface reflectance, a high solar absorptance, and a low infrared emittance is deposited on a high infrared reflectance surface. One important property of the absorbing coating is the absorptivity as a function of incident angle. If the coatings absorb radiation at high incident angles, the need for tracking is minimized and diffuse radiation is more effectively absorbed. Figure 8 shows the angleof-incidence effect on the solar absorptance of a ChromOnyx electroplated coating.

Photovoltaic Materials use n-p junctions to give charge separation when the incident radiation is absorbed by excitation of electronhole pairs. 27,28 The solar absorption coefficient is also an important factor in material selection, since if the absorption coefficient is low. the carriers will be generated over an appreciable depth in the material, and carrier mobility and lifetime will have to be high in order for the carrier to reach a junction. Carrier loss by recombination results in serious degradation of solar-cell efficiency.

There are two junction designs that may be used for charge separation. In the homojunction cell, the junction is formed by changing the dopant of the base material. The silicon solar cell is an example of the homojunction device. Since the optical-absorption coefficient in silicon (indirect gap semiconductor) is rather low,<sup>28</sup> the thickness of the cell must be large (> 150  $\mu$ m) in order to absorb the solar radiation. Therefore, the number of recombination centers must be low. Hence the desirability

#### TABLE 5 PRESENT STATUS OF PHOTOVOLTAIC JUNCTION DEVICES

		Cell Structure <sup>a</sup>	Efficiency (%)	
Material	$E_{g}$ (eV)		Theoretical/	Experimental <sup>b</sup>
Silicon ( <i>n</i> - <i>p</i> )	1.11	1-X PX	20	16 <sup>32</sup> 2
nCdS/pCu <sub>2</sub> S	2.40/1.2	TF – VD TF – ChS	16	833 534
nCdS/pInP	2.40/1.3	TF - VD/1-X		11-1435
nCdS/pCuInSe <sub>2</sub>	2.40/1.23	TF - VD/1-X		11-1436
nCdS/pCdTe	2.40/1.44	TF – VD		5-637
nZnSe/pGaAs	2.67/1.43	TF – VD	13	138
$Ga_{1}$ $AI_{x}$ (GaAsp-n)	1.43	LPE		21
$nCu_2 Te/pCdTe$	1.0/1.44	TF – VD		4-537

<sup>a</sup>1-X = single crystal, PX = polycrystalline, TF = thin film, VD = vacuum deposited, ChS = chemical spray, LPE = liquid phase epitaxy.

<sup>b</sup>Superior numbers refer to the references at the end of this paper.

of single-crystal or very largegrained polycrystalline material. Single-crystal silicon is prepared by growing a boule, then slicing and polishing. Attempts are being made to grow single-crystal slabs by pulling from the melt (ribbon growth) or growth on a web (dendritic web).<sup>28</sup>

In the *heterojunction cell* the junction is formed by two semi-

conductor materials in contact. One n-type material with a large energy gap (> 2 eV) may act as a "window" for the incident solar radiation. A direct-gap p-type semiconductor material with an energy gap of near 1.4 eV strongly absorbs the radiation in the junction region. Charge separation is obtained by the action of the junction. Since the carriers are generated near the



Figure 11 Schematic construction of single and polycrystalline silicon solar cells and a front  $(Cu_2 S \text{ side})$  and back surface (CdS side) illuminated thin-film CdS/Cu<sub>2</sub> solar cell.

junction region, carrier lifetime and mobility are of lesser importance than in the homojunction materials; therefore, polycrystalline thin films may be used to form the junction devices, although carrier recombination at the interfacial region should be minimized.

Table 5 summarizes some of the homojunction and heterojunction systems that have been investigated and the fabrication processes used in their construction. Figure 11 shows the construction of singlecrystal and polycrystalline silicon cells, as well as front- and backsurface illuminated thin-film CdS/Cu<sub>2</sub>S cells. Thin-film cells may be formed by vacuum deposition, sputter deposition, or spray pyrolysis. Solar cells must be protected by encapsulation. In addition, cell efficiency is temperature dependent; thus, adequate cooling must be supplied, particularly if concentration schemes are used to give multi-sun illuminations.

Semiconductor materials have high indices of refraction (for Si, n = 4.0), which give high reflectivity (40 per cent from Si) from smooth surfaces. In order to increase the transmission into the cell, antireflection coatings or surface treatment, such as those used to form "black silicon."<sup>12</sup> are used.

For backsurface cells such as the thin-film CdS/Cu<sub>2</sub>S cell, antireflection coatings or treatments are needed to improve the transmission of the glass. A glass having high solar transmission (low iron impurity) is desired. The transparent electrode material must have a high solar transmission and good electrical conductivity. Figure 4 shows the transmission and electrical properties of doped tin oxide (10  $\Omega/\Box$  ), which may be used as a transparent electrode material. The CdS layer should have a high solar transmission.

