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The preparation of textured Te thin films with pronounced acicular morphology and concomitant high absorptivity

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The dependence of surface morphology, and resultant absorptivity, on deposition angle for vacuum deposited Te films has been studied. A deposition angle of 80° was found to yield surface morphologies comprised of acicular crystallites of appropriate dimension and geometry for the trapping of solar incident radiation through multiple reflection. Solar absorptivities across the visible spectrum as high as 95% are manifested by such surfaces.

1. Introduction

The unusual textures of thin films produced by obliquely-angled vapour deposition conditions were noted as early as 1936 [1]. The mechanism by which the unusual columnar morphologies result from this method is considered to be that the vapour deposited material strikes the substrate as a uniform distribution and that the resultant nuclei are evenly dispersed. As the deposition proceeds, crystallites forming on these nuclei shadow the areas behind them. A low material self diffusion constant is necessary for these shadowed areas to remain clear. Condensation subsequently takes place preferentially on the upper surfaces of the crystallites, which thus tend to grow more rapidly in the direction of the vapour beam [2]. This self shadowing model of columnar growth in oblique angle-vapour deposited films was confirmed in 1960 [3].

The morphologies resulting from this method of vapour deposition have been noted and studied for their unique anisotropic mechanical, optical, and electrical properties [4]. However, the unusual thin films yielded by this method of vapour deposition have not typically been considered useful. Recently, selective absorber research by Cuomo [5] and Horwitz [6] employing surface morphologies allowing for high absorption of solar spectra through multiple reflection of incident light suggests a practical application for obliquely deposited vapour films.

Cuomo suggested that high absorption of solar light could be achieved with a microstructure similar in geometry to anechoic surfaces used in acoustic studies. Cuomo's suggested surface would consist of a dense forest of aligned needles whose diameters would be of the order of one average wavelength of visible light while the spacing between the needles would be the equivalent of several wavelengths. Efficient absorption is achieved through multiple reflection of incident photons between the acicular growths on the surface [5]. Horwitz suggested the use of a surface uniformly distributed with holes, whose approximate diameter is equal to the average wavelength in the solar spectra, to capture light through multiple reflection. Horwitz had difficulty in producing this surface and consequently obtained absorptivities less than 40% [6]. Cuomo had better success in obtaining densely forested columnar structures employing chemically vapour deposited tungsten. Absorptivities obtained by Cuomo with these surfaces were over 95% in some instances [5].

Elemental Te, because of its environmental stability, favourable energy gap, and applicability to self shadowing vapour deposition (e.g., low self-diffusion constant [7] and preferred growth direction [8]) was chosen for study in the context

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of a morphological absorbing surface. Absorptivities as a function of deposition angle were determined to ascertain the optimum absorptivity, α, versus this angle. X-ray studies were performed to determine direction of preferred orientation.

2. Experimental procedures

The Te used in these experiments was 99.999% pure semiconductor grade material*. Deposition was carried out using a Pyrex boat–tantalum heating element configuration. Polished substrates of Aluminum Association Type 5052 Al (Al–2.5% Mg–0.25% Cr) were used as substrates for all absorptivity samples. The substrates for absorptivity measurement were flat sheets. In addition, a commercially pure copper tube was similarly coated with Te in an effort to produce a continuous surface which would show the alteration in surface morphology with changing deposition angle. This specimen was used for scanning electron micrograph studies of morphological change with angle. All Te films were deposited at a bell jar pressure of approximately 10^{-5} Torr. Flat absorptivity samples were coated at angles (ϕ) of 0°, 30°, 60°, 80°, and 85° as measured between the line from the sample centre to the deposition boat and the line normal to the surface on which deposition occurs (Fig. 1). The boat to centre-of-substrate distance was 4 cm. The copper tube substrate for morphology studies was centred directly above the deposition boat at a distance of 4 cm as measured from the lip of the boat to the centre of the tube (see Fig. 2). All Te layers produced had mass/area densities of 3.1777×10^{-4} g cm^{-2} or greater. Separate experiments had shown that, for layers of this amount, absorptivity did not increase with increasing with increasing amounts of tellurium deposited. Thickness measurements of Te layers were not possible because of the extremely textured nature of the layers.

Normal spectral reflectivities, r_n as a function of wavelength (0.4 to 0.7 μm) were measured on a Bausch and Lomb Spectronic 20 spectrophotometer. Absorptivity values, a, as a function of wavelength were calculated from: $a = 1 - r_n$. Total solar absorptivity for each deposition angle was calculated for an air mass of 2 using the methods outlined by Moon [9, 10].

