Determination of thin film thickness and its optical properties by the Swanepoel method*

A.C. Escobar-Fajardo,[1] J.J. Támara-Isaza,[1] and Vladimir Vargas-Calderón[1]

[1] *Characterization techniques A - Universidad Nacional de Colombia - Bogotá*

In this assignment we determined the optical properties and film thickness of an unknown thin film. We used the Swanepoel method to extract its key parameters: refractive index, the extinction coefficient and thickness, the former two as functions of wavelength. The aforementioned method is based on the study of the envelopes' properties in each important region of the transmittance spectrum which is compared with the transmittance spectrum of the substrate. In order to apply this method, we used computer programs for analyzing the available data of the thin film. We found that the film thickness is $d = 1030$ nm, the refractive index is $n \approx 2.7$, the extinction and absorption coefficients are $k \sim \alpha \approx 0$ and the band gap is around $E_g = 2.0$ eV, possibly corresponding to GaSe.

I. INTRODUCTION

Thin films have many applications, from decorations to depositing solar cells' materials over a substrate. Thin films' thickness vary from a few nanometers to tens of micrometers. Usually, the most important applications are found in technology, where it is required to determine their optical properties as well as the thickness of the films.

The parameters which are determined to establish the optical properties are the refractive index and the extinction coefficient as a function of the incident radiation wavelength. With this information, we can study the photoelectric and electric behavior of the material in a laboratory and then it is possible to compare this behavior with the theoretical predictions.

There are many methods to find the data required to get the important parameters of a thin film, for example, the typical method for this is spectroscopic ellipsometry. With the data from this method, it is possible to find the thickness and other optical properties. Also, with techniques like X-ray reflectometry and S-UV it is possible to determine some of those parameters. The usual data obtained from these methods is the transmittance at each wavelength, also known as transmittance spectrum, from which the key optical parameters mentioned before can be extracted with the help of computer programs.

In this work, we extracted the optical properties and thickness from a dataset that represents the transmittance spectrum of an unknown thin film, to which we apply the Swanepoel method. We considered different regions of the spectrum which have different characteristics that allow a simplification of the method's equations.

II. SWANEPOEL METHOD

This section contains the main remarks shown in Swanepoel's original article [1], where each of the equations hereafter are explained thoroughly.

To be able for determine the optical properties (refractive index n and extinction coefficient k) and the thickness (d) of a thin film, it is necessary to characterize the substrate optical properties. The Swanepoel method is useful if the substrate has an extinction coefficient approximately equal to zero. With this in mind, we must find the refractive index to establish completely the optical properties of the substrate. For this, we use the equation:

$$T_s = \frac{2n_s}{n_s^2 + 1} \tag{2.1}$$

where T_s and n_s correspond to transmittance and refractive index for the substrate. Finally, we get n_s from equation (2.1).

$$n_s = \frac{1}{T_s} + \sqrt{\frac{1}{T_s} - 1}. \tag{2.2}$$

Now, we can study the transmittance spectrum of the system conformed by substrate and thin film to determine the optical properties for the film and its thickness. The equation for the system's transmittance is given by:

$$T = \frac{Ax}{B - Cx\cos(\phi) + Dx^2}. \tag{2.3}$$

Where A, B, C, D are constants which depend on n_s and n, and are given by:

$$A = 16n^2 n_s, \tag{2.4}$$

$$B = (n-1)^3(n + n_s^2), \tag{2.5}$$

$$C = 2(n^2 - 1)(n^2 - n_s^2), \tag{2.6}$$

$$D = (n-1)^3(n - n_s^2). \tag{2.7}$$

Also we have that $\phi = 4\pi nd/\lambda$ and $x = \exp(-\alpha d)$, where α is the absorption coefficient, defined through its relation with the extinction coefficient $k = \alpha\lambda/4\pi$.

