



Effect of α -Irradiation of Energy 0.5 MeV on Hydrogen Bonding in a-Si: H and Ultrathin Layers of a-Si: H/a-Ge: H

N.M. Abdel-Moniem

Physics Department, Faculty of Science, Tanta University, Tanta, Egypt

Received 15th Jul. 2018
Accepted 19th Feb. 2019

The Effect of α -irradiation and Ge content on a-Si: H and a-Si: H/a-Ge: H with different layer films are studied using infrared (IR) spectra. The integrated intensity of the oscillator strength of Si-H and Ge-H vibrations is determined. It is found that the integrated intensities of IR vibrational bands are enhanced significantly after the bombardment by 0.5 MeV α -particles. These observations are explained in terms of the change in the oscillation strength of the vibrational modes induced by defects created near the vibration complex during bombardment. The results revealed the effect of Ge content on the infrared spectra before and after irradiated films by α -particles of energy 125KeV/n. The defects created by bombardments, induce an increase in the oscillator strengths for some of Si-H and Ge-H vibrations due to decrease in the refractive index. The dangling bonds, formed in the range of 2700-3100 cm^{-1} in a-Si: H/a-Ge: H, are attributed to the presence of OH groups or due to the preferential attachment of hydrogen and deuterium to Si atoms rather than the Ge ones. The irradiated a-Si: H/a-Ge: H lead to decreasing the absorption band due to the increase in the hydrogen content bonded to Ge atoms. Therefore, the disorder is decreased and the crystalline state is increased.

Keywords: α -irradiation particles/ Thin films/ a-Si: H/a-Ge: H/ Infrared

Introduction

Hydrogenated amorphous silicon, a-Si: H, is the most extensively studied and also the best understood amorphous semiconductor. The basic discoveries have made it possible to use amorphous silicon as the base material for electronic devices. The most important result is the incorporation of hydrogen as a monovalent bond terminator. This allows one to reduce large densities of the electronically active dangling bond defects in pure amorphous silicon [1].

Large number of Si: H vibrational modes display two important properties. The first, they are spatially localized on the hydrogen atom and its nearest silicon neighbors. The second, the

vibrational frequencies are above the highest frequencies of the silicon host material. These types of vibrations are local modes [2-5].

Hydrogenated amorphous silicon-germanium alloys have gained a considerable interest because of their potential application in the photovoltaic technology [6]. Hydrogenated amorphous silicon-germanium (a-SiGe: H) alloys have potential applications in devices, in particular in multi-junction solar cells [7].

The vibrational modes in these alloys are the same as those found in the binary alloys a-Si: H and a-Ge: H, but with the absence of some types which depend on the details of the deposition process. Extensive studies of infrared properties for a-Si_{1-x}Ge_x: H films prepared by glow discharge system

were carried out [8,9]. The absorption of infrared radiation through intersubband transitions in a quantum well was studied extensively in the past few years, because of its possible application in infrared detectors [10].

The Si/SiGe: H system has attracted much attention. For a pseudomorphically grown SiGe alloy film on a Si substrate, nearly the entire band offset occurs between the valance band edge of Si and SiGe. Therefore, from the technological point of view, it is preferable to employ valance-band transitions in SiGe quantum wells, since such structures can be grown directly on a silicon substrate without the need of an alloy buffer [11]. The aim of this present work is to study the effect of α -irradiation on hydrogen bonding in a-Si: H and ultrathin layers of a-Si: H/a-Ge: H.

Experimental Technique

Thin films of a-Si: H and a-Si: H/a-Ge: H ultrathin layers ($n=60$) were prepared by alternating deposition from SiH_4 and GeH_4 plasmas in a computer-controlled four chamber glow-discharge deposition system with capacitive coupled diode reactors (the electrode diameter=7cm). At a substrate temperature 200°C , the RF was 13.6 MHz with a power of 10W at a pressure of about 0.18 mbar. In SiH_4 chamber the gas flow rate and the pressure were 5 sccm/sec (standard cubic cm per sec) and 0.32 mbar respectively. While in GeH_4 chamber, the gas flow rate of H_2 - GeH_4 was 0.25-2 sccm/sec. The a-Si: H/a-Ge: H multilayer films were grown on crystalline Si for composition analysis. The individual thickness of the a-Si: H layers was kept constant at 5°A , while the layer thickness of a-Ge: H

