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Germanium selective solar absorber surfaces

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Thin Ge films, produced by evaporation through 0.3, 1 and 3 torr pressures of argon onto polished aluminum substrates were found to exhibit selective absorption behaviour. Maximum absorptance to emittance ratios of 13:1 were measured, with values of 8:1 for films having solar absorptances of 0.9. Film structures were significant in determining collection efficiency. Films deposited at 0.3 torr showed better overall properties due to a larger particle size of about 1 μm compared with an approximate 0.1 μm size measured with films deposited at 1 and 3 torr.

1. Introduction

A good selective absorber surface is characterized by high absorptivity at solar radiation wavelengths (0.3 to 2 μm) and low emissivity for the infra-red spectrum radiated at about 550 K (5 to 10 μm) [1]. The development of these surfaces is of great technological importance since they allow a more efficient conversion of sunlight to thermal energy.

Among several methods which can be used to produce selectively absorbing surfaces, vacuum evaporation of a suitable semiconductor onto a reflective metal substrate offers attractive possibilities [2]. A suitable semiconductor is one with a band gap which will absorb strongly in the solar spectrum while being transparent in the infra-red. Germanium has a band gap of 0.67 eV which converts to a optical absorption edge of 1.86 μm. Since 95% of the solar spectrum is at wavelengths shorter than 1.86 μm, the theoretical collection efficiency of Ge is very high. Thin-film semiconductors which allow the transmission of low-energy wavelengths will allow the infra-red emitting characteristics of the polished metal substrate to determine the long wavelength emissivity of the overall composite (film plus substrate) structure.

Theoretically a germanium–polished metal substrate composite meets the criteria for a good selective absorber with low emission characteristics. However, most semiconducting materials have high indices of refraction (> 2) which means that a significant quantity ($> 20\%$) of the incident light will be reflected from, for example, a cleaved crystal surface [3]. This drawback may be circumvented by the production of thin semiconducting films composed of small particles having sizes and spacings of the order of the incident solar radiation wavelengths [4]. Such texturing promotes the forward reflection of the incident radiation and enhances the natural absorptivity of the semiconductor. These types of textured surfaces have been produced using gold [5] and chromium [6] as metal smokes produced by gas evaporation. The gas evaporation method entails evaporation and deposition through a substantial pressure (0.5 to 50 torr) of inert gas. One of the present authors [7] reported the gas evaporation of tellurium onto polished surfaces and the measurement of absorptance (a_s) to emittance (ϵ) ratios as high as 33:1.

Gilbert *et al.* [8] satisfied the need to reduce reflectivity by etching thick sputtered germanium films in hydrogen peroxide and reported an absorptance of 0.97. The emittance was not specified. Mattox and Kominiak [2] vacuum evaporated amorphous germanium films and reported high absorptance of 0.98 together with a poor emittance of 0.48. Gittleman *et al.* [9] sputter-etched single-crystal wafers of silicon to produce absorbing textured surfaces with emittances of about 0.25. This latter value is typical of bulk single-crystal silicon, and suggests that the composite reflecting

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substrate–textured crystalline semiconductor approach may offer a better method of reducing emissivity than the surface treatment of bulk samples. We have, therefore, carried out an initial study of the absorptive and emissive behaviour of gas-evaporated germanium thin films onto polished aluminum substrates as a function of inert gas pressure and film area density.

2. Experimental procedure

The polished ends of 4 cm sections of 2.5 cm diameter aluminum rod were used as substrates. Polishing was followed by ultrasonic cleaning in acetone and rinsing in methanol. Films were deposited in a vacuum system with a base pressure of 10^{-5} torr and a measured leak rate less than 3×10^{-4} torr h^{-1}. 99.999% pure Ge was evaporated using boats machined from spectroscopically pure graphite. A tungsten ring contained the molten Ge ensuring good heat transfer and allowing deposition rates as high as 0.04 mg cm^{-2} sec^{-1} to be obtained. 99.998% pure argon gas pressures of 0.3, 1 and 3 torr were maintained during evaporation with a source to substrate distance of 4 cm. Deposition times and excessive substrate heating were controlled by the use of a mechanical shutter between the Ge and the substrate.

Absorptances were measured using a modified Beckman DK2-A spectrophotometer. This modification, the addition of an integrating sphere* which has an Eastman 6080 (barium sulphate) coating, allowed a combined measurement of both specular and diffusive radiation. An absorptance, a_s, could be calculated after weighing, by the AM2 solar spectrum according to ASTM standard number E424.

Emittance measurements were made at 90° C using a Melectron† P3-1 detector equipped with a KRS-5 lens having a band pass from 0.5 to 50 μm. Normal emittance at 90° C, was determined dividing the radiated intensity of the sample by the intensity of a black body cavity at the same temperature.

