Journal of Non-Crystalline Solids 35 & 36 (1980) 213-218
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RETARDING CRYSTALLIZATION OF CVD AMORPHOUS SILICON BY ALLOYING *

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Amorphous silicon holds considerable promise as a photothermal absorber, but high-temperature-induced crystallization limits its usefulness. To attempt to retard the crystallization, we produced CVD a-Si films alloyed with C, N, B, or Ge. These films crystallized differently than did the non-intentionally doped amorphous material. The crystallization temperature was increased from 680 C to 950 C for 18 at.% C-alloyed a-Si, and even then more than 10 hours were required for crystallization. This retardation of crystallization gives alloyed a-Si absorbers sufficient life expectancy for converters operating at temperatures up to 700 C.

INTRODUCTION

Efficient conversion of solar radiation into high-temperature heat requires surfaces capable of high absorption over the solar spectrum, and low thermal emission losses in the infrared[1-3]. A standard approach to the problem employs the tandem action of a semiconductor absorber deposited on top of a reflector[4]. Silicon has been a favored candidate for the absorber material, since its absorption edge falls approximately between the solar spectrum and the spectral range of the thermal reemmision[5]. Using chemical vapor deposition(CVD), we have developed a spectrally selective surface based on a silicon absorber than can function at a temperature of 500 C[6,7].

Initially the silicon absorber was polycrystalline, but the absorption edge of this material was shallow and permitted too many infrared solar photons to pass through unabsorbed[8]. The absorption profile of amorphous silicon is superior to that of polycrystalline silicon with respect to steepness and spectral position, thereby providing larger solar absorptance[9-11]. Sputtered or evaporated amorphous silicon, however, was known to crystallize rapidly at 550 C[12]; selective surfaces incorporating this material would have too short a lifetime at the required high operating temperatures of photothermal converters.

However, chemical vapor deposition of amorphous silicon improved the situation. Incomplete decomposition of the silane molecule led to the incorporation of hydrogen in the growing film. The resultant material, having a hydrogen content of 1 at.% or less, did not crystallize as rapidly as its sputtered or evaporated counterparts.

Detailed studies showed that crystallization in amorphous silicon is a gradual process that depends on length and temperature of anneal, and proceeds exponentially at higher temperatures. With this in mind, a "crystallization temperature" of 680 C for CVD amorphous silicon was assigned for comparison with the crystallization temperature of 550 C previously observed for sputtered or evaporated amorphous silicon films[13].

The thermally activated crystallization kinetics of CVD amorphous silicon implied,

* This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under contract ER-78-S-02-4899.

however, that a converter operated at 500 C would still have an insufficient lifetime. The coincidence of increased resistance to crystallization with the presence of hydrogen in amorphous silicon suggested that intentional dopants could retard even further the crystallization of CVD amorphous silicon. This paper describes a study of the effects of chosen dopants - C, N, or B - on the crystallization behavior of CVD amorphous silicon. Carbon was given the greatest attention because not only does the solar absorptance of the alloyed material exceed that of the non-intentionally doped(NID) material, but the crystallization is retarded to a point where lifetimes of decades at temperatures above 700 C can be predicted.

SAMPLE PREPARATION AND CHARACTERIZATION

Samples were prepared by the pyrolytic decomposition of silane and dopant gases onto fused quartz substrates in a horizontal, radiation heated atmospheric pressure reactor. A helium carrier gas flow rate of typicaaly 4 ℓ/min was used. Of the total gas flow, silane constituted typically 0.5% and the dopant gases 0.05%. The dopant gases were NH_3(100%), C_2H_2, B_2H_6, and GeH_4, the latter three diluted to 1% in helium. Deposition temperatures ranged from 550 C to 750 C and were determined with an accuracy of ± 5 C. Deposition rates ranged from 350 A/min to 1300 A/min. The film thicknesses were measured with a Mirau two-beam interference objective on a Leitz microscope[14], with most films having a thickness of 1.0 ± 0.2 μm.

Optical properties of the silicon films were determined from transmittance and reflectance measurements made on two Perkin-Elmer spectrophotometers, model 137 ($2.5\ \mu m \leq \lambda \leq 15.0\ \mu m$) and model 450 ($0.35\ \mu m \leq \lambda \leq 2.7\ \mu m$). The refractive indices of the films were calculated from interference fringe maxima and minima, in the wavelength region where the absorption coefficient α was less than $5 \times 10^4\ cm^{-1}$. The absorption coefficients were computed from the transmittance[15] with values of α reported only for $\alpha > 10^3\ cm^{-1}$. For details on the determinations of refractive index and absorption coefficient, the reader is referred to the work of Booth, et al.[14].

