Ellipsometric analysis for CVD thick films on weakly absorbing substrates

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Abstract - Ellipsometry is a traditional technique for the thickness and the optical constants of CVD films determination, and if *in situ* film control is impossible, the best way is to use spectroellipsometry. The novel method for quick estimation of the film parameters in the case of weakly absorbing thick film (80 - 600 nm) on nonabsorbing substrate, using spectroellipsometry is presented. The experimental results for electron-beam assisted CVD ZrO_2 films on quartz, PECVD diamond and a-B/C:H films on Si (100) are reported and the influence of substrate absorption and intermediate layers presence is discussed. Both the thickness and the wave dependence of the film optical constants were calculated from the azimuth of polarization spectra in the range of 360-660nm.

1. - Introduction.

Recent CVD technologies enable to produce films of various compositions, thickness and optical properties. Moreover one can alternate these characteristics just during deposition to obtain multi-layer systems. Ellipsometry is a traditional technique for such systems analysis, and if *in situ* surface control is impossible, for example because of high deposition rate, the best way is to study deposits using spectroellipsometry [1].

We report here the method for thickness and optical constants determination in the case of transparent and weakly absorbing films on transparent substrate. The method is based on the azimuth of polarization measurement, so it is good not only for automatical spectroellipsometers, but for manual ones, equipped with high aperture monochromators.

2. - Theory.

The general ellipsometric equation, describing the reflection of polarized light from a film with thickness d and complex refractive index $n_f = n_f - ik_f$ on a transparent substrate, is [2]

$$\text{tg}\Psi \exp(i\Delta) = (\tilde{r}_1^p + \tilde{r}_2^p \beta) (1 + \tilde{r}_1^s \tilde{r}_2^s \beta) / (\tilde{r}_1^s + \tilde{r}_2^s \beta) (1 + \tilde{r}_1^p \tilde{r}_2^p \beta) \quad (1)$$

where $\beta = \exp[-i4\pi d \lambda^{-1} (\tilde{n}_f^2 - \tilde{n}_0^2 \sin^2 \varphi)^{1/2}]$

$\tilde{r}_1^p, \tilde{r}_1^s$ - Fresnel coefficients for the ambient/film interface (p, s

denote the polarization directions parallel and perpendicular to the plane of incidence);

r_1^p, r_2^s - Fresnel coefficients for the film/substrate interface,

Ψ, Δ - relative amplitude attenuation and relative phase shift between p and s components of the light wave, induced by reflection.

n_s - refractive index of the substrate, φ - the angle of incidence of light and λ is the wavelength.

If the film is transparent, Ψ changes periodically with the wavelength within Ψ_-, Ψ_+ limits (Fig.1)

$$\Psi_{\pm} = \arctg[(r_1^p \pm r_2^p)(1 \pm r_1^s r_2^s)/(r_1^s \pm r_2^s)(1 \pm r_1^p r_2^p)], \quad (2)$$

which correspond to λ values, given by

$$\lambda_j = 4\pi d \alpha / j, \quad j=1, 2, \dots \quad (3)$$

where $\alpha = (n_f^2 - n_s^2 \sin^2 \varphi)^{1/2}$.

At these points $\Delta = 0^\circ$ or 180° depending on φ value and on the optical constants of the film and the substrate. Positions of the neighboring extremums correlate

$$j \lambda_j = (j+1) \lambda_{j+1}. \quad (4)$$

and shift with the angle of incidence. By measuring Ψ spectra for two different angles φ_1 and φ_2 or registering peaks positions in azimuth of polarization spectrum $\chi(\lambda)$ (for $\Psi_{\pm} = \chi_{\pm}$) one can determine the refractive index of the film from

$$n_f = n_s [(\lambda_{\varphi_1}^2 \sin^2 \varphi_2 - \lambda_{\varphi_2}^2 \sin^2 \varphi_1) / (\lambda_{\varphi_2}^2 - \lambda_{\varphi_1}^2)]^{1/2}, \quad (5)$$