3. Results and discussion

The effect of film area density on absorptivity for Ge films evaporated in argon atmospheres maintained at 0.3, 1 and 3 torr is presented in Fig. 1. In general, absorptance, a_s, increased with increasing film area density towards a saturation value of about 0.94 for densities greater than 0.5 mg cm^{-2}. Films deposited at 0.3 torr exhibited marginally lower maximum a_s values. However, for film area densities less than about 0.3 mg cm^{-2}, deposits made at an argon pressure of 0.3 torr had adsorptances significantly higher than those measured with films deposited at the higher argon pressures.

Fig. 2 shows emittance, ϵ_{90}, against film area density for the same series of samples. Again films deposited at 0.3 torr differ significantly from those deposited at 1 and 3 torr. For each gas pressure, emittance values decrease with decreasing film area density towards a lower boundary set by the emissive characteristics of the polished aluminium substrate. However, films deposited at 0.3 torr allow more dominance of the polished substrate for films having area densities up to 0.4 mg cm^{-2} as shown by the generally lower emittances measured

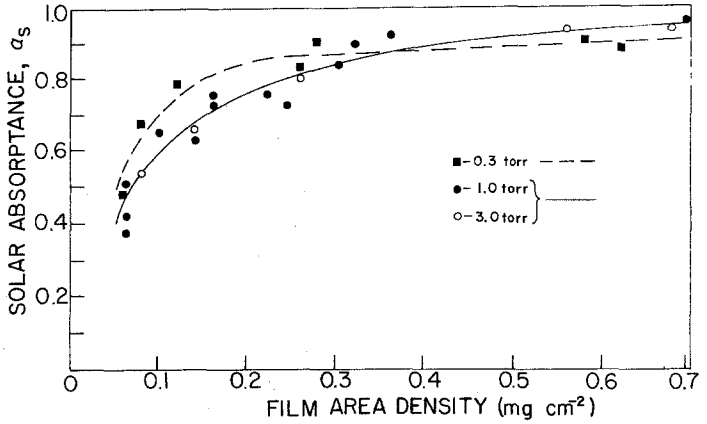

Figure 1 Solar absorptance, a_s, against film area density.

*Labsphere Inc., P.O. Box 1196, New London, New Hampshire 03859, USA.
†Molectron Corp., 177 North Wolfe Rd, Sunnyvale, CA 94086, USA.

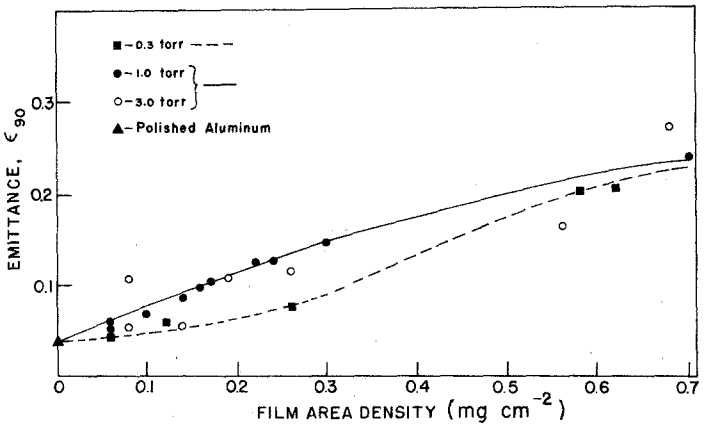

Figure 2 Infra-red emittance, ϵ_{90}, against film area density.

with these films. With increasing film area density ϵ_{90} for all films tends towards a saturation value of 0.22.

By combining absorptance and emittance in the ratio a_s/ϵ_{90}, an estimate of the relative performance of these selective absorber surfaces is obtained. This ratio is plotted against film area density in Fig. 3. Each series shows a maximum in a_s/ϵ_{90} at low film area densities. Films deposited at 0.3 torr argon pressure show higher a_s/ϵ_{90} ratios at all but the highest film area densities. A maximum a_s/ϵ_{90} ratio of 13:1 occurs at a film area density of about 0.15 mg cm^{-2}. However, at film area densities of about 0.35 mg cm^{-2}, where the absorptance approaches the satisfactory 0.9 value, the a_s/ϵ_{90} ratio is reduced to about 8:1.