Samples were annealed in a flowing N_2H_2 atmosphere at 70 cc/min, the H_2 content being 8.5%. Hydrogen was necessary to prevent the rapid oxidation of the silicon samples which were necessarily annealed at temperatures in excess of 900 C. The annealing temperature of a given sample was monitored to ± 1 C. Before and after each anneal, the optical transmittance and reflectance, and the X-ray diffraction pattern, were measured. After insertion into the annealing furnace, the samples reached anneal temperature within 3 minutes. No overshoot in temperature was observed, and the anneal time began when the samples were inserted into the furnace.

X-ray diffraction measurements insured that the as-deposited material was amorphous, and also monitored the

TABLE I

Representative compositions and CVD process parameters for alloyed amorphous silicon

Composition (at.%)	Substrate temperature (C)	Molar ratio of dopant gas to silane *	Deposition rate (A/min)
3.4 C	630	0.0040	1050
11.5 C	630	0.021	700
18.5 C	630	0.060	840
27.0 C	630	0.096	520
35.0 C	630	0.11	520
15.5 C	630	0.060	1020
13.0 C	700	0.060	1330
23.0 C	750	0.060	640
17 N	575	0.63	640
34 N	630	0.56	740
<0.5 B	600	0.006	1040
0.7 B	600	0.056	680
1.8 Ge	630	0.23	680
11 Ge	600	1.12	820

* Silane at rate of 0.02 ℓ/min added to helium carrier to give a total flow rate of approximately 4.4 ℓ/min.

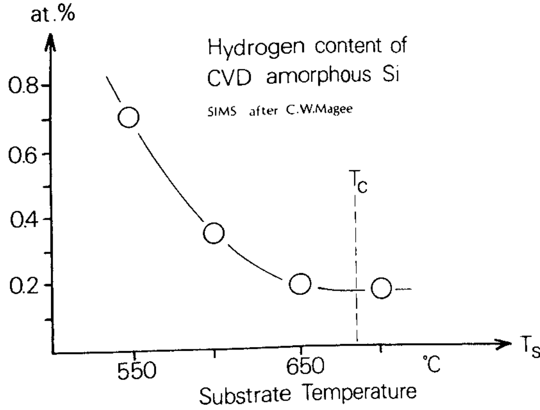

Figure 1
Hydrogen content of NID a-Si films, determinded by SIMS[17].

progress of crystallization during high temperature anneals. The absence of the Si{111} diffraction peak (Cu K_α at $2\Theta=28.4°$) was regarded as evidence of an amorphous structure. On selected samples scans were made over a wide range of angles up to 90° to confirm that no crystalline phases were formed. All of our as-deposited alloyed silicon films are amorphous, except for samples having a high B concentration. The average diameter of coherently scattering regions as determined from the angular with of {111} peak is 20 A, as is the case for the NID material[13].

Transmission electron microscopy revealed the microscopic changes which occur in C-alloyed a-Si(15 at.%) during high temperature anneal[16]. Quantitative elemental analysis was performed by an electron microprobe. Table I summarizes the compositions of various alloyed a-Si films. Certain deposition parameters are included for purposes of comparison.

The hydrogen content of NID a-Si has been determined by secondary ion mass spectroscopy(SIMS) by C.W. Magee of RCA Labs[17]. In Figure 1 the hydrogen content of NID a-Si is shown as a function of deposition temperature. Due to the much higher substrate temperature, pyrolytically deposited amorphous silicon contains less hydrogen than material made by rf glow discharge, which typically contains 2-30 at.% hydrogen in as-deposited films[18].

EXPERIMENTAL RESULTS AND DISCUSSION

Janai, et al.[13] report that CVD a-Si, unlike all other a-Si films deposited at temperatures much below 600 C, is anneal-stable below the onset of crystallization. In contrast, CVD a-Si films alloyed with C, N, or B apparently differ in their crystallization properties, as judged from the response of the x-ray spectra and the optical properties to different anneal temperatures and times. In the NID material the crystallization proceeds throughout the entire volume, starting from random crystallization centers embedded in the amorphous matrix. The hydrogen impurity concentration of a sample about to crystallize is low (Figure 1), and diffuses rapidly enough so that it does not impede the growth of the crystals.

