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CHEMICAL VAPOR DEPOSITED AMORPHOUS SILICON FOR USE IN PHOTOTHERMAL CONVERSION

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Abstract

Efficient photothermal conversion requires surfaces of high solar absorptance and low thermal emittance. This can be accomplished by the tandem action of a good infrared reflector overlaid by a film of sufficient solar absorptance that is transparent in the infrared. Crystalline silicon is a suitable candidate for the absorber layer. Its indirect band gap, however, results in a shallow absorption edge that extends too far into the visible. In contrast, the absorption edge of amorphous silicon is steeper and located farther into the infrared, resulting in a larger solar absorptance. We report on the fabrication of amorphous silicon absorbers by chemical vapor deposition (CVD). Their optical and structural properties are determined as a function of the deposition temperature. We describe the effects of a progressive crystallization during anneal above 650 C and report the performance of converter stacks that are identical "twins" except for the use of a polycrystalline silicon absorber in one and an amorphous absorber in the other.

Introduction

Much of the current research on spectrally selective surfaces for photothermal solar energy conversion is centered around the dark mirror concept, wherein a layer of material of high infrared reflectance is overlaid with a layer of meterial of high visible absorption. This absorbing layer must be transparent to the infrared to let the reflecting layer "look through" in the infrared, thereby reducing thermal losses. Silicon has been the preferred material for a variety of reasons. It is abundant in supply and inexpensive; important factors in view of the large quantities of material that will be required to produce the large surfaces for spectrally selective photothermal converters. Also important is the large amount of scientific and technological knowledge that exists for silicon, as a result of its use in the microelectronics industry. Silicon has been widely studied for its electronic properties, but little investigation has been devoted to its use as an absorbing material. Silicon has an indirect bandgap resulting in a shallow absorption edge located too near the center of the solar spectrum, resulting in a loss of solar absorptance. Semiconductors with a direct gap and an absorption edge farther out in the infrared absorb a larger fraction of the solar spectrum than does crystalline silicon, and are superior in this respect. Our amorphous silicon has been shown to possess a sharper absorption edge, which is shifted to the red, enabling it to absorb a larger fraction of the solar spectrum.

Amorphous Silicon as a Photothermal Absorber

Interest in the use of amorphous silicon as a model system of an elemental amorphous material arose in the early 1970's. As its optical properties and fabrication processes became better known, the use of amorphous silicon as an absorber became of interest.[1-3] Amorphous silicon has an intrinsically higher absorption coefficient, leading to greater solar absorptance. Its absorption edge is shifted to the red, allowing a greater fraction of the solar flux to be absorbed. The number of free carriers is reduced, resulting in good infrared transmittance that is maintained to elevated temperatures.

There are four primary processes for depositing amorphous silicon: sputtering, electron beam evaporation, RF glow discharge, and chemical vapor deposition (CVD). Of these, all but one, CVD, are vacuum-based methods with the inherent size and geometry limitations of the systems. CVD proceeds at atmospheric pressures in open ended tubes and has the ability to coat many varied and large substrates in a continuous, flow-through manner. CVD therefore shows significant promise for producing the large-scale optical coatings necessary for thin film selective surfaces. The CVD process also exposes stacks to fabrication temperatures above operating temperatures, permitting early detection of stack failure.

We have made polycrystalline silicon by CVD, but deposition of amorphous silicon was deemed unlikely to succeed because it was known that amorphous silicon produced by sputtering and electron beam evaporation crystallized at 500 C, whereas CVD of silicon required a minimum temperature of 600 C for reasonable deposition rates. Our understanding of the situation changed when RF glow discharge produced silicon containing substantial amounts of hydrogen (1 to 20%) was found to resist crystallization at temperatures up to 680 C.[4] This hydrogenated silicon thus suggested to us the possibility of producing an amorphous silicon by CVD, by indicating a region of overlap of 600 to 680 C where the silicon would remain amorphous and the CVD process would work. At this point we began preliminary work on CVD silicon deposited at 600 C. We found that this silicon was indeed amorphous, and further research has shown that this silicon is amorphous to 670 C, confirming early reports in the literature that CVD silicon crystallized at temperatures of 650 C to 700 C.[5,6]

Preparation and Measurements of the Amorphous Silicon

Our amorphous silicon films are produced by pyrolytic decomposition of silane gas in a radiation-heated, horizontal reactor (Applied Materials AMH 704). The carrier gas is helium at a nominal gas flow of 10 l/min. The silane concentration is 0.25% to 1.0%. Deposition temperatures range from 500 C to 800 C, determined with an accuracy of ±5 C. Thicknesses vary from 0.5 to 4.0 μm, with the majority of the films in the 1.0 to

