Evidence for the void size related IR absorption frequency shifts in hydrogenated amorphous germanium films

Yu-Pin Chou, Si-Chen Lee*

Department of Electrical Engineering, National Taiwan University, Room 440, No. 1, SEC 4, Roosevelt Road, Taipei, Taiwan, ROC

Received 7 September 1999; accepted 20 September 1999 by M. Cardona

Abstract

Hydrogenated amorphous germanium alloys (a-Ge:H) have been prepared by plasma enhanced chemical vapor deposition at a substrate temperature of 200°C. The films tend to oxidize as soon as they are taken out from the chamber and exposed to air. The oxidation process is found to follow a percolation channel formed by a continuous linkage of large voids that is evidenced by the observation of the decline of the intensity of Ge–H stretching mode at 1980 cm⁻¹ to zero while the other peak at 1890 cm⁻¹ does not change. This means that the peak at 1980 cm⁻¹ corresponds to the Ge–H stretching mode in large voids while that at 1890 cm⁻¹ corresponds to Ge–H stretching mode in isolated small voids. Thus, the frequency shifts of the stretching mode should arise from the difference of the void size where Ge–H bonds are situated. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: A. Disordered systems; A. Semiconductors; A. Thin films

In the past decades, the origins of the IR absorption frequency shifts in the stretching mode of Si–H or Ge–H bonds in amorphous silicon- or germanium-based alloys have been studied [1–10]. Usually, the origins are attributed to two possible mechanisms. The first one is the Ligand effect, or to be more concise the induction effect. The ligand effect was first proposed by Lucovsky [1] to explain the frequency shifts of Si–H bonds in hydrogenated amorphous silicon based alloys such as a-Si, a-SiN_x and a-SiO_x. Since, as the electronegativities of the nearest neighbors of Si–H bond increase, the Si–H bond would be more polarized which, in turn, shortens the Si–H bond length and increases the effective force constant, thus the vibration frequency. Another mechanism is the solid-state effect. Since for hydrogenated amorphous silicon (a-Si:H) or germanium (a-Ge:H) alloys, the frequency shifts due to the difference of nearest neighbor electronegativity would be rather small. But the stretching mode of Si–H (Ge–H) bonds still shows two main absorption peaks centered at 2000 (1890) and 2090 (1980) cm⁻¹. These two peaks were initially assigned to different configuration of silicon hydrides, i.e. 2000 cm⁻¹

for Si–H and 2090 cm⁻¹ for Si–H₂ [2–4], but the shift is rather large compared to that of Si–H bonds on crystalline silicon surface measured by high resolution electron energy loss spectroscopy (EELS) [5]. Besides, there is no clear correspondence between the oscillator strength of the 2090 cm⁻¹ stretching mode and SiH₂ scissors mode at 890 and 845 cm⁻¹ [6,7], thus the unique assignment of 2090 cm⁻¹ peak to Si–H₂ was disputed. By taking the IR absorption frequency shifts for Si–H bonds in higher silane into consideration, Wagner et al. [8] proposed that the 2090 cm⁻¹ peak should correspond to Si–H bonds on internal surfaces while 2000 cm⁻¹ peak corresponds to Si–H bonds in the bulk. In this paper, evidence for the IR absorption frequency shifts of Ge–H bonds originated from the size of voids is given.

In the experiments reported here, a-Ge:H films were prepared by plasma enhanced chemical vapor deposition (PECVD) on unpolished silicon wafers. The reason for using unpolished silicon wafers is to avoid interference during infrared absorption measurement. The deposition parameters are as follows: RF power density 0.11 W/cm², substrate temperature 200°C, chamber pressure 0.4 Torr, Ge–H₄ flow rate 5 sccm, and H₂ flow rate 2 sccm. The growth rate of a-Ge:H is 0.98 nm/s. The IR spectra were

*Corresponding author. Fax: +886-2-23697337.

Fig. 1. The IR spectra of a-Ge:H deposited at substrate temperature of 200°C exposed to atmosphere for different periods of time: (a) 1750–4000 cm⁻¹; and (b) 400–1800 cm⁻¹.

measured with a Nicolet Magna-IR model 550 FTIR spectrometer with an undeposited c-Si wafer cleaned by the same process as reference. The resolution of the IR spectra is 0.5 cm⁻¹.

