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Study of Ge_YSi_{1-Y}:H films deposited by low frequency plasma

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Abstract

In this work, we report a study of the optical properties measured through spectral transmission and spectroscopic ellipsometry in Ge:H and Ge_YSi_{1-Y}:H ($Y \approx 0.97$) films deposited by low frequency (LF) PE CVD with hydrogen (H) dilution. The dilution was varied in the range of $R=20$ to 80. It was observed that H-dilution influences in a different way on the interface and bulk optical properties, which also depend on incorporation of silicon. The films with low band tail characterized by its Urbach energy, E_U, and defect absorption, α_D, have been obtained in Ge:H films for $R=50$ with $E_U=0.040$ eV and $\alpha_D=2\times10^3$ cm^{-1} ($h\nu \approx 1.04$ eV), and in Ge_YSi_{1-Y}:H films for $R=75$ with $E_U=0.030$ eV and $\alpha_D=5\times10^2$ cm^{-1} ($h\nu \approx 1.04$ eV).

Keywords: Germanium; Silicon; Plasma processing and deposition; Optical properties; Amorphous materials

1. Introduction

Germanium–silicon films deposited by plasma are very attractive as materials because its optical gap is narrower than that for silicon films. They are also completely compatible with the standard silicon CMOS technology. These films can be used for different device applications i.e., solar cells [1] detectors [2], micro-bolometers [3], etc. However growth, structure and electronic properties of these films have been significantly less studied in comparison with silicon films. Typically RF glow discharge at a frequency $f=13.56$ MHz is used for its deposition. Dalal [4] has reported that deposition conditions providing higher ion bombardment during growth, resulted in good quality Ge:H and Ge_YSi_{1-Y}:H films. These conditions can also be reached in a low frequency (LF) discharge. Growth and properties of Ge_YSi_{1-Y}:H films deposited by LF PE CVD have been reported in Refs. [5,6]. In the latter, the effect of argon (10:1) and hydrogen (20:1) dilution has been studied over the entire range of Ge concentrations. The deposition and study of nano-crystalline films by LF discharge with a very high degree of hydrogen dilution (from 170:1 to 400:1) have been reported in Ref. [7]. Also, the morphology and some electronic properties of LF PECVD films have been reported in Refs. [8,9].

The goal of this work is to study optical properties of germanium–silicon films deposited by LF PECVD with hydrogen dilution in the range of $R=20$ to 80.

2. Experimental

The Ge:H and Ge_YSi_{1-Y}:H films were deposited by LF PECVD at a substrate temperature of $T_s=300$ °C and discharge frequency $f=110$ kHz from SiH_4 and GeH_4 feed gases diluted with hydrogen. Hydrogen dilution defined as $R=Q_{H2}/[Q_{SiH4}+Q_{GeH4}]$, where Q_{H2}, Q_{SiH4}, and Q_{GeH4} are the gas flows of hydrogen, silane and germane, respectively, was varied in the range of $R=20$ to 80. The Ge_YSi_{1-Y}:H films were deposited with a fixed flow of $Q_{SiH4}=25$ sccm and $Q_{GeH4}=25$ sccm. The composition of the films was studied using secondary ion mass spectroscopy (SIMS). The spectral dependence of the optical absorption coefficient, $\alpha(h\nu)$, was calculated from optical transmission $T(h\nu)$ measurements (with a "BRUCKER"

