Optica Applicata, Vol. XLII, No. 3, 2012
DOI: 10.5277/oa120320

Ellipsometric investigation of CdTe films

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Ellipsometric parameters of CdTe films prepared by "hot-wall" vacuum-epitaxy method on single crystal Si substrates were measured at the wavelength of 632.8 nm. Refractive index, extinction coefficient and thickness of the films were determined. Based on the Maxwell–Garnett approximation of inhomogeneous material containing inclusions of different components (cavities, oxides) the refractive indices and extinction coefficients of effective media were calculated. Optical parameters of the film were found to depend on its thickness, which could be explained by different volume concentration of the substance in the film depth.

Keywords: cadmium telluride thin films, film thickness, optical parameters.

1. Introduction

Semiconductor films are widely used in different branches of micro- and optoelectronics for producing sun energy converters, signal transmitting devices, *etc*. In particular, CdTe-based devices are used as electroluminescent emitters or coatings for surface passivation of the solid-state sun radiation detectors in the near IR spectral region. Knowledge of the film properties such as optical constants and thickness uniformity throughout the sample area, film radiation and chemical stability is necessary for construction of multilayer devices.

Determination of CdTe film optical constants is of individual interest because these films are widely used in photo-micro-electronics but their optical properties have been studied insufficiently. It was shown in [1–6] and in our earlier papers [7, 8] that surface structure and values of film optical parameters considerably depend on methods and conditions of film deposition. Particularly, it was found that CdTe film refractive index is always smaller than that of the bulk single-crystal CdTe. In [5], this fact was explained by the film porosity and in [2, 4] by a high sensitivity of optical parameters

to the deviation from the stoichiometric composition of the film within sample surface. Hexagonal phase formation in thick films [1] or in the films grown at high substrate temperature was found as well. In [9], it was detected that refractive index in long-wave region of visible spectrum increases with the film thickness. This fact is due to changes in the film structure. At the same time, it is known that the optical spectra of semiconductors are most sensitive in the region of fundamental absorption.

The aim of this investigation was to study the dynamics of CdTe film optical parameter changes with increasing the evaporation time and thickness, correspondingly, and to make an attempt to connect the singularity of the film optical parameter behaviour with the film inhomogeneity.

2. Experiment

Thin CdTe films were obtained using the vacuum "hot-wall" epitaxy device. Si(100) single-crystal wafers with approximate size of 1×0.5 cm^2 were used as substrates. Substrate wafers were obtained by conventional method that includes polishing in chemical etching agent until the surface reaches a high optical quality. Before loading into the growth chamber the samples were chemically etched in HF acid and washed in acetone for oxide and impurity removal. CdTe film formation was conducted in high vacuum of 10^{-7} mmHg. For obtaining thin film growth conditions that approximate the balanced ones to the greatest extent possible, evaporation was conducted in semi-closed space formed by the source, wall and substrate, which were kept at different temperatures. These temperatures were as follows: $T_{source} = 653$ K, $T_{wall} = 673$ K, $T_{substrate} = 323$–393 K. The time of evaporation was varied for obtaining films of different thickness. Nominal thickness of CdTe layers was obtained by the continuous growth of a thin layer during the whole evaporation time. Films were deposited for fixed durations of 6, 10 and 14 minutes. Each sample was grown separately. Under these circumstances we obtained three samples with different interference color throughout the area, which obviously pointed to different thicknesses at different points of the film. Three series of such samples were obtained.

Morphological and X-ray examination of such films grown in the same growth chamber is described in [10]. XRD measurements showed that all the samples had a well-pronounced crystalline structure.

