

## Effect of annealing and substrate temperature on structural and optoelectronic properties of a-SiGe:H thin films

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**Abstract:-** Hydrogenated a-Si<sub>0.47</sub>Ge<sub>0.53</sub> thin films were prepared at 200 and 250°C by the glow-discharge deposition technique from SiH<sub>4</sub> and GeH<sub>4</sub> gases. The Structural changes of the films were characterized using IR, XRD and SEM after annealing at 300°C for 8h. Remarkable structural degradation was observed upon annealing because of the formation of hydrogen bubbles which give rise to surface bumps. The influence of annealing on the electrical conductivity and optical energy gap of a-Si<sub>0.47</sub>Ge<sub>0.53</sub>:H thin films was discussed. The results revealed that the electrical conductivity is increased with increasing the annealing temperatures and /or annealing time, while optical energy gap is decreased. On the other hand it was found that the activation energy of crystallization deduced from the annealing time dependence of the conductivity using Avrami's equation is structural dependent.

**Keywords:** *Optical properties, electrical properties, a-SiGe:H, hydrogen content and crystallization.*

### I. INTRODUCTION

Amorphous silicon and its alloys of Group IV elements, like germanium, have gained importance due to their applications in various photonic devices, e. g., solar cell, photodetector, and light emitting diode. Hydrogenated amorphous silicon – germanium (a-SiGe:H) are used as a narrow band gap materials for amorphous silicon-based solar cells. High efficiency solar cells are necessary to convert solar energy to electrical energy at low cost. Since the quality of a-Si<sub>1-x</sub>Ge<sub>x</sub>:H is not as good as that of a-Si:H, some attempts were carried out to improve the optical and electrical properties of a-Si<sub>1-x</sub>Ge<sub>x</sub>:H by changing the preparation conditions and by annealing the samples [1-7]. In this study, the effect of annealing temperature on structural, electrical and optical properties of a-Si<sub>0.47</sub>Ge<sub>0.53</sub>:H alloys was investigated.

### II. EXPERIMENTAL

Thin films of a-Si<sub>0.47</sub>Ge<sub>0.53</sub>:H were prepared by glow-discharge deposition system with capacitively coupled diode reactors from SiH<sub>4</sub> and GeH<sub>4</sub> plasmas. At a substrate temperature of 200 and 250°C, a RF power of 13.6 MHz, a RF power of 10 W, a pressure of about 0.18 mbar and a gas flow of 5 sccm, a-Si<sub>0.47</sub>Ge<sub>0.53</sub>:H thin films were grown on quartz substrates for optoelectronic characterization and on crystalline Si for composition analysis. Infrared absorption spectra were measured in the range between 400 and 2200 cm<sup>-1</sup> using a Nicolet Fourier transform infrared spectrometer ( model 740 ). After base line correction, the IR absorption peaks were fitted by Gaussian to obtain the integrated absorption intensity I\*. As the film thickness was usually below 1 μm, the correction proposed by Langford et al. [8] was employed to obtain the integrated absorption I. The optical band gap E<sub>g</sub> was deduced from transmission and reflection measurements using JASCO V-570 UV-Vis Spectrophotometer-Instructions. The samples were investigated by the scanning electron microscopy ( SEM ) after annealing at 300°C for 8 h. For electrical measurements, a co-planer method was used for the dark and photo-conductivity in vacuum. The light source of a tungsten lamp of 100 mW/cm<sup>2</sup> was employed.

### III. RESULTS AND DISCUSSION

#### 3.1 Infrared Absorption Spectra

Figure (1) shows the infrared (IR) absorption spectra of a-Si<sub>0.47</sub>Ge<sub>0.53</sub>:H films prepared from SiH<sub>4</sub> and GeH<sub>4</sub> gases at substrate temperature (T<sub>s</sub>) 200 and 250 °C, respectively. For a-SiGe:H films, the wagging, bending and stretching modes of Si-H and Ge-H bonds occur in the 500-750,750-950 and 1800-2200 cm<sup>-1</sup> ranges, respectively. The modes near 2000 and 2100 cm<sup>-1</sup> are stretching modes associated with Si-H vibrations. The corresponding stretching modes for Ge-H vibrations are at 1880 and 2000 cm<sup>-1</sup>. The bending modes for Si-H<sub>2</sub> vibrations appear near 845 and 890 cm<sup>-1</sup>, while the corresponding bending modes for Ge-H<sub>2</sub> vibrations appear at 775 and 835 cm<sup>-1</sup> [9-11].

