

## Study on Structural Stability of Hydrogenated Amorphous Germanium-Nitrogen Alloys

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**Abstract** A series of hydrogenated amorphous germanium-nitrogen alloys have been synthesized by r. f. glow discharge process. The chemical bonding configurations and their thermal stability have been investigated by means of Raman Scattering and Fourier Transform Infrared techniques and compared with those samples produced by reactive sputtering method. It was found that the Ge—N and N—H bonds stay stable in the alloy network and the structure is more stable than that of sputtered-samples especially for high nitrogen content alloys.

**PACC:** 7280N, 4630L

Hydrogenated amorphous silicon (a-Si : H) and its related alloys, such as a-SiN : H, a-SiC : H etc, have been widely studied for many years since the pioneering work of Spear and LeComber<sup>[1]</sup>. However, hydrogenated amorphous germanium-nitrogen (a-GeN : H) alloys are less understood compared with a-SiN : H alloys though it has been reported that stoichiometric Ge<sub>3</sub>N<sub>4</sub> can be utilized as an insulating layer in GaAs MIS devices<sup>[2]</sup>. Some groups have investigated the fundamental properties of a-GeN : H alloys produced by reactive sputtering method<sup>[3,4]</sup>, it was found that inclusion of nitrogen into a-Ge : H network induces the important change in the optical and electric properties, which may be useful for obtaining high-efficiency amorphous solar cells<sup>[5]</sup>. In this paper, a-Ge<sub>1-x</sub>N<sub>x</sub> : H alloys with different N content  $x$  were prepared in a conventional plasma enhanced chemical vapor deposition (PECVD) system, their structure and thermal stability were studied by using Fourier Transform Infrared (FT-IR) and Raman scattering techniques.

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Received 16 July 1996, revised manuscript received 17 October 1996

A series of a-GeN : H alloys were fabricated by using gas mixture of GeH<sub>4</sub> and NH<sub>3</sub> in a PECVD system. During the deposition, the substrate temperature, pressure and total gas flow rate was kept at 200°C, 26.7Pa and 60sccm, respectively. The gas ratio of NH<sub>3</sub> to GeH<sub>4</sub> (5% in H<sub>2</sub>) is carefully controlled by mass flow meter. The r. f. power density is about 26.4mW/cm<sup>2</sup> and the film with 500nm thickness was deposited on c-Si wafers and Corning' 7059 glass substrates for different measurements. The chemical composition of prepared alloys was determined by using X-ray photoelectron spectra (XPS) by integrating the intensity of N 1s and Ge 3d signals. With increasing ratio of [NH<sub>3</sub>]/[GeH<sub>4</sub> + NH<sub>3</sub>] from 0 to 85%, the N content  $x$  in the a-Ge<sub>1-x</sub>N<sub>x</sub> : H alloys is increased from 0 to 0.44. Correspondingly, the optical band gap deduced from Tauc plot varies in a quite wide range of 1.0~3.0eV.

Raman and FT-IR techniques were used to characterize the bonding configurations of as-grown a-GeN : H alloys. In Raman spectra, an amorphous Ge-Ge mode ( $\sim 275\text{cm}^{-1}$ ) can be observed when the N content  $x$  is less than 0.3, and above this, the peak is disappeared and the Raman spectra become featureless in the examined range since the structure is changed from Ge-Ge-like to Ge-N-like network<sup>[6]</sup>. In FT-IR spectra, absorption bands of Ge-H, Ge-N and N-H can be identified and it is found that, with increasing the N content  $x$ , the intensity of Ge-N signal is significantly enhanced.

The structural stability of a-GeN : H samples was investigated by annealing treatment at various temperatures of 300°C, 500°C and 600°C for 30min in N<sub>2</sub> ambient, respectively. It is found that a-Ge : H has been crystallized at the annealing temperature of 300°C since the crystallized Ge-Ge signal ( $\sim 300\text{cm}^{-1}$ ) is appeared in Raman spectra. Figure 1 gives the Raman spectra for different samples annealed at 500°C. At this annealing temperature, a-Ge : H should be further crystallized while no obvious crystallized signal can be observed from a-Ge<sub>1-x</sub>N<sub>x</sub> : H samples with  $x = 0.15$  and 0.44, which suggests that amorphous phase is dominant in those alloys after annealing treatment at 500°C for 30min.

