COMPARISON OF THE EFFECTS OF SUBSTRATE TEMPERATURE AND 2% MOLECULAR HYDROGEN ANNEALING ON THE OPTICAL GAP OF a-Ge THIN FILMS

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The effects, of substrate temperature, T_S, and 2% molecular hydrogen annealing on the optical gap, E_O, of evaporated a-Ge thin films on borosilicate glass substrates are compared. As T_S increases from 100°C to 200°C, E_O increases from 1.13 eV to 1.43 eV. However, as T_S increases further to 400°C, Eo decreases to 1.27 eV. This trend is not observed when an as-deposited film is annealed in steps from 100°C to 400°C in an atmosphere of 98% nitrogen and 2% hydrogen. In the latter case, a non-linear increase of E_O is observed.

I. Introduction

Efforts are being directed towards using microcrystalline tetrahedral semiconductor material for better efficiency in thin film solar cells.[1] Since microcrystallinity is associated with increasing deposition temperature and annealing temperature, the effect of both these temperatures on the optical bandgap would be interesting to be compared. There is considerable interest on whether an annealed tetrahedral semiconductor thin film sample in an atmosphere of molecular hydrogen has similar properties, particularly the optical bandgap as that as microcrystalline samples made at an initially elevated substrate temperature.

We report here the change of the optical energy gap with elevated substrate temperature in a-Ge thin films with comparison to increasing annealing temperature in an atmosphere of 2% molecular hydrogen.

II. Experimental Techniques

Thin a-Ge films are obtained by thermal evaporation of high-purity (99.999%) germanium lumps from a tungsten boat kept at a distance of 20 cm from ultrasonically cleaned borosilicate glass substrates in pressure better than 10^{-6} torr.

Six samples of thickness ~ 1 μm are deposited at substrate temperatures of 100°C, 150°C, 200°C, 250°C, 300°C and 400°C. The rate of deposition is maintained at 120Å/s - 150 Å/s.

An as-deposited sample STF20 (T_S ~ 27^0C) is annealed in steps at 100^0C, 200°C, 300°C and 400°C in an atmosphere of 98% nitrogen and 2% hydrogen for 10 minutes. Optical measurements are taken at room temperature with a double-beam spectrophotometer. The optical gap is obtained by Tauc plot.

III. Results and Discussion

The optical gap increases from 1.13 eV to 1.43 eV as the substrate temperature increases from 100°C to 200°C. However, when T_S is increased further to 250°C, 300°C and finally to 400°C, E_O decreases to 1.38 eV, 1.31 eV and 1.27 eV respectively. Table 1 shows the changes of E_O with T_S.

No.	Sample	Ts (°c)	Eo (eV)
1	SH 10	100	1.13
2	SH 20	150	1.34
3	SH 30	200	1.43
4	SH 40	250	1.38
5	SH 50	300	1.31
6	SH 60	400	1.27

Table 1: The change of optical bandgap values, E_O, with substrate temperature, T_S.