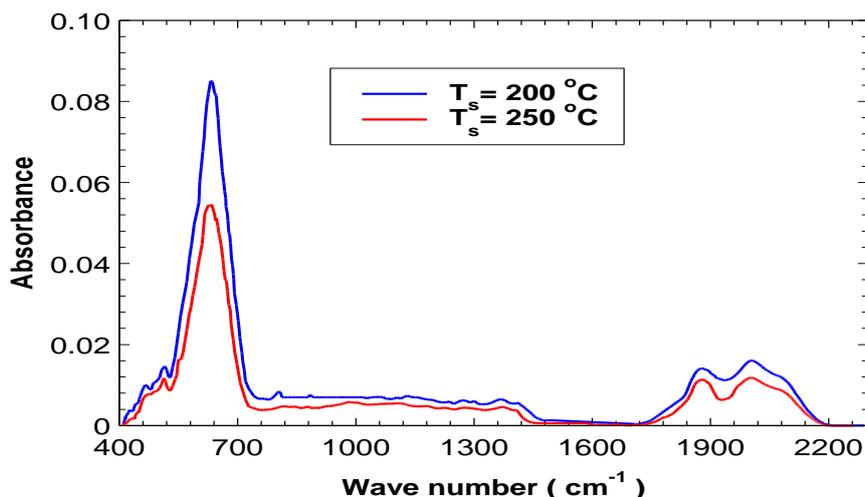


Figure (1): IR- spectra of a-Si<sub>0.47</sub>Ge<sub>0.53</sub>:H prepared at 200°C and 250°C

From figure (1) it is seen that with raising substrate temperature ( $T_s$ ) from 200 to 250 °C, the hydrogen related absorption lines decrease in intensity and the bending modes that are due to dihydride groups (Si-H<sub>2</sub> and Ge-H<sub>2</sub>) appeared at 845 and 890 cm<sup>-1</sup> in a highly hydrogenated materials ( $T_s = 200^\circ\text{C}$ ) disappear while the Si-H stretching mode at 2000 cm<sup>-1</sup> increases in intensity relative to the 2100 cm<sup>-1</sup> stretching mode and becomes dominant. Also, the 1880 cm<sup>-1</sup> stretching mode associated with Ge-H vibration in the bulk shows dominance at higher substrate temperature ( $T_s = 250^\circ\text{C}$ ) while the Ge-H stretching mode at 2000 cm<sup>-1</sup> disappears [1]. Thus, the formation of microvoides in a-Si<sub>0.47</sub>Ge<sub>0.53</sub>:H alloys is accompanied by a transition of Si-H stretching mode from 2000 cm<sup>-1</sup> to near 2100 cm<sup>-1</sup> and the appearance of the 2000 cm<sup>-1</sup> Ge-H stretching mode. Accordingly, the 2000 cm<sup>-1</sup> stretching mode appeared in a-Si<sub>0.47</sub>Ge<sub>0.53</sub>:H alloys is associated with vibrations of both Si-H bonds in the dielectric medium and hydrogen bound to Ge surfaces [1]. Infrared (IR) absorption spectra of a-Si<sub>0.47</sub>Ge<sub>0.53</sub>:H thin films prepared at 200 and 250°C before and after annealing at 300°C for 8 h are shown in figures (2) and (3), respectively. It is shown that the integrated intensity of the wagging, bending and stretching bonds decreases. In the stretching mode range of the wave number, the spectra show that the integrated absorption intensity of Ge-H and Si-H stretching bonds is decreasing after annealing at 300°C for 8h. It is seen also that the 2000 cm<sup>-1</sup> band increases in intensity relative to the 2100 cm<sup>-1</sup> stretching mode indicating that hydrogen moves around in the network and is partially evolved, thus causing a change in the atomic density of the SiGe network. The hydrogen evolved from the films leads to structural relaxation caused by the annealing [4-7].