Ellipsometric measurements were conducted *ex-situ* in the open air using a LEF-3M-1 laser null ellipsometer at a 632.8 nm wavelength and fixed angle of incidence $\varphi = 65°$. The measured parameters Δ and ψ are the phase difference between *p*- and *s*-components of electric vector of reflected light wave and the arctangent of the ratio of reflective coefficients in the *p*- and *s*-planes of the sample, correspondingly. The measurements of Δ and ψ were conducted at several places on the surface of each sample with different interference colors. Sample 6 had 4 places, sample 10 had 2 places and sample 14 had 6 places near the center of the film. Film parameters were determined with the help of ellipsometric software package, where $\cos\Delta$ and $\mathrm{tg}\,\psi$ were used as experimental values.

3. Experimental results

Figure 1 illustrates the results of measurements at the wavelength of 632.8 nm, where measured values of ellipsometric parameters cosΔ and tgψ lie along the orthogonal axes of nomogram.

One can see that the experimental points obtained (couples of ellipsometric parameters) for samples at different evaporation time are located in different areas of the diagram and form certain curves. Particularly, curve 3 was obtained for the same sample as curve 2 but after one-year exposure to the air.

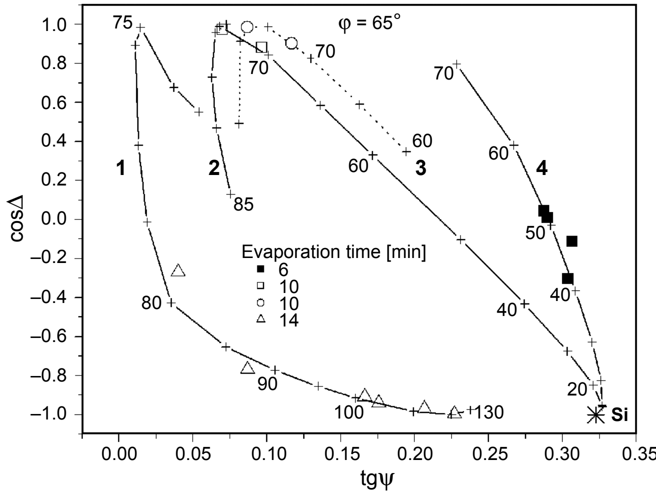

Fig. 1. Experimental points (symbols) obtained for the samples at different evaporation time in comparison with the results of theoretical calculations of the curves of film thickness change. Numbers near the marks on the curves show the film thickness in nm. Curve calculation parameters: 1 – n = 2.68, κ = 0.273; 2 – n = 2.59, κ = 0.23; 3 – n = 2.54, κ = 0.23; 4 – n = 2.4, κ = 0.2.

For interpretation of the experimental results obtained we used a one-layer homogeneous film model. Optical parameters (refractive index and index of extinction) and film thickness in each section of the film are the parameters to be determined.

We developed a special method [11] based on ellipsometric software package “ellipsometric calculator” [12], for determination of optical parameters and film thickness at every measured point. Values of refractive index n = 3.9 and extinction index κ = 0.04 of the single crystal silicon substrate were used for determination of film parameters [13].

Without going into details described in [11], we will quote only those peculiarities of the method which allowed us to interpret the data obtained. This method allows to determine optical parameters of the film at different places of the same sample if places have equal optical constants and different film thickness. In the first stage of ellipsometric data processing, the data array of film optical parameters n and κ, which correspond to each couple of ellipsometric parameters obtained in each place

of the film, and different film thicknesses d were calculated with the help of the program. On the diagram with coordinates n and κ this array has the form of curve (thickness curve), with thickness d changing along this curve. The number of such curves equals the number of working places where measurements were taken.

Obviously, all thickness curves on the diagram mentioned will intersect at one point if film optical parameters are the same at all points under study. If the film is heterogeneous with respect to both the thickness and the optical parameters, then curves will lie separately and will not intersect. This circumstance was actively used for calculation and interpretation of the experimental results.

Solutions including the film parameters were found for all the samples studied. Results of calculations are presented in Tab. 1; some data for films obtained using the same technique and published by us are also presented in this table. The intervals within which the thickness of each film changes over their surface area are also presented in Tab. 1.

Table 1. Refractive index n, extinction index κ and thickness d for CdTe films at different time of evaporation.

