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BLACK GERMANIUM SOLAR SELECTIVE ABSORBER SURFACES*

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Semiconductor films with an appropriate bandgap (approximately 0.5–1.25 eV) have a high absorption coefficient in the solar spectral region and high transmission in the IR thermal emission region and thus make nearly ideal selective absorbers when coated on polished metal surfaces with low IR emittance. However, owing to their high refractive index, semiconductor films have high reflectance (approximately 45%) which limits their total solar absorption. We have shown that by controlling the sputtering preparation conditions of non-crystalline germanium films the surface microstructure can be drastically altered by simply etching in 30% H_2O_2. The resulting surface has a total reflectance of less than 3% in the solar spectrum. This flat-back surface appearance is shown to be due to a dense array of aligned needle-like protrusions which have an extremely high aspect ratio and both a cross-sectional area and a separation between needles of the order of the wavelength of solar radiation.

1. INTRODUCTION

An ideal selective solar absorber surface would absorb all incident solar radiation and would not re-radiate any of the photothermally converted energy. Because of the overlap of the solar spectrum and the radiation spectrum of a warm body in the temperature range of interest (350–1000 K) no single layer can be truly ideal. Thus the functional definition of an ideal solar absorber surface is usually considered to be that surface which has zero reflectivity at wavelengths less than that (λ_c) at which the solar and warm-body radiation spectra are equal and 100% reflectivity at longer wavelengths[1,2]. Metal films are both highly absorbing in the visible and highly reflecting in the IR and thus are prime candidates as selective surfaces. However, they are also highly reflecting in the visible. Several schemes have been used to reduce this reflectivity—surface roughening[3], antireflection top coatings[4], cermet films[5] and combinations—the most successful being that of electrodeposited black chrome.

Another approach is to coat a layer which is both highly absorbing in the visible

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and highly transmitting in the IR onto a metal surface which has low IR emittance (or, by Kirchhoff's law, a high IR reflectance)[6, 7]. For this type of selective absorber a semiconductor with a sharp band gap at λ_c would be ideal if it were not for the high visible reflectance resulting from its high refractive index. Again the same schemes discussed above for reducing the surface reflectance of metals can be used for semiconductors.

(1) Antireflection coatings are highly angular and wavelength dependent, and are a stepped refractive index approach. More than one layer can be used in order to broaden the visible reflection minimum or, as suggested by Seraphin[7], a graded antireflection coating can minimize reflection even further. Such additional layers require rather stringent process control and can impose rather severe economic limitations.

(2) Dispersion of a semiconductor in a visible and IR transmitting material of low refractive index leads to a layer of lower refractive index than the semiconductor. Such refractive index lowering can apparently be described by the Maxwell-Garnett theory[8]. One method involves dispersion of fine mesh semiconductor powder in a silicone binder[9]. All binders to date, however, have unacceptably high IR emittance. Another method is to codeposit a semiconductor with some lower index insulator, *e.g.* Ge–Al_2O_3 [5, 7]. However, there are a number of potential drawbacks: the dilution effect of the mixing cannot reduce the visible extinction coefficient to any large extent; the thermal conductivity may be too low; the semiconductor and insulator must be immiscible and must not react under operating conditions[5]; the absorption edge cannot shift appreciably from λ_c [5–8].

(3) Porous or rough surfaces result in a graded refractive index, the exact grading depending on the detailed microstructure of the surface. The roughness must be of the order of solar radiation but much smaller than IR wavelengths, which puts a maximum separation of about 2 μm. Stephens and Cody[10] have pointed out that the multiple-reflection-type absorption model is not complete when surface features smaller than the wavelength of light are considered and they have made an exact calculation of the boundary conditions through an iterative procedure which simulates a graded refractive index. They show that an ideal absorber would have a graded dielectric constant with no discontinuities.

