

Spectroscopic ellipsometric study of Ge nanocrystals embedded in SiO₂ using parametric models

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Ge-rich SiO₂ layers on top of Si substrates were deposited using plasma enhanced chemical vapour deposition. Ge nanocrystals embedded in the SiO₂ layers were formed by high temperature annealing. The samples were measured and evaluated by spectroscopic ellipsometry. Effective medium

theory (EMT) and parametric semiconductor models have been used to model the dielectric function of the layers. Systematic dependences of the layer thickness and the oscillator parameters have been found on the annealing temperature (nanocrystal size).

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1 Introduction Dielectric layers with embedded semiconductor (Si, Ge, etc.) nanocrystals (NCs) on top of Si substrates are nowadays in the focus of interest mainly because of their possible usage as charge storage mediums in non-volatile semiconductor memories and their promising possibilities in light emitting applications [1]. The electronic (capacitance-voltage [2-4], current-voltage [5], charge storage properties [6]) and optical features (photo- and electroluminescence [7, 8], laser effect [9], optical transmission [10, 11], and characterization with spectroscopic ellipsometry [12, 13]) are widely studied at different layer structures and composition. However, the exact charge transport mechanism to/from the NCs is still not clear in the case of electronic measurements, and the device structure (including layer thicknesses, composition, and NC sizes) still have to be optimized. That is why there is an important role for non-contact, non-destructive, fast and precise qualification methods, such as spectroscopic ellipsometry (SE).

The key moment in applying SE on these structures is the appropriate selection of the parametric model during the evaluation, since the exact dielectric function of the layers containing NCs is not known. More complex models provide more reasonable results, but it is important to note

that with increasing the complexity of the applied model (which often means increasing the number of model parameters) it becomes more complicated for the fit to converge. A good compromise and a widespread model for the dielectric function of NCs is the Tauc-Lorentz model.

2 Experimental Multilayer films were grown in a plasma enhanced chemical vapour deposition (PECVD) reactor (model PlasmaLab 8510C) on Si substrates using 180 sccm SiH₄ (2% in N₂), 225 sccm NO₂ and varying flow rates of GeH₄ (2% in He) as precursor gases, at a sample temperature of 350 °C, a process pressure of 1000 mTorr under an applied RF power of 10 W. The samples were then annealed in N₂ atmosphere in an alumina oven at temperatures ranging from 650 °C to 850 °C for 5 minutes. The samples were loaded and unloaded with ramp times of 1 minute. It has been obtained by earlier cross-sectional transmission electron microscope studies [14] that the size of the NCs depended systematically on the annealing temperature (see Table 1). The expected layer structure is illustrated in Fig. 1.

2. SiO ₂ layer
1. SiO ₂ layer with Ge NCs
0. Si substrate

Figure 1 The expected layer structure of the samples.

The samples were measured with a Woollam M2000 rotating compensator ellipsometer in the photon energy range over 1.2–5.0 eV at angles of incidence of 70°, 75°, and 80° at room temperature.

Table 1 Annealing temperatures of the present studied samples and corresponding NC size obtained during earlier studies [14].

Annealing temperature (°C)	NC diameter (nm)	Error (nm)
650	2.5	0.6
770	3.2	1.0
850	7.4	1.6

3 Ellipsometric modeling The dielectric function of the top SiO₂ layer is represented by the simplified non-absorbing Cauchy model. It is a slowly varying function of the wavelength as can be seen in Eq. (1).

$$n(\lambda) = \alpha + \frac{\beta}{\lambda^2} \quad (1)$$

The Tauc-Lorentz model was used for the parametrization of the dielectric function of Ge NCs inside the SiO₂ layers. It consists of one single transition (its amplitude (A), broadening (C) and position (E₀)), the energy gap (E_g) and a constant that corresponds to the contribution of transitions outside the measured spectral range (ε₁(∞)) (see Eq. (2)). Note, that the real part of the dielectric function is calculated by the Kramers-Kronig transformation of the imaginary part.