and then its thickness from eq(3). The measurements should be made in rather wide range, because it needs at least two $\Psi_{\pm}$ values to determine j . The accuracy of n_f and d calculations depends on the accuracy of λ and φ measurement and for most cases is better than 2-3%. In the case of absorbing film β is complex, the alternations of Ψ become weaker and decrease with wave frequency, λ_j values differ from those of transparent film. But if $n_f k_f < 0.1$, the difference is negligibly small, and k_f can be calculated from

$$k_f = -\alpha \ln D / 4\pi d n_f, \quad (7)$$

D is given by the equation $aD^2 + bD + c = 0$,

where $a = r_2^p r_2^s (r_1^p \tg \Psi - r_1^s)$,

$$b = (-1)^j [\tg \Psi (r_2^s + r_1^p r_2^p r_1^s) - (r_2^p + r_1^p r_1^s r_2^s)]$$

$$c = \tg \Psi r_1^s - r_1^p.$$

The accuracy of k_f determination is better than 4-5% even for $k_f = 0.1$.

Obviously, the approach enables direct calculation of the film characteristics, but it should be corrected if a dispersion takes place. Let us assume that the refractive index of a film is n_f at λ_j , and it is $(n_f + \Delta n_f)$ at λ_{j+1} . If $\Delta n_f/n_f < 0.1$, the shift of the extremum point λ_j due to dispersion will be

$$\Delta \lambda_{j+1} = \Delta n_f n_f \lambda_{j+1} / \alpha^2, \quad (8)$$

So, the dispersion $\delta n / \delta \lambda$ inside the interval λ_j, λ_{j+1} is given by

$$\delta n / \delta \lambda = -[\alpha(j+1) / \lambda_j]^2 \Delta \lambda_{j+1} / j n_f, \quad (9)$$

Thus, if there is n_f dispersion, it is better to operate in the narrow range of λ . With this in mind the measurement near to the Brewster angle seems to be more preferable, for in this case we can calculate n_f and d from the equation

$$\chi(\lambda) = 0. \quad (10)$$

For two neighboring roots of the eq(10) it holds

$$1/\lambda_i + 1/\lambda_{i+1} = i/2d\alpha, \quad (11)$$

and the dispersion can be neglected, because the points λ_i, λ_{i+1} are situated much closer than the points λ_j, λ_{j+1} from eq(4). The accuracy of n_f and d determination only depends on the accuracy of φ and $\lambda \delta d$ - justment, and for the case presented in Fig.1 is: $\delta n_f = 0.08\%$, $\delta d = 0.45\%$.

Fig.1 χ -spectra of ZrO_2 film on fused silica.

Fig.2 χ -spectra of CVD films on Si, $\varphi = 60^\circ$: a) $n_f = 1.86, d = 500\text{nm}$, b) linear $n_f = 1.46 - 2.0$ profile, c) 10nm a-Si interlayer.

If one deals with an absorbing substrate, for example Si, GaAs, other semiconductors, computer search should be performed in order to determine film parameters (especially k_f). We operated in accordance with the following scheme. First Ψ, Δ values were measured at two different angles of incidence and at a fixed wavelength and the solution of eq. 1 (n_f, k_f, d) was found at this wavelength by the computer searching (n_s values were taken from [8]). Then we varied n_f and k_f (d was fixed) to fit the experimental $\chi(\lambda)$ curve. χ -spectrum is very sensitive to the film parameters, the presence of intermediate layers and film optical constants profile (Fig. 2) and we used it in computer simulations instead of traditional ψ or Δ spectra.

3. - Experimental procedure.

The measurements have been carried out using Gaertner L119XUV manual ellipsometer with Bausch & Lomb grating monochromator (650 grooves/mm, exit slit 1.5 mm) in the range of $\lambda = 360$ -660 nm.

ZrO_2 films were deposited on fused silica ($n_s = 1.46$) by electron-beam assisted evaporation in vacuum ($p \approx 5 \cdot 10^{-5}$ torr) from Zr target, at the substrate temperature 100°C , deposition rate being 1nm/s . The samples were aged in air over 1.5-2 months.