We have found that non-crystalline (NC) germanium films prepared under certain sputtering conditions turn black under visual observation during etching in hydrogen peroxide (30%). This drastic decrease in surface reflectance from approximately 45% to less than 3% is due to a surface microstructure which develops during the etching. The range of sputtering conditions over which such black films are attained is quite wide. The exact surface microstructural details, and thus the reflectance spectra, are found to depend on the sputtering conditions. In general, the surface roughness is of the order of the wavelength of light and has a high aspect ratio (*i.e.* ratio of height to width of the individual protrusions).

As we have shown previously, the properties (density, argon and oxygen content, stress etc.) of NC germanium sputtered films can have large variations depending on the exact preparation conditions[11]. We have also shown that under certain conditions NC germanium can crystallize "explosively"[12]. The present report is yet another interesting and potentially important phenomenon of NC germanium films.

2. EXPERIMENTAL CONDITIONS

Germanium was sputtered in a turbomolecular-pumped r.f. sputtering system (Ultek model 3140-6J) with a base pressure of 2×10^{-7} Torr using argon purified with a titanium getter. The target was a 5 in disk of polycrystalline 40 Ω cm germanium. The substrates, cleaned Corning 2947 microslides (25 mm × 75 mm × 1 mm) and Corning #2 cover glass (8 mm × 8 mm × 0.1 mm), were placed on a water-cooled J-arm with a target-to-substrate distance of either 26 or 52 mm. The sputtering pressures used were 10×10^{-3}, 20×10^{-3} and 40×10^{-3} Torr, which corresponded to flow rates of 105, 225 and 310 cm^3 min^{-1} of argon through the system. Measurement of the substrate surface temperature T_s was made with an annealed resistance-calibrated NC germanium film[11].

All property measurements were made with films deposited near the center of the target in order to eliminate all radial and edge effects of the target. Because of the minimum weight necessary for the density measurements, films ranged in thickness from 20 to 40 μm. These thicknesses were determined by examining a fractured edge and by comparing it with a ruled grating under an optical microscope. All films were measured from $2\theta = 20°$ to $2\theta = 80°$ in a GE diffractometer with Cu Kα radiation to determine the degree of crystallinity. Densities were measured first by dissolving the glass substrate with hydrofluoric acid and by then using an Archimedes technique in a Roller–Smith precision torsion balance with weighings of the free-standing films in air and toluene. The results were compared with a crystalline density of 5.35 g cm^{-3} for germanium. As a check to determine that the HF etch was not altering the germanium film densities, several films sputtered at lower r.f. powers onto polished KCl substrates were found to agree with those deposited on glass. KCl substrates could not be used for high power level runs owing to bombardment-induced decomposition of the substrate. The precision of the density measurement was dependent on the total film weight and varied from 1% to 4%. Scanning electron micrographs of film surfaces and cross sections were taken with an M-7 International Scientific Instruments microscope. Reagent grade hydrogen peroxide (30%) was used to etch the germanium films. Room temperature etch rates were obtained by measuring film weight before and after etching and by using the measured thickness to determine rates.

Reflectance measurements were performed on a Beckman DK-2A spectrometer with an integrating sphere for measuring total reflectance (specular plus diffuse). A lead sulfate powder was used as a reflectance standard.

3. RESULTS

A systematic series of films were prepared at varying r.f. power levels, gas pressures and substrate-to-target separations (Table I). All films were non-crystalline as deposited. In addition to measuring substrate temperature during film preparation, deposition rate and film density, each film was etched in 30% H_2O_2 and the etch rate was measured and the resulting surface visual appearance was qualitatively recorded. Many of the films turned a flat-black, some within several minutes after immersion. X-ray diffraction analysis of the black germanium surface showed no traces of any crystalline phase. Energy dispersive analysis of the X-rays generated by an electron beam indicated no impurities (< 3 at.%).