Silicon and CdS/Cu<sub>2</sub>S cells are the most widely discussed candidates for direct conversion to electricity. One reason for this is that the materials for these cells are in plentiful supply. Calculations have shown that maximum conversion efficiency should be achieved for materials having an energy gap of 1.4 eV.<sup>29</sup> Materials with this energy gap include GaAs (1.4 eV) and CdTe (1.4 eV). These materials may be made either n or p type so homojunction cells can be fabricated from these materials, but their sharp absorption edge leads to strong absorption near the surface. and strong surface recombination in these materials gives low efficiency. Other compound semiconductors can only be fabricated as one type or have either too small or too large an energy gap to match the solar spectrum. For these reasons, most new concepts involve the use of heterojunctions.

A variation of the heterojunction that now allows GaAs to be a contender is the use of a "heterobase" material, which essentially protects the active region of the cell.<sup>30</sup> Examples are  $pGa_xA1_{1-x}As$  or pA1As on pGaAs/nGaAs.

Generally these potential thinfilm systems use materials that are more costly than silicon, sulfur, copper, or cadmium, so their economics are subject to question.

Instead of using a p-n semiconductor junction for change separation, a near-surface space-charge region (Schottky barrier) may be used.<sup>31</sup> In this design, a direct gap semiconductor is used to absorb the radiation in the near-surface region and charge separation is obtained across the space-charge region. A transparent electrode or electrode



PHOTO-ELECTROLYTIC DECOMPOSITION OF WATER

Figure 12 Schematic diagram for photoassisted electrolytic decomposition of water using a semiconductor surface in contact with an aqueous electrolyte. grid is used on the front surface and a metal counter electrode is used on the back.

Photoelectrochemical Cells. If, as shown in Figure 12. the front surface is in contact with a solar transparent aqueous electrolyte instead of a solid electrode, photo-assisted electrolysis of water can be obtained.<sup>34</sup> The photoelectrochemical conversion at a semiconductor-electrolvte interface provides a direct conversion scheme that generates both electrical and chemical (hydrogen-oxygen) energy. For the electrochemical decomposition of water, a potential difference greater than 1.24 eV is necessary between the anode electrode and the cathode electrode. This means that, conceptually, the solar radiation with a wavelength of less than  $1 \,\mu m$ (~ 80 per cent AM2) is capable of decomposing water.

The semiconductor-electrolyte interface acts similarly to a metal semiconductor rectifying junction and is explained by band-bending and formation of a depletion layer. Electron-hole generation by photon absorption allows charge separation and the generation of a potential. If the semiconductor is n type (TiO<sub>2</sub>, ZnO, CdS), oxygen is evolved; if ptype (GaP), hydrogen is evolved. Only one electrode must be a semiconductor, but higher efficiencies can be obtained by using n- and ptype semiconductors or heterojunctions.

At present, TiO<sub>2</sub> ( $E_g = 3.2 \text{ eV}$ ) seems to be the most successful semiconductor electrode, since other semiconductor materials degrade under photolysis conditions. The large energy gap of the TiO<sub>2</sub> means that only a very small portion of the solar spectrum (< 1 per cent) can be utilized for the photolysis of water. The measured incident radiation-to-current conversion efficiencies at wavelengths < 3750 Å for the Pt-TiO<sub>2</sub> is greater than 70 per cent.

This conversion system is interesting since, in addition to electrical energy, the electrolysis of water produces hydrogen and oxygen, which can be collected at high pressures and stored. Storage and distribution of this chemical energy may be significantly cheaper than for electrical energy. So far, suitable semiconductor electrode materials are limited, and their properties are such that the solarconversion efficiency is poor.

Photogalvanic cells<sup>33,34</sup> rely on the excitation of a molecule in solution by a photon to induce chemical reactions resulting in high-energy products. These highenergy products can then lose their energy electrochemically, as in an ordinary battery: thus they behave as electrochemical cells, which are recharged by light. The photons are absorbed in a solution between two electrodes, and the optical properties of the molecules in solution determine the absorption and excitation states. So far, the solar conversion efficiency of these types of cells is low (1-2 per cent).

# **FABRICATION TECHNIQUES**

**Reflecting Surfaces** 

The principal concerns in the fabrication of materials for solar-energy application are fabrication costs, materials costs, and fabrication rates. To have a significant impact on the energy economy, millions of m<sup>2</sup> of collector surfaces will have to be fabricated each year. A fabrication rate of 1.3 x 10<sup>8</sup>  $m^{2}$ /year is equivalent to a 1-m-wide strip moving at 240 m/min continuously throughout the year. Industrial processes exist for fabricating some types of materials of interest at these rates.35 Table 6 shows some desired solar optical materials and possible ways of fabricating the materials.