The complete dielectric function of the bottom layer containing the NCs was modeled by the Effective Medium Approximation (EMA) mixture of the Tauc-Lorentz dielectric function and dielectric function of SiO₂ obtained for the top layer. The method of EMA (Bruggeman or Maxwell-Garnett) was varied to see which one could be applied best for this structure. The Bruggeman EMA could be applied best if the two components are dispersed homogeneously in the layer. Maxwell-Garnett assumes that one component is embedded in the other which is the host matrix.

4 Results and discussion Already a systematic dependence of the ψ and Δ functions was observed as a function of the annealing temperature (see Fig. 2).

$$\varepsilon_2(E) = \begin{cases} \frac{AE_0C(E-E_g)^2}{(E^2-E_0^2)^2+C^2E^2} \frac{1}{E} & E > E_g \\ 0 & E \leq E_g \end{cases}$$

$$\varepsilon_1(E) = \varepsilon_1(\infty) + \frac{2}{\pi} P \int_{E_g}^{\infty} \frac{\xi \varepsilon_2(\xi)}{\xi^2 - E^2} d\xi \quad (2)$$

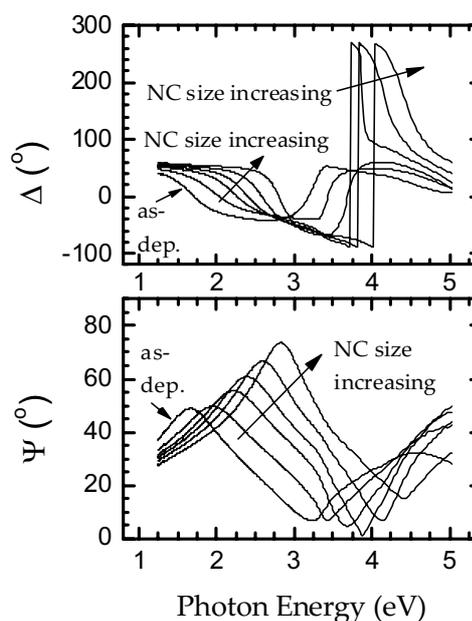


Figure 2 The ψ and Δ ellipsometric angles measured at 70° incident angle on different samples depending on the annealing temperature (NC size).

It has been obtained that the Cauchy parameters exhibited minor changes due to annealing. The Cauchy parameter α was typically between 1.42 and 1.53, while β was between 0.002 and 0.01.

It was found that the fit quality is better by using the Maxwell-Garnett model instead of the Bruggeman in the EMA in the case of the annealed samples (with Ge in the nanocrystalline form). However, in the case of the as-deposited sample, or the sample annealed at the lowest temperature (with Ge in amorphous form), the Bruggeman approximation was found to be more adequate. This is in correspondence with the observation that nanocrystals are formed only during the annealing process and not during deposition. The Mean Squared Error (MSE) of the fits using different EMA models are plotted in Fig. 3. Note, that during this study, dielectric spectra found in the literature was used for SiO₂ [15].

Table 2 Results of the ellipsometric evaluation obtained for different samples, depending on the annealing temperatures: the layer thickness of the top SiO₂ layer (d₂) and the bottom SiO₂ layer with Ge NCs (d₁), the Ge NC volume fraction in this layer and the parameters of the Tauc-Lorentz model that are used to parametrize the dielectric function of the Ge NCs.