For the material heavily doped with foreign atoms, the x-ray diffraction spectra as well as the transmission electron micro-

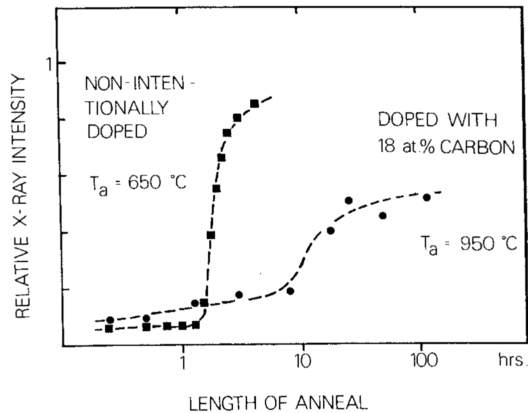

Figure 2
Intensity of the Si{111} diffraction peak (normalized) vs. anneal time T_a.

TABLE II

Crystallization times for alloyed amorphous silicon

Composition (at.%)	Anneal temp(C)	Crystallization time*(hours)
11 C	1040	0.3 ± 0.1
18 C	950	14 ± 4
18 C	990	>2
18 C	1040	0.4 ± 0.1
27 C	1040	≈10
35 C	1040	>10
17 N	950	>90
17 N	990	> 2
17 N	1040	2 ± 1
< 0.5 B	730	< 0.25

* See text for definition.

graphs indicate that the already crystallized areas contain a smaller concentration of dopant atoms than the remaining areas outside. The crystallization is apparently accompanied by a rejection of the dopant into the still amorphous matrix. With the increasing dopant enrichment of the remaining amorphous volume during anneal, the rate of crystallization is progressively retarded. One is reminded of the purification of a growing crystal in the floating zone process, although the limited diffusivity in the solid phase limits the analogy. We see in Figure 2 the intensity of the Si{111} x-ray diffraction peak plotted as a function of the length of anneal, relative to that of a CVD polycrystalline film. The NID film annealed at 650 C starts to crystallize after less than 2 hours, in agreement with the results of Janai, et al.[13]. In contrast, a film alloyed with 18 at.% C withstands an anneal at 950 C for up to 10 hours before substantial crystallization begins.

The anneal curves in Figure 2 show that the crystallization proceeds quite differently for alloyed films compared to NID a-Si films. For example, whereas the {111} peak in the NID material does not appear during an initial induction period, in C-alloyed films it grows from the beginning of the anneal. The overall change is much slower, however, in spite of the much higher temperature. Even after long-term anneal, the heights of the {111} diffraction peak fall short of the level eventually observed in crystallized NID material. In the alloyed film, the crystallization apparently leaves a certain fraction of the volume amorphous, due to the residual high concentration of the dopant. Further growth of the crystalline regions subsequently advances at such a small rate that it effectively ceases before all of the alloyed a-Si is crystallized.

In order to describe the crystallization process in quantitative terms, we defined "crystallization time" as the time at which the inflection point occurs in the curves of Figure 2. Table II summarizes the crystallization times for the dopants and anneal temperatures investigated. Plotted as a function of reciprocal absolute temperature, the logarithms of the crystallization times given in Table II fall on a straight line. This suggests expressing the rate of crystallization in terms of an Arrhenius equation. From analysis of this and similar data(Janai, et al.[13]), we obtained activation energies of 78 kcal/mole (3.4 eV/atom) for the NID material[19] and 110 ± 20 kcal/mole(4.8±1 eV/atom) for a-Si alloyed with 18 at.% C. Note that these activation energies are roughly twice the bond energies of the Si-Si bond(42 kcal/mole) and the Si-C bond(69 kcal/mole)[20].

Figure 3 compares the absorption coefficients of the NID a-Si films after Janai et al.[13] with those of films alloyed with B, N, C, and Ge, respectively. Note that all four dopants generate a low-energy tail in the absorption coefficient of the alloyed material, absent in the NID material. Figure 4 plots the absorption coefficient of films alloyed with C at various concentrations. In films alloyed with a higher C concentration, the profile of the absorption coefficient drops below that of the NID a-Si above photon energies of 1.6 eV.

Another frequently used quantity for comparing the optical properties of amorphous semiconductors is the optical gap E_0, defined by $\alpha h\nu = A(h\nu - E_0)^2$ where α is the absorption coefficient, A a constant, and E_0 is the energy of the band gap. For our alloyed samples, we found values of E_0 from 1.50 eV to 1.65 eV, compared to 1.60 eV for the NID a-Si. In contrast, rf glow discharge a-Si:carbon films show values of 2.25 eV to 3.0 eV as reported by Anderson and Spear[21].