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We can apply the equation (2.3) to the superior and inferior envelope of the transmittance spectrum, which are obtained in the equation when $\phi = 2m\pi$ and $\phi = (2m+1)\pi$, respectively. This is

$$T_M = \frac{Ax}{B - Cx + Dx^2}, \tag{2.8}$$

$$T_m = \frac{Ax}{B + Cx + Dx^2}. \tag{2.9}$$

With the equations (2.8) and (2.9), an analysis of the principle characteristics of each region can be done:

A. Transparent region

In this case we have that the absorption coefficient is zero. This means $\alpha = 0$ and implies $x = 0$. Then, we can replace this condition over T_M and T_m and evaluate A, B, C and D for each one and finally we get

$$T_M = \frac{2n_s}{n_s^2 + 1}, \tag{2.10}$$

$$T_m = \frac{4n^2 n_s}{n^4 + n^2(n_s^2 + 1) + n_s^2}. \tag{2.11}$$

Then we know that (2.10) is completely known because n_s was determined from (2.2) and finally for (2.11) we can find the solution which is given by (2.12).

$$n = \sqrt{M + \sqrt{M^2 - n_s^2}}, \tag{2.12}$$

$$M = \frac{2n_s}{T_m} - \frac{n_s^2 + 1}{2}.$$

B. Weak and medium absorption region

In this region, we cannot consider $\alpha = 0$ and we have that the envelopes of the spectrum are decreasing and the peaks' height are different, then we have x¡1. This is the most general region, whose treatment cover the other regions. Consider the difference between the reciprocal of the equations (2.8) and (2.9):

$$\frac{1}{T_m} - \frac{1}{T_M} = \frac{2C}{A}. \tag{2.13}$$

Then we can replace A and C from (2.4) and (2.6), respectively, and solving for n we get

$$n = \sqrt{N + \sqrt{N^2 - n_s^2}}, \tag{2.14}$$

$$N = 2n_s \frac{T_M - T_m}{T_m T_M} + \frac{n_s^2 + 1}{2}.$$

Here we can get T_M and T_m in the same way as in the transparent region. To obtain x, we can find the sum among the reciprocal of the equations (2.8) and (2.9), which yields:

$$\frac{2T_M T_m}{T_m + T_M} = T_i = \frac{ax}{B + Dx^2} \tag{2.15}$$

or

$$x = \frac{F - (F^2 - (n^2-1)^3(n^2 - n_s^4))^{1/2}}{(n-1)^3(n - s^2)}, \tag{2.16}$$

$$F = \frac{8n^2 n_s}{T_i}.$$

C. Strong Absorption region

For this zone, the envelopes disappear; neither we can calculate n and x independently in this region using just the transmission spectrum. The T_m,T_M and T_i converges to a single function. For this region we can neglect the interference effects and we can consider $x << 1$. Then we have:

$$T_0 \approx \frac{Ax}{B} = \frac{16n^2 n_s}{(n-1)^3(n + s^2)}. \tag{2.17}$$

From each region we can get important information about the optical properties, but, we can also determine the thickness of the thin film by considering two contiguous maxima or two minima from the two first regions:

$$d = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)}. \tag{2.18}$$

Finally, the energy gap might be estimated using a Tauc plot [2] which is a plot of $(\alpha h\nu)^n$ vs the photon energy $h\nu$, where $\lambda\nu = c$, for $n = 2, 2/3, 1/2, 1/3$ corresponding to electron-hole recombination of allowed direct, forbidden direct, allowed indirect and forbidden indirect transitions, respectively.

III. METHODS AND MATERIALS

The values of transmittance were obtained from the spectrophotometer Cary 5000 in a wavelength range between 300 nm and 1100 nm.

The spectrophotometer Cary 5000 employs three different lamps (deuterium, tungsten and mercury) to cover a wavelength range from near infrared to ultraviolet. The electromagnetic radiation passes through a system of diffraction gratings to separate them in different wavelengths. Then it is separated in two different channels:

one for the reference(i.e. substrate) and the other one for the sample (i.e. substrate and thin film). Lastly, toroidal lenses help to focus that radiation in the detectors.

With the transmission data obtained from Cary we computed the envelope functions. In order to compute them, we used a code provided by prof. Ángel Miguel, wrote by Marjorie McClain et al. [3] at NIST [4].