The absorptances shown by these films follow from the combined effect of the band gap of germanium and the textured structure of the deposit. The textured structure acts to reduce the degree of reflection expected from the high refractive index of Ga [4.0(1 to 10 μm)], by promoting forward reflection of the incident radiation. The results show that the particle formation conditions, namely, homogeneous nucleation from a supersaturated vapour in the presence of a scattering gas, play a significant role in the structure produced. (These films were confirmed to be crystalline by X-ray diffraction analysis and comparison with the ASTM index cards for Ge.) Fig. 4a and b are typical scanning electron micrographs showing the appearance of films made at high and low argon pressures, respectively. Higher argon pressure ensures more scattering of the evaporated Ge cluster before condensation on the substrate. Hence the particle size (< 0.1 μm) is approximately an order of magnitude smaller than that obtained at 0.3 torr. This smaller particle size produces a surface which is more reflective to solar radiation, and has a correspondingly smaller absorptance than that produced at 0.3 torr.

The emissivity characteristics of the deposited films were, as expected, controlled by the extent to which the polished substrate qualities for low infra-red radiation were permitted to dominate.

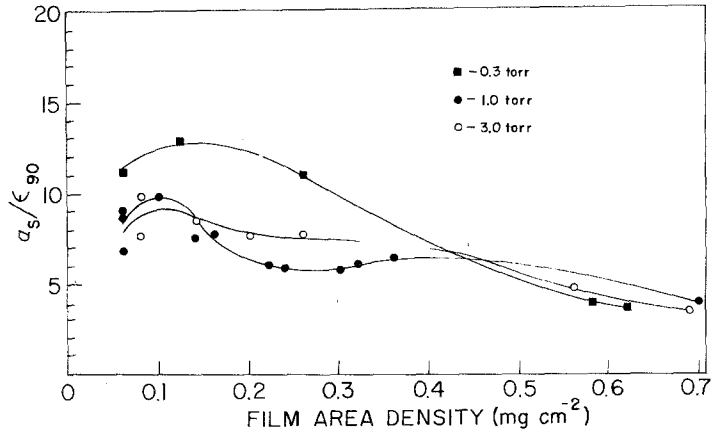

Figure 3 Absorptance to emittance ratio against film area density.

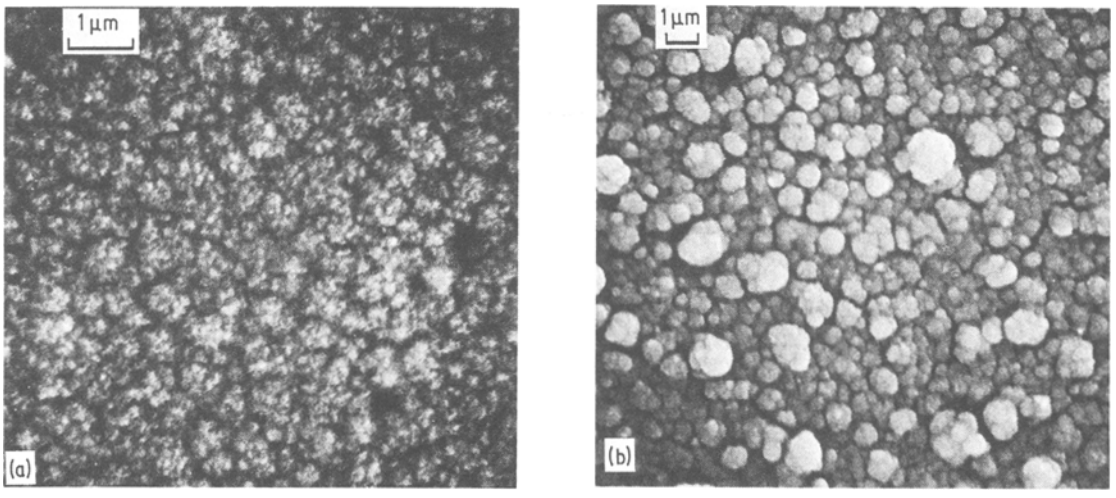

Figure 4 Scanning electron micrographs showing typical surface morphologies of films produced at (a) 1 torr and (b) 0.3 torr.

Although the difference was not great, the large particle size of the films deposited at 0.3 torr allowed emittance values of less than 0.1 to be obtained up to moderate film densities.

4. Conclusions

Textured Ge films produced by evaporation through significant pressures (0.3 to 3 torr) of argon have been shown to possess selective absorber behaviour. A maximum solar absorptance, a_s, to infra-red emittance, ϵ_{90}, ratio of 13:1 was measured. The most effective collectors were deposited at argon pressures of 0.3 torr. These deposition conditions produced a coarser structure (approximately 1 μm particle size) than that produced at 1 and 3 torr (approximately 0.1 μm particle size). The best absorptivity to emissivity ratios for absorptances of at least 0.9 was approximately 8:1.

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