

## HYDROGEN INCORPORATION IN AMORPHOUS $\text{Ge}_x\text{Se}_{100-x}$ FILMS PREPARED BY PLASMA-ENHANCED CHEMICAL VAPOUR DEPOSITION

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### 1. Introduction

It is well known that the amorphous silicon prepared by plasma-enhanced chemical vapour deposition (PECVD) is a high quality material for photovoltaic cells and other electronic devices. During the deposition in the hydrogen-rich plasma hydrogen atoms are incorporated in the silicon matrix and their concentration depends mainly on temperature. The hydrogen atoms passivate the dangling bonds, thus yielding a material with a low defect density.

In this study we prepared amorphous  $\text{Ge}_x\text{Se}_{100-x}$  films by PECVD starting from the hydrides as precursor gases. It can be expected that hydrogen will be incorporated in the matrix of the chalcogenide film but the effect of hydrogen incorporation on the basic physical properties is probably not drastical. It is generally accepted that neutral dangling bonds are transformed into positively and negatively charged dangling bonds, pinning the Fermi level close to the middle of the bandgap. From a previous study of Raman spectra in the  $\text{Ge}_x\text{Se}_{100-x}$  system [1] we concluded that films prepared by PECVD exhibited a closer resemblance in their structure to bulk glasses than to films prepared by thermal evaporation. This means that PECVD films contain less wrong bonds and defects than thermally evaporated films.

### 2. Experimental procedure

We have deposited thin amorphous  $\text{Ge}_x\text{Se}_{100-x}$  films in a plasma discharge stainless steel reactor, having a construction similar to that commonly used for the deposition of amorphous Si. The experimental arrangement consisting of the reactor, deposition control units and pumps was described in ref. [2]. The precursor gases were high purity germanium hydride ( $\text{GeH}_4$ ) and hydrogen selenide ( $\text{H}_2\text{Se}$ ) diluted in hydrogen (15 vol.% of the hydrides). A low pressure plasma of 0.1 mbar was created by an rf discharge of 13.57 MHz between two parallel plate electrodes. The RF power coupled into the reactor was  $1.6 \text{ W cm}^{-2}$ . The deposition time was 30 min., yielding films with a thickness of about 1  $\mu\text{m}$ . Crystalline silicon and glass substrates were fixed on both electrodes and first cleaned by etching in an argon plasma. The chemical composition was measured by means of electron microprobe analysis. IR transmission spectra were recorded in the wavelength range from 4000 to  $150 \text{ cm}^{-1}$  on films deposited onto polished crystalline Si wafers. Raman spectra were recorded with the help of a Bruker 66 V spectrometer in reflection mode using a  $1.06 \mu\text{m}$  YAG  $\text{Nd}^{3+}$  laser source.

### 3. Results and discussion

The chemical composition of the films deposited on the grounded electrode expressed in atomic % of Ge,  $x$ , was equal to 65.8, 48.8, 35.5, 32.5, 26.4 and 22.8.

Infrared and Raman spectroscopy are powerful techniques to detect hydrogen bonds in a material. The vibrational spectra of hydrogen bonds in amorphous Ge have been the object of considerable study. The interest mainly arises from the role of hydrogen in passivating dangling bonds. In hydrogen-rich material, the Ge films may contain polygermane groups,  $(\text{GeH}_2)_n$ , giving rise to bending vibrations. The vibrational modes of the hydrogen bonds lie in the middle-infrared between 2000 and 500  $\text{cm}^{-1}$ . They are given in Table 1.

Table 1  
Germanium-hydrogen vibrational modes in hydrogenated amorphous germanium.

Wavenumber ( $\text{cm}^{-1}$ )	Origin
$\sim 2000$	stretching vibration of $(\text{GeH}_2)_n$ or surface bonded hydrogen
$\sim 1900$	stretching vibration of the monohydride Ge-H
825	scissor vibration of $(\text{GeH}_2)_n$
765	wagging vibration of $(\text{GeH}_2)_n$
560	rocking vibration of $(\text{GeH}_2)_n$

For the band situated at 2000  $\text{cm}^{-1}$ , commonly observed in hydrogen-rich material, two explanations have been given: either the stretching vibration of Ge dihydride  $(\text{GeH}_2)$  groupings [3] or a Ge-H stretching mode arising from surface-bonded hydrogen inside of cavities [4]. There was general agreement about the band at 1900  $\text{cm}^{-1}$ , which arises from vibrations of Ge-H in a monohydride group. Amorphous Ge films containing polygermane groups showed bending vibrations at 825, 765 and 560  $\text{cm}^{-1}$ . The Se-H stretching vibration is located at 2240  $\text{cm}^{-1}$ .

