Determination of the complete set of optical parameters of micron-sized polycrystalline CH₃NH₃PbI₃–ₓClₓ films from the oscillating transmittance and reflectance spectra

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Abstract
The complete set of optical parameters of micron-sized polycrystalline CH₃NH₃PbI₃–ₓClₓ films deposited by the vacuum co-evaporation of lead iodide and methylammonium chloride is determined by analysis of oscillating optical transmittance and reflectance spectra in the wavelength range 400–1000 nm. It is shown that for a medium and weak absorption region the envelope method is valid for the extraction of refractive index, extinction and absorption coefficient when using only transmittance spectra. As well thickness of the film is determined from transmittance and reflectance spectra with interference-effect. The absorption coefficient for the strong absorption region and optical band gap (direct transition at E_{opt} = 1.62 eV) are calculated based on transmittance and reflectance spectra by using conventional approximated formulas.

1. Introduction
Application of films of various materials in electronics assumes knowledge of such parameters as thickness (d), refractive index (n), extinction (k) and absorption coefficient (α) and optical band gap (E_{opt}) in the case of semiconductors and dielectrics. For films of the same material deposited in different ways, these parameters can be very different. Therefore, the express determination of these parameters for technology development is quite important.

Desire to determine the complete set of optical parameters by a minimum number of measurements has led to a unified (all-in-one) solution for this problem based on the oscillating optical spectra. These oscillations are caused by the interference phenomenon occurring due to the relative difference between substrate and film refractive indices and thicknesses. Note that these developed express methods for determining the complete set of optical parameters of films are based only on spectrophotometric measurements, which are the simplest compared to other methods and doesn’t require special external conditions. Besides, in the case of air/film/substrate/air configuration and normal incident of light, the formulas based on the solution of the inverse problem of thin-film optics are very simple.

The basis for determining the optical parameters of films only from transmittance spectra with interference-effect is an envelope method developed by Swanepoel [1]. In terms of Swanepoel’s method, which is based on the idea of Manifacier et al [2], n, k, and α of films deposited on transparent finite thickness substrate can be calculated in the medium and weak absorption region by creating upper and lower envelopes of transmittance spectra. Then, the envelopes around the maxima and minima are considered as a continuous spectrum versus wavelength. Also, E_{opt} and α in the strong absorption region (none oscillation region) are calculated by conventional approximated formulas. This method is applicable to any transmission spectrum showing an appreciable interference pattern. The major limitation is applicability to relatively thick films since at lower film
thickness the interference extremes are spaced further apart and interpolation between these extremes becomes more difficult. Swanepoel’s method is very practical for quick determination of a complete set of optical parameters of films, although the accuracy is limited by an absence of the right way to construct envelopes between interference extremes. It is appropriate to note that observation of oscillates on optical spectra strongly depends on film geometrical properties and suggests a homogeneous smooth surface with uniform thickness and homogeneity of the refractive index regardless of crystalline structure. If the thickness of the film, for example, is not uniform or is slightly wedge-shaped all interference effects are destroyed, and so the existence of oscillations on optical spectra for the relatively thick film is the primary indicator for the quality of film-formation technology.

The validity of Swanepoel’s method was demonstrated on various films, such as a-Si:H, As-S, Ge-Sb-Se and similar chalcogenides, CdTe, ZnO, Cu₃N [1, 3–9]. In this article, a complete set of optical parameters of micronsized polycrystalline CH₃NH₃PbI₃−ₓClₓ (MAPbI₃−ₓClₓ) perovskite films are determined for the first time from independently measured oscillating transmittance (T) and reflectance (R) spectra via calculations based mainly on Swanepoel’s method. The main interest in such organic-inorganic halide materials is caused by the possible use of them in solar cells. Efficiencies of photovoltaic devices based on these materials have reached over 20% (22.1% efficiency on CH₃NH₃PbI₃ absorber [10]). The serious obstacle for perovskite solar cells is their not sufficiently high stability to the humidity and ultraviolet radiation. But, it should be noted that mixing of CH₃NH₃PbI₃ compound with other halogens (chlorine and bromine) leads to an increase of stability to degradation [11, 12] and also affects significantly on the physical properties. For example, MAPbI₃−ₓClₓ films show suited bandgap (1.6 eV), long electron and hole diffusion lengths (>1 μm [13, 14]), and therefore are in demand for solar cell applications.

