On the Influence of Deposition Temperature on the Microvoid Structure and Hydrogenation of a-Ge:H Films

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The nanometer scale structure of RF sputtered a-Ge:H thin films has been investigated using small angle X-ray scattering (SAXS) and infrared spectroscopy (IR). The microvoid size distribution and the relative amounts of hydrogen bonded to Ge in voids having the size of a vacancy (bulk-like Ge-H bonds) and H bonded to the internal surfaces of larger size voids (surface-like Ge-H bonds) were determined as a function of substrate temperature for a fixed hydrogen partial pressure and deposition rate. The results show that for low deposition temperatures a less dense material is obtained, with a polgdispcrse void population and a greater amount of surface-like bonded hydrogen.

I. Introduction

Hydrogenated amorphous seiniconductors are very attractive materials for application in thin film devices such as solar cells and photosensors. As a consequence, considerable attention lias been devoted to the study of their electrical and optical properties, as well as to their dependence on deposition conditions. In orcler to gain a deeper understanding of this relationship, detailed studies of film microstructure are essential. Tlie existence of inhomogeneities due to Ge concentration fluctuations and the presence of microvoids are two important structural features which certainly influence the optoelectronic propertics. Previous works on a-Si:H[1], a-SiC:H[2], a-SiGe:H[3-5] and a-Ge:H[6] have given valuable information on tlie porous nature of films deposited by glow discharge under non-optimized conditions.

In the present work me focused our attention on a-Ge:H samples grown by rf reactive sputtering ill an Ai. plus H_2 atmosphere. The main advantage of this deposition method is that it enables to control the amount of hydrogen into the deposition chamber during growth. As a. consequence it is possible to study the hydrogenation process and its influence on the structure in a separate way. The glow discharge system, on the contrary, does not present this possibility since the films are obtained from tlie decomposition of the corresponding semiconductor hydrides, ie. silane (SiH_4) or germane (GeH_4).

IR. transmission spectroscopy and SAXS measurements have been used to obtain in'formation on the nanoscale structure of rf sputtered a-Ge:H films as a function of deposition temperature. The relationship between rnicrovoid size distribution and hydrogenation is discussed.

II. Experimental

Hydrogenated amorphous germanium films were prepared by the rf reactive sputtering method (13.56 MHz) in a hydrogen-argon atmosphere. The background pressure of the sputtering apparatus was 10^{-6} mbar. Tlie total pressure of the hydrogen-argon mixture was kept constant at 14.7 x 10^{-3} mbar. The hydrogen partial pressure was 1.4×10^{-3} mbar in all cases. The substrate temperature was varied between 75 and 340°C (see Table I), and the deposition rate was approximately 1.1 Å/s.

The samples were clepositecl onto crystalline silicon wafers for IR transmission, on Corning 7059 glass for VIS-NIR optical transmission and dark conductivity(as function of the temperature) and on thin aluminum foils

Table I - Deposition temperatiire, hydrogen concentration, microstructural parameter R and void volme fraction Q of rf-sputtered a-Ge:H samples.

Sample	Substrate Temperature (°C)	C_H%	R	Q
A	75	13.5	1.1	2.04
B	120	11.7	1.3	1.57
C	220	7.4	1.9	1.16
D	340	4.8	3.4	0.54
E	220	(non hydrogenated)		1.00

for SAXS measurements. Typical film thickness is 1 μm. Ten A foils were stacked for X-ray transmission experiments. These were performed with a line focus geometry and Ni filtered Cu (Kα) radiation from a rotating anode generator (Rigaku-RU200). The experimental set-up include a vacuum path and a linear position sensitive detector. Infrared spectroscopy was performed using a Fourier Transform infrared spectrometer (FT 1600 Perkin Elmer model) in the 400 - 4000 cm^{-1} wave number range. NIR-VIS optical transmission measurements were performed with a λ9 Perkin Elmer spectrometer in tlie 800-2500 nm wavelenght range.