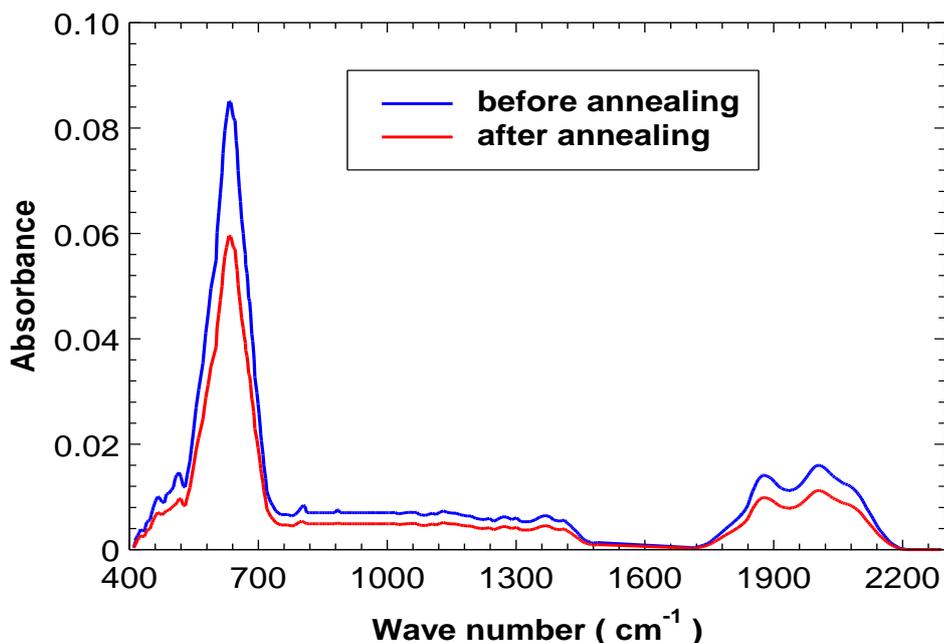


Figure (3): IR- spectra of a-Si<sub>0.47</sub>Ge<sub>0.53</sub>:H prepared at 200 °C before and after annealing at 300°C.

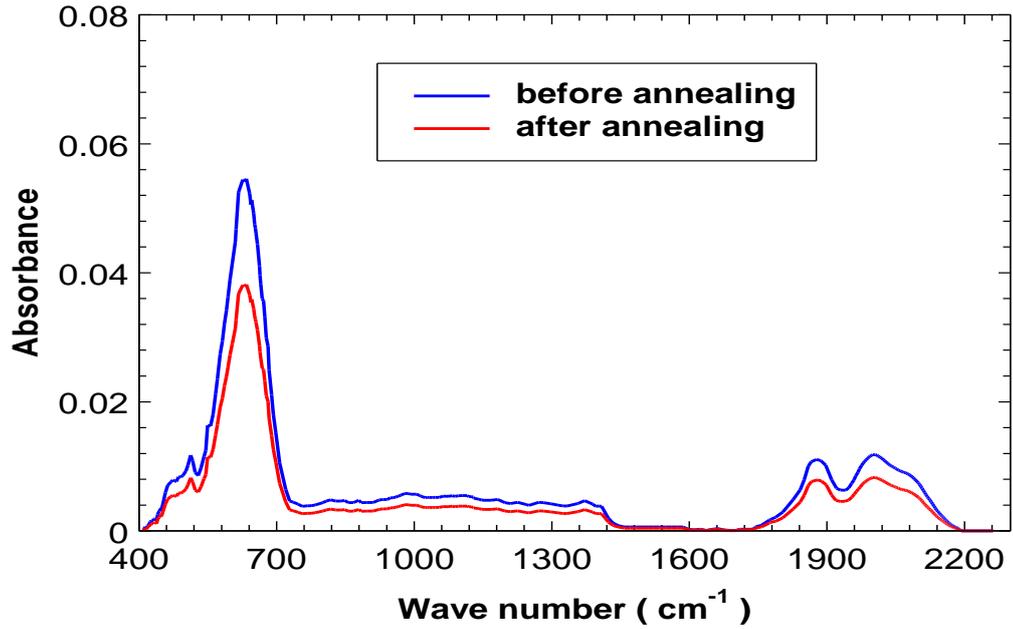


Figure (3) : IR-spectra of a-Si<sub>0.47</sub>Ge<sub>0.53</sub>:H prepared at 250°C before and after annealing at 300°C.

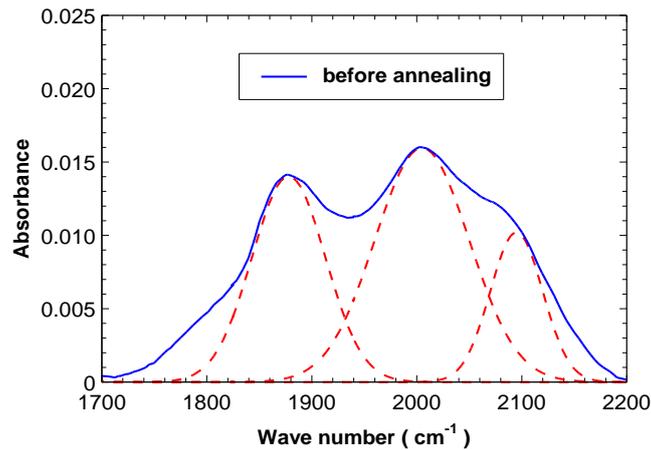


Figure (4): Fitting for IR- spectra in the stretching mode of a-Si<sub>0.47</sub>Ge<sub>0.53</sub>:H prepared at 200°C before annealing.

