Thin Solid Films 541 (2013) 12–16

Contents lists available at SciVerse ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Advanced modeling for optical characterization of amorphous hydrogenated silicon films

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ARTICLE INFO

Available online 2 May 2013

Keywords:
Ellipsometry
Spectrophotometry
a-Si:H
Urbach tail
Localized states
Sum rule

ABSTRACT

Amorphous hydrogenated silicon (a-Si:H) films deposited on glass and crystalline silicon substrates are analyzed using a multi-sample method combining ellipsometry and spectrophotometry in a spectral range of 0.046–8.9 eV, utilizing an analytical dispersion model based on parametrization of joint density of states and application of sum rule. This model includes all absorption processes from phonon absorption to core electron excitations. It is shown that if films deposited on both substrates are characterized together it is possible to study both phonon absorption and weak absorption processes below the band gap, i.e. the Urbach tail and absorption on localized states.

1. Introduction

Ellipsometry and spectrophotometry are excellent non-destructive methods for material characterization since they provide information about both geometrical properties of samples (thickness, roughness, etc.) and dielectric response, i.e. electron/phonon structure of the material. In order to obtain more than just optical constants and thickness, i.e. something related to the sample structure, it is necessary to apply advanced modeling. Such modeling includes application of proper structural models that take into the account boundary roughness, non-uniformity, anisotropy and the like. It is necessary to use physically correct dispersion models that fulfill Kramers–Kronig relations, time-reversal symmetry and f-sum rule [1]. The f-sum rule for the imaginary part of the dielectric function $\varepsilon_{\rm i}(\omega)$ is

$$\int_0^\infty \varepsilon_{\rm i}(\omega)\omega d\omega = \frac{\pi}{2}\frac{e^2\mathcal{N}_{\rm e}}{\epsilon_0 m_{\rm e}}\mathcal{U}, \tag{1}$$

where ω, $\mathcal{N}_{\rm e}$, e, $m_{\rm e}$ and ϵ_0 are the light frequency, density of electrons, elementary charge, electron mass and vacuum permittivity. The constant $\mathcal{U}\approx 1.000274$ represents a correction to finite mass of nuclei [2]. Unlike the first two conditions, the sum rule is not often discussed in relation to dielectric response, nevertheless, it introduces a useful additional information concerning density of the material.

In order to use Eq. (1) correctly it is necessary to cover all the absorption processes. If, for instance, the sum rule is simply applied only to valence electron excitations the density of electrons is overestimated because of higher effective contribution of valence electrons [3,2].

The advanced modeling should be applied to experimental data measured over wide spectral range. It requires the combination of measurement using different devices. Moreover, it is advantageous to combine ellipsometry/polarimetry, providing polarization state and degree of polarization (3 quantities for an isotropic system of the probing light), with spectrophotometry giving the intensity. It brings a complete information about reflected or transmitted light, i.e. Stokes vector [4]. The modeling should also take into account instrument non-idealities such as light non-monochromaticity, non-collimated light beam and non-ideal optical elements.

In this work the advanced modeling is utilized for characterization of thin films of amorphous hydrogenated silicon (a-Si:H) that are of technological interest [5–7]. Ellipsometric and spectrophotometric data measured on a-Si:H films deposited on crystalline silicon (c-Si) which were analyzed in a previous work [8] are combined with data measured on an a-Si:H film deposited on glass substrate which is transparent in different regions than c-Si and lead to increased optical contrast between the film and the substrate. All data are fitted simultaneously using multi-sample method [9]. It is shown that this approach permits characterizing the weak absorption below the band gap.

2. Experimental details

The sample of a-Si:H film (#1663) was prepared by plasma enhanced chemical vapor deposition on Corning glass substrate at the same deposition conditions as three a-Si:H films on c-Si substrate

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http://dx.doi.org/10.1016/j.tsf.2013.04.129

(#1654–1656) characterized in our previous paper [8]. The radio frequency discharge at 13.56 MHz was employed in the capacitive mode. The powered electrode had the diameter of 95 mm and the opposite heated electrode, used as the substrate holder, was at the floating potential. The distance between the electrodes was 18 mm. The vacuum chamber was pumped by a turbo-molecular pump. Prior to the deposition the chamber was degassed by heating under vacuum. The minimum pressure achieved before the deposition was 10^{-6} Pa. Discharge was ignited in pure silane of purity 5.0 (99.999%) at the pressure of 25 Pa and flow rate of 30 sccm. The rf power density was 0.06 W cm^{-2} and substrate temperature during the deposition was 220 °C. The deposition time of sample #1663 was 90 min that corresponded to film thickness of 1.2 μm.

The ellipsometric data were measured in the spectral region of 0.6–6.5 eV using phase modulated Jobin Yvon UVISEL ellipsometer (five angles of incidence 55–75°). The reflectance data were measured from both sides at near-normal incidence of 6° with Perkin Elmer Lambda 45 spectrophotometer in the spectral region of 1.24–6.2 eV and at 10° with spectrophotometer Bruker VERTEX 80v in the spectral region of 0.046–0.93 eV (360–7500 cm^{-1}). The normal-incidence transmittances were measured by the same spectrophotometers in the spectral regions of sample transparency, 1.13–2.2 eV and 0.24–0.93 eV (2000–7500 cm^{-1}).