Fig. 1(a) and (b) displays the IR spectra of hydrogenated amorphous germanium alloys deposited at a substrate temperature of 200°C exposed to atmosphere for different periods of time. As it is seen clearly in Fig. 1, as the specimen is taken out from the vacuum chamber and exposed to atmosphere for only 15 min, a broad peak ranging from 2800 to 3700 cm⁻¹ emerges. This broad peak should correspond to the stretching mode of both the Ge–OH and H₂O as is justified by the existence of the bending mode of H₂O at 1640 cm⁻¹. Two peaks at 1890 and 1980 cm⁻¹ are related to Ge–H_n ($n = 1$ or 2) stretching modes, in addition, two small peaks at 2025 and 2055 cm⁻¹ also appear. Compared to the corresponding Si counterpart [1,10], the two peaks should be the stretching mode of O₂Ge–H_n and O₃Ge–H, respectively. After 45 min, a peak at 890 cm⁻¹ emerges, while the O–H related peaks at 3400 cm⁻¹ becomes higher. At this time, some buried-in peaks in the region of 700–860 cm⁻¹ have pushed the polygermane chain double peaks at 830 and 760 cm⁻¹ higher. After 100 min, the O–H related peak at 3400 cm⁻¹ grows higher and the absorption peak of Ge–H_n stretching mode at 1980 cm⁻¹ almost vanishes. However, the Ge–H stretching mode at 1890 cm⁻¹ does not change. Also, due to the further oxidization of O₂Ge–H_n without enhancement from the oxidation of Ge–H, the intensity of O₂Ge–H_n absorption peak gradually diminishes. At the same time, the double peaks corresponding to the polygermane chain at 830 and 760 cm⁻¹ decrease to nearly zero and a peak positioned at 765 cm⁻¹ emerges. This new peak may not be the bending mode of Ge–H₂ because there is no corresponding intensity of stretching mode at 1980 cm⁻¹ and the shape of the peak becomes rather broad. It is suggested to be the Ge–O– stretching mode where the oxygen atom is not two-fold coordinated for the following two reasons. First, it emerges after the oxidation of the polygermane chain. Second, similar peak also appears in the spectrum of crystal GeO₂ after being irradiated by X-ray [11]. After 25 h, the broad GeO–H peak at 3400 cm⁻¹ starts to decrease and a new peak at 860 cm⁻¹ emerges, together with a peak at 1430 cm⁻¹. The 860 cm⁻¹ peak was identified by Lucovsky et al. [12] as the Ge–O–Ge stretching mode by incorporating O₂ or H₂O into plasma. This could be explained by the dehydration of germanium hydroxyl group in the following reaction:

Since the peak at 1430 cm⁻¹ emerges after the appearance of the Ge–O–Ge 860 cm⁻¹ peak, it may correspond to the vibration mode of some complex molecular cluster related to the Ge–OH₂. As the atmospheric exposure time increases, the intensity of this OH related peaks increase rapidly, accompanied with the decrease in the intensity of the Ge–H stretching mode at 1980 cm⁻¹. While the oxidation

proceeds, the oscillator strength of the Ge–H bonds at 1890 cm^{-1} experiences almost no change, even after being exposed to air for 50 days.

It is known that for an oxidation process in solid films to take place the water molecules should be able to percolate through the extended channel formed by interconnected voids. Therefore, the disappearance of 1980 cm^{-1} peak suggests that the corresponding bands are located inside these interconnected voids. On the contrary, the preservation of the Ge–H stretching mode at 1890 cm^{-1} indicates that they are positioned inside the isolated small voids. How small is the void size? It is believed [9] that the 1890 cm^{-1} peak is related to the Ge–H bonds situated inside a one-germanium vacancy. Once the void is enlarged to two-germanium vacancies with six Ge–H bonds inside, the vibration frequency of the Ge–H_n ($n = 1, 2$) stretching mode shifts to 1980 cm^{-1} . If this model is correct, then the oxidation results suggest that only the one germanium vacancies are isolated, all the larger voids form an interconnected percolation channel such that the water molecules can percolate through the channel and oxidize all the Ge–H bonds in them. Since 1890 and 1980 cm^{-1} peaks correspond to Ge–H bonds situated in different size of voids, the frequency shifts between them must arise from the difference in the size of the voids.

In conclusion, it has been observed that a-Ge:H alloys deposited by PECVD at a substrate temperature of 200°C tend to oxidize when they are exposed to atmosphere. As the oxidation process proceeds, the intensity of Ge–H stretching mode at 1980 cm^{-1} declines to zero while that at 1890 cm^{-1} does not change. This means that the peak at 1980 cm^{-1} corresponds to Ge–H_n stretching modes in large voids while that at 1890 cm^{-1} corresponds to Ge–H stretching

mode in small voids. Thus, the frequency shifts of the Ge–H stretching mode should come from the difference of the void size where Ge–H bonds are situated.

Acknowledgements

This work is supported by the National Science Council of the Republic of China under Contract no. NSC86-2215-E-002-030.

References

- [1] G. Lucovsky, Solid State Commun. 29 (1979) 571–576.
- [2] M.H. Brodsky, M. Cardona, J.J. Cuomo, Phys. Rev. B 16 (1977) 3556.
- [3] E.C. Freeman, W. Paul, Phys. Rev. B 18 (1978) 4288.
- [4] G. Lucovsky, R.J. Nemanich, J.C. Knights, Phys. Rev. B 19 (1979) 2064.
- [5] Y.J. Chabal, E.E. Chaban, S.B. Chrisyman, J. Electron Spectrosc. Relat. Phenom. 29 (1983) 35.
- [6] W. Paul, Solid State Commun. 34 (1980) 283.
- [7] H. Shanks, C.J. Fang, L. Ley, M. Cardona, F.J. Demond, S. Kalbitzer, Phys. Stat. Sol. (b) 100 (1980) 43.
- [8] H. Wagner, W. Beyer, Solid State Commun. 48 (1983) 585–587 See also M. Cardone, Phys. Stat. Sol. (b) 118 (1983) 463.
- [9] W.J. Sah, H.K. Tsai, S.C. Lee, Extended Abstract Of International Conference On Solid State Devices and Materials, Tokyo, Japan, 1988 (unpublished), p. 243.
- [10] Y.P. Chou, S.C. Lee, J. Appl. Phys. 83 (1998) 4111–4123.
- [11] J. Tauc, A. Anderson, R. Zallen, M. Slade, J. Non-Cryst. Solids 4 (1970) 279–288.
- [12] G. Lucovsky, S.S. Chao, J. Yang, J.E. Tyler, R.C. Ross, W. Czubatyj, Phys. Rev. B 31 (4) (1985) 2190–2197.