As discussed in ref. [3], this algorithm smooths a given oscillatory data (i.e. transmission) with a least-squares spline fitting subroutine in order to estimate the tangent points of the upper and lower envelopes. In the end it returns the upper and lower envelopes data from an interpolation.

Finally, based on Swanepoel's method, we found the refractive index, the extinction coefficient, the absorption coefficient, the film thickness and the band gap energy.

IV. RESULTS AND DISCUSSION

The envelopes obtained from the code are shown in figure 1.

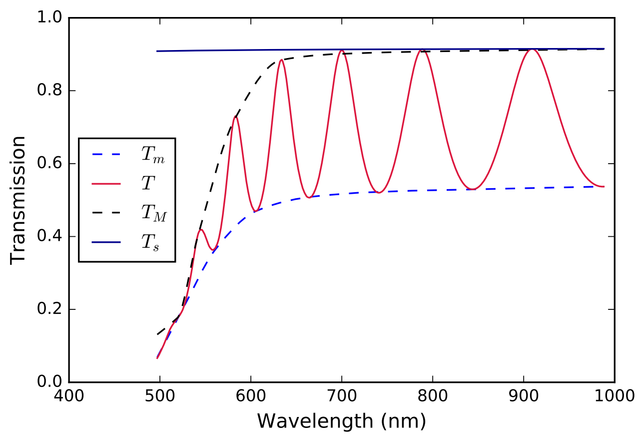

FIG. 1. Transmission data of the substrate and the thin film. Curves T_M and T_m corresponds to top and bottom envelopes.

Using these envelopes, we can compute from equation (2.14) the refractive index, which is shown in figure 2 by the blue dots. As suggested in §II C, in the strong absorption region ($\lambda < 550$nm) this calculation fails, which is the reason of the abnormal behavior of n in the figure.

We used three approaches or methods to determine the film thickness: the first method consisted in using equation 2.18 with the transmittance maxima and minima, the second method consisted in computing the thickness from linear regression of $l/2$ vs n/λ as suggested in ref. [1] and the third and last method minimized the difference between the transmittance spectrum and the predicted spectrum given by Swanepoel's method.

The average thickness found using the first method was $\overline{d_1} = 994$ nm and the standard deviation $\sigma_1 = 50$. The

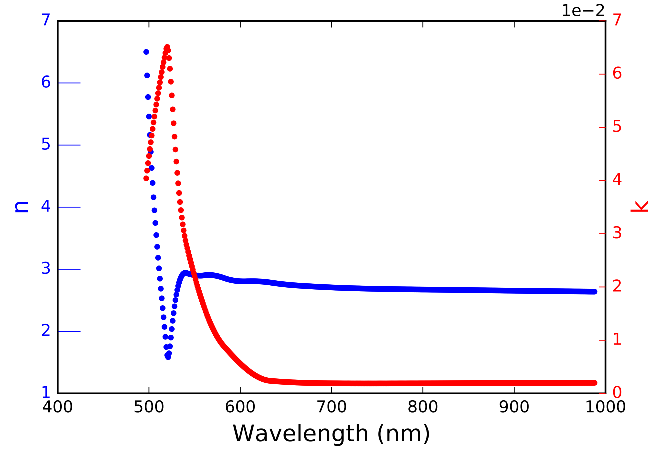

FIG. 2. Real(n) and imaginary (k) part of the complex refractive index for each wavelength.

complete results are shown in table I.

TABLE I. Critical points of transmission data and thickness from equation (2.18).

λ (nm)	n	d_1 (nm)
497	6.50	53
519	1.75	240
524	1.90	321
540	2.94	926
561	2.90	915
582	2.86	977
606	2.81	986
633	2.79	936
664	2.74	1021
700	2.71	1048
740	2.69	1048
789	2.68	1046
845	2.65	1036
911	2.65	
988	2.64	

When using the second method, we found the refractive index n for each critical point (maximum or minimum of the transmittance spectrum). From the relation $l/2 = 2d(n/\lambda) - m$, plotted in figure 3, and from the fitting coefficients of the data $l/2$ vs $n/2$, we found $l/2 = 1984n/\lambda - 5.237$. Hence $d_2 = 992$ nm and $\sigma_2 = 19$.