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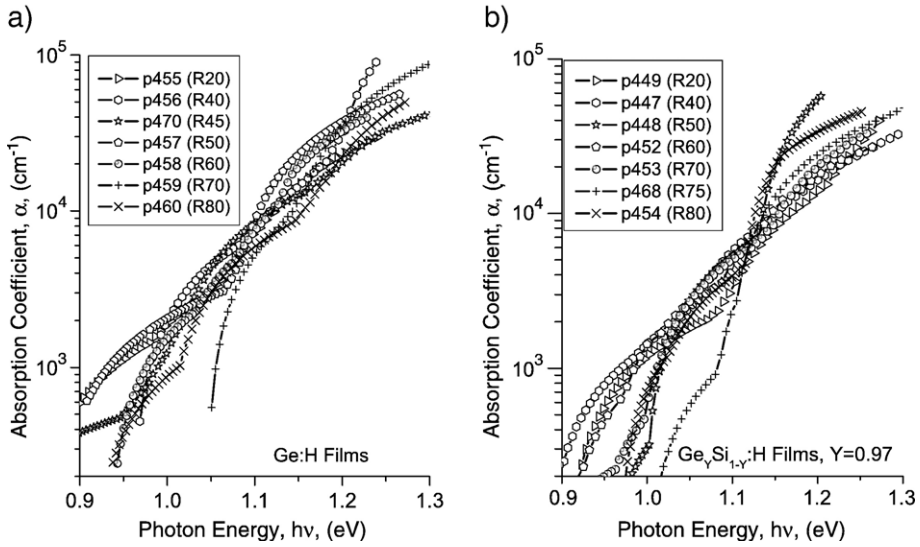

Fig. 1. Spectral dependence of optical absorption coefficient $\alpha(h\nu)$ for different hydrogen dilution R for a) Ge:H and b) Ge_YSi_{1-Y}:H, $Y=0.97$, films.

spectrophotometer model Vector-22) using the model described in Ref. [10] for obtaining the set of optical parameters. Spectroscopic ellipsometry measurements were performed in the $h\nu=1.0$–4.5 eV photon energy range.

3. Results

3.1. Optical characteristics obtained by spectral transmission, T(hν), measurements

Fig. 1 shows the spectral dependence of the absorption coefficient, $\alpha(h\nu)$, for the Ge:H and Ge_YSi_{1-Y}:H films deposited in the aforementioned hydrogen dilution range. $\alpha(h\nu)$ was determined from spectral transmission $T(\lambda)$ measurements. The $\alpha(h\nu)$ curves demonstrate significant effect of hydrogen dilution on the spectral dependence of the optical absorption, dependence which is related to density of states in the films. The three main regions in $\alpha(h\nu)$ spectra of Fig. 1, are due to: a) band-to-band transitions that correspond to the transitions from valence to conduction band; b) transitions related to valence and conduction band tails and c) defect related transitions. It should be noted that in non-crystalline materials there is no un-ambiguous definition of optical gap, in contrast to crystalline semiconductors. There are several definitions for optical gap and conventionally Tauc optical gap, E_g, is used among others. In this work, in order to characterize optical properties we have used the following parameters: E_{03} and E_{04} energies corresponding to $\alpha=10^3$ cm^{-1} and $\alpha=10^4$ cm^{-1}, respectively, $\Delta E=E_{03}-E_{04}$ is the energy characterizing the slope of $\alpha(h\nu)$, the refraction index for long wavelengths, n_∞, the Tauc optical gap, E_g, and the Urbach energy,