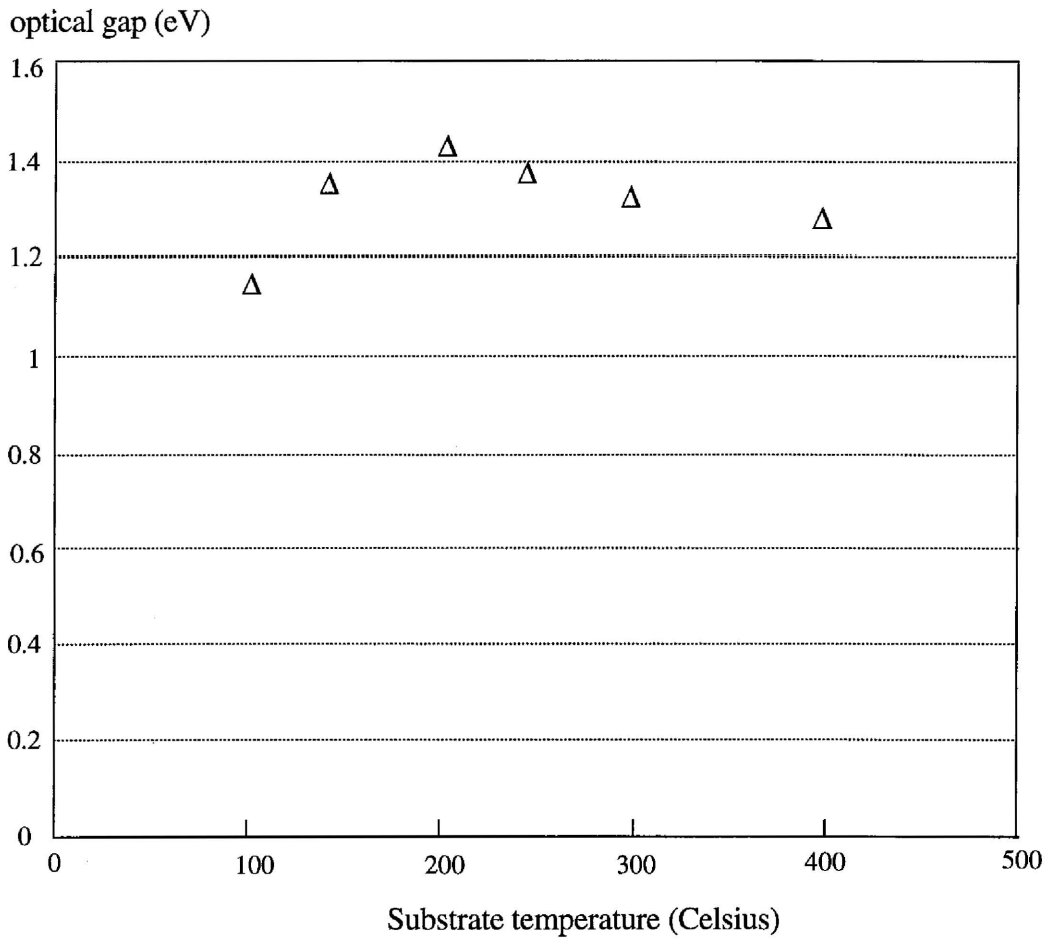

Fig 1: The change of E_o with T_s

When the as-deposited sample STF 20 is annealed in steps from 100°C to 400°C, the optical bandgap increases from 0.81 eV to 0.89 eV. Table 2 shows the change of E_o values with annealing temperature in 2% hydrogen.

Annealing temperature (^{0}C)	Eo (eV)
(as-deposited)	0.78
100	0.81
200	0.81
300	0.83
400	0.89

Table 2: The change of E_o values with annealing temperature, T_a.