To determine the absorption coefficient, we solved equation (2.16) which immediately relates to α through the relation $x = \exp(-\alpha d)$. From α, we are able to compute the extinction coefficient $k(\lambda) = \alpha(\lambda)\lambda/4\pi$. The validity of the values for k is evidently related to a correct calculation of d. With $\alpha(\lambda), n(\lambda), d$ and $n_s(\lambda)$ found with the substrate transmittance spectrum via equation (2.1), we are able to compute the predicted spectrum with the equation (2.3). The transmittance for each thickness (i.e. d_1 and d_2) is shown in figure 4. The agreement of both curves with the experimental curve is similar but there is

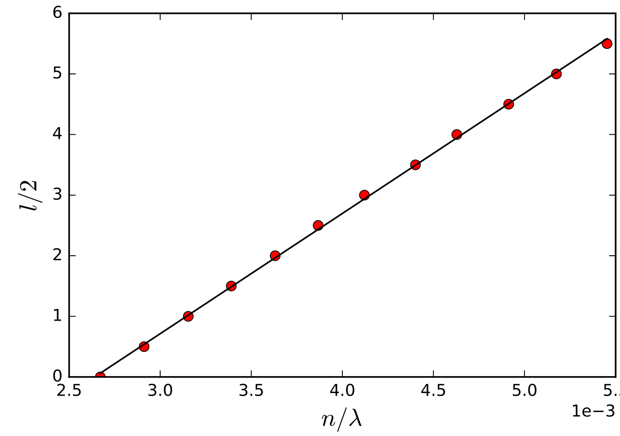

FIG. 3. Plot of $\frac{l}{2}$ as a function of $\frac{n}{\lambda}$.

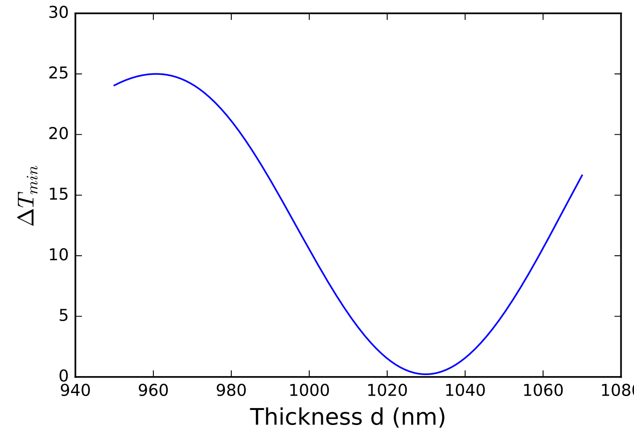

FIG. 5. Minimum difference between simulated and data transmission for each thickness.

a shift or sliding of the maxima and minima compared to the experimental curve. Probably, as suggested by prof. Ángel Miguel, this is caused by a disagreement with the real or true value of thickness. For this reason, the third method was employed to ameliorate the agreement with experimental data.

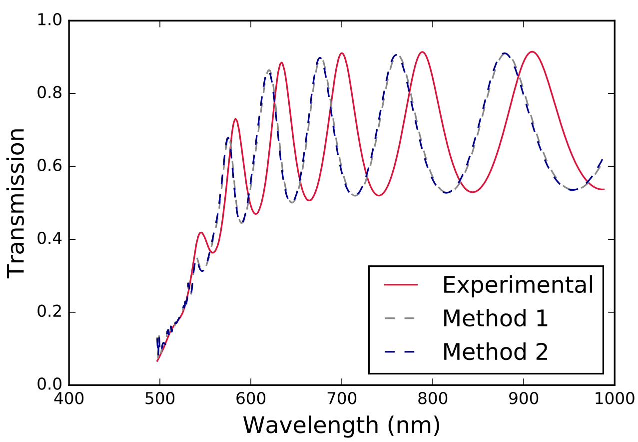

FIG. 4. Simulated transmission according to method 1 and method 2.