layer was varied by changing the hydrogen dilution ratio $[\text{H}_2]/[\text{GeH}_4]$ as well as changing the deposition time. The growth rate was kept near $1^\circ\text{A}/\text{sec}$ for a-Si: H and ranged from 1 to $4^\circ\text{A}/\text{sec}$ for a-Ge: H layers. The total film thickness measured by the Dektak surface profiler was in the range 2500 - 2600°A , whereas the multilayer periods ranged from 9 to 17.6°A . It has been reported that the multilayer with periods below 20°A can be viewed as a completely mixed a-SiGe: H alloy [12]. A Nicolet Fourier transform infrared (IR) spectrometer (model 740) was used for infrared absorption measurements.

Each sample was irradiated by Am^{241} source of activity $0.924 \mu\text{Ci}$ and a surface area of 19.63

mm^2 . The collimated beam of diameter 5mm and energy 125 KeV/n was obtained normal to the film surface. The irradiation time was 70 hours yielding an α -particle beam of fluence $\sim 0.04 \times 10^8 \text{cm}^{-2}$. The irradiation was performed under vacuum ($\sim 10^{-2}$ Pa) at room temperature. The infrared spectra were measured for the samples before and after bombardment by the α -particle beam.

Results and Discussion

The infrared of a-Si: H and a-Si: H/a-Ge: H films depend upon the substrate temperature. These films were deposited at a substrate temperature of 200°C . Figures (1a, b and c), show the infrared spectra of a-Si: H before and after bombardment with α -particle beam of energy 125 KeV/n. The absorption modes of silicon-hydrogen vibrations occur in the ranges 500-850, 1040-1160 and 2280-2460 cm^{-1} , respectively. These absorption modes have attributed to silicon-hydrogen Wagging bending and stretching modes, respectively [13, 14]. The results illustrate that the Wagging modes appear near to 610 and 750 cm^{-1} , bending modes near to 1100 cm^{-1} and stretching modes near to 2360 cm^{-1} respectively. The absorption peaks increase after bombardment of the film by α -particle beam, which leads to creation of defect density responsible for these peaks [15]. Figure (1a) shows the absorption peak near to 610 cm^{-1} relates to the Si: H Wagging mode. Assuming that at 640cm^{-1} , any hydrogen bond contributes to Si-H Wagging mode [16]. This means that there is some hydrogen effusion dependence on absorption strength. It is supposed that α -bombardment creates new defects near the infrared-active site hydrogen. Defect creation by α - bombardment of a-Si: H means additional disorder such as dangling bonds and weak bonds between Si atoms. These defects increased the oscillator strengths due to the decrease of the refractive index [16]. The oscillator strength is increased after bombardment of a-Si: H films which arises from the creation of new voids and is not a direct transfer of hydrogen atoms from one site to other.

The silicon-hydrogen stretching mode lies in the wavenumber range of 1040-1160 cm^{-1} is shown in Fig. (1b). The peak intensity is shifted to a lower wavenumber, and FWHM is increased from 5 cm^{-1} to 6 cm^{-1} after irradiated.

In Figure (1c), the 2360 cm^{-1} peak, the line width at half maximum, full width at half maximum (FWHM) was 3 cm^{-1} and was increased to 5 cm^{-1}

after irradiation of the films. This means that the peak intensity is sufficient to trace the concentration of the defect with respect to the irradiation dose. The peak intensity is shifted from 2380 cm^{-1} to 2360 cm^{-1} after irradiation. Hence, the complexes responsible for the 2380 cm^{-1} peak include two H atoms. This conclusion is consistent with the fact that hydrogen atoms doped with the method adopted in this study are not in an isolated atomic state, but rather in a molecular state, and hydrogen molecules, are regarded to be immobile during irradiation, since the migration energy of H_2 is about 0.78 eV [17]. The composite bands between 2360 cm^{-1} and 2380 cm^{-1} have been assigned to silicon-hydrogen stretching modes of $\equiv\text{SiH}(\omega_1^*)$ and $\text{SiH}_2(\omega_2^*)$ in particular structural environments [16].