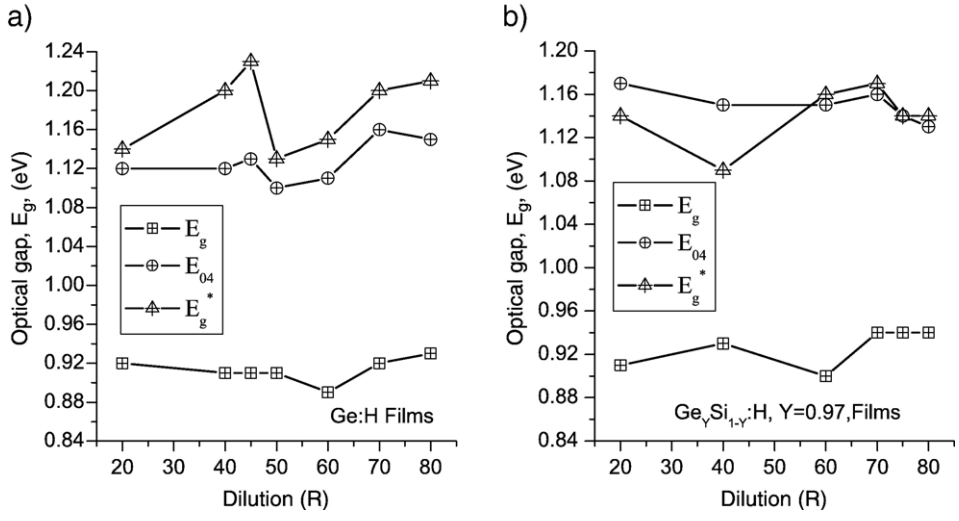

Fig. 2. Optical gaps, E_g and E_g^* determined from spectroscopic ellipsometry and spectral transmission measurements, respectively, and the energy, E_{04}, as function of H-dilution for a) Ge:H and b) Ge_YSi_{1-Y}:H films. Solid line is a guide to the eyes.

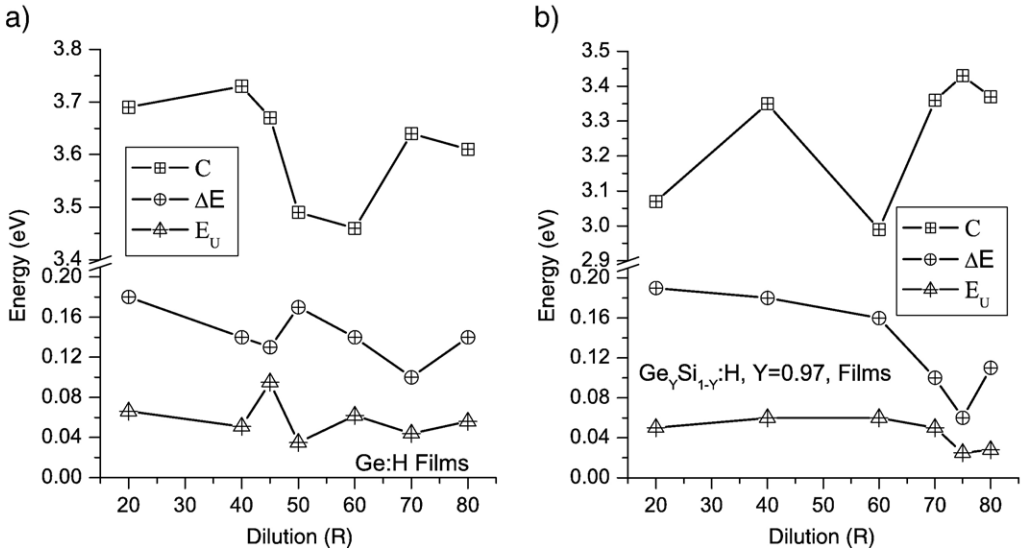

Fig. 3. Broadening parameter, C, energy, ΔE, and Urbach energy, E_U, for a) Ge:H and b) Ge_YSi_{1-Y}:H films. Solid line is a guide to the eyes.

E_U. The Urbach energy was determined in the region $h\nu \leq E_g^*$, where absorption can be described as $\alpha(h\nu)=\alpha_g \exp(h\nu - E_g^*/E_U)$ where α_g is the absorption coefficient at $h\nu = E_g^*$. These parameters are plotted in Figs. 2–4 in comparison with the data obtained from spectroscopic ellipsometry.