In the third method we minimized the difference between the transmittance spectrum and the predicted spectrum. The only variable parameter in the minimization was d because n is computed from the envelopes of the spectrum, n_s is also a known function of λ, x depends on n and n_s and α depends on d. The difference between the predicted and experimental spectra is shown in figure 5, which is minimum at $d = 1030$nm.

The predicted and experimental spectra from this method using the aforementioned value of d are shown in figure 6.

From the good fit of the transmittance spectrum, we conclude that the true value of d is very near to 1030nm.

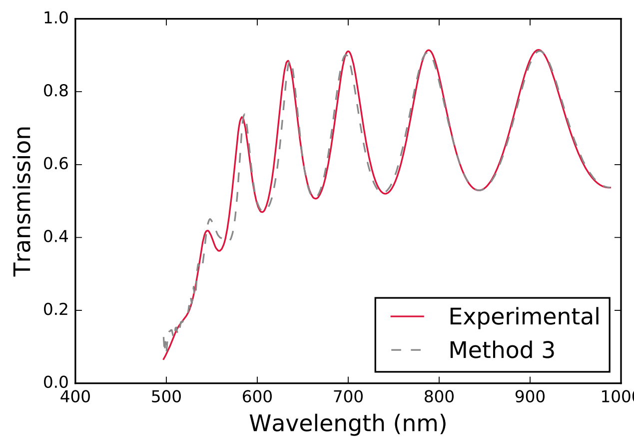

FIG. 6. Simulated transmission according to method 3.

Note that this value is quite near to the thicknesses d_1 found in table I for large wavelengths. With this value we were able to calculate the absorption coefficient α that is shown in figure 7, and correspondingly we compute the extinction coefficient, which is shown in figure 2. This is in accordance with what is expected since as the frequency decreases the absorption increases drastically. Also there is a difference of two orders of magnitude between n and k so there is less attenuation than propagation in this frequency range. The coefficients n and k are fairly constant ($n \approx 2.7$ and $k \approx 0$) in a wavelength range from 620 nm to 1000 nm.

It is worth noting that we also embarked on making a brute-force fit of equation (2.3) at each λ with the parameters n, α, n_s and d, which yielded a perfect fit. However, a perfect fit was achieved both for $d = 100$ nm as well as $d = 1000$ nm at the cost of a very non-smooth function $n(\lambda)$. Because of this, we consider that such brute-force fit is worthless but we think that if smoothness conditions on n and α are imposed, this could be a novel approach

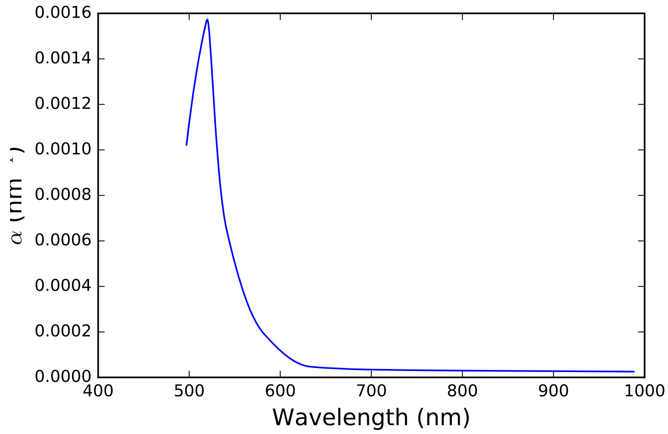

FIG. 7. Absorption coefficient α for each wavelength.

to finding the thickness of amorphous thin films, as well as their optical properties.

Also, we estimated the band gap energy using Tauc plots shown in figure 8. The orange dots represent data which we consider to be linear. We fitted a straight line to these points and obtained the green lines which satisfy the equation $(\alpha h\nu)^n = A(h\nu - E_g)$.