Sample number	Time of evaporation [min]	n	κ	d [nm]	Notes
2	8	1.99	0.42	65–90	[7]
3	8	2.2	0.36	40–83	[7]
6	6	2.4	0.204	42–52	Current paper
5	10	2.59	0.23	72–76	Current paper
5	10	2.54	0.23	72–76	Current paper
7	14	2.68	0.27	80–120	Current paper
10/1	10	2.36	0.225	56–68	Current paper

Instrumental accuracy of ellipsometric parameter measurements in this method approaches the optical parameter errors $\Delta n \approx \pm 0.05$, $\Delta\kappa \approx 0.03$, $\Delta d \approx 3$–5 nm [11]. Errors obtained in this work from the experimental results treated by the same technique are close to the values mentioned. This means that optical parameters of the films studied are actually equal in different places of the sample surface in the limits of aforementioned errors.

Theoretical curves calculated upon the experimentally obtained values of film optical parameters are presented in Fig. 1. Such curves take their beginning from the point that corresponds to substrate optical parameters and describe the variation ellipsometric parameters with the film thickness growth. It is obvious that curves go through the experimental points on the diagram of measured values, which demonstrates the appropriateness of the film parameter calculations.

From the data presented in Tab. 1 one can see that certain dependence of optical parameters on the film thickness is observed for samples 5–7 studied in this work. In particular, sample 7 that has the greatest film thickness also has the greatest values of refractive index and extinction index.

At the same time, the samples studied by us in [7] show a notably smaller refractive index and notably greater extinction index than the films studied in this work.

4. Interpretation of results and discussion

Thickness heterogeneity over the film could be explained by the heterogeneity of the source thermal field, which resulted in different substrate temperature in different regions during film formation.

Most films obtained by the vacuum methods have lacunary column structure [14]. Then, the parameters of film optical have a physical meaning of optical constants of the composition of the host material, CdTe in our case, and the cavities between separate columns or grains of the host material which can be filled by oxide or a mixture of oxides.

Porous structure of the films studied in this work can appear as a result of great difference between lattice constants of Si (5.4282 Å) and CdTe (6.477 Å). That is why growing films can be stressed and the centers of stress localization can become the centers of predominant material deposition and film growth.

The Maxwell–Garnett approximation is often used [14] for describing the dependence of optical constants of equivalent medium that replace the matrix of host substance *a* with sphere form inclusions *b*, on the fraction portion:

$$\frac{\varepsilon - \varepsilon_a}{\varepsilon + 2\varepsilon_a} = f_b \frac{\varepsilon_b - \varepsilon_a}{\varepsilon_b + 2\varepsilon_a} \tag{1}$$

where ε_a and ε_b are the dielectric constants of the matrix and its inclusions, respectively, ε is the dielectric constant of the effective medium, and f_b is the volume fraction of inclusions.

The formula for dielectric constant of effective medium can be obtained from (1) as:

$$\varepsilon = \varepsilon_a \frac{\varepsilon_b(1 + 2f_b) + 2\varepsilon_a(1 - f_b)}{\varepsilon_b(1 - f_b) + \varepsilon_a(2 + f_b)} \tag{2}$$

In the case of absorptive substances, the dielectric constant is a complex value and is expressed by the refractive index *n* and extinction index κ

$$\varepsilon = (n - i\kappa)^2 = \varepsilon_1 - i\varepsilon_2 \tag{3}$$

where ε_1 and ε_2 are the real and imaginary parts of the dielectric function, respectively, and

$$\varepsilon_1 = n^2 - \kappa^2, \qquad \varepsilon_2 = 2n\kappa \tag{4}$$

Consequently, the dependence of refractive and extinction indices on the volume portions of the components is specified by Equations (2)–(4).

We have calculated the dependence of the optical constants of the composition on the fraction of host substance CdTe for several probable values of refractive and extinction indices of the other substance. Results are presented in Fig. 2 as the curves, each of which begins from point 0 that corresponds to the optical parameters of bulk CdTe $n = 2.94$, $\kappa = 0.38$ [15]. Fraction of the host substance decreases along each curve, with fraction of the other substance increasing correspondingly.