TABLE I

SPUTTERING CONDITIONS AND RESULTING FILM PROPERTIES

Sputtering variables		*Substrate temperature* (°C)	*Deposition rate* (Å $\mathrm{min^{-1}}$)	*Density* (g $\mathrm{cm^{-3}}$)	*Etch rate* (µm $\mathrm{min^{-1}}$)	*Visual appearance*[a]
R.f. power (W $\mathrm{cm^{-2}}$)	*Ar pressure* ($\times 10^{-3}$ Torr)					
Substrate separation 52 mm						
5	10	120	280	5.3	0.31	SB
10	10	180	470	5.2	0.07	UC
15	10	210	620	5.3	0.09	UC
20	10	230	770	5.3	0.22	B
2.5	20	80	160	5.0	0.92	B
5	20	130	280	4.7	1.1	B
7.5	20	160	380	5.0	0.87	B
10	20	190	660	5.2	1.3	B
12.5	20	210	660	5.3	1.9	B
15	20	220	790	5.2	1.4	B
17.5	20	240	810	5.0	0.87	B
20	20	240	1600	5.0	1.5	B
5	40	160	310	4.6	0.25	B
10	40	220	610	5.4	1.5	B
15	40	260	770	5.3	1.5	B
20	40	290	860	5.0	0.27	B
Substrate separation 26 mm						
5	20	60	440	5.4	1.0	SB
7.5	20	120	550	5.0	0.31	SB
10	20	160	750	5.2	0.98	B
15	20	200	1000	5.0	1.3	B

[a] B, black; SB, slightly black; UC, unchanged.

As seen in Table I, the black germanium films could be prepared under a wide range of sputtering conditions, especially at higher gas pressures ($P_{\mathrm{Ar}} > 10 \times 10^{-3}$ Torr) and larger substrate-to-target separations (52 mm). There were no clear correlations, however, between the black visual appearance and either the substrate temperature, deposition rate or film density. Other film characteristics such as oxygen and argon inclusion during film preparation are known to be substantial and to be highly dependent on the exact film preparation conditions[11] but were not measured in this study.

The black germanium could be regenerated. After polishing a black layer to reveal a smooth reflecting NC germanium film, a second immersion in hydrogen peroxide again resulted in a black film at about the same etch rate. This process could be continued until the film was completely dissolved.

There was very little difference between the qualitative visual appearance of most of the black germanium films. In most cases there was no observable visible reflection over a very wide viewing angle, as much as 60° from normal. Thus we chose three different black germanium films for more detailed investigation. The various etched black germanium layers had less than 3% total integrated reflectance over the solar spectrum (Fig. 1). Films 2 and 3 were black while film 4 appeared gray but not reflecting at all angles of observation. For comparison, the reflectance spectra of carbon black, of a commercial black chrome* coating on a copper substrate and of an unetched NC germanium film on a glass substrate are also presented. The unetched NC germanium had a visible spectral reflectance of approximately 45%.

The corresponding surface microstructures of the black germanium films are shown in Fig. 2. The unetched film 6 has a slight but discernible surface roughness. The etched films 2 and 3 both have a fine-grained surface structure with a separation between surface asperities of less than 1 μm and with a distribution in the heights of the asperities. As seen in this figure and in Fig. 3, the surface structure is the result of a dense array of aligned needle-like protrusions which have an extremely high aspect ratio, a cross-sectional area of the order of visible wavelengths and a separation between needles of the order of the wavelength of light. Film 4, however, had a much coarser surface structure which appeared to be the result of a high density of conical etch pits (see Figs. 2(c) and 3(d)). There is a distribution in the depths of these various conical pits and thus in the cross-sectional size of the pits at the surface. The smaller ones have an average diameter of 0.5–2 μm while the larger pits are 2–4 μm and predominate in the overall surface structure. The sides of the pits are quite steep giving a high aspect ratio to the protruding material.