Almost all kinds of thin-film technologies are applicable to the fabrication of organic-inorganic halide films. But, we adhere to the opinion that vacuum technologies are more controllable for the synthesis of such complex films. Besides, vacuum deposition leads to the formation of void-free and good crystalline films, which are important factors for functional electronic devices. This is already shown in the article [15], where authors determined that the main x-ray diffraction (XRD) peaks are in identical positions for both solution-processed and vapor-deposited films which indicate that both techniques have produced the same MAPbI₃−ₓClₓ perovskite film, but vacuum-deposited films were relatively uniform, dense and void-free. As a precursor, they used methylammonium iodide (CH₃NH₃I; MAI) and lead chloride (PbCl₂). In this article, MAPbI₃−ₓClₓ films were synthesized by dual-source thermal evaporation technique in co-evaporation mode from precursors lead iodide (PbI₂) and methylammonium chloride (CH₃NH₃Cl; MACl) in contrast to [15]. During the co-evaporation of MACl and PbI₂, the process of chemical reaction and formation of MAPbI₃−ₓClₓ film on a glass substrate occurs. Optical quality polycrystalline films were produced without additional annealing, which confirms by the oscillation nature of optical spectra and XRD investigations.

2. Sample preparation and investigation details

Dual-source vacuum thermal evaporation technique was used to grow of MAPbI₃−ₓClₓ films from MACl and PbI₂ precursors on glass substrates at room temperature. For the evaporation of precursor materials, quartz crucibles were used. As much as both materials well sublimated, evaporating temperatures were adjusted bellow of PbI₂ melting point (412 °C) and MACl flashpoint (208 °C), which allows a suitable control of the deposition process. During the co-evaporation of precursors (source-substrate distance 5–10 cm and residual vacuum in chamber ~10⁻⁵ torr), the process of chemical compound synthesis on a glass substrate occurs (growth rate 100–200 nm min⁻¹). Finally, as-deposited (PbI₂ + MACl) films were annealed in air at 100 °C for up to 1 h.

The basic investigations of as-deposited and annealed films were carried out by (i) thickness and roughness measurements (Mitutoyo Surftest SJ-410 surface profilometer); (ii) investigation of morphology and structure (Magellan 400 scanning electron microscope (SEM) and x-ray Mini Diffractometer MD-10 with CuKα radiation source (radiation wavelength λ = 1.54 Å), respectively); (iii) independent measurements of T and R at the near-normal incidence of light (spectrophotometer Filmetrics F20 (spectral range 400–1000 nm)). Films with a thickness of 1 to 4 μm were investigated.

The main result of the technological route is that as-deposited and annealed film practically similar by structural and optical quality, are void-free and mainly composed of nanorod-like crystals (figure 1(d)). The surface roughness of annealed micron-sized film (measured on arbitrary areas across a length 500 μm) corresponds to ~7–8 nm and differs a little from the glass substrate roughness (~3–4 nm). XRD patterns of as-deposited and annealed film figures (1(a), (b)) exhibit the same additive-free polycrystalline CH₃NH₃PbI₃-like tetragonal structure [16]. Also, the optical measurements related to T spectra did not reveal any noticeable changes (figure 1(c)).
3. Optical characteristics of MAPbI$_3$–xCl$_x$ films

Only optical properties of annealed films deposited onto transparent glass substrate were studied in the case of air/film/substrate/air configuration and near-normal incident of non-polarized light (figure 2) since as-deposited and annealed films are practically similar by structural and optical quality (see figures 1(a)–(c)).

Figure 3(a) shows $T$ spectra of films with different thicknesses. It is seen that films exhibit high absorption and a sharp edge below 750 nm. The existence of oscillations is explained by the interference effect occurring due to $d_f \ll d_s$ and $n_f \approx n_s$ under the conditions that $d_f$ and $n_f$ respectively are uniform and isotropic. Such conditions are met in our measurements. Note also that relatively thick films were investigated since at lower film thickness interpolation between extremes becomes more difficult. Beforehand we say that an explicit dependence of optical properties on film thickness is not observed. Therefore, the possibility of determining a complete set of optical parameters is shown for one of the films (figure 3(b)).