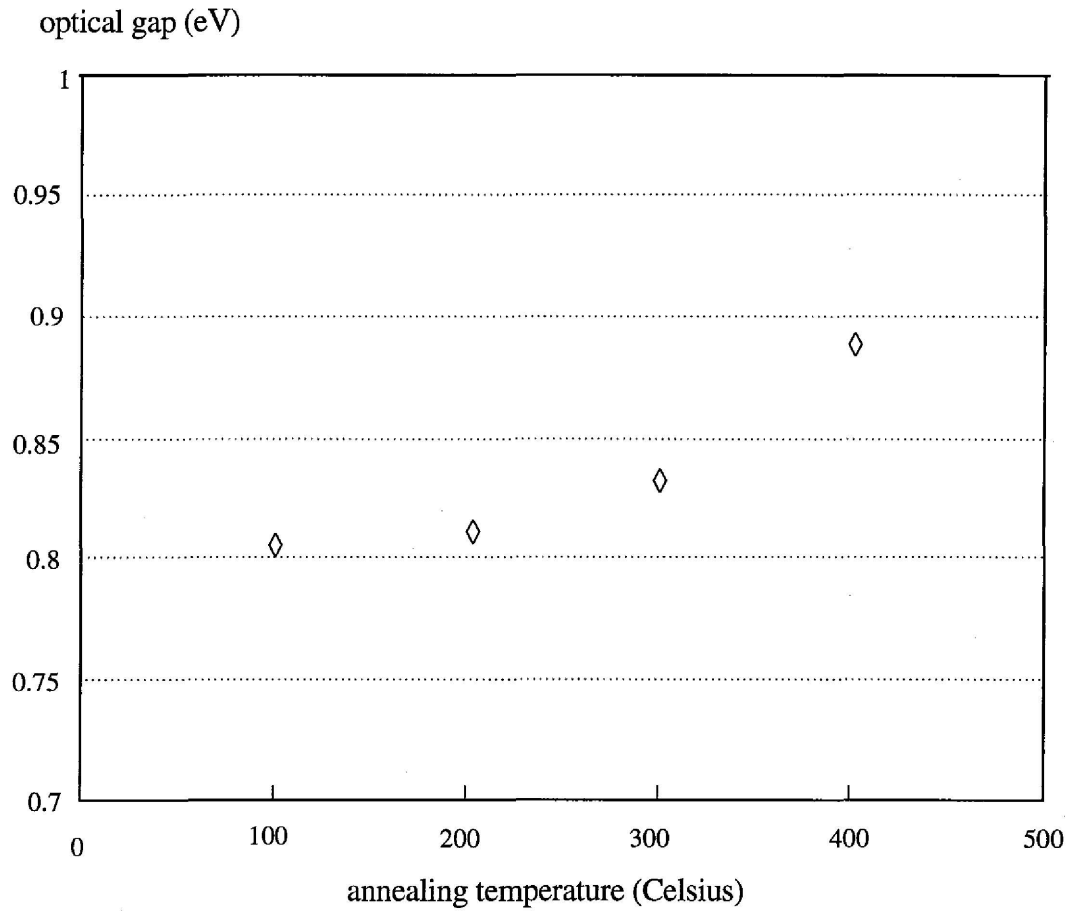

Figure 2: The change of E_o with T_a in 2% hydrogen

The change of optical bandgap values is strongly related to the structure of the films. Evaporated a-Ge films of thickness ~ 1 μm on glass substrates at T_s < 240°C show only a broad X-ray diffraction peak at $2\theta = 49°C$, which is typical of the amorphous phase.[2] However, when $T_s > 240°C$, two narrow lines at $2\theta = 53.7°$ appear in the spectra superimposed on the broad peak, indicating the presence of microcrystals embedded in the amorphous phase.

Upon increasing T_s, the strength of the narrow lines keeps growing while the broad peak decreases. Finally, at $T_s \sim 285°C$, the amorphous phase no longer exists. Laue photographs, however, indicate the amorphous nature of all the samples. This may be due to the crystalline nuclei not large or numerous enough for the characteristic crystalline pattern.

The variations of the optical gap presented here differ from previous observations of the asymptotic behavior of the optical gap with higher substrate temperature. The initial trend where E_O varies more rapidly with T_S at lower values, however, is similar. F. Evangelisti et al[2] reported an increase of local order as a function of T_S in a-Ge samples grown at T_S<240°C with the sudden appearance of microcrystals with relatively large size of the order of 200Å or more at $T_S \approx 240$°C. For substrate temperatures between 100°C and 240°C, a large percentage of material with a narrower distribution of the second-neighbour average distances exist. For T_S>240°C, crystallites of the order of 200Å or more are distributed in the amorphous phase. Using Raman scattering, all samples grown at $T_S \geq$ 245°C exhibit a shift of ~ 2.0 - 2.5 cm^{-1} towards lower energy. Because the shift is constant from sample to sample and the crystallite dimension is already large (D>300Å) and increasing with T_S, this shift is attributed to strains present in the material.

A relatively large optical gap (1.43 eV) is obtained at the initially high T_S (~ 200°C) and may be due to increasing network order. A pronounced optical gap of 1.7 eV in microcrystal silicon film obtained by P.H. Fang et.al. created considerable interest in photovoltaic applications.[3] Richter and Ley[4], however, reported microcrystalline silicon films with E_O ~ 1.1 eV at the substrate temperature of 350°C; a much smaller gap than that observed by P.H. Fang et. al.[3] The decrease in gap values of a-Ge films with further increase in T_S may be due to strains in the network. Furthermore, the presence of oxygen cannot be ruled out and may have also caused the optical gap to be lowered in the high T_S samples obtained by Richter and Ley. The role of oxygen in causing strains in the a-Ge network needs to be investigated. Short-range order variations associated with changes in the bond-angle distributions may also directly modify the optical gap.

Modifications of bond-angle distribution may result in changes in both dihedral angle distribution and ring statistics that in turn affect the optical gap. Since topological disorder in evaporated a-Ge films is at the minimum at T_S > 200°C, the lowering of E_O at T_S>250°C may be due to quantitative disorder. The effects of topological and quatitative disorder on the band gap are discussed by Yonezawa.[5]

Annealing generally increases the optical gap. The values presented here are lower than those obtained by Theye[6] using similar temperature range. However, one must also take into considerations the rate of deposition[7,8] and film thickness.[9,10] Annealing is believed to reduce voids and bond distortions. The optical gap values do not decrease even when $T_a \sim 400°C$, implying the possibility of no phase change even at 400°C. A non-linear increase of E_o is observed. The role of molecular hydrogen in annealing, however, is not fully understood. Hydrogen may be expected to play a significant role as in chemical annealing.[11] Similarly deposited a-Ge films annealed in N_2 only have lower optical gaps.

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