Our infrared spectra gave direct evidence for the presence of hydrogen. In the films with  $x=65.8$ , 48.8, 35.5 (Ge-rich) and 32.5 (nearly stoichiometric) absorption bands were observed at 2050, 820, 760 and 560  $\text{cm}^{-1}$ . This is shown in Fig. 1 for the film with the highest Ge concentration ( $x=65.8$ ). The intensity of the bands decreased with decreasing Ge concentration. In the Se-rich samples with  $x=26.4$  and 22.8 the germanium-H bands were completely absent. The stretching vibration was found at slightly higher wavenumber (2050  $\text{cm}^{-1}$ ) than the expected one from Table 1. This is probably due to the presence of selenium in the matrix. The Se-H stretching vibration located at 2240  $\text{cm}^{-1}$  was observed in the sample with  $x=35.5$ , 32.5 and the two Se-rich films with  $x=26.4$  and 22.8, having a maximum intensity at  $x=22.8$ .

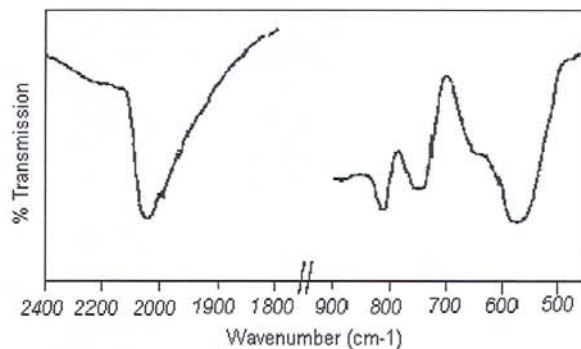


Fig. 1 Infrared absorption bands due to Ge-hydrogen bonds in amorphous  $\text{Ge}_{65.8}\text{Se}_{34.2}$ .

From these infrared results one can conclude that Ge-H bonding is present only in Ge-rich films, Ge-H and Se-H bonds are present in films with composition around stoichiometry ( $\text{GeSe}_2$ ), while Se-H only arises in Se-rich films.

The Raman measurements led to the same conclusions concerning the hydrogen incorporation. A typical Raman spectrum of a film with  $x=35.5$  is shown in Fig. 2. This figure clearly indicates that germanium - hydrogen and selenium - hydrogen bonds are present and their signatures are given by a Raman band at  $2030$  and  $2240\text{ cm}^{-1}$ , respectively. In pure amorphous Se prepared by PECVD no hydrogen was detected.

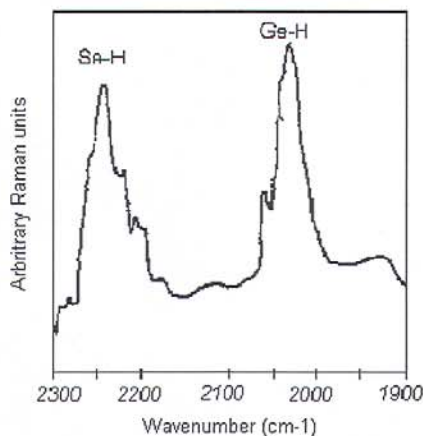


Fig. 2 Raman spectrum of a  $\text{Ge}_{35.5}\text{Se}_{64.5}$  film indicating the incorporation of hydrogen.