Boron-carbon and diamond-like films (90% sp^3 bonds) were deposited on silicon wafers Si(100) by PECVD. Boron-carbon films were prepared in dc glow discharge plasma at 0.1-5 Pa, $T = 50$ - 250°C , from carborane as precursor. The ion energy was 20 eV, the ion flux 3 - $6 \cdot 10^{18} \text{cm}^{-2}\text{s}^{-1}$, deposition rate about 0.4nm/s , all the deposition procedure is described in details in [3,4].

Fig. 3. χ -spectra of a-B/C film on Si(100), B/C=4, $\phi=60^\circ$

Fig. 4. Light absorption in PECVD a-B/C films on Si(100).

All the calculations were performed on PC 286 AT/XT using own computer programs, the main algorithm published in [5].

4.- Results and discussion.

The ZrO_2 films parameters at $\lambda=590\text{--}620\text{nm}$ were calculated using azimuth of polarization spectra at $\phi_1=45^\circ$ and $\phi_2=70^\circ$, they are: $n_f = 1.96 - i0.02$, $d = 513\text{nm}$; the n_f dispersion in the range $\lambda = 430\text{--}477\text{nm}$ was $\delta n/\delta \lambda = 5 \cdot 10^{-4}\text{nm}^{-1}$.

The χ -spectra of the ZrO_2 film, measured at near to the Brewster angles are presented in the Fig.1, the film parameters calculated from eq(11) are: $n_f = 1.9 - i0.01$, $d=571\text{nm}$. The film porosity $(1-q)$ was estimated from the Lorenz-Lorentz equation [6]

$$(n_f^2 - 1)/(n_f^2 + 2) = q(n_b^2 - 1)/(n_b^2 + 2), \quad (12)$$

where $n_b = 2.17$ is the bulk value of ZrO_2 refractive index [7]. For the films investigated the porosity was $\sim 16\%$.

Optical parameters of diamond-like films were calculated using $\Psi(\lambda)$, $\Delta(\lambda)$ curves and $\chi(\lambda)$ as well, the calculations yield $n_f = 2.255 - i0.00$ for films 33.6nm thick.

χ -spectrum of a-B/C film ($B/C=4$) on silicon is shown in Fig. 3. together with theoretical curve built using the computer calculated film parameters and silicon optical constants from [8]. The calculations showed the increasing film absorption in the short wavelength range of spectra. Although the films with high B/C ratio exhibited higher absorption (Fig. 4).

All a-B/C films had refractive indices lying between those of diamond $n=2.25$ and graphite $n=1.8$. The higher B/C ratio in the film was, the closer was its refractive index to that of diamond. This fact is in good agreement with data on the films structure and the type of chemical bonds in it [9].

When studying a-B/C films produced under 500V bias an intermediate a-Si:H layer was detected and its thickness was in the range from 5 to 10nm for different samples.

5.- Conclusion.

The ellipsometric method for quick estimation of the film parameters in the case of weakly absorbing $80 - 600\text{ nm}$ films on nonabsorbing and weakly absorbing substrates is presented. It provides CVD films analysis including the determination of their thickness, optical constants and microporosity.

References.

- [1] Arwin H., Aspnes D.E., Thin Solid Films 138 2 (1986) 95.
- [2] Azzam R.M.A. and Bashara N.M., Ellipsometry and Polarized Light, North-Holland Amsterdam (1977) 583.
- [3] Kanaev A.I. et al., Dok. Acad. Nauk SSSR 318 (1991) 342
- [4] Kanaev A.I., Rybakov S.Yu., Churaeva M.N, ibig.
- [5] Churaeva M.N., Zorin Z.M., Interface modelling in ellipsometry. Moscow (1985) BINITI Dep. N1050-85, N1051-85.
- [6] Churaeva M.N., Zorin Z.M., Persiantseva V.P., Poverkhnost 2 (1985) 132.
- [7] Wood D.L., Nassan K., Appl.Opt. 21 (1982) 2978.
- [8] Aspnes D.E., Studna A.A, Phys.Rev.B 2 (1983) 985.
- [9] Alimov V.Kh. et al. J.Nucl.Mat. 196-198 (1992) 670.