3. Results and discussion

Fig. 3 shows the effect of deposition angle on total solar absorptivity of Te films deposited on flat substrates. In all cases, the absorptivity was found to vary by less than 0.035 over the entire wavelength range over which it was measured. In most cases, the maximum variation was approximately 0.005. At an oblique deposition angle of approxi-

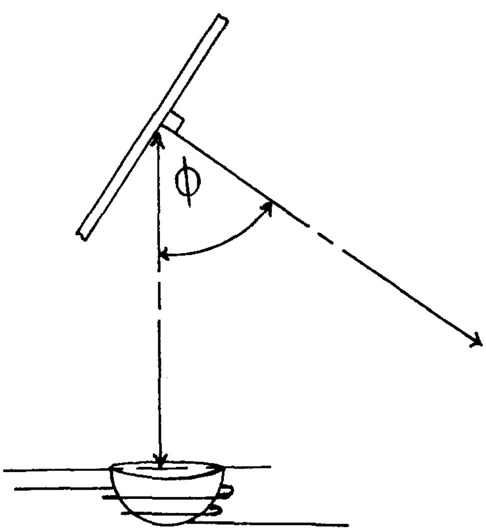

Figure 1 Aluminium substrate–evaporation boat orientation.

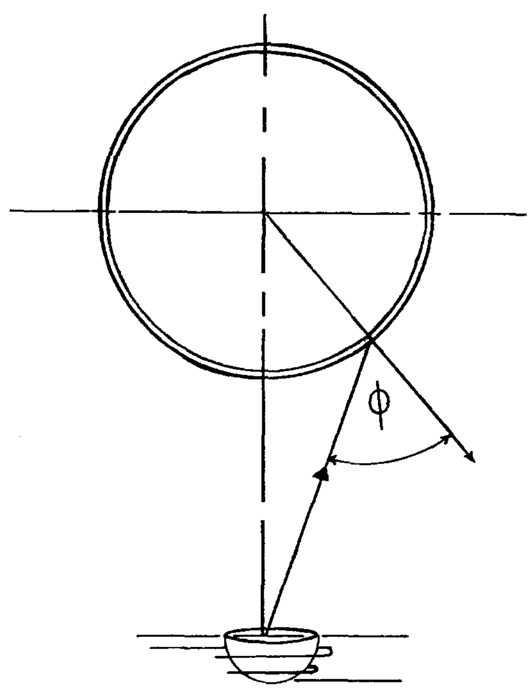

Figure 2 Copper tube–evaporation boat orientation.

*Ventron Corporation, Alfa Division, P. O. 299, 152 Andover Street, Danvers, MA 01923, USA.

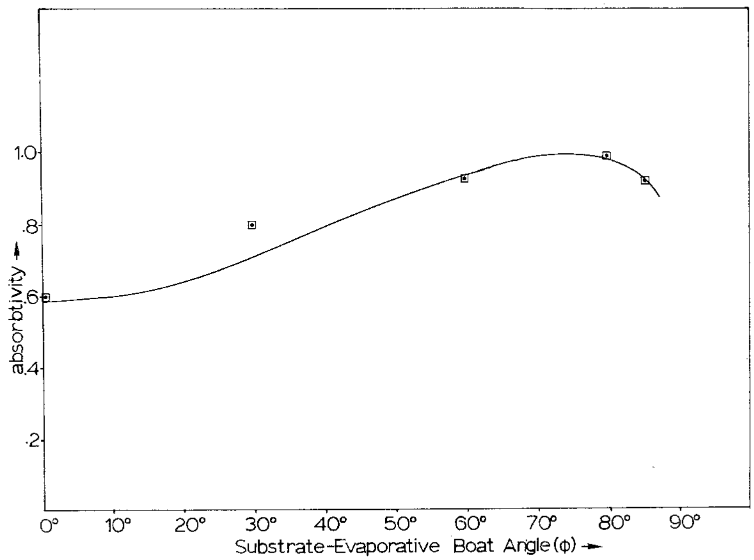

Figure 3 Graph of absorptivity versus substrate–evaporation boat angle.

mately 80° the absorptivity is maximum with an absorptivity greater than 95%.

As shown in Fig. 4, the morphology at 10° is seen to be slightly nodular and almost smooth. At 60° the nodular surface (Fig. 5) texture has developed a more acicular structure. At 80° a densely packed forest of needle-like crystallites (Fig. 6) is evident. These crystallites are seen to be of the approximate order of size as the average wavelength of solar radiation, and interstices between them are several wavelengths in dimension. The high absorptivities manifested by the samples deposited at angles of 80° is attributable to the needle-like morphology which provides for multiple reflections of incident photons. The low absorptivities observed in less obliquely angled substrates is the result of the smoother, more highly reflective nodular morphology which does not effectively promote multiple reflection of incident photons and consequent trapping of solar spectra.