Figures (2a, b and c), show the infrared absorption spectra of a-Si: H/a-Ge: H film before, and after being irradiated by α -particle beam. Major absorption peaks between 500 and 930 cm^{-1} , Fig. (2a), is attributed to the Si-H and Ge-H Wagging modes [18]. The absorption peak between 1950 and 2050 cm^{-1} , Fig. (2b), is due to Si-H and Ge-H stretching modes, while the absorption peaks between 2650 and 3100 cm^{-1} , Fig. (2c), are attributed to two components that can contribute to Ge-H or Ge- H_2 groups at void surfaces and Si-H groups in compact material. Figure (2a) shows the absorption band of the irradiated sample which is lower than that of the sample before being irradiated in the range of 500 - 700 cm^{-1} . The absorption band occurs at 610 cm^{-1} , this band is attributed to Wagging modes. This band is corresponding to either Ge-H or Si-H vibrational modes which occur at lower frequency. It is seen that the irradiated samples lead to decreasing the absorption band due to the increase of the hydrogen content bonded to Ge atom. The disorder is decreased and the samples transform to the crystalline state in the range of 500 - 700 cm^{-1} , therefore, the hydrogen content bonded in Si is decreased. Whereas, a continuous wave of α -beam particles induced crystallization of a-Si: H/a-Ge: H. An important result is that the existence of threshold intensity for crystallization above yields to drastic changes in the physical properties of the irradiated material [19]. At intensities below the threshold, clusters are created which can increase in the number and size, attaining microcrystalline depending on the power level. Up to this stage, the system is reversible, i.e. without further input of

radiation energy, and the clusters can relax back to the amorphous state. After the threshold is reached, the clusters can coalesce and form polycrystalline which then remain stable. While creating peaks near to 740 , 810 and 900 cm^{-1} after irradiated sample for Si- H_2 bending modes lead to increase the absorption coefficient.

Figure (2b) shows the absorption peak of the irradiated sample which is lower than the absorption peak before irradiation and the FWHM changes from 6.5 cm^{-1} to 3.5 cm^{-1} . Also, the peak is shifted from 1990 cm^{-1} to 1980 cm^{-1} after irradiation of the sample.

Due to the removal of disorder for films containing hydrogen up to 40%, it is tentatively assigned to loss of consecutiveness of amorphous network. This stretching frequency was first identified by Connel and Pawlick [20] in a-Ge: H at 1975 cm^{-1} . They attributed that to the higher energy vibration at 1975 cm^{-1} to Ge-H and Ge- H_2 bonds located at surface of voids. For the absorption peak near 2000 cm^{-1} , two components can contribute to Ge-H or Ge- H_2 groups at void surfaces and Si-H groups in the compact material.

Figure (2c) shows the 2910 cm^{-1} peak which has not been reported. The FWHM of the 2910 cm^{-1} peak is about 4 cm^{-1} . The broad absorption band is created after irradiation of the films due to the formation of dangling bond in the range 2700 - 3100 cm^{-1} which is attributed to either presence of OH groups or due to the preferential attachment of hydrogen and deuterium to silicon atoms rather than to germanium ones. Because this feature is present for both a-Ge: H and a-Ge: D [16, 21], the hydrogen in the OH groups apparently does not originate from the hydrogen incorporated in the films during the deposition process but it must come from outside.

Conclusions

The results of the present investigation revealed the effect of Ge content on the infrared spectra before and after irradiation of the films by α -particles of energy 125 KeV/n . The defects created by the bombardment induce an increase in the oscillator strengths for some of Si-H and Ge-H vibrations due to decrease in the refractive index. The dangling bonds were formed in the range 2700 - 3100 cm^{-1} in a-Si: H/a-Ge: H and are attributed to the presence of OH groups or due to the preferential attachment of hydrogen and deuterium to Si atoms rather than the Ge ones.

The irradiation a-Si: H/a-Ge: H leads to a decrease in the absorption band due to the increase in the hydrogen content bonded to Ge atoms, therefore

the disorder is decreased and the crystalline state is increased.