3.1. The region of strong absorption

This region is characterized by interference-free transmittance and reflectance spectra. Taking into account absorption and single reflection for air/film/substrate/air configuration (see figure 2) $\alpha$ can be calculated from
individually measured $T$ and $R$ data by using of $\alpha d_p = \ln[(1 - R)/T]$ approximated relation, where $d_p$ is the thickness of film measured, for example, by a profilometer. Note that this relation almost completely eliminates residual disturbance from the optical interference-effect and is applicable to any films, as long as the film is a homogeneous single layer [17]. Figure 4(a) shows the dependence of $\alpha$ (semi-logarithmic scale) from photon energy ($E$) for MAPbI$_{3-x}$Cl$_x$ film (thickness $d_p \approx 2.7 \mu m$) calculated from $T$ and $R$ data. In order to establish the nature of optical transitions, $\alpha$ was approximated by power-law $\alpha E = B(E - E_{opt})^m$. This approximation shows that there is a direct ($m = 1/2$) transition at 1.62 eV (figure 4(b)).

There is no way to calculate $n_t$ and $\alpha$ independently in this region from the transmission spectrum alone. $n_t$ can be estimated by extrapolating the values calculated in the other parts of the spectrum or by solving a quadratic equation $R = [(n_t^2 - 1 + k_t^2)/[(n_t^2 + 1 + k_t^2)]$, where $R$ is measured reflectance and $k_t = \alpha \lambda / 4 \pi$. But, if the relation $(1 - R)/T$ completely eliminate residual oscillations from the optical interference-effect when $\alpha$ calculated, yet residual oscillations on $R$ leads to errors for $n_t$ data. Therefore, only an estimation is done for $n_t$ at 630 nm by using experimental determined values $R = 0.0864$ and $k_t = 0.085 (n_t = 1.7$).

3.2. The region of medium and weak absorption

The optical characterization of films in this region is given mainly based on Swanepoel’s method [1] from independently measured existence $T$ and $R$ spectra (see figure 3(b)). For this region $\alpha = 0$ and $\exp(-\alpha d_p) < 1$. In terms of Swanepoel’s method, the optical parameters of films can be calculated in the medium and weak absorption region by creating upper and lower envelopes of $T$ spectra. Then, the envelopes around the maxima and minima are considered as a continuous spectrum versus wavelength ($T_M$ and $T_m$) via fitting by the mathematical program. In our case, fitting of $T_M$ and $T_m$ is carried out by a polynomial function of the third-order (figure 5(a)). $n_t$ of film can be calculated by equation $n_t = [N + (N^2 - n_t^2)^{1/2}]^{1/2}$, where $N = 2n_s (T_M - T_m) / (T_M T_m + n_s^2 + 1)/2$ and $T_M$, $T_m$, $n_s$ are fitted smooth curves and substrate (glass) refractive index ($n_s = 1.53$). The results of simple calculations for $n_t$ is shown on figure 5(b). For comparison, the same graph gives values of refractive index for MAPbI$_3$ and MAPbI$_{3-x}$Cl$_x$ taken from [18, 19] respectively. It can be seen that there is a good agreement of refractive index values for MAPbI$_{3-x}$Cl$_x$.

If $n_t$ is known, $\exp(-\alpha d_p)$ can be calculated again by Swanepoel’s method from relation $\exp(-\alpha d_p) = [F - ([F^2 - \alpha^2 \lambda^2 (n_t^2 - n_s^2)^{1/2}]/(n_t - 1)^2 (n_t - n_s^2))] / [(n_t - 1)^2 (n_t - n_s^2)]$, where $F = 8 n_t^2 n_s / \alpha T_1$ and $T_1 = 2 T_M T_m (T_M + T_m)$. Figure 5(c) shows the dependence of $\alpha$ from the light wavelength. Note that $T_1$ represents a curve passing through the fitted $T_M$ and $T_m$ smooth curves (figure 5(a)). Then, $k_t$ is calculated from $k_t = \alpha \lambda / 4 \pi$ relation (average value is 0.006 in 800–1000 nm wavelength region).

Figure 3. (a) $T$ spectra of MAPbI$_{3-x}$Cl$_x$ films with various thicknesses, (b) $T$ and $R$ spectra for 2.7 $\mu$m thick MAPbI$_{3-x}$Cl$_x$ film.

Figure 4. (a) $\alpha$ and (b) $(\alpha E)^2$ dependencies from photon energy for 2.7 $\mu$m thick MAPbI$_{3-x}$Cl$_x$ film in the strong absorption region.
3.3. Thickness determination

Determination of $d_f$ is the number one problem for any film-formation technology. Advanced methods, such as scanning, transmission electron and atomic force microscopy, are applicable for this task, but there are not so practical, such as optical methods, which are very easy in technical performance. For example, in vacuum technologies, which are more flexible in comparison to others, the determination of $d_f$ on test-samples is fine carried out in situ at a certain wavelength by a spaced apart light-emitting diode containing optocoupler. However, this method needs a calibration, which is mainly performed by ex situ profilometer measurement. Also were used, but relatively infrequently, spectrophotometric measurements of oscillation existed $T$ and/or $R$ spectra. Let’s see how it is done in the case of oscillation spectra shown in figure 6 (our case).