The thermal stability of the etched films was similar to that for the unetched films. Films crystallized upon annealing at 550 °C for 2 h while films annealed at 400 °C for 2 h remained non-crystalline. The unetched 400 °C annealed films still turned black upon etching. Also the etched 500 °C annealed crystalline films

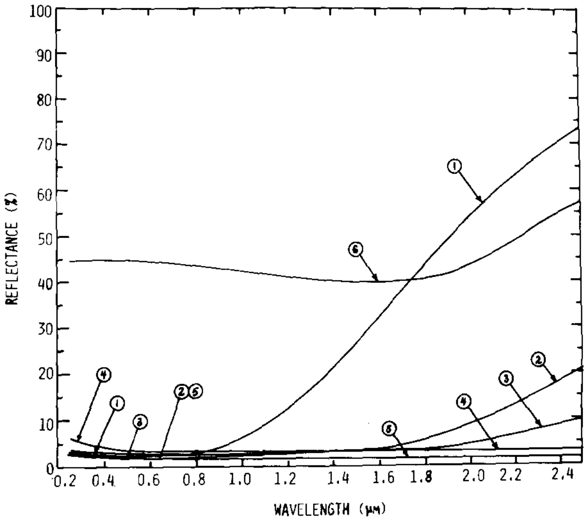

Fig. 1. Total (diffuse plus specular) reflectance spectra of several etched black germanium films on glass substrates (2, 3, 4) together with the spectra for black chrome (1), carbon black (5) and an unetched NC germanium film on glass (6) for comparison.

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* SolarStrip (Berry Solar Products, Edison, N.J. 08817, U.S.A.).

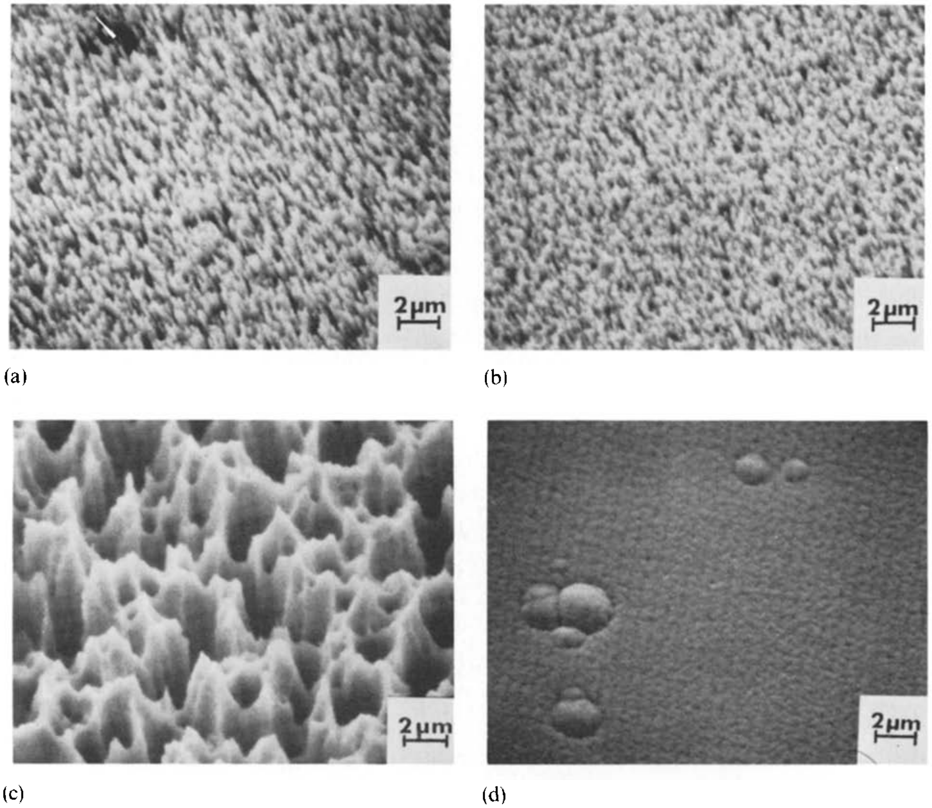

Fig. 2. Scanning electron micrographs of the top surface (at 30° tilt) of etched (films 2, 3 and 4) and unetched (film 6) NC germanium films: (a) film 2; (b) film 3; (c) film 4; (d) film 6. These are the same films as those in Fig. 1 with the same numbering.

remained black and adherent after crystallization; these are thus a possible thermally stable semiconductor coating configuration.