Figure 2 shows the Raman spectra of a-Ge<sub>0.85</sub>N<sub>0.15</sub> : H alloys annealed at different temperature. It is found that the shape of Raman spectra from samples annealed at 300°C and 500°C is almost the same as that from as-deposited sample, and the crystallized Ge-Ge signal appears obviously in Raman spectra by annealing at 600°C for 30min. The structural stability of a-Ge<sub>1-x</sub>N<sub>x</sub> : H with N content  $x$  of 0.44 is also investigated by Raman scattering technique, no any structural change can be found in Raman spectra even annealed at 600°C for 30min. The Raman spectra for a-Ge<sub>0.56</sub>N<sub>0.44</sub> : H keep the same at different annealing temperature as in the case of 500°C annealing which has been shown in Fig. 1. These results indicated that introducing nitrogen into a-Ge : H network improves the structural stability and this stability is enhanced with increasing the N content  $x$  in the a-Ge<sub>1-x</sub>N<sub>x</sub> : H alloys. It was known that the bonding energy of Ge-N and N-H is larger than that of Ge-Ge and Ge-H, and in a-GeN : H alloys, nitrogen is strongly bonded with germanium and hydrogen to form Ge-N and N-H bonds, which stay stable in the alloy net-

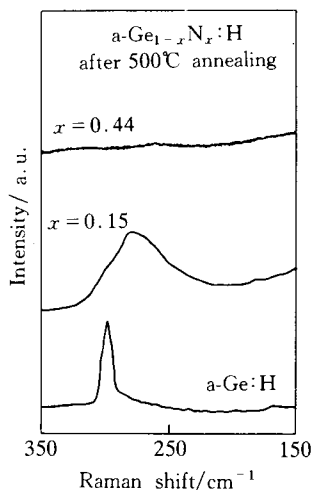


Fig. 1 Raman spectra of  $a\text{-Ge}_{1-x}\text{N}_x\text{:H}$  samples with different  $x$  annealed at  $500^\circ\text{C}$  for 30min

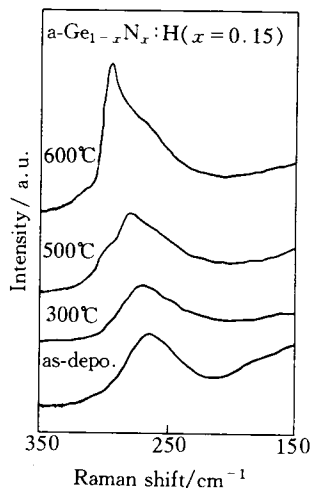


Fig. 2 Raman spectra of  $a\text{-Ge}_{0.85}\text{N}_{0.15}\text{:H}$  alloys annealed at different temperatures

work<sup>[4]</sup>. With increasing the N content in the alloys, the bonding number of Ge-N and N-H is increased as verified by FT-IR spectra, thus the structure become more stable as nitrogen content increases.

It has been reported that in  $a\text{-GeN:H}$  alloys prepared by reactive sputtering method, the N-H bonds were broken when annealed at temperature below  $600^\circ\text{C}$  for 20min<sup>[4]</sup>. However, as shown in Fig. 3 in our present samples produced by PECVD, with increasing

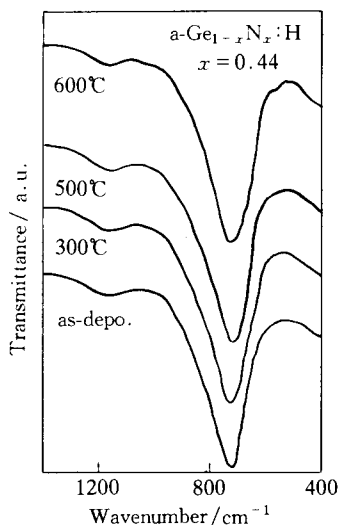


Fig. 3 FT-IR Spectra of  $a\text{-Ge}_{0.56}\text{N}_{0.44}\text{:H}$  alloys annealed at different temperatures

the annealing temperature, no obvious changes can be observed in FT-IR spectra. The absorption intensity of Ge-N stretching mode ( $\sim 700\text{ cm}^{-1}$ ) and N-H bending mode ( $\sim 1115\text{ cm}^{-1}$ ) remains unchanged even at the annealing temperature of  $600^\circ\text{C}$ . It means that the structure of alloys prepared by PECVD is more stable than that of sputtered samples. The possible reason may be related to the content of back bonding nitrogen, since it can effectively enlarge the bonding force of Ge-N or N-H bond in off-stoichiometric  $a\text{-Ge}_{1-x}\text{N}_x\text{:H}$  films<sup>[3,5]</sup>. It is worth note that the nitrogen content in our samples is higher than that prepared by reactive sputtering method.

In conclusions, the thermally structural stability has been studied for off-stoichiometric hydrogenated amorphous germanium-nitrogen compounds prepared by PECVD method. The bonding configurations and structure have been investigated and it is shown that by intro-

ducing nitrogen into a-Ge : H network not only enlarges the optical band gap but also increases the structural stability of the materials. The network of the present films is more stable than those samples produced by reactive sputtering method.

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