Our study of the crystallization of C-alloyed films had shown that noticeable

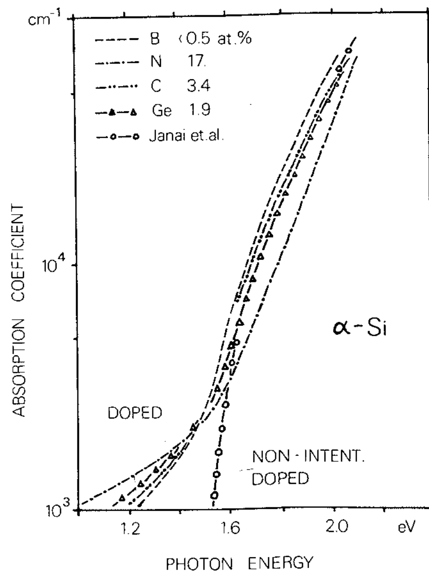

Figure 3
Absorption coefficient as a function of photon energy for a-Si alloyed with B, N, C, or Ge.

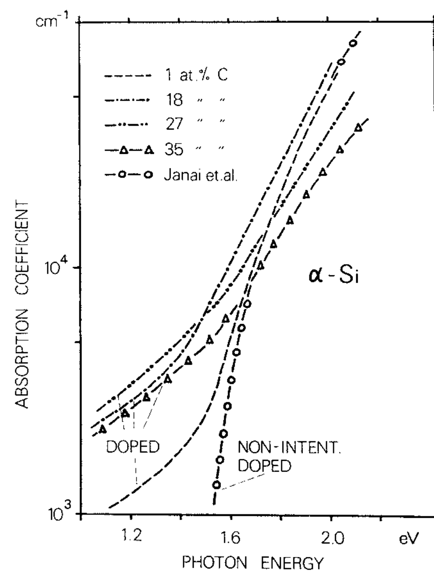

Figure 4
Absorption coefficient as a function of photon energy for a-Si:C alloys at various concentrations.

changes could only be expected in a reasonable laboratory time frame, if an anneal was performed close to 1000 C. Consequently, we measured the changes in absorption coefficient and index of refraction that accompany the crystallization after anneals of various length at 990 C. The results are shown in Figures 5 and 6 for a set of films alloyed with 18 at.% C. Based on the data from Table II we calculated a crystallization time of about 2 hours for an anneal temperature of 990 C. The optical changes shown in Figures 5 and 6 occurred in times that were shorter by an order of magnitude. We also note that the low energy tail of the absorption coefficient does not substantially shift with annealing, in agreement with results from annealed rf glow discharge a-Si films[22].

The electron spin reasonance for a number of NID and C-alloyed samples was also measured[23]. For the NID samples deposited at comparable substrate temperatures, the results are in agreement with Hirose[24]. For the C-alloyed samples, the spin density increased with increasing C concentration, beginning with the NID density value.

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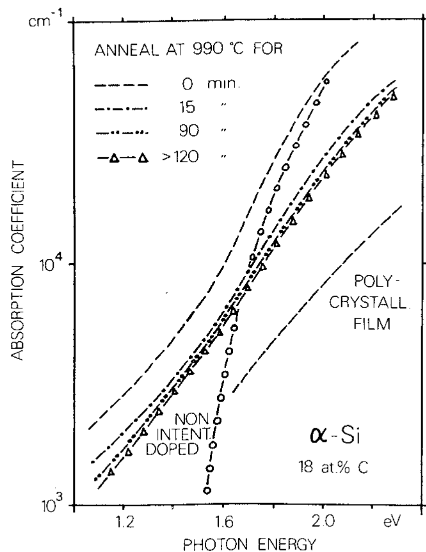

Figure 5
Absorption coefficient as a function of anneal time at 990 C for an 18 at.% C a-Si alloy.

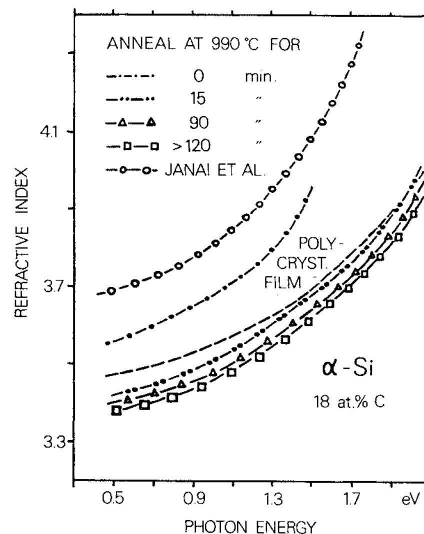

Figure 6
Refractive index as a function of anneal time at 990 C for an 18 at.% C a-Si alloy.

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