The hydrogen content ( $N_H$ ) calculated by fitting the stretching mode before and after annealing for samples prepared at 200 °C and 250°C is given in table (1). For brevity see figure (4) of a-SiGe:H prepared at 200 °C before annealing. The fitting was done by using the Gaussian distribution for calculating the hydrogen content and is written as :

$$y(x) = \frac{\beta}{\sqrt{2\pi}(x)} \exp\left(-\frac{(\omega-\omega_0)^2}{2x^2}\right) \quad (1)$$

Where  $\beta$ ,  $\omega$ ,  $\omega_0$ ,  $x$ , are the titration value, the frequency, the peak frequency, also  $x= 2.35$  FWHM, where (FWHM) is full width of half maximum.

Table (1): Hydrogen content of a-Si<sub>0.47</sub>Ge<sub>0.53</sub>:H thin films before and after annealing at 300°C for 8 h.

The samples	T <sub>s</sub> (°C)	Hydrogen content (N <sub>H</sub> ) cm <sup>-3</sup> before annealing	Hydrogen content (N <sub>H</sub> ) cm <sup>-3</sup> after annealing
a-SiG:H	200	3.76 x10 <sup>21</sup>	2.63x10 <sup>21</sup>
a-SiG:H	250	3.00 x10 <sup>21</sup>	2.18 x10 <sup>21</sup>

It is seen from table (1) that the total hydrogen content ( $N_H$ ) is decreasing upon annealing due to the evolution of hydrogen from the network.

### 3.2 Scanning Electron Microscopy (SEM)

The samples were investigated by the scanning electron microscopy (SEM) after annealing at 300°C for 8 h. Figures (5) and (6) show the SEM images of a-Si<sub>0.47</sub>Ge<sub>0.53</sub>:H thin films prepared at 200°C and 250°C, respectively. The surface of the films illustrates close bubbles with the hydrogen. The hydrogen forming the bubbles arises from the rupture of the Si-H and Ge-H bonds activated by the thermal energy of the annealing temperature [13] and by the energy released from the recombination of thermally generated electron hole pairs [14,15].

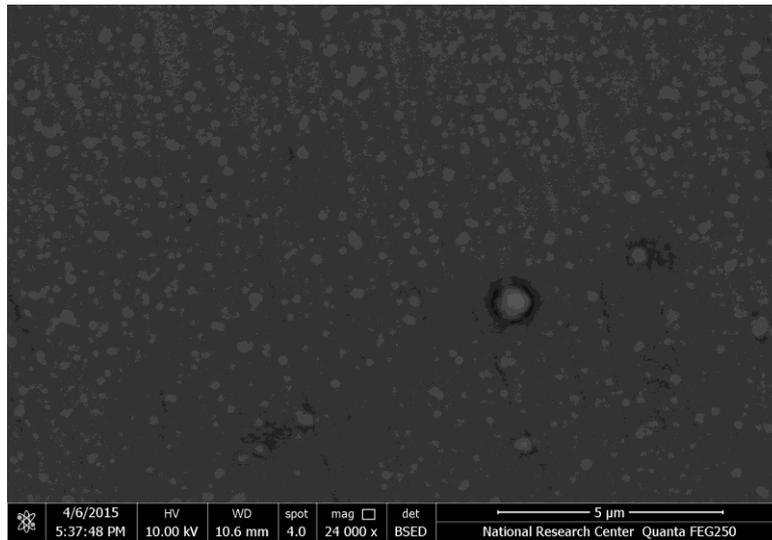


Figure (5): The SEM image of a-Si<sub>0.47</sub>Ge<sub>0.53</sub>:H prepared at 200°C and annealed at 300 °C for 8 h.