Annealing temperature (°C)	d ₂ (nm)	d ₁ (nm)	Ge NC per SiO ₂ volume fraction (%)	A	C (eV)	E ₀ (eV)	E _g (eV)	ε ₁ (∞)
as-deposited	6.5	115.5	25.1 ± 0.3	103.47 ± 1.2	9.08 ± 0.04	2.43 ± 0.01	1.39 ± 0.01	2.00
650	35.3	80.5	35.5 ± 0.3	122.12 ± 2.3	9.07 ± 0.12	1.88 ± 0.01	1.60 ± 0.01	0.83
700	33.4	76.2	21.8 ± 0.8	138.47 ± 6.2	7.80 ± 0.24	1.25 ± 0.06	1.25 ± 0.06	0.00
750	34.6	73.0	15.7 ± 0.5	133.26 ± 10.0	4.32 ± 0.09	3.59 ± 0.11	0.83 ± 0.09	0.07
800	37.2	65.0	14.2 ± 0.9	136.44 ± 0.1	2.51 ± 0.01	3.51 ± 0.21	1.05 ± 0.18	0.50
850	36.4	59.3	14.2 ± 0.7	148.79 ± 20.2	2.75 ± 0.10	4.18 ± 0.14	1.47 ± 0.11	0.18

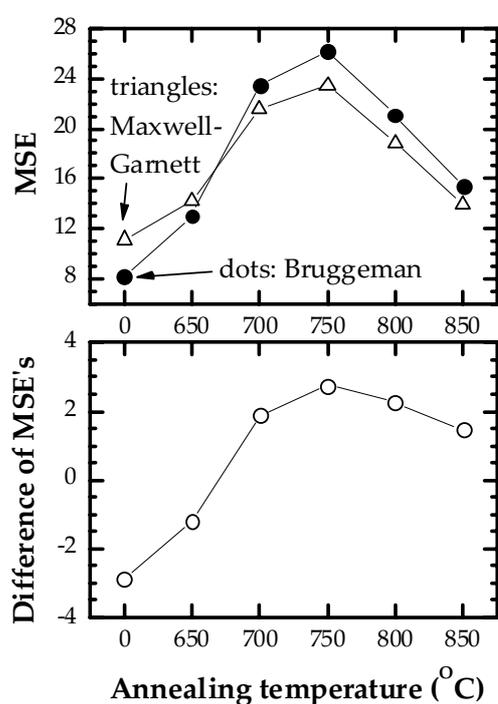


Figure 3 The MSE for fits using Bruggeman or Maxwell-Garnett EMA models as a function of annealing temperature corresponding for the samples.

There were systematic changes of the Tauc-Lorentz oscillator parameters and the layer thicknesses as a function of the annealing temperature (see Table 2).

The change of the layer thicknesses indicates that the interface between the pure SiO₂ and the SiO₂ with embedded Ge NCs moves towards the Si substrates as the annealing temperature increases. Moreover, the volume fraction of the Ge-rich layer shows decreasing Ge content with increasing annealing temperature, while the total thickness of the multilayer decreases as well. These suggest Ge departure from the multilayer that needs to be explained. As a matter of fact, thermal diffusion of Ge atoms in SiO₂ towards the substrate was found to be notable in the literature in the case of annealing at high temperatures [17, 18].

The results probably suggest that the used ellipsometric model does not take into account the Ge accumulation close to the Si substrate which could be responsible for the departure of Ge from the multilayer.