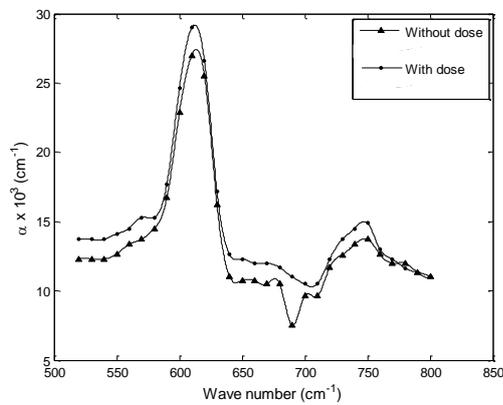


Fig. (1a): The variation of the absorption coefficient with the wave number range of 610 - 750 cm^{-1} for a-Si: H films before and after irradiated by α -particles of energy 0.5 MeV

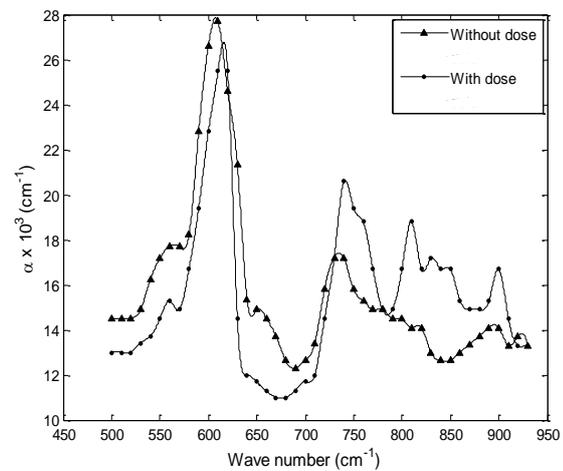


Fig. (2a): The variation of the absorption coefficient with wave number range 500 -930 cm^{-1} for a-Si: H/ a-Ge: H films before and after irradiated by α -particles of energy 0.5 MeV

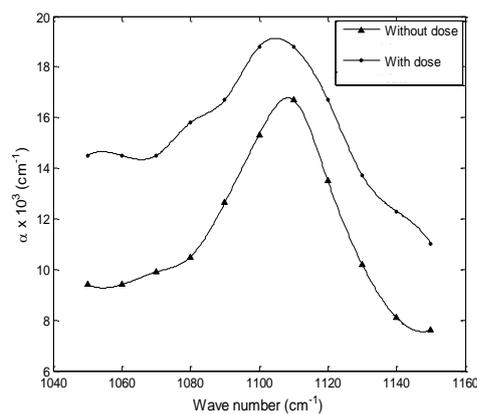


Fig. (1b): The variation of the absorption coefficient with the wave number range of 1040 – 1160 cm^{-1} for a-Si: H films before and after irradiated by α -particles of energy 0.5 MeV

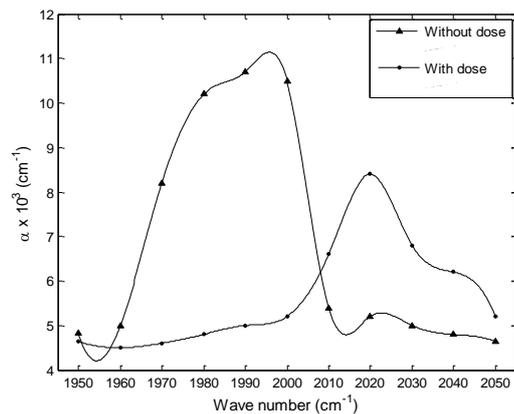


Fig. (2b): The variation of the absorption coefficient with wave number range 1950 -2050 cm^{-1} for a-Si:H/ a-Ge:H films before and after irradiated by α -particles of energy 0.5 MeV