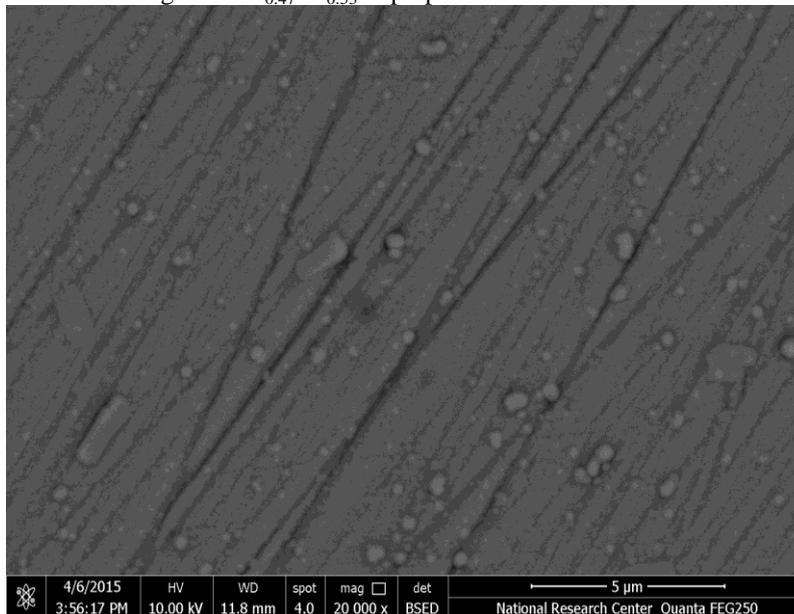


Figure (6): SEM image of a-Si<sub>0.47</sub>Ge<sub>0.53</sub>:H prepared at 250°C and annealed at 300°C for 8 h.

### 3.3. Optoelectronic data

The optical band gap is useful material parameter that allows comparison of a-SiGe:H thin films based materials regarding their light absorption properties. Figures (7) and (8) shows the relation between  $(\alpha h\nu)^{1/2}$  and  $(h\nu)$  of a-Si<sub>0.47</sub>Ge<sub>0.53</sub>:H prepared at 200 and 250°C, respectively. According to Tauc's relation, the optical energy gaps deduced from the plots are given in tables (2) and (3) for the two samples before and after annealing.

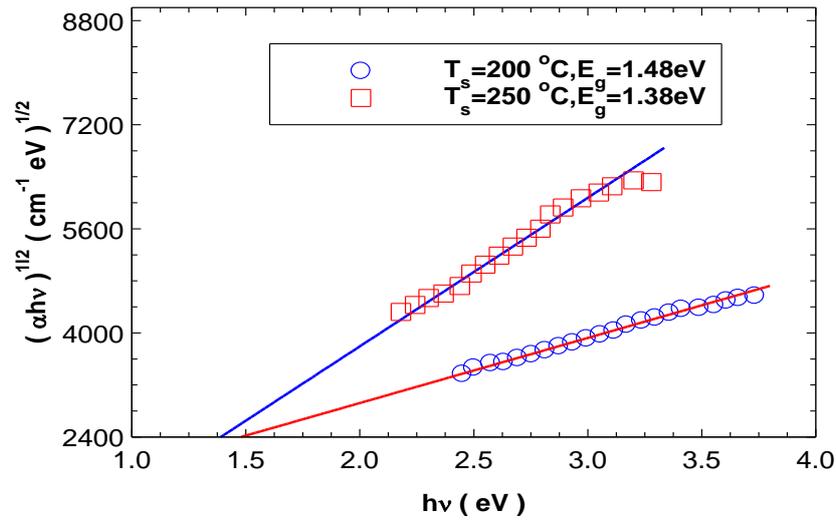


Figure (7) :  $(\alpha hv)^{1/2}$  vs  $hv$  for samples prepared at 200 °C and 250 °C, before annealing.