An X-ray evaluation of polycrystalline Te deposit produced at a deposition angle of 80° the relative reflection intensities shown in Table I. If this deposit were crystallographically random, the relative intensities would, of course, be those shown for the American Society for Testing and Materials (ASTM) powder diffraction standard pattern. As may be seen, this tellurium deposit shows a preferred orientation with (1 0 2) planes being preferentially oriented parallel to the substrate surface.

4. Conclusion

High absorptivity values (95%) were obtained using Te vapour deposited at oblique angles on Al substrates. The angle of deposition which yielded the highest α values was 80°. SEM photomicro-

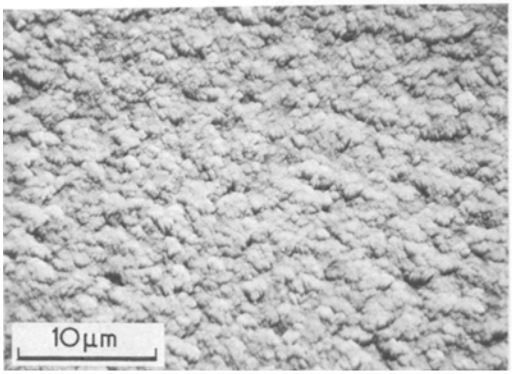

Figure 4 Scanning electron micrograph of silver specular band region of Te on Cu tube (angle = 10°) (× 1680).

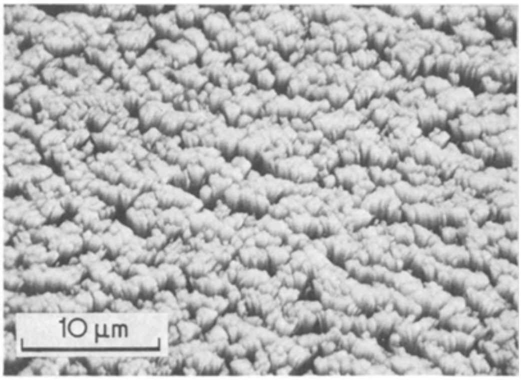

Figure 5 Scanning electron micrograph of gray band region of Te on Cu tube (angle = 10°) (× 1680).

TABLE I Te Miller indices, corresponding ASTM intensity ratio, and self shadowed Te measured intensity for a typical sample deposited at an angle of 80°, and a vacuum ~ 10^{-5} Torr.

Miller indices ($h\ k\ l$)	ASTM intensity ratio	Self shadowed Te measured intensity ratio
100	20	13
101	100	40
102	37	100
110	31	8
111	11	–
003	8	31
200	4	–
201	20	–
112	7	–
103	2	14
202	12	6
113	13	12
210	8	–
211	8	–
104, 203	7	17

*From powder Diffraction Card File # 4-554.

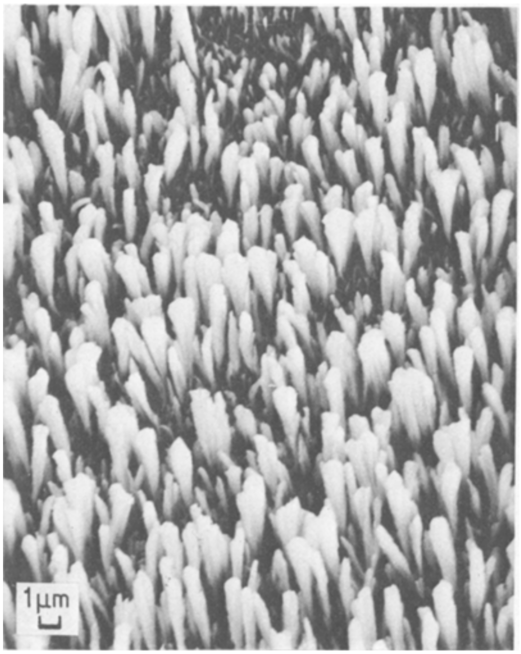

Figure 6 Scanning electron micrograph of black band region of Te on Cu tube (angle = 10°) (X 2180).

graphs demonstrated that this high absorptivity was largely due to the development of needle like dendrites which act as light traps through multiple reflection of incident radiation. It may be possible that other materials which possess low self diffusion constants and show preferred growth directions and also lend themselves to vapour deposition techniques may be employed in producing surfaces of high absorptivity. If obliquely angled vapour deposited films can be made sufficiently thin so that the emissive characteristics of metallic substrate are manifested while retaining the high absorptivity of the overlying textured film, a highly efficient selective absorbing surface will result.

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