We studied the thermal stability of the hydrogen bonds by heating the films for 30 minutes at increasing temperatures and measuring the Raman spectra after each annealing step. In Fig. 3 the Raman spectra of a film with the composition  $\text{Ge}_{35.5}\text{Se}_{64.5}$  are shown. As mentioned before, in the virgin material two bands due to Ge-H ( $2030\text{ cm}^{-1}$ ) and Se-H vibrations ( $2240\text{ cm}^{-1}$ ) are present. The intensity of the Ge-H peak already decreased at  $100^\circ\text{C}$ , which means that bond breaking started at  $100^\circ\text{C}$  and was complete at  $200^\circ\text{C}$ . The Se-H bond is slightly more stable. Breaking of this bond started  $50^\circ\text{C}$  higher at  $150^\circ\text{C}$  and was nearly complete at  $225^\circ\text{C}$ .

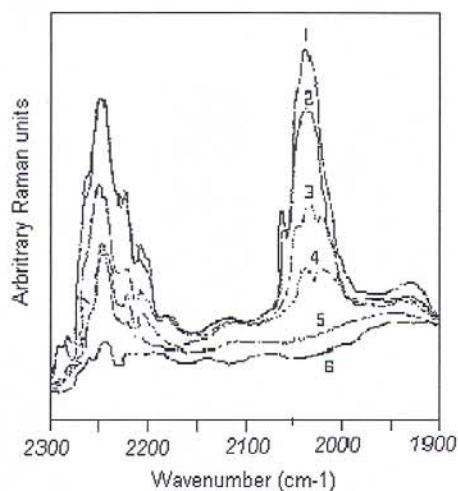


Fig. 3 Hydrogen bands in Raman spectra before and after annealing treatments: (1) virgin, (2)  $100^\circ\text{C}$ , (3)  $150^\circ\text{C}$ , (4)  $175^\circ\text{C}$ , (5)  $200^\circ\text{C}$ , (6)  $225^\circ\text{C}$ .



We calculated the area of the Ge-H and Se-H peaks as a function of the annealing temperature. The results are shown in Fig. 4. Here, it can be seen easily that the Ge-H bond is less stable than the Se-H bond.

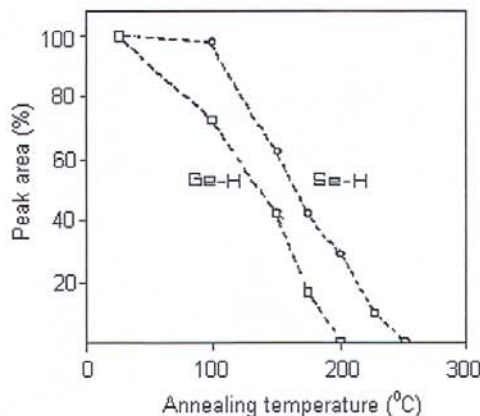


Fig. 4 Peak area of the Se-H ( $2240\text{ cm}^{-1}$ ) and Ge-H bands ( $2030\text{ cm}^{-1}$ ) as a function of the annealing temperature.

Hydrogen evolution in amorphous hydrogenated Ge was studied by Beyer et al.[5]. They observed one evolution peak at  $200^{\circ}\text{C}$  for an a-Ge film prepared below  $150^{\circ}\text{C}$ , while hydrogen evolution mainly occurred in the  $400\text{--}800^{\circ}\text{C}$  temperature range for films prepared at higher temperature. They attributed the low temperature evolution to a surface desorption process in a void-rich material and the high temperature evolution to a diffusion-limited process in the bulk material. The highest hydrogen stability was obtained for compact undoped material. If we follow their ideas, then we can assume that the hydrogen loss in our germanium-selenide samples originates from the rupture of Ge-H and Se-H bonds at the surface. This indicates that most of the hydrogen incorporated during the deposition process is bonded at the surface of voids.

#### 4. Conclusions

Infrared and Raman spectra measured on amorphous  $\text{Ge}_x\text{Se}_{100-x}$  films prepared by PECVD gave direct evidence for the incorporation of hydrogen. Ge-H bonds are present in Ge-rich material, while Se-H bonds appear in Se-rich material. Around stoichiometry, bands of both types of hydrogen bonds are observed. In pure selenium no hydrogen was found. Thermal annealing experiments showed the rupture of hydrogen bonds at low temperature, starting at  $100^{\circ}\text{C}$  for Ge-H and at  $150^{\circ}\text{C}$  for Se-H. This indicates that most of the hydrogen incorporated during the deposition process is bonded at the surface of voids.

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