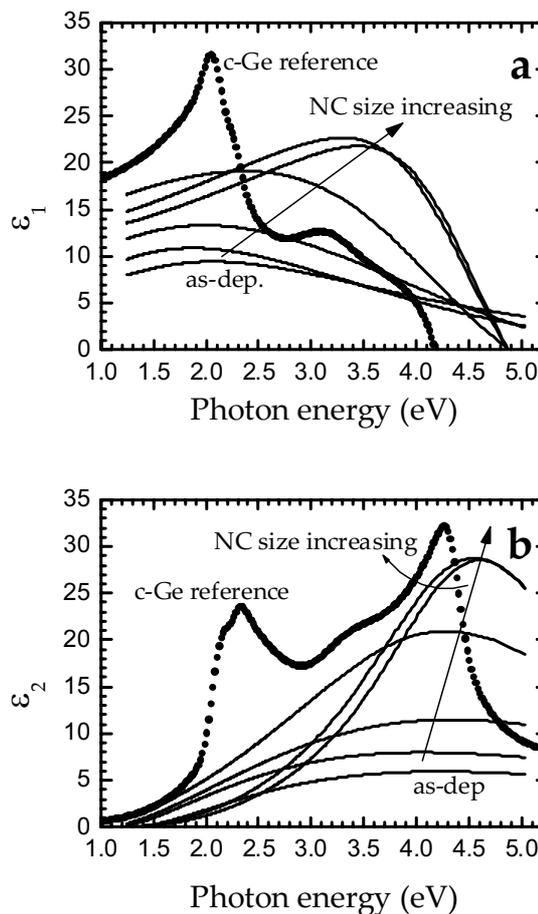


Figure 4 Real (a) and imaginary (b) part of dielectric function of the Ge NC component in the Tauc-Lorentz model for all studied samples along with the dielectric function of the considered c-Ge reference [16].

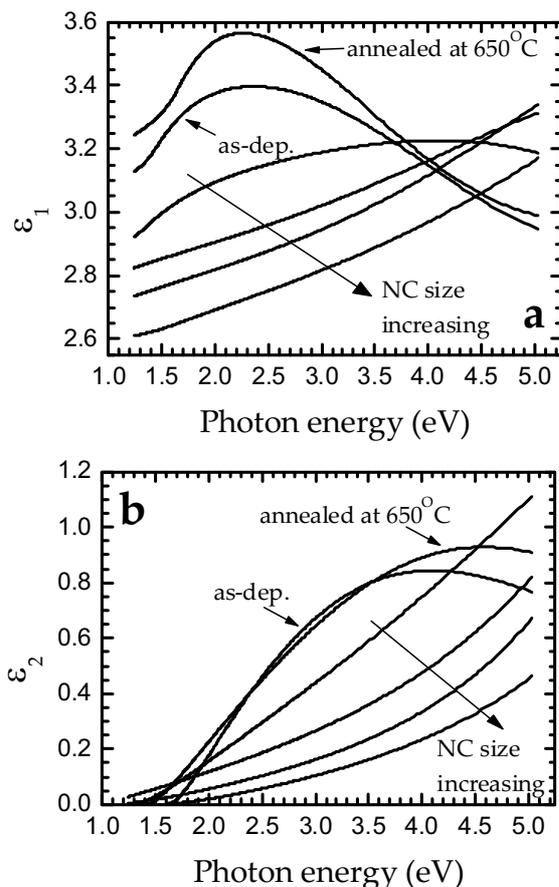


Figure 5 Real (a) and imaginary (b) part of dielectric function of the Maxwell-Garnett mixed (Cauchy-SiO₂ + Tauc-Lorentz-Ge) bottom layer for all studied samples.

The change of the Tauc-Lorentz parameters can be best followed in Fig. 4. Despite the correlation between the parameters, it can be seen that as the annealing temperature increases, the dielectric function of the germanium approaches the dielectric function of the crystalline germanium (c-Ge) reference. It is in correspondence with the observation, that the Ge nanocrystal size increases with increasing annealing temperature (see Table 1). The most significant effect is the systematic decrease of the broadening (C) and the systematic increase of the amplitude (A) of the Tauc-Lorentz oscillator. A similar effect on the oscillator amplitude and broadening as a function of the nanocrystal size has been published recently on Si nanocrystals embedded in Si₃N₄ [12].

Figure 5 shows the Maxwell-Garnett mixed (Cauchy-SiO₂ + Tauc-Lorentz-Ge) dielectric function of the bottom layer as a function of annealing temperature (i.e. NC size).

It can be seen, that this dielectric function is a monotonous function of the NC size for NC sizes above 2.5 nm (or, for annealing temperatures above 650 °C). As a matter of fact, according to our investigation (see Fig. 3) the Maxwell-Garnett approximation was valid only in the very

same regime, above Ge NC sizes of 2.5 nm. Therefore, that could be the reason for the break in the monotony if going lower with the annealing temperature, towards 650 °C.