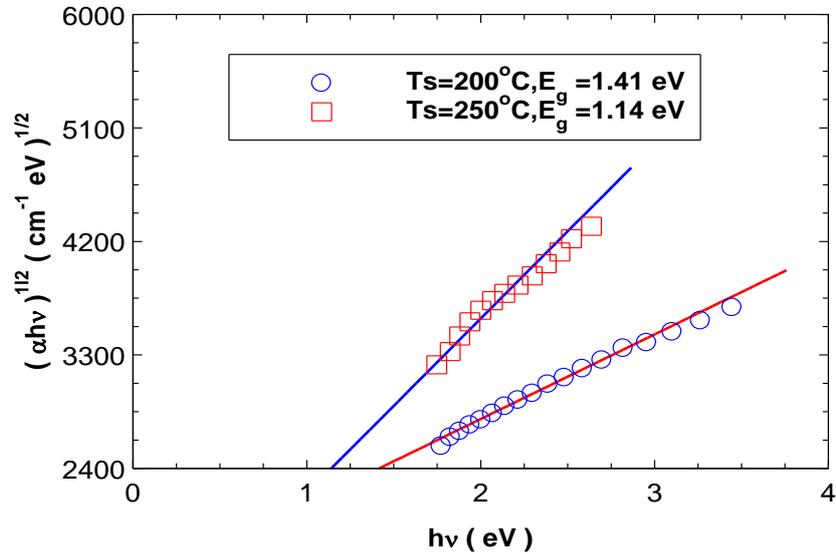


Figure (8) :  $(\alpha hv)^{1/2}$  vs  $hv$  of prepared at 200 °C and 250 °C, after annealing.

The calculated Urbach energy  $E_u$  for the two samples is also given in tables (2) and (3). The data shows that the optical energy gap is decreased with rising the substrate and/or annealing temperature while the Urbach energy is increased mainly due to the decreased total hydrogen content in agreement with previous works [16–18].

Table (2): The data of optical band gap  $E_g^{Opt}$  and Urbach energy  $E_U$  before annealing.

The sample	$T_s$ (°C)	Hydrogen content ( $N_H$ ) $cm^{-3}$	$E_g^{Opt}$ (eV)	$E_U$ (meV)
a-Si <sub>0.47</sub> Ge <sub>0.53</sub> :H	200	$3.76 \times 10^{21}$	1.48	68
a-Si <sub>0.47</sub> Ge <sub>0.53</sub> :H	250	$3.00 \times 10^{21}$	1.38	85

Table (3): The data of optical band gap  $E_g^{Opt}$  and Urbach energy  $E_U$  after annealing.

The sample	$T_s$ (°C)	Hydrogen content ( $N_H$ ) $cm^{-3}$	$E_g^{Opt}$ (eV)	$E_U$ (meV)
a-Si <sub>0.47</sub> Ge <sub>0.53</sub> :H	200	$2.63 \times 10^{21}$	1.41	93
a-Si <sub>0.47</sub> Ge <sub>0.53</sub> :H	250	$2.18 \times 10^{21}$	1.14	125

The dark and photo- conductivities as a function of temperature for a-Si<sub>0.47</sub>Ge<sub>0.53</sub>:H prepared at 200 and 250°C in the temperature range 303- 423 K are shown in figures (9) and (10), respectively. It is seen that the relation between the electrical conductivity and the temperature obey Arrhenius type equation:

$$\sigma = \sigma_0 \exp(-E_a/k_B T) \quad (2)$$

where  $\sigma$  is electrical conductivity,  $E_a$  is the activation energy and  $k_B$  is the Boltzmann's constant. The conductivity measured at 303 K and the activation energy calculated from the slopes of the lines are given in table (4). It is seen that the electrical conductivity increases and the activation energy decreases by rising the substrate temperature. This is due to the decrease of hydrogen content as shown in table (1).

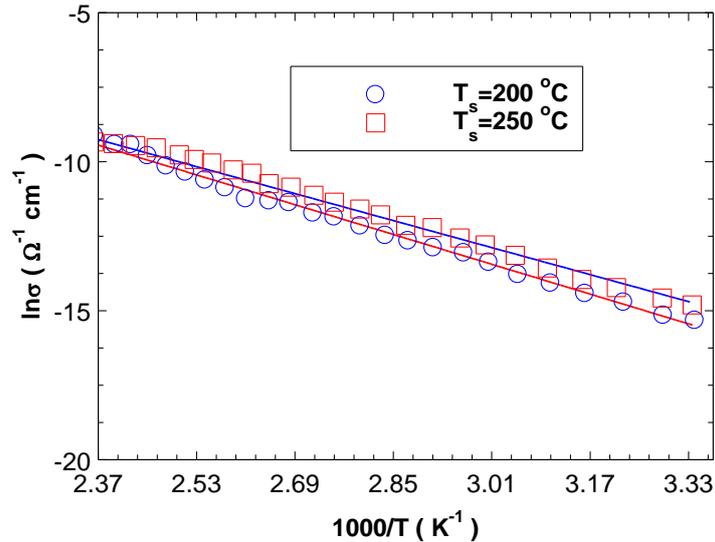


Figure (11): Dark conductivity vs. inverse of the temperature for a-Si<sub>0.47</sub>Ge<sub>0.53</sub>:H thin films.