4. DISCUSSION

Semiconductor coatings, with an absorption edge between 1 and 2 μm, on highly reflecting metal surfaces have been recognized as efficient photothermal converters[6, 7]. The primary drawback to such selective surfaces is their high reflectivity due to the high refractive index of the semiconductor layer.

Other factors, such as shifts in the absorption edge, thermal stability under operating conditions, thermal conductivity, mechanical stability and IR absorption[13] are important also, but these will not be discussed here at any length. The absorption edge of a semiconductor shifts to lower energy with increasing temperature. In addition, the absorption edge varies with preparation conditions and with the resulting film properties such as density[11] and hydrogen content[14]; in both cases the shifts result from extended "tail" states presumably due to defect states (*i.e.* dangling bonds) at the internal void network surfaces. Thus the

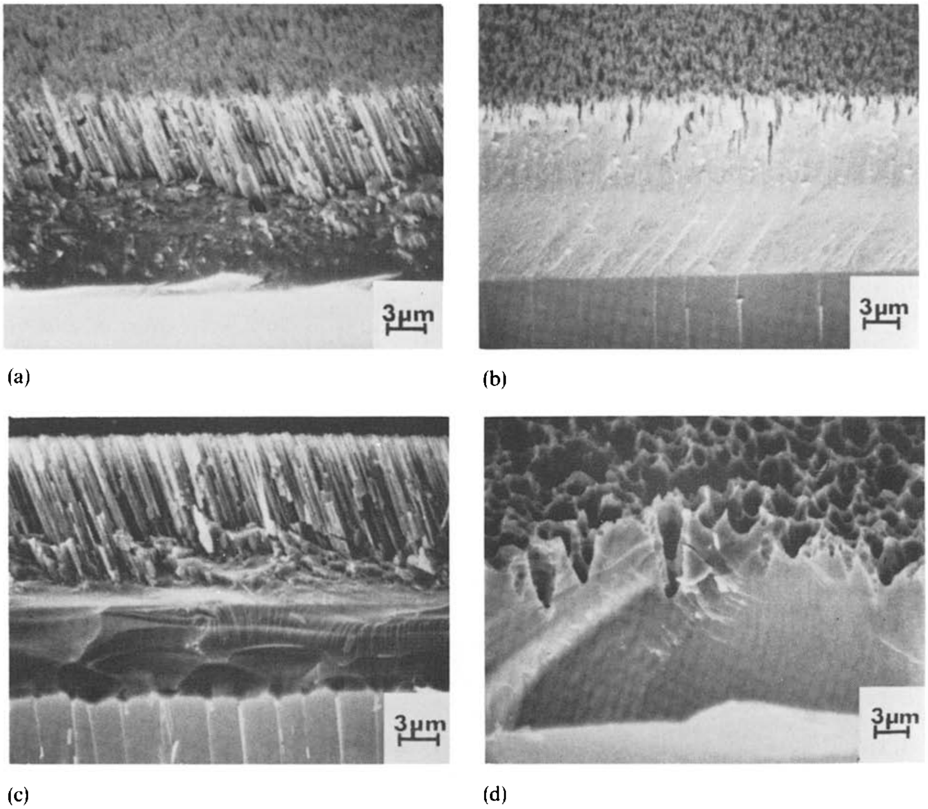

Fig. 3. Scanning electron micrographs of the fractured edges of the same etched films as in Figs. 1 and 2: (a) (c) film 2; (b) film 3; (d) film 4. In films 2 and 3 the bottom portion of the micrographs are the glass substrates while in film 4 the film is overhanging the glass substrate.

absorption edge must be controlled through choice of both semiconductor material and its preparation conditions in order to optimize device operating efficiency for a particular temperature application. It has been shown previously that with increased annealing and increasing film density the absorption edge becomes sharper and moves to higher energy while the IR refractive index decreases and approaches that of crystalline germanium[15].