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2.0 μm range. The deposition rates range from 2 to 40 Å/sec depending on both the deposition temperature and silane concentration. It has been found that CVD silicon can be produced at temperatures as low as 550 C with deposition rates of 2 to 4 Å/sec. At a deposition temperature of 600 C and a silane concentration of 1%, the deposition rate was 15 Å/sec. This rate increases as the temperature is raised, to about 675 C where the rate begins to decrease as the crystallization temperature is approached. These very substantial CVD deposition rates at temperatures below the crystallization temperature eliminated a major concern of ours regarding the CVD of amorphous silicon.

The film thickness growth is monitored in situ by an emissometer at a wavelength of 2 μm. An interference method is employed that measures the thickness of the growing films by monitoring the modulation of the emissivity by the growing silicon film.

Thickness of the films was determined by etching a step in the silicon film and then using a Mirau two-beam interference objective. The interferograms were recorded on film, enlarged, and measured. This was done with both white and monochromatic (5460 Å) light.

The refractive index of the films was calculated from spectral positions of the minima of the interference fringes of the reflected light. The reflectance was measured with a Perkin-Elmer double-beam spectrophotometer model 137 ($2.5\ \mu m \leq \lambda \leq 15\ \mu m$) and a model 450 ($0.35\ \mu m \leq \lambda \leq 2.7\ \mu m$). The refractive index was determined in the wavelength region in which the absorption coefficient is less than $2 \times 10^4\ cm^{-1}$, so the contribution of the imaginary part of the refractive index is negligible. The value of the refractive index was determined with an accuracy of ±1.5%, limited by the accuracy of the determination of the sample thickness.

The absorption coefficient alpha was calculated from the transmittance. In the near infrared the interference fringes were averaged by taking into account the values of the transmittance at wavelengths that correspond to the mean values of the wave-numbers of two adjacent maxima and minima only. Values of alpha were determined only for $\alpha \geq 1000\ cm^{-1}$. Lower values of the absorption coefficient are difficult to determine using thin film samples.

The structure of the films was determined by a GE XRD-5 x-ray diffractometer, using a Cu target and a Ni filter ($\lambda = 1.54$ Å). The angular resolution of the detector was 0.2^o.

Crystallization processes were studied by annealing the samples in a flowing helium atmosphere at elevated temperatures between 550 C and 800 C.[7]

Review of Measured Properties

The quantities of interest we have studied include refractive index, absorption coefficient, and crystallization. These were first studied on as-deposited samples, and then as the samples were annealed.

Films deposited at temperatures in the range 550 C to 560 C all showed, within experimental error, the same profile of absorption coefficient (Figure 1). Films deposited at substrate temperatures between 650 C and 750 C show a shift toward crystalline values of absorption coefficient, with films deposited at 680 C having a value midway between values for 650 and 750 C. Films deposited at temperatures above 750 C again all show similar values of the absorption coefficient.

The refractive index was measured for a sample deposited amorphous, and then annealed in several steps at 650 C. As shown in Figure 2, as the sample begins to crystallize, the refractive index begins shifting toward the crystalline values. (Curve 7 is the value of crystalline silicon.)

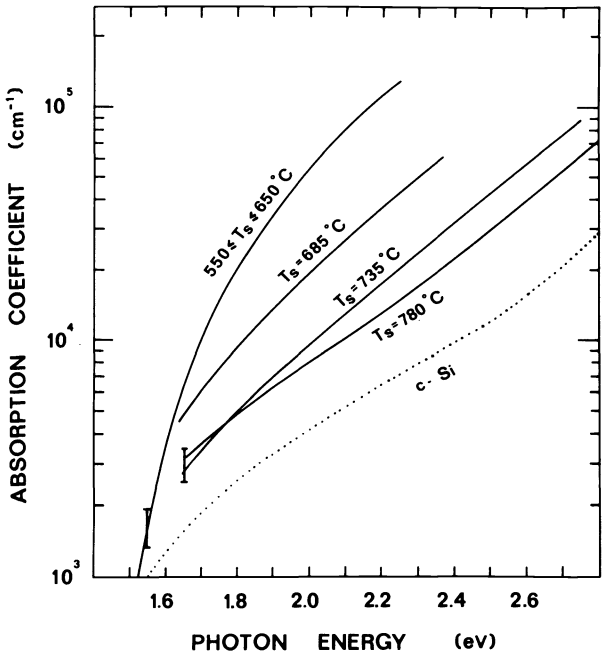


Fig. 1. Absorption constant as a function of photon energy for different deposition temperatures (from ref. 7).