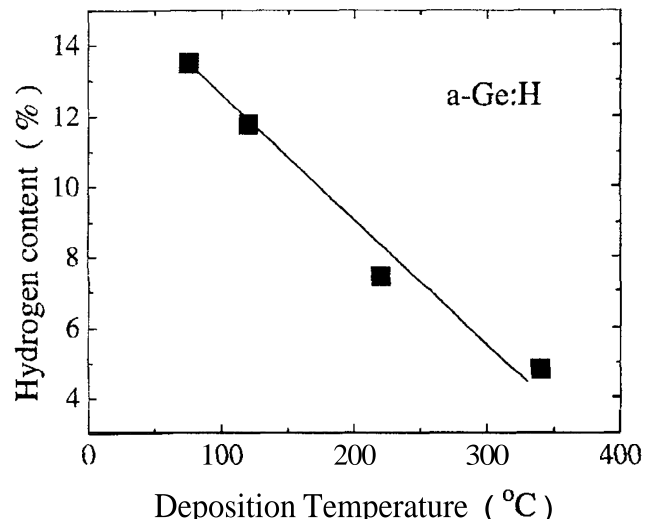

Figure 1: Hydrogen content (from IR absorption) of rf-sputtered a-Ge:H films as a function of deposition temperature.

III. Results and discussion

The amount of bonded hydrogen was determined from tlie integrated absorption of the Ge-H wagging mode at 565 cm^{-1} [7]:

$$C_H = A \int \alpha(\omega)/\omega \; d\omega,$$

where A = 1 1 $\times$ 10^{19} cm^{-2}, α is the absorption coefficient, and ω is the wavenumber.

Figure 1 shows the fraction of hydrogen bonded to the a-Ge network as a function of substrate temperature. All increase of the hydrogen content is measured in films depcsited at low deposition temperatures. As expected, no absorption bancls were detected for tlie non-liydrogeriated E sample (see Table I). An absorption band appearing at 825 cm^{-1} in samples A and B was related to the hending vibration mode of the Ge-H_2 bond[8]. The increased hydrogenation of samples deposited at low temperatures produces an increase of tlie Tauc's optical gap[9], which varied from 1.02 to 1.17 eV. A simultanous increase of the activation energy of the dark conductivity up-to 0.47 eV was measured.

Previous work on RF sputtered a-Ge:H indicates that the Ge-H stretching mode may be associated to two different local environments. The first mode at 1880 cm^{-1} *(bulk-like* Ge-H stretching *mode)* has been associated to isolated Ge-H bonds in microvoids having the size of a vacancy. The second stretching mode at 1980 cm^{-1} (surface-like Ge-H stretching *mode)* corresponds to Ge-H groups forming clusters of 5 or more H atoms located in the internal surfaces of larger voids. These larger voids may appear at low deposition temperature and/or high hydrogen fluxes and are representative of a low quality material[10]. Figure 2 displays the absorption coefficient of the Ge-H stretching mode. As already explained, the absorption band can be deconvoluted into two gaussians originating from Ge-H vibration in different environments (bulk-like and surface-like

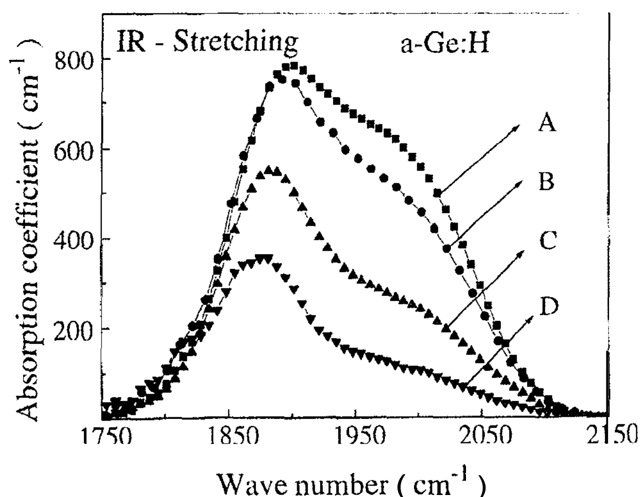

Figure 2: Absorption coefficient corresponding to the stretching mode of the Ge-H vibration of samples deposited at different temperatures. Note the evolution of the *bulk-like* and of the *surface-like* contributions to the overall absorption.