Float-glass plants produce glass by pouring molten glass on a bed of molten tin, then allowing the glass to cool as a continuous sheet. Production rates from one such plant are 2.6 x  $10^7$  m<sup>2</sup> of glass sheet per year.<sup>36</sup> Conceptually, such a plant could be expanded to allow the spray pyrolysis deposition of metallic reflector surfaces, semiconductor infrared reflector surfaces, or CdS/Cu<sub>2</sub>S<sup>37</sup> solar cells at a rather low areal cost.

In the electrodeposition of 10 000 Å of tin on strip steel, plants exist that have a capacity of 1.8 x  $10^{\text{s}} \text{ m}^2$  per 8-h shift or about 1.8 x

 $10^8 \text{ m}^2/\text{year.}^{38}$  These plating lines coat strip steel moving at a speed of 500 m/min. There are about 1.8 x  $10^9 \text{ m}^2$  of strip steel tinplated in the United States per year. This technology might be applicable to the electrodeposition of selective solar-absorbing coatings or the metallization of flexiable materials.

In the vacuum-coating industry, there exist air-to-air strip coaters capable of coating a 1.5 m-wide plastic sheet with 500 Å of aluminum at a rate of 180 m/min with a throughput of about 4.6 x 10<sup>7</sup> m<sup>2</sup> per year. A batch-type roll coater has a smaller throughput but a lower capitalization cost.<sup>39</sup> Flexible substrates can be coated at a higher rate than can rigid substrates.

To coat individual rigid pieces requires an operation that is more labor intensive than the continuouscoating systems. One glass company has a continuous lock-type batch coater for depositing a twoor three-layer film on  $3 \times 3.7$ -m glass panels. This system is reported to have a throughput of about 7.4 x  $10^5$  m<sup>2</sup>/year and uses electron-beam evaporation sources.<sup>40</sup> Sputter deposition systems for coating glass panels have been constructed.<sup>9</sup>

The Energy Research and Development Administration is now placing emphasis on the development of low-cost, single-crystal, silicon solar cells. To be economically competitive, the fabrication cost of silicon cells must be lowered by at least a factor of 100.<sup>1</sup> Attempts to achieve this cost reduction include lowering the cost of solar-grade silicon, devising fabrication processes that eliminate processing steps, and developing lower-cost fabrication techniques.<sup>28</sup>

The cost and availability of raw materials are very important considerations. A square mile of 1000 Å film contains  $2 \times 10^5$  cm<sup>3</sup> of material. As a general rule of thumb, this is equivalent to about one ton per square mile per 1000-Å film (assuming a density of 5

#### TABLE 6 SOLAR-OPTICAL MATERIAL FABRICATION TECHNIQUES

Vacuum Deposition	Vacuum Deposition		
Sputter Deposition	Sputter Deposition		
Rolling (Polished)	Chemical Leaching		
Spray Pyrolysis	Chemical Etching		
Solar Transparent/ir Reflectors	Solar Selective Absorbers		
Sputter Deposition	Electrodeposition		
Spray Pyrolysis	Chemical Conversion		
Glow Discharge Decomposition/Reaction	Thermal Oxidation		
	Vacuum Deposition		
	Sputter Deposition		
Silicon Solar Cells	CdS/Cu <sub>2</sub> S Solar Cells		
Ribbon Growth	Vacuum Deposition		
Web Growth	Spray Pyrolysis		
Slice/Polish			

Antireflection Surfaces

g/cm<sup>3</sup>). Obviously rare, costly, or exotic materials cannot be used if hundreds of square miles of material are required.

Fabrication costs are difficult to obtain. Tin plating of steel is done for several cents a square meter because of the high volume. A similar batch-type electroplating would cost \$3.00 a square meter.<sup>41</sup> Multilayer interference coatings on glass may cost as little as \$3.00 a square meter, but chemical leaching may cost much less. Plastics may be metallized at a cost of about \$0.03 a square meter at high volume. If the fabrication of solar material can be combined with an existing production facility, the cost may be appreciably lower than if solar material is processed in a separate operation. This would be the case in adding a spray pyrolysis capability to a float-glass plant. It should be recognized that the optical materials used will be determined by the economics, which in turn will be determined by the production technology and marketing costs. Many attractive materials/systems will fail in the economic analysis.

#### SUMMARY

The fabrication and properties of optical materials for solar energy applications will play an important role in solar-energy applications. There will be important tradeoffs between desirable properties and the economics of production. There is a need to study the properties of optical materials produced by mass production techniques and to develop analytical techniques, processes, and process controls applicable to high-volume production. In particular, needs exist for lowcost and environmentally stable optical materials for mirrors, windows that are solar transparent but are infrared reflectors, photochromic windows that will darken with increasing sunlight, hightemperature-high-efficiency photovoltaic materials, and solar selective coatings that can be easily applied during manufacture. An additional desirable feature for these materials would be field-repair capability.

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