5 Conclusion Ge nanocrystals embedded in SiO₂ layers on top of Si substrates were investigated by spectroscopic ellipsometry and modeled using effective medium theory (EMT) and parametric semiconductor models. The Maxwell-Garnett approximation was found to be more adequate to model the SiO₂ layers with embedded Ge nanocrystals than the Bruggeman if the Ge NCs have sizes larger than 2.5 nm. Systematic dependences of the layer thickness and the Tauc-Lorentz oscillator parameters (the amplitude and the broadening) have been found on the annealing temperature (i.e. the nanocrystal size). The dielectric function of the single Tauc-Lorentz modeled Ge component, and also the Maxwell-Garnett mixed SiO₂+Ge NC layer is presented as a function of Ge NC size.

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References

- [1] Zs. J. Horváth, *Current Appl. Phys.* **6**, 145 (2006), and references therein.
- [2] M. Kanoun, C. Busseret, A. Poncet, A. Souifi, T. Baron, and E. Gautier, *Solid-State Electron.* **50**, 1310 (2006).
- [3] P. Basa, Zs. J. Horváth, T. Jászi, A. E. Pap, L. Dobos, B. Pécz, L. Tóth, and P. Szöllösi, *Physica E* **38**, 71 (2007).
- [4] A. Salonidou, A. G. Nassiopoulou, K. Giannakopoulos, A. Travlos, V. Ioannou-Sougleridis, and E. Tsoi, *Nanotechnology* **15**, 1233 (2004).
- [5] M. L. Ciurea, *J. Optoelectron. Adv. Mater.* **8**, 13 (2006).
- [6] C. Y. Ng, T. P. Chen, D. Sreeduth, Q. Chen, L. Ding, and A. Du, *Thin Solid Films* **504**, 25 (2006).
- [7] P. Photopoulos and A. G. Nassiopoulou, *J. Phys.: Condens. Matter* **15**, 3641 (2003).
- [8] A. A. Shklyaeve and M. Ichikawa, *Appl. Phys. Lett.* **80**, 1432 (2002).
- [9] L. Pavesi, L. Dal Negro, C. Mazzoleni, G. Franzo, and F. Priolo, *Nature* **408**, 440 (2000).
- [10] V. Em. Vamvakas and S. Gardelis, *Surf. Coat. Technol.* **201**, 9359 (2007).
- [11] M. Righini and L. Razzari, in: *Semiconductor Nanocrystals; Proc. 1st Int. Workshop on Semiconductor Nanocrystals SEMINANO2005*, Sept. 10-12, 2005, Budapest, Hungary (Eds. B. Pődör, Zs.J. Horváth, P. Basa), Vol. 2, pp. 251-254, 2006; <http://www.mfa.kfki.hu/conferences/seminano2005/>
- [12] P. Basa, P. Petrik, M. Fried, L. Dobos, B. Pécz, and L. Tóth, *Physica E* **38**, 76 (2007).
- [13] L. Ding, T. P. Chen, Y. Liu, and C. Y. Ng, *J. Cryst. Growth* **288**, 87 (2006).

- [14] A. Dana, I. Akca, O. Ergun, A. Aydinli, R. Turan, and T. G. Finstad, *Physica E* **38**, 94 (2007).
- [15] E. Palik (Ed.), *Handbook of Optical Constants of Solids*, Vol. 1 (Academic Press), p. 759.
- [16] Tabulated at University of Nebraska-Lincoln (UNL) (multiple data sets fit).
- [17] H. Tsuji, N. Arai, N. Gotoh, T. Minotani, K. Kojima, K. Adachi, H. Kotaki, T. Ishibashi, Y. Gotoh, and J. Ishikawa, *Nucl. Instrum. Methods Phys. Res. B* **257**, 94 (2007).
- [18] T. Kobayashi, T. Endoh, H. Fukuda, S. Nomura, A. Sakai, and Y. Ueda, *Appl. Phys. Lett.* **71**, 9 (1997).