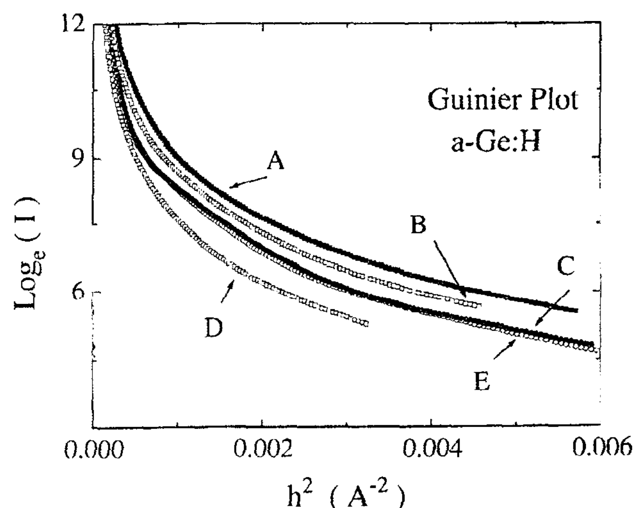

Figure 3: Guinier plots for the whole series of rf-sputtered a-&:I-I sarnples.

bonded hydrogen). The ratio of the integrated absorption of the two vibrations (S_{1880}/S_{1980} = R,) for the present a-Ge:H series is shown in Table 1, which indicates that low deposition temperatures produce films having a. large density of microvoids.

SAXS intensity curves were obtained as a function of the absolute values of tlie scattering vector $h(=4\pi sin\theta/\lambda)$, where 2θ is the scattering angle and λ the wavelength of the incident X-rays. Corrections to the experimental data were introduced taking into account the background scattering due to the substrate, thc absorption by the sample, and the incident beam geometry (linear focus). A general data treatment program due to Svergun[11] was used to perform the last correction and tlie subsequent calculation of the radius of gyration of the voids, as well as their size distribution function $D(r)$, considering the samples as polydisperse systems of spheres. Figure 3 shows the Guinier plots $[Ln(I(h))vs.h^2]$ obtained foi tlie desmeared intensity curves[12]. Since there is not a clear linear dependence foi. the whole range of measured angles, the system has to be treated as polydisperse. Nevertheless, two linear regions can be identified for the smaller and the larger values of the scattering vector. A calculation of the radius of gyration for these two extreme cases gives the values R_{gmin} = 14Å and R_{gmax} = 300Å. The tail end of tlie scattering curves of the present samples (larger values of the scattering vector) obeys Porod's power law $\mathbf{I} = Ch^{-4}$ (where C is a constant). This experimental finding leads ris to conclude that the void-matrix interface can be considered smooth.

Small angle X-ray scattering results were interpreted considering the samples as being a two-phase system: the solid phase with constant electron density ρ_s occupying a definite volume fraction v, and the voids with electron density ρ_f with a corresponding volume fraction $v_f = 1 -$ v,. The integrated (h^2 weighted) desmeared SAXS intensity curves can be related to the void volume fraction by the equation[13]:

$$Q = \int h^2 I(h)dh = K(\Delta\rho)^2 v_f(1 - v_f)$$

where $\Delta\rho = \rho_s - \rho_f$, and $K \equiv$ constant.