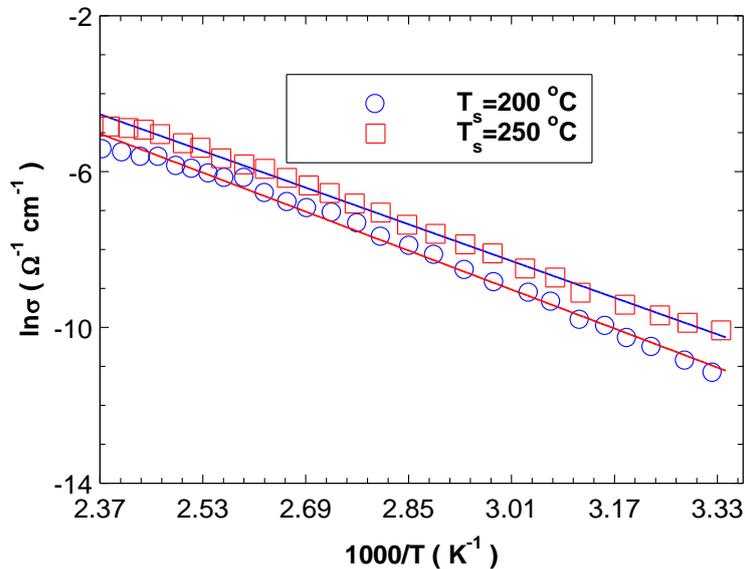


Figure (12) : Photo- conductivity vs. inverse of the temperature for a-Si<sub>0.47</sub>Ge<sub>0.53</sub>:H thin films.

Table (4): Dark and photo-conductivity measured at 303 K and the activation energy of a-Si<sub>0.47</sub>Ge<sub>0.53</sub>:H.

The sample	T <sub>s</sub> (°C)	σ <sub>d</sub> (Ω <sup>-1</sup> .cm <sup>-1</sup> )	σ <sub>ph</sub> (Ω <sup>-1</sup> .cm <sup>-1</sup> )	E <sub>a,d</sub> (eV)	E <sub>a,ph</sub> (eV)
a-Si <sub>0.47</sub> Ge <sub>0.53</sub> :H	200	2.07 X 10 <sup>-7</sup>	1.80 X 10 <sup>-5</sup>	0.54	0.51
a-Si <sub>0.47</sub> Ge <sub>0.53</sub> :H	250	3.97 X 10 <sup>-7</sup>	4.72 X 10 <sup>-5</sup>	0.48	0.47

The electrical conductivity of a-Si<sub>0.47</sub>Ge<sub>0.53</sub>:H system as a function of annealing times were recorded at different temperatures 493, 523, 553 and 573 K. The results obtained for the two samples as shown in Figure (11), and Figure (12) illustrate that the electrical conductivity increases with increasing the annealing time at

constant annealing temperature and is attributed to partially to evolution of hydrogen from internal surfaces of voids and partially to crystallization effects depending on the annealing temperature since the crystallization temperature of a-Ge is near 300°C.

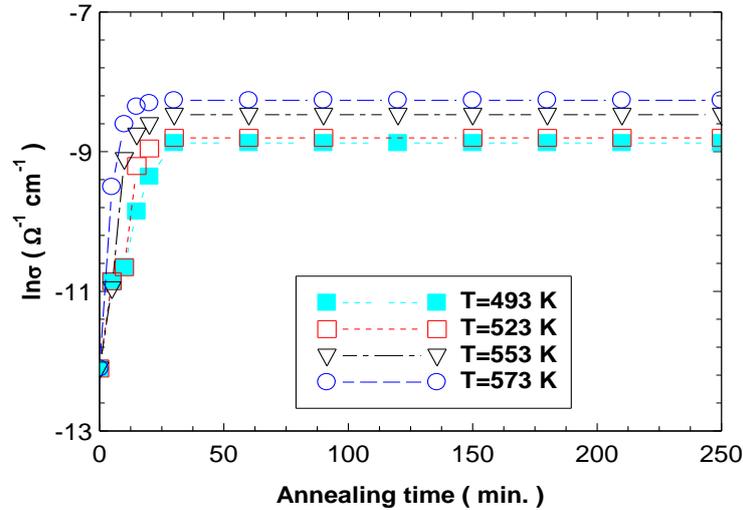
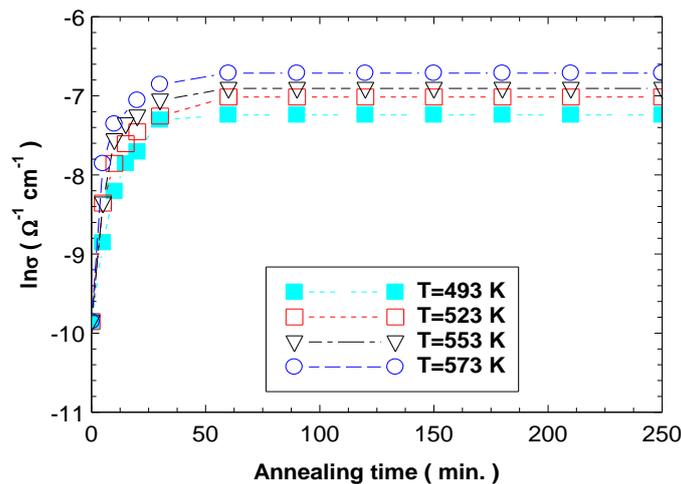