If $n_1$ and $n_2$ are the refractive indexes for two neighboring extrema at $\lambda_1$ and $\lambda_2$, the film thickness may be calculated by the relation $d = (\lambda_1 \lambda_2) / 4(n_1 n_2 - \lambda_1 \lambda_2)$, which is withdrawn from the basic equation for interference $2nd = m\lambda$, where $m$ is an integer for maxima and half-integer for minima. Although this relationship is correct, it is very sensitive to $n_1$ data. In our case, there is no way to calculate $d_f$ since we have big errors in comparison with profilometer measured data. However, since $n_1$ has a weak dispersion in an 800–1000 nm wavelength region, we can use the approximate expression $d = (\lambda_1 \lambda_2) / 4n_0 (\lambda_1 - \lambda_2)$, where $n_0 = 2.15$ is average refractive index. The calculated results for each pair of neighboring extrema $\lambda_1$ and $\lambda_2$ are presented in

Figure 5. (a) $T$ and fitted curves, (b) $n_1$ and (c) $\alpha$ for 2.7 $\mu$m thick MAPbI$_3$–$x$Cl$_x$ film in the region of medium and week absorption.

Figure 6. $T$ and $R$ spectra for 2.7 $\mu$m thick MAPbI$_3$–$x$Cl$_x$ film in the region of medium and week absorption.

$\lambda_1$, $\lambda_2$
Table 1. Average data for df obtained from R and T curves are 2.806 and 2.82 μm respectively. These values are in a good agreement with the data dp = 2.7 μm measured on a surface profilometer.

| Pair of λ, nm | df calc. from R, μm | Pair of λ, nm | df calc. from T, μm |
|--------------|---------------------|--------------|-------------------|
| 816.75       | 2.814               | 817.99       | 3.022             |
| 845.28       | 844.57              | 844.57       | 2.831             |
| 845.28       | 2.901               | 844.57       | 2.823             |
| 874.92       | 874.92              | 907.63       | 2.607             |
| 908.1        | 2.726               | 907.63       | 2.607             |
| 944.7        | 945.92              |              |                   |

3.4. About the accuracy of determined optical parameters and thickness

Although the application of the envelope method to determine the optical parameters of films from transmittance spectra with interference-effect leads to some inaccuracies associated with an absence of the right way to construct envelopes between interference extremes, it can be understood that the practicality of this method lies in the quickly determining of the complete set of optical parameters using only the spectrophotometric measurements of T and R.

Most often the obtained calculated results are compared with more accurate measurements of these parameters by ellipsometry. However, we give some estimates based on the accuracy of our measuring instruments.

For the extracting of nf, kf and α in the region of weak and medium absorption when is using only T spectra with interference-effect the values of TM and Tm must be obtained. The maximum absolute accuracy of TM and Tm measured on spectrophotometer Filmetrics F20 is not more than 1%. A similar situation is well described by Swanepoel in [1], where it is shown that 1% accuracy of TM and Tm yields a relative error not more than 3% for the accuracy of the calculated values of nf and α. The results of our calculations with such accuracy were compared with the results of other authors performed by using ellipsometry and spectrophotometry [19–21] and there is a good agreement.

Although non-contact profilometers (for example, SJ-410 series) have certain difficulties in thickness measuring since always require a substrate-film border, they are highly precise (1 nm resolution) for the ex situ thickness and roughness measurement. Therefore, the thickness of the film extracted from the oscillating transmittance and reflectance curves (see section 3.3) was compared with profilometer data. Although the accuracy of determined wavelengths of neighboring extrema is precise (less than 1.5 nm), there are big errors for calculated df data which are explained via absolute accuracy (not better than 1%) of measured TM and Tm. The relatively better result compared to profilometer data gives when we use an average refractive index for this wavelength region.

4. Summary

In this article, the optical parameters of optical quality micron-sized polycrystalline MAPbI3−xClx perovskite films are determined by using the spectrophotometric measurements of T and R. For these films it is shown at the first time, that in the medium and weak absorption region envelope method is valid for the extraction of nf, kf and α with an accuracy not worse than 3% when is using only T spectra with interference-effect. Also, α and Eopt are calculated for the strong absorption region by using conventional approximated formulas.

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