3.2. Spectroscopic ellipsometry (SE) measurements

Spectroscopic ellipsometry (SE) measurements were performed in the photon energy range $h\nu = 1.0$–4.5 eV. The analysis of SE data was performed using a two-layer model (ambient/surface roughness/bulk/substrate). The surface roughness was modeled as 50–50% mixture of the bulk material and voids. For modeling the bulk material, Tauc–Lorentz dispersion law was used. In this model, which combines Tauc's expression for absorption above the band edge of an amorphous material and standard quantum mechanical approach, imaginary part of the dielectric function is expressed as:

$$\varepsilon_{\infty}^{TL} = \frac{AE_0C(h\nu - E_g)^2}{\left((h\nu)^2 - E_0^2\right) + C^2(h\nu)^2}\frac{1}{(h\nu)} \quad (1)$$

where E_g is the Tauc optical band gap, A is the amplitude factor proportional to the density of the material and the optical transition matrix elements, E_0 is the peak transition energy (energy distance between maxima of density of states in valence and conduction bands), C is the broadening parameter proportional to material disorder. These characteristics are shown in Figs. 2–4 in comparison with those determined from spectral transmission measurements for the films deposited with hydrogen dilution varied in the range of $R = 20$–80.

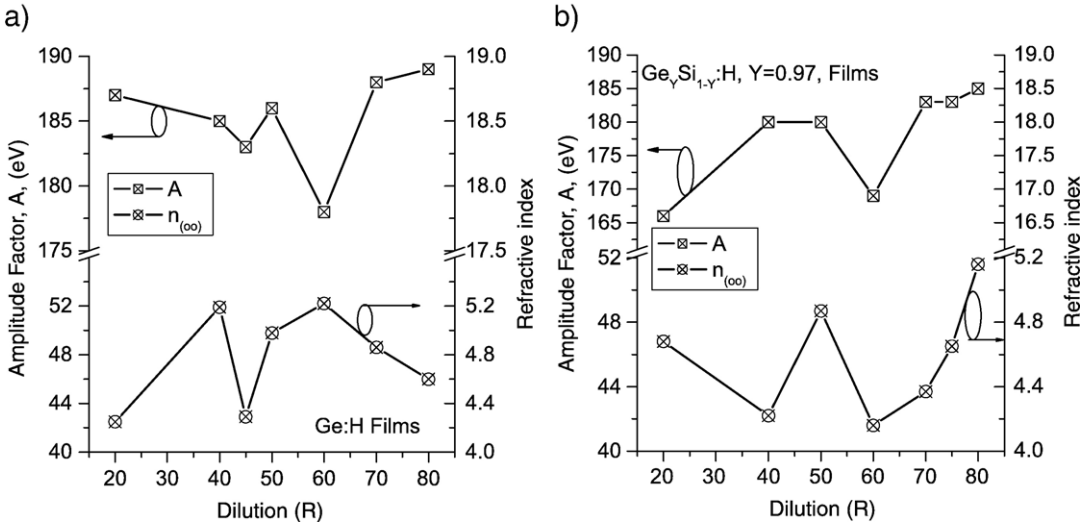

Fig. 4. Amplitude factor, A, and refractive index, n_∞, as a function of hydrogen dilution for a) Ge:H and b) Ge_YSi_{1-Y}:H films. Solid line is a guide to the eyes.

4. Discussion

Hydrogen dilution is found to influence significantly, as shown in Fig. 1a) and b), on both band-tail related absorption at photon energies in the range of $h\nu = 1.05–1.15$ eV and defect related absorption at photon energies $h\nu = 0.9–1.0$ eV.

In order to characterize optical gap from transmission measurements we employed E_g^* value determined as a boundary energy between the region related to Urbach absorption, which is characterized by E_U and band-to-band transitions in the region of high absorption ($\alpha > 10^4$ cm^{-1}). The conventionally used Tauc gap energy was also calculated for the films studied, provided the values determined by defect (and tail) rather than band-to-band absorption. Determined in this way E_g^* values were close to the E_{04} values and demonstrated very similar behavior with R as shown in Fig. 2a) and b).