Figure (11): Dark conductivity of a-Si<sub>0.47</sub>Ge<sub>0.53</sub>:H prepared at 200°C Vs. annealing time at constant annealing temperature.



constant Figure (16) : Dark conductivity of a-Si<sub>0.47</sub>Ge<sub>0.53</sub>:H prepared at 250°C Vs. annealing time at annealing temperatures. It is known that the electrical conductivity of the ordered system is higher than that of amorphous one and the ordered systems exhibit lower activation energy than the amorphous one [19]. Thus the electrical conductivity measurements as a function of annealing time at constant temperature are used to study the thermal crystallization kinetics using Johnson-Mehl-Avermi's (JMA) equation [20] in the form:  $\chi = 1 - \exp[-(kt)^n]$  (3)

where  $\chi$  is the volume fraction of the crystalline phases transformed from the amorphous state at time t, n refers to the order of reaction and k is the effective overall reaction rate, which actually reflects the rate of crystallization [21, 22] and is given by:

$$k = k_0 \exp [-E_c/RT] \quad (4)$$

Here  $k_0$  indicates the number of attempts to overcome the energy barrier. From the results of the conductivity as a function of annealing time the volume fraction  $\chi$  is calculated from the relation:

$$\chi = (\sigma_t - \sigma_0) / (\sigma_\infty - \sigma_0) \quad (5)$$

where  $\sigma_0$  is the electrical conductivity at zero time,  $\sigma_t$  the electrical conductivity at any time t and  $\sigma_\infty$  is the electrical conductivity at the end of saturation (full crystallization). According to JMA equation the value of n can be obtained from the slopes of the plots of  $\ln[-\ln(1 - \chi)]$  vs.  $\ln t$  are given in table (5) for the studied films a-Si<sub>0.47</sub>Ge<sub>0.53</sub>:H, measured at 493, 523, 553 and 573 K. Since the volume fraction of the crystallized phases is assumed to depend on the conductivity of the material at any annealing time we found that the value of n does not depend on the composition and the annealing time as seen in table (5). The values of k according to JMA equation were obtained from the slopes of the plots of  $-\ln(1 - \chi)$  vs.  $(t^n)$  and are given in table (5) for all films.

According to equation (5) the values of the activation energies  $E_c$  of crystallization deduced from the slopes of the plots of  $\ln k$  versus  $1000/T$  for the a-Si<sub>0.47</sub>Ge<sub>0.53</sub>:H are also given in table (5). It seen that the activation energy of crystallization depends on the substrate temperature.

Table (5): Values of n, k and  $E_c$  of a-Si<sub>0.47</sub>Ge<sub>0.53</sub>:H thin films .

annealing temperature (T)		n				K				$E_c$ kJ/mol
		493 (K)	523 (K)	553 (K)	573 (K)	493 (K)	523 (K)	553 (K)	573 (K)	
samples	$T_s$ (°C)									
a-SiGe:H	200	1.09	1.19	1.28	1.37	$5.79 \times 10^{-5}$	$3.03 \times 10^{-4}$	$4.09 \times 10^{-4}$	$6.45 \times 10^{-4}$	67.1
a-SiGe:H	250	0.796	0.774	0.627	0.671	$0.563 \times 10^{-2}$	$0.716 \times 10^{-2}$	$2.01 \times 10^{-2}$	$1.89 \times 10^{-2}$	41.24

#### IV. CONCLUSIONS

The substrate temperature and annealing play an important role for determining the optical absorption edge and electrical conductivity of a-SiGe:H. The results showed considerable improvements for electrical conductivity of a-Si<sub>0.47</sub>Ge<sub>0.53</sub>:H by controlling the hydrogen content and hydrogen configuration upon annealing.

#### V. Acknowledgements

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