3. Results and discussion

The optical data of all four samples were fitted using a structural model including surface roughness described by the Rayleigh–Rice theory [10–12], lateral non-uniformity [13–15] and the analytical PJDOS-2EX (parameterized joint density of states—two excitons) dispersion model described in detail in previous paper [8], assuming that the optical constants of all four films were identical. This model included following absorption processes: core electron excitations, excitations of extended (delocalized) valence electrons σ to the conduction σ^* and higher energy bands ξ^*, transitions of valence electrons from localized to extended states and vice versa (Urbach tail), i.e. $\sigma \to \lambda^*$ and $\lambda \to \sigma^*$, absorption on localized (defect) states $\lambda \to \lambda^*$ and phonon absorption. The fitted values of free parameters of the dispersion model are summarized in Table 1 together with their short descriptions. The remaining dispersion parameters, such as hydrogen content, quantity describing the core level excitation or high-energy limit of the extended valence electron excitations, were fixed in the same values as in [8]. The values of the structural model parameters determined by this fit are listed in Table 2.

The optical measurements on a-Si:H film prepared on glass exhibited larger contrast of optical constants than a-Si:H on c-Si as shown for ellipsometric data in Fig. 1 displayed as associated ellipsometric parameters I_s, I_{cII} and I_{cIII}. These parameters are for a depolarizing sample related to the classical ellipsometric parameters azimuth Ψ, phase change Δ and degree of polarization P as follows: $I_s = P \sin 2\Psi \sin\Delta$, and $I_{cIII} = P \cos 2\Psi$, hence, $P = \sqrt{I_s^2 + I_{cII}^2 + I_{cIII}^2}$ [16]. The spectrophotometric quantities, i.e. reflectance from film side R, reflectance from substrate side R' and transmittance T measured for a-Si:H films are also plotted in Fig. 1 and show a similar contrast improvement. The measurement error of reflectance, transmittance and associated ellipsometric parameters is approximately 0.01, about 1% of amplitude in the case of the film on glass and 10% for c-Si substrate. This contrast allowed one to obtain more reliable data about weak absorption below the band gap, i.e. the Urbach tail and absorption on localized states.

Table 1
Values and standard deviations of free fitting parameters of a-Si:H dispersion model, i.e. the fundamental macroscopic parameter N_a together with the parameters describing electron and phonon excitations.

Fundamental macroscopic parameter		
N_a (eV^2)	114.2 ± 1.0	Density parameter
Extended valence electron excitations		
E_g (eV)	1.824 ± 0.005	Band gap of $\sigma \to \sigma^*$
A_{c1}	36 ± 5	Amplitude of exciton 1
E_{c1} (eV)	3.504 ± 0.002	Central energy of exciton 1
B_{c1} (eV)	1.116 ± 0.003	Width of exciton 1
A_{c2}	1.0 ± 0.3	Amplitude of exciton 2
E_{c2} (eV)	2.628 ± 0.008	Central energy of exciton 2
B_{c2} (eV)	0.64 ± 0.03	Width of exciton 2
α_x	0.138 ± 0.010	Relative strength of $\sigma \to \xi^*$
Urbach tail		
α_u	0.045 ± 0.003	Relative strength
E_{uj} (eV)	0.749 ± 0.0006	Urbach energy
absorption on localized states		
α_{loc} (10^{-6})	17.1 ± 0.9	Relative strength
E_{loc} (eV)	1.393 ± 0.005	Peak position
B_{loc} (eV)	0.134 ± 0.007	Peak width
Phonon absorption		
α_{S1}	0.1146 ± 0.0017	Stretching SiH
α_{S2}	0.191 ± 0.0006	Stretching SiH_2
α_{S3}	0.0000 ± 0.0005	Stretching SiH_3
α_{B2}	0.0103 ± 0.0011	Bending SiH_2
α_{B3}	0.0067 ± 0.0010	Bending SiH_3
α_W	0.268 ± 0.004	Wagging modes
α_R	0.000 ± 0.002	Rocking modes
α_{TO}	0.000263 ± 0.000019	TO mode

The model for the Urbach tail applied to the data on a-Si:H/c-Si alone tended to describe rather interband transitions which resulted in large variations of obtained Urbach tail parameters depending on the model and for some models the Urbach energy even had to be fixed [8]. The simultaneous fitting of all data led to the Urbach energy of 74.9 meV which is relatively close to the typical value of 50 meV for amorphous semiconductors [17]. The obtained relative strength of the Urbach tail was 0.045. It can be understood as a degree of disorder that is an important characteristic of the material.

The parameters describing the absorption on localized states determined in this work differed significantly from those determined in [8]. The absorption on localized states is much more narrow and close to the band gap E_g which appears more realistic as can be seen in Fig. 2. The accuracy of determination of the optical constants in region of weak sub-gap absorption is given by the accuracy of determination of the nodes rather than the extrema. The extrema are influenced by various effects such as roughness, non-uniformity, and refractive index profile. The positions of nodes are determined by phase

$$\phi = \frac{4\pi}{\lambda} nd, \tag{2}$$

where λ, n and d are wavelength, refractive index and film thickness, respectively. The sensitivity of optical quantities on absorption on localized states is demonstrated in Fig. 3 for I_s. In this figure I_s is plotted together with ΔI_s which is equal to the difference between theoretical data calculated with and without $\lambda \to \lambda^*$ transitions. It can be seen that the difference ΔI_s, which is approximately anti-symmetrical about the central energy of $\lambda \to \lambda^*$ transitions E_{loc}, has an overall

Table 2
Values of structural model parameters of individual samples.

Par.	#1654	#1655	#1656	#1663	Description
d_o (mm)	2.43	2.43	2.43	2.43	Overlayer thickness
d_f (nm)	547	54	205	1210	Film thickness
σ (nm)	0.94	0.31	1.12	2.96	rms of the heights
τ (nm)	4.8	1.0	6.2	41.0	Autocor. length