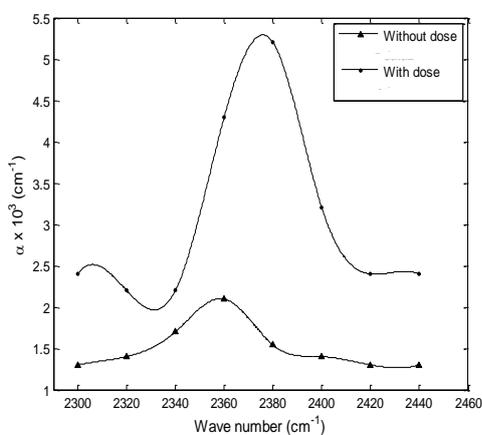


Fig. (1c): The variation of the absorption coefficient

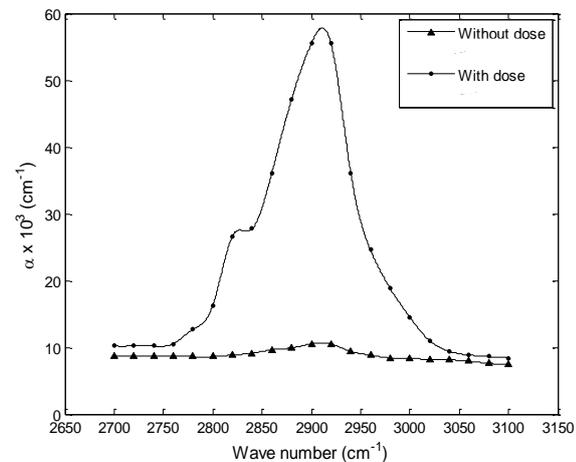


Fig. (2c): The variation of the absorption coefficient with wave

with wave number range of 2300 - 2440 for a-Si: H films before and after irradiated by α -particles of energy 0.5 MeV number range 2650 -3100 cm^{-1} for a-Si: H/ a-Ge: H films before and after irradiated by α -particles of energy 0.5 MeV

ACKNOWLEDGEMENT

It is a pleasure to thank Prof. Dr. El-sayed M. Farag, Professor of amorphous semiconductor materials, Basic Science Engineering Department, Faculty of Engineering, Shebin El-Kom, Menoufia University, Egypt, for his kind help in implementing the experimental investigation of the present work.

REFERENCES

- 1- W.E. Spear and H. L. Steemers, *J. Non-Cryst. Solids*, 66 (1984)163.
- 2- E. Martinez and H. Cardona, *Phys. Rev. B*, 28 (1983) 880.
- 3- W.B. Pollard, *Phys. Rev. B*, 29 (1984) 857.
- 4- J.T. Harris, J.L. Hueso, and B.A. Korgel, *Chem. Mater.*, 22 (23) (2010) 6378.
- 5- A. Seyhan, T. Altan , Ö.C. Ecer, R. Zan, *IOP Conf. Series: Journal of Physics: Conf. Series* 902 (2017) 012024.
- 6- S.Z. Weirz, M. Gomez, J.A. Muir, O. Resto, R. Perez, Y. Goldstein and B. Abeles, *Appl. Phys. Lett.*, 44 (1984) 634.
- 7- K. Tanaka and M. Matsuda, *Thin Solid Films*, 163 (1988) 123.
- 8- D.K. Paul, B. Von Roedern, J. Blake and W. Paul, *J. Appl. Phys. Suppl. A*, 49 (1980) 1261.
- 9- K.D. Mackenzie, J.R. Eggert, D.J. Leopold, Y.M. Li, S. Lin, and W. Paul, *J. Phys. Rev. B*, 31 (1985) 2198.
- 10- B. F. Levine, *Semicond. Sci. Technol.*, 8 (1993) 8400.
- 11- T. Fromherz, E. Koppensteiner, M. Helm, G. Bauer, J. Nützel and G. Abstreiter, *J. Appl. Phys.*, 33 (1994) 2361.
- 12- J.P. Conde, V. Chu, D.S. Shen and S. Wagner, *J. Appl. Phys.*, 75 (1994) 1638.
- 13- M. Cardona, *Phys. Status Solidi B*, 118 (1983) 463.
- 14- M. Grundner and H. Jacob, *Appl. Phys. A*, 39 (1986) 73.
- 15- M. Suezawa, *Phys. Rev. B*, 63 (2000) 035201.
- 16- W. Beyer and M.S. Abo-Ghazala, *J. Materials Research Soci.*, 507 (1998) 601.
- 17- V.P. Markevich and M. Suezawa, *J. Appl. Phys.*, 83 (1998) 2988.
- 18- M.S. Abo-Ghazala, *Physica B*, 293 (2000) 132.
- 19- I. Abdulhalim, R. Beserman and R. weil, *Phys. Rev. B* 39, 2 (1989) 1081.
- 20- G.A.N. Connell and J.R. Pawlik, *Phys. Rev. B*, 13 (1976) 787.
- 21- C.J. Fang, K.J. Gruntz, L. Ley and M. Cardona, *J.Non-Cryst. Solids* 35-36 (1980) 255.