HORIBA Scientific

Application Note

Photovoltaic

Spectroscopic Ellipsometry

SE31

Characterization of silicon nanoparticles (Si-nps) embedded in a silicon-nitride matrix by spectroscopic ellipsometry

Silicon nanoparticles (Si-nps) show different optical properties than bulk silicon. A strong correlation has been established between the particle size and the band-gap for example [1]. These particular properties offer potentialities of application in optoelectronics, silicon based memories and third generation solar cells [2].

For this last application, nanoparticles embedded in a dielectric matrix are used to enhance the photovoltaic effect. The approach consists in reducing the losses of single band-gap solar cells, namely the ability to absorb photons with energies less than the band-gap and the losses by thermalization of the photons with energies higher than the band-gap. Thus, varying the particle size enables to optimize the absorption of light. In another hand, a precise determination of the optical properties of these nanoparticles is required for a better optimization of the efficiency of the resulting solar cells. From this point of view Spectroscopic Ellipsometry represents a technique of choice for the characterization of the optical and structural properties of these layers [2].

Experiments

Silicon-Rich silicon Nitride (SRN) layers with silicon excess deposited on silicon substrate were prepared by remote-controlled ECR-PECVD. These SRN layers were obtained by the deposition of a mixture of pure silane (SiH_4) and ammonia (NH_3) on a silicon substrate. The gas flow ratio NH_3/SiH_4 gives the silicon excess amount with regard to Si_3N_4 stoichiometry. The samples are then annealed in order to induce the crystallization of the Si-nps in the SRN layers (figure 1).

Figure 1

Ellipsometry measurements

The ellipsometric measurements were carried out with a UVISEL spectroscopic ellipsometer in the visible range [1.5– 6.5 eV]. This ellipsometer, based on phase modulation technology, is equipped with photomultipliers covering the UV-Visible spectral range for a better sensitivity and higher signal/noise ratio. In addition phase modulation technology ensures fast measurements. The experiments have been performed at an angle of incidence of 70°. The obtained observables, known as I_s and I_c, are related to the ellipsometric angles (Ψ, Δ) through the following equations.

$$I_s = \sin 2\Psi . \sin \Delta$$
$$I_c = \sin 2\Psi . \cos \Delta$$

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Modeling Results

The analysis of the ellipsometric experimental data aimed at the determination of the layers thicknesses, volume fractions and the optical properties of the Si-nps. The analysis has been undertaken over two steps. The first one focused the attention on the determination of the thicknesses of the SRN Layers and the volume fractions of the Si-nps by using the Bruggeman Model also refereed to as EMA (Effective Medium Approximation). The optical properties of the Si-nps and the silicon nitride were fixed to reference data known for crystalline silicon (c-Si), amorphous silicon (a-Si) and silicon nitride. The purpose from using these fixed reference data instead of dispersion formulas is to decrease the number of parameters in order to get higher accuracy. The analysis took also into account the roughness thickness witch was considered as a mixture of air (50 %) and silicon nitride (50 %).

In the second step, the thicknesses and the volume fractions have been fixed as obtained form the first step and a Tauc-Lorenz dispersion formula has been used to refine the optical properties of the silicon nano-particles. Table 1 reports on the values obtained for the SRN layers and roughness thicknesses in addition to the volume fractions of the Si-nps.

Sample	t_{film} (nm)	t_{rough} (nm)	$f_{Si\text{-}nps}$ (%)
S1	99.9	6.8	27.6
S2	102.5	6.8	19.4
S3	113.5	4.6	13.7
S4	123.0	3.1	9.0

Table 1

Figure 2 shows the variation of refractive index and extinction coefficient of the Si-nps obtained from the SRN single layers, refereed to as S1, S2, S3 and S4 compared to those of the crystalline silicon (c-Si) and amorphous silicon (a-Si).

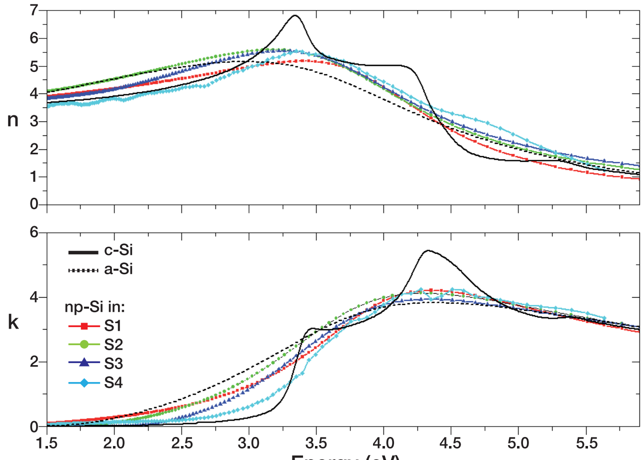

Figure 2

In addition to the refractive index and the extinction coefficient, the optical band gap of the Si-nps has been estimated by using the Tauc representation after the absorption coefficient α is obtained from the ellipsometric measurement.

$$(a \,.\, E)^{½} = A \,.\, (E - E_g^{Tauc})$$

Where A is the slope and E_g^{Tauc} is the Tauc's band gap. Moreover, from the band gap, the mean size of the Si-nps has been deduced according to zunger's formula. Table 2 shows the values obtained for the estimated band gap and the size of the Si-nps within the SRN layers. From table 1 and 2 we can deduce that the energy band gap increases when the volume fraction of Si-nps decreases. This observation was confirmed by measurements carried out with other techniques. In addition, the size distribution of the Si-nps as obtained from sample S_2 by SE is consistent with the results obtained by Ef-TEM shown in figure 3.

$$d \approx 26.34 \,.\, (E_g^{Tauc} - 1.167)^{-0.73}$$

Sample	R	E_g^{Tauc} (eV)	d_{zunger} (nm)
S1	1.36	1.80	3.7
S2	1.50	1.95	3.1
S3	1.64	2.00	3.0
S4	1.79	2.12	2.7

Table 2

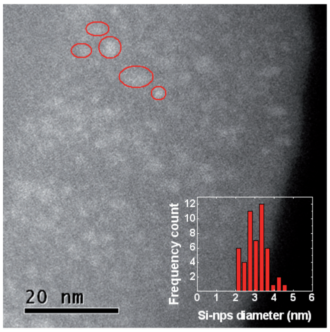

Table 3

Conclusion

Spectroscopic ellipsometry technique has been successfully applied to the characterization of SRN thin layers. These analyses enabled the extraction of various information as the layers thicknesses, the optical constants of the Si-nps and their volume fraction in the silicon-nitride matrix. Moreover, the band gap of the Si-nps and their mean size have been deduced form the ellipsometric results by using respectively the Tauc representation and Zunger's formula.

[1] F. Delachat et al., Nanotechnology 20 (2009) 415 608
[2] F. Delachat et al., Spectroscopic ellipsometry analysis of silicon-rich silicon nitride layers for photovoltaic applications. 24th European Photovoltaic Solar Energy Conference, 21-25 September 2009, Hamburg, Germany