The function Q, known as the invariant, is very useful in giving an indication of the relative void volume fraction in the samples. The curves $h^2I(h)$ vs. h obtained from the analysis of the present samples are shown in Fig. 4a. They indicate that high Q values correspond to low deposition temperatures, and consequently to less dense material. Fig. 4b shows the values of tlie invariant Q as a function of the substrate temperature for all thc studied samples. An almost linear behavior is obtained. It is worth stressing here that tlie relative void volume fraction of samples deposited at 220°C does not depend on hydrogenation. Samples C (hydrogenated) and E (non-hydrogenated) deposited under identical conditions have almost the

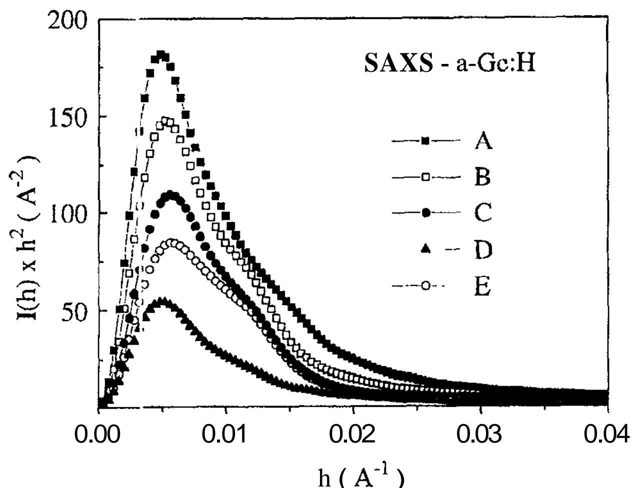

Figure 4a: $I(h).h^2$ versus (h) curves used in the calculation of tlie invariant Q. Note that the areas are proportional to the void volume fraction.

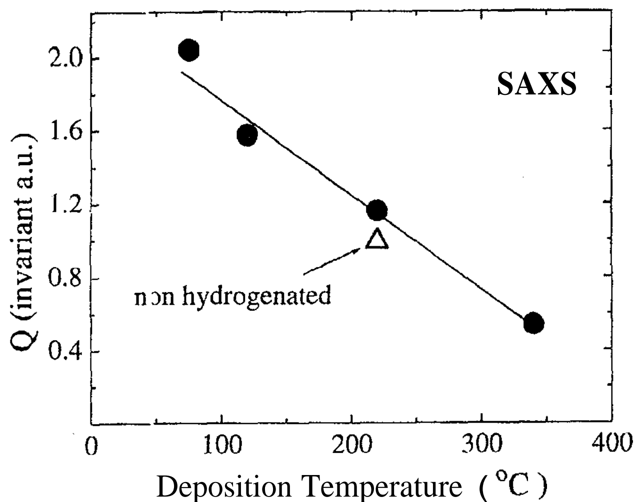

Figure 4b: Void volume fraction [invariant Q] as a function of tleposition temperature for rf-sputtered a-Ge:H samples. Notice that at $T_s = 220°C$ the volume void fraction is almost independent af hydrogenation.

same Q value, an indication of a similar void volume fraction.

The calculation of the void size distribution function $D(r)$ is shown in Fig. 5 for the five series of studied samples. The function $D(r)$ is related to the scattered intensity by[11,12,13]:

$$I(h) = \int D(r)\sigma(h,r)dr,$$

with

$$D(r) = \mathrm{m}^2(r)N(r)$$

where $m(r)$ is the scattering length, $N(r)$ is the number of particles (voids) of size r and $\sigma(h, \mathrm{r})$ is the form factor