Reduction of the reflectivity of a rough surface occurs as a result of reflection and scattering processes, both of which depend in different ways on the exact dimensions (aspect ratio, spacing, depth) of the surface features. When the spacing of the surface features is much smaller than the wavelength of light, scattering processes predominate and the reflection process is best described in terms of a graded refractive index film[10] in which the depth of the grade is the important parameter. For larger spacings of surface features where the wavelength of the light is of comparable or smaller size, multiple-reflection processes will predominate and can be calculated from purely geometrical considerations such as the aspect ratio.

For the black germanium films (see Fig. 2) there is an intermediate situation owing to the size distribution within just a single film and the larger variations possible from film to film and also owing to the distribution of wavelengths over the solar spectrum (0.3–2.5 μm). Thus both processes are needed to describe the reflectance spectra of black germanium films. The "gray" germanium film (Fig. 2(c)), however, with its much larger surface feature spacing, can be described almost totally by a multiple-reflection process which can account for the extremely low reflection even at the longer wavelengths (see Fig. 1). The high aspect angle for these films can reasonably account for the wide angle of low reflection.

Stephens and Cody[10] show that by controlling the grade depth or height of the surface features the reflection at any wavelength can be accounted for. Thus by controlling this grade depth the wavelength at which the reflectivity begins to rise should be adjustable. As seen in Fig. 3, the grade depth can be controlled by simply changing the time for etching. A 1.5 μm grade (Fig. 3(b)) has a similar microstructure to a 10 μm grade (Fig. 3) and there appears to be no limitation on even smaller grade thicknesses.

More detailed modelling of these structures is, of course, needed to understand the exact details of the reflectance spectra. However, from the above qualitative parameters controlling solar reflectance it is apparent that the sizes and shapes of the microstructures for black germanium films are at least of the right order of magnitude.

The etching behavior is extremely anisotropic. The etching rate perpendicular to the surface would have to be 10–50 times greater, along some as yet unspecified "channels", than the etch rate in the plane of the film in order to explain this observed behavior. Since the films are non-crystalline there can be no grain boundaries. The fractured edge of the unetched portion of a black germanium film (see film 2, Fig. 3(c)) shows conchoidal fracturing and does not reveal any macroscopic structural anisotropy. However, it has been suggested that thick germanium films have low density rod-like regions over 2000 Å long and about 30 Å in diameter which are oriented perpendicular to the surface[16]. It is reasonable that such an anisotropic structure could account for the etching behavior observed in this study. The explanation would then be as follows: hydrogen peroxide etches rapidly along the aligned rod-like low density regions[16] while etching of the remaining higher density material will proceed perpendicular to these rod-like regions at a considerably lower rate; the final result will be a needle-like structure with each needle having a large aspect ratio. Such an anisotropic thin film model has also been suggested by others in order to explain an anomalously high oxygen uptake deep into NC germanium films[17,18]. Since the etching mechanism of hydrogen peroxide involves an oxidation step to form a germanium oxide which is water soluble, the strong oxidation phenomenon could explain the observed anisotropy in etching behavior.

The anisotropic structures for NC germanium noted above have been shown to depend on the angle of incidence of the vapor species during film formation[19] and thus show a non-perpendicular anisotropy. It is interesting to note that the needle-like structure of the black germanium films is not always aligned exactly perpendicular to the film surface (see Fig. 3). This anisotropic alignment along the direction of the impinging vapor species has most recently been shown by Weston *et al.*[19]

If the above model is correct then the etching behavior is essentially a bulk phenomenon. As noted in the previous section, the film could be regenerated through polishing and re-etching with the same microstructure attained each time. Such a result can only be accounted for by a bulk effect and is again consistent with the model.

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