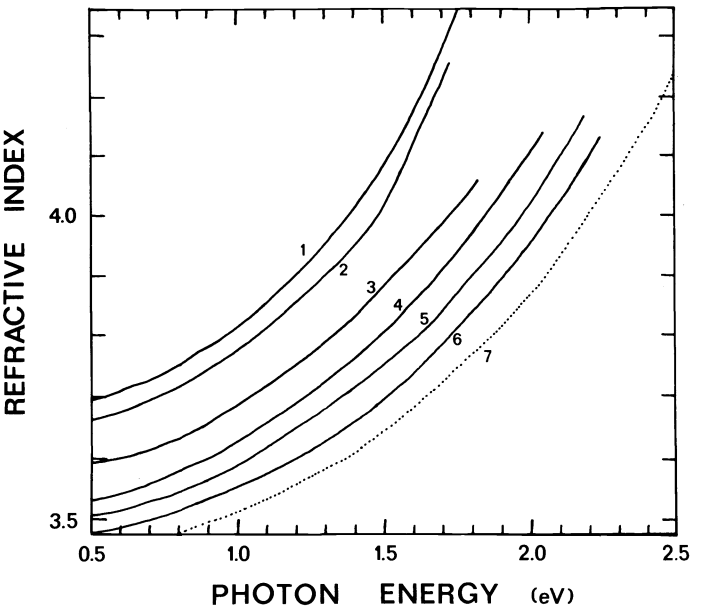


Fig. 2. Index of refraction as a function of photon energy for a sample annealed at 650 C for successive annealing times (from ref. 7).

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X-ray diffraction studies of the films prepared below 650 C indicate an amorphous structure. The average diameter of the coherently scattering regions is approximately 20 Å, as obtained from the angular width of the <111> peak. For deposition temperatures of ∿670 C, small and relatively broad peaks appear. These peaks narrow and their intensity increases gradually with increasing deposition temperature. At 685 C the average particle size is 70 Å and reaches ∿200 Å at 715 C deposition temperatures. X-ray diffraction patterns indicate a gradual change from amorphous to polycrystalline structure.

Surface quality is also strongly affected by deposition temperature. Samples produced on fused quartz show highly reflective (i.e., low scattering) surfaces when deposited at temperatures between 550 and 650 C. At temperatures at which the silicon is partially crystallizing (650 to 750 C), the surface is rough and strongly scattering. Samples deposited above 750 C are again specular and show very small amounts of scattering.

Comparison of the Solar Absorptance of Crystalline and Amorphous Silicon

One of the primary arguments that has been made for amorphous silicon in photothermal solar energy conversion is its higher absorption coefficient. As shown in Figure 1 the absorption coefficient is from 0.8 to 1.3 orders of magnitude larger for amorphous silicon. An increase in solar absorptance therefore should be possible with properly prepared samples.[3]

In addition to the increased absorption coefficient, amorphous silicon has an absorption edge that is steeper than crystalline silicon and is shifted toward the infrared. This should permit amorphous silicon to better match the spectral profile of an ideal solar absorber.

In order to compare the performance of an amorphous silicon photothermal converter with that of a polycrystalline one, we made theoretical calculations of the reflectance of photothermal stacks with amorphous and crystalline silicon using a multilayer thin film analysis program. We then produced actual "twin" stacks whose only difference in fabrication was the use of amorphous or crystalline silicon in the absorber layer.

Theoretical Design

For the theoretical calculations, reflectances were calculated in the region 350 nm to 2600 nm using the refractive indices and optical constants of the components of the photothermal converter stacks. Optical constants for silver are from the AIP Handbook, while the constants for silicon are from experimental data (Figures 1 and 2) extrapolated where necessary for calculations. Values of the refractive index for the AR coating were taken from the CRC Handbook. Four reflectances were calculated: 0.65 μm thick polycrystalline silicon absorber layer, 0.65 μm thick amorphous silicon layer, 1.42 μm thick polycrystalline silicon layer, and 1.42 μm thick amorphous silicon layer. These reflectance data were then plotted on a distorted wavlength scale. Because of the distortion of the wavelength scale in correspondence to the spectral profile of the sun, the area under the curve gives directly the solar absorptance with no need for performing a numerical integration. The areas of the distorted wavelength plots were measured by planimetry.