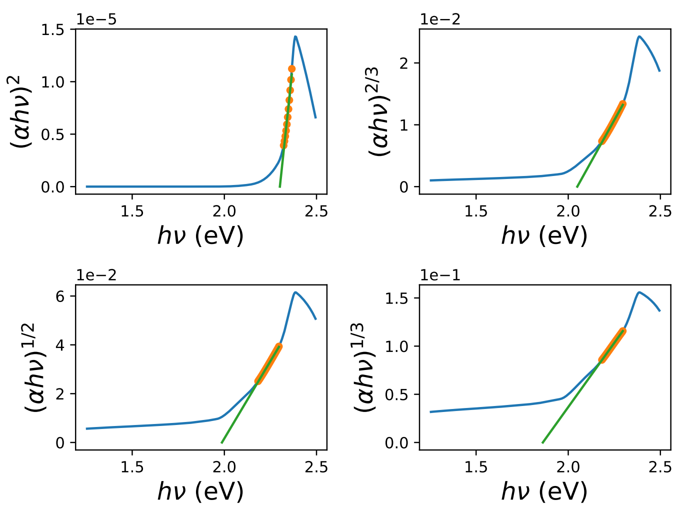

FIG. 8. Tauc plots for allowed and forbidden, direct and indirect transitions.

With these linear fits, we obtained the optical transition energies found in table II.

Finally, using the results from ref. [5], where the refraction index of GaSe was measured to be about 2.9 for the wavelengths we worked with, and also using the results from ref. [6], where the forbidden direct and indirect transitions in GaSe were found to be 2.1 and 2.0 eV, respectively, we hypothesize that the material of the thin film is GaSe.

TABLE II. Transition energies of the thin film given by the Tauc plots in figure 8.

Transition	Energy gap (eV)
Allowed Direct	2.3
Forbidden Direct	2.0
Allowed Indirect	2.0
Forbidden Indirect	1.9

V. CONCLUDING REMARKS

A transmittance spectrum of an unknown thin film, obtained from a spectrophotometer from the physics department of National University of Colombia, was used to determine its thickness, refractive index, absorption and extinction coefficient, and band gap energy. We used Swanepoel's method, which proved to be a good model for the transparent and weak and medium absorption region of the spectrum.

Apart from the two methods mentioned in Swanepoel's original paper, we proposed a minimization technique of the difference between the predicted and the experimental spectra, which yielded a very good fit, enhancing the Swanepoel's methods. We emphasize that Swanepoel's method might work as well by discarding the thicknesses corresponding to short wavelengths.

We found that the thickness of the thin film is $d = 1030$ nm, its refractive index is about 2.7 in the region 620-1000 nm. In the same region, the absorption and extinction coefficient is about 0.

Lastly, the band gap energy for forbidden transitions was found to be 2.0 and 1.9 eV for direct and indirect transitions, respectively, which allowed us to conclude, along with the information of the refractive index, that the thin film is possibly made of GaSe.

The code used for this work can be found in the open repository `https://github.com/VolodyaCO/swanepoel`.

[1] R Swanepoel. Determination of the thickness and optical constants of amorphous silicon. *Journal of Physics E: Scientific Instruments*, 16(12):1214, 1983.

[2] J. Tauc. Optical properties and electronic structure of amorphous ge and si. *Materials Research Bulletin*, 3(1):37 – 46, 1968.

[3] Marjorie McClain, Albert Feldman, David Kahaner, and Xuantong Ying. An algorithm and computer program for the calculation of envelope curves. *Computers in Physics*, 5(1):45–48, 1991.

[4] The code is actually deprecated for current Fortran compilers such as gfortran because it uses deprecated flags. We decided to convert the important parts of the code to Fortran 90 and worked with it.

[5] N. Piccioli, R. Le Toullec, M. Mejatty, and M. Balkanski. Refractive index of gase between 0.45 μm and 330 μm. *Appl. Opt.*, 16(5):1236–1238, May 1977.

[6] J V McCanny and R B Murray. The band structures of gallium and indium selenide. *Journal of Physics C: Solid State Physics*, 10(8):1211, 1977.