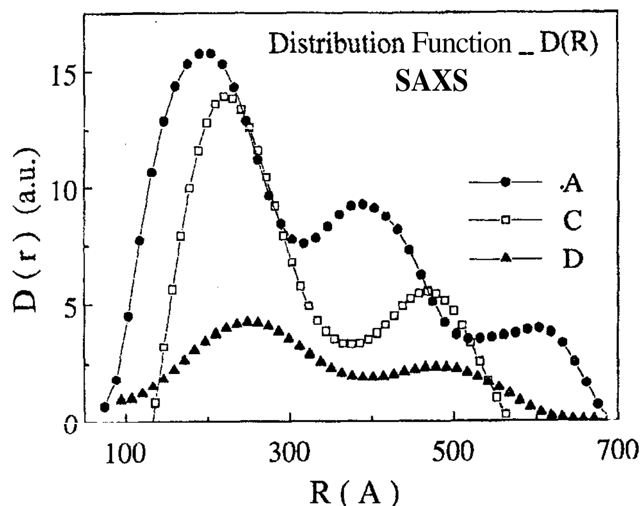

Figure 5: Void size distribution of different a-Ge:H samples as calculated from SAXS data.

of the particles (voids).

The $D(r)$ curves shown in Fig. 5 indicate that the size distribution function, within the (100 - 650 Å) r range, contains a large contribution from a void population having r $\approx 200Å$ and smaller contributions from one or two populations having bigger sizes. The $D(r)$ curve of sample E is not shown in Fig. 5. Its shape is practically the same as that of sample C. The oscillations found in the calculated $D(r)$ curves are under study. It is not yet known if they are a computer programming artifact or a true indication of a bimodal or trimodal void size distribution.

Experimental data show that samples grown at high temperatures have a low void density and a small hydrogenation. At first sight, these results may induce to think that the hydrogenation process of the a-Ge network is responsible for the structural changes. That this is not the case may be seen in Fig. 4b, showing that an almost identical void volume fraction is obtained for hydrogenated and non-hydrogenated samples deposited at 220°C. This result suggests, on the contrary, that the deposition temperature and the deposition rate control the structural properties. Rising the substrate temperature increases the ad-atom mobilily of the impinging species. If the deposition rate is low enough, they can diffuse and accomodate in highly stable configurations or, in other words, in places of minimum potencial energy. A less strained bonding configuration is thus favored leading to a denser film, as observed.

It is well known that hydrogen may eitlier satisfy dangling bonds at the growing surface, or may break weak bonds in tlie strained network. The increase of deposition temperature and of ad-atoms mobility produce less strained Ge-Ge bonds. The decrease in strained Ge-Ge bonds density leads to a. decrease of bonded hydrogen iii the growing material.

In this way, it is concluded that the structural evolution of ainorphous germanium during the growth process is what determines hydrogenation ancl not the opposite. The main findings of the present work are confirmed by structural studies made on a-Ge samples grown under different. deposition conditions, i.e., a couple of series in which the substrate temperature was held constant ancl, either the hydrogen partial pressure in tlie chamber, or tlie rf power fed into the plasma was varied at a time[14].

IV. Conclusions

The amount of bonded hydrogen *(13.5%* to 4.8%): as well as its bonding characteristics to the a-Ge:H network (*bulk* or *surface-like*), were determined by FTIR spectroscopy in samples deposited a.t different temperatures (75-340°C range). Lower deposition temperatures produce material having a. large amount of liydrogen bonded to internal surfaces of microvoids. Considering a-Ge:H films as a. two phase system, SAXS results indicate that: a) the interface void-matrix is smooth, and b) for low deposition temperatures there is an increase in tlie void volume. As a consequence, tlie films deposited at low temperatures are l e s dense. The overall effect has been attributed to the lower ad-atom mobility during tlie deposition process.

It has been found that a.t a substrate temperature of 220°C hydrogen does not contribute to void formation, its role being mainly the passivation of dangling bonds. The present results allow us to conclude that hydrogenation and void formation in a-Ge:H films appear to be almost independent processes, both being strongly dependent on deposition temperature. These conclusions have been corroborated in samples in which the substrate temperature was held constant and either tlie hydrogen partial pressure in the chamber or the rf power fed into the plasma was varied a.t a time[14].

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