In Ge films both E_g^* and E_{04} had minimum at $R = 50–60$ which correlates with minimum E_g, as can be seen in Fig. 2a). In Ge–Si films E_g showed also minimum at $R = 60$, but E_g^* had minimum values at $R = 40$ and 75–80, while E_{04} showed minimum only at $R = 80$. It is interesting to analyze the parameters which described the band tail absorption: C, ΔE and E_U. They are shown in Fig. 3 as a function of dilution. In Ge films we can see that E_U has minimum at $R = 50$ in correlation with C and at $R = 70$ in correlation with ΔE. In Ge–Si films both E_U and ΔE show a minimum at $R = 75$, while C showed minimum only at $R = 60$. The density of the films is revealed in A and n_∞ characteristics shown in Fig. 4. In Ge films A has two minima at $R = 45$ and 60. The former correlates with minimum of n_∞ at $R = 45$. In Ge–Si films n_∞ shows two minima at $R = 40$ and 60 and only the latter correlates with minimum A at $R = 60$.

Taking into consideration that SE measurements are very sensitive to the surface or interface regions, while transmission provides information about bulk properties, the data discussed allow us to suggest that hydrogen dilution influences on interface and bulk region in a different way, depending also on both the degree of H-dilution and the incorporation of Si. The latter effects slightly on the data obtained by spectral ellipsometry (compare E_g, C and A in Figs. 2–4). The effect of H-dilution on the bulk properties is more significant, providing the observed $\alpha(h\nu)$ characteristics with small Urbach energy $E_U = 0.040$ eV (Ge:H, $R = 50$) and $E_U = 0.030$ eV (Ge–Si:H, $R = 75$) and, small values of defect absorption $\alpha_D = 2 \times 10^3$ cm^{-1} ($h\nu \approx 1.04$ eV) for Ge:H films with $R = 50$ and $\alpha_D \approx 5 \times 10^2$ cm^{-1} ($h\nu \approx 1.04$ eV) for Ge–Si:H films with $R = 75$. To our knowledge such small values have not been reported in literature so far.

5. Conclusions

The optical characteristics measured in this work by spectral transmission and spectroscopic ellipsometry measurements on LF PECVD Ge:H and Ge–Si:H films, deposited with different hydrogen dilution have demonstrated that the dilution influences on the bulk and the interface optical properties in a different way, an influence which also depends on silicon incorporation. At $R = 50$ for the Ge:H and $R \approx 75$ for the Ge_YSi_{1-Y}:H films, both, low band tail and defect absorption have been obtained.

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References

[1] J.K. Rath, F.D. Tichelaar, R.E.I. Schropp, Sol. Energy Mater. Sol. Cells 74 (2002) 533.
[2] M. Krause, H. Stiebig, R. Carius, Mater. Res. Soc. Symp. Proc 664 (2001) A26.5.1.
[3] M. Garcia, R. Ambrosio, A. Torres, A. Kosarev, J. Non-Cryst. Solids 338–340 (2004) 744.
[4] V.L. Dalal, Curr. Opinion Solid State Mater. Sci 6 (2002) 455.
[5] B.G. Budaguan, A.A. Sherchenkov, G.L. Gorbulin, V.D. Chernomordic, Physica B 325 (2003) 394.
[6] A. Kosarev, A. Torres, Y. Hernandez, R. Ambrosio, C. Zuniga, T.E. Felter, R. Asomoza, Y. Kudriavtsev, R. Silva-Gonzalez, E. Gomez-Barojas, A. Ilinski, A.S. Abramov, J. Mater. Res 21 (1) (2006) 88.
[7] P.R. Poulsen, M. Wang, J. Xu, W. Li, K. Chen, G. Wang, D. Feng, J. Appl. Phys 84 (6) (1998) 3386.
[8] L. Sanchez, A. Kosarev, A. Torres, T. Felter, A. Ilinskij, Mater. Res. Soc. Symp. Proc. 862 (2005) A18.5.
[9] L. Sanchez, A. Kosarev, A. Torres, T. Felter, A. Ilinskii, Y. Kudriavtsev, R. Asomoza, Mater. Res. Soc. Symp. Proc. 910 (2006) 0910–A07–02.
[10] G. Birgin, I. Chambouleyron, J.M. Martinez, J. Comput. Phys 151 (1999) 862.