Theoretical Results and Discussion

The results from the calculations show that for the samples with a thin silicon absorber, the amorphous silicon stacks had an increased absorptance of approximately 7% over the polycrystalline silicon stacks. For the samples with a thick silicon absorber, the amorphous silicon stacks had an increased absorptance of approximately 3%. We would expect this type of behavior to be due to thickness, because for the thicker absorber layers the polycrystalline samples have a greater chance to trap the incoming solar flux.

Experimental Design and Results

We fabricated stacks consisting of fused quartz substrate, evaporated silver reflector, evaporated chromium oxide barrier to protect the silver against agglomeration, silicon absorber, and an antireflection layer of evaporated antimony trioxide (Figure 3). The first sequence was the deposition of silver and chromium oxide onto the fused quartz substrates. Then silicon was deposited at 600 C two samples at a time so that all parameters, including thickness, were the same for each sample of a twin. Then one sample from each pair was annealed for 5 minutes at 800 C, a procedure which initiates crystallization of the silicon as evidenced by the x-ray diffraction patterns of the <111> peak. The samples were antireflected with evaporated antimony trioxide. Among the twins, the silicon absorber thickness varied from 0.64 μm to 1.42 μm.

The near normal specular reflectance was measured in the range 0.35 μm to 2.70 μm at room temperature. The solar absorptance measurements were made by averaging adjacent fringe minima and maxima and plotting the results on a distorted wavelength plot, as was done for the theoretical case described above.

The results of these measurements are pending due to fabrication problems which altered the twin nature of these stacks. Initial calculations show a strong dependence on the location of the anti-reflection coating interference minima and on the comparative reflectivity of the silver between the twins. Some samples show a deterioration of the silver reflectance, due to pinholing and agglomeration, which introduces false absorption.

Conclusions

The theoretical results are encouraging and indicate that amorphous silicon photothermal converter stacks can perform substantially better than polycrystalline stacks. This is especially true if thin (∿0.5 μm thick) absorber layers of amorphous silicon are used. More calculations should be done to determine an optimal

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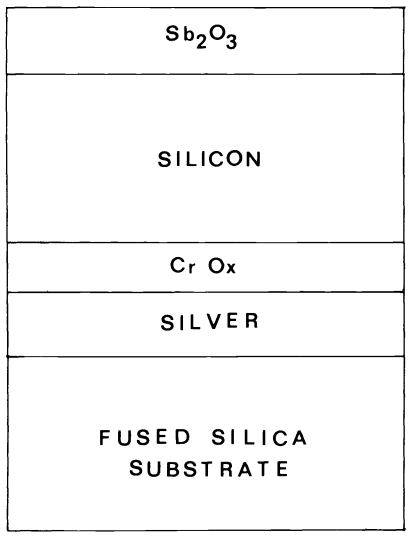


Fig. 3. Schematic of photothermal converter stack construction.

thickness for maximum absorptance. Additionally, placement of the anti-reflection fringe minimum in the visible (solar emission spectrum) should be carefully studied to determine the best location with respect to the absorbing properties of the amorphous silicon layer.

The experimental results have not yet given us a valid comparison, but rather have indicated areas of fabrication that have a strong effect on the performance of the photothermal converter stacks. Special care must be taken to insure the twin nature of the stacks if valid comparison of data is to be accomplished. This implies special care to maintain reflectivity of the reflecting layer, reduction of any surface scattering (required for specular measurements), and equivalence of absorber thickness.

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References

1. Seraphin, B. O., Proceedings of the Symposium on Material Sciences Aspect of Thin Solid Films in Solar Energy Conversion, Tucson, Arizona, 20-22 May 1974, NSF-RANN Grant GI-43-795, p. 7. 1974.
2. Seraphin, B. O., J. Jap. Soc. Phys., Vol. 44, p. 11. 1975.
3. Griffith, R. W., in Sharing the Sun--Solar Technology in the Seventies, Winnepeg, Canada, 15-20 August 1975, International Solar Energy Society, Vol. 6, p. 205. 1976.
4. Brodsky, M. H., IBM Research Report, RC 6278 (#26902), November 11, 1976.
5. Emmanuel, A., and Pollock, H. M., J. Electrochem. Soc., Vol. 120, p. 1586. 1973.
6. Nagasima, N., and N. Kubota, J. Vac. Sci. Tech., Vol. 14, p. 54. 1977.
7. Janai, M., D. D. Allred, D. C. Booth, and B. O. Seraphin, Solar Energy Materials, Vol. 1. 1978, to be published.

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