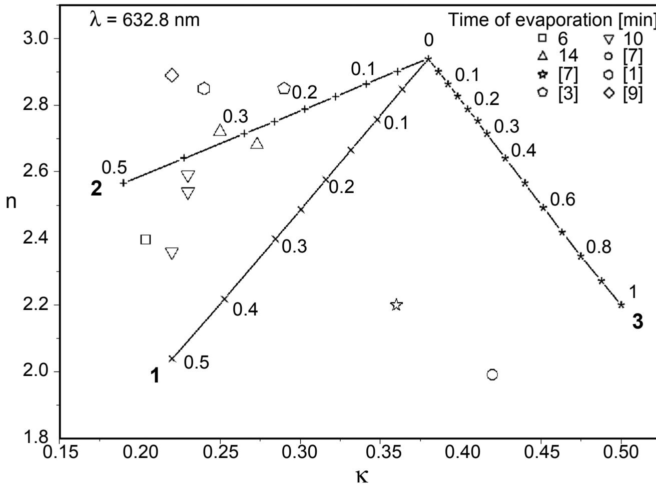

Fig. 2. Comparison of the model optical constants found from the ellipsometric measurements (symbols) and the effective optical constants calculated in Maxwell–Garnett approximation (solid lines). Optical parameters of the other component of the composition: 1 – $n = 1$, $\kappa = 0$ (voids); 2 – $n = 2.2$, $\kappa = 0$; 3 – $n = 2.2$, $\kappa = 0.5$. Numbers near the curves indicate portion of voids in the film.

In the context of present investigation we calculated a similar diagram for the same system in the Bruggeman approximation, which was thought [16] to be more acceptable than the Maxwell–Garnett approximation, particularly in the range of large values of volume fraction of inclusions. Curves of Bruggeman approximation differ from those presented in Fig. 2 by the value that is considerably smaller than the error of optical constant calculation in this paper.

Each curve on the diagram in Fig. 2 ends with the point that corresponds to the optical parameters of the other component. For instance, curve 1 describes dependence of the optical parameters on the fraction of host substance for composition of CdTe and voids; correspondingly, curve 2 describes composition of CdTe and hypothetical transparent substance with refractive index of 2.2; curve 3 describes composition of CdTe and absorptive substance with parameters pointed in the caption to Fig. 2.

It is necessary to mention some rules that describe location of the curves on the diagram that corresponds to other values of optical parameters of the substance. Curves for the transparent substances with different values of refractive index $n \geq 1$ are situated above curve 1 because at $q_a = 0$ it ends with the point $n = 1$, $\kappa = 0$. Curves

that correspond to substances with relatively small absorption can be imposed upon the same area.

Those curves which correspond to substances with relatively large values of extinction index lie to the right of curve 1.

Measured values of refractive index and extinction index are given on such diagram as symbols. Since a great number of curves that correspond to different values of the optical parameters of the other component can pass through this point, then these constants, in general case, can be determined only when volume fraction of the substance in the film is known. Refractive index and volume fraction of the other component can be determined simultaneously only when voids are filled with transparent substance.

Ellipsometry is not a direct method, so, optical parameters obtained with the help of it are realistic only if the chosen model of reflecting system represents the facts. The experimental points obtained in the present work in the light reflection from places of the film with different thickness, coincide quite well with a single theoretical curve which is described by only one pair of optical parameters (see Fig. 1). This points to the homogeneity of the film properties over its area, obviously, in the limits of the obtained errors of optical constants.

In [7], using multi-angle measurements carried out on the films of the system mentioned, we showed that in the limits of central places the film is homogeneous over its depth.

All these considerations confirm the validity of the choice of the effective medium model for description of CdTe films grown on Si.

Obtained in this work the experimental points in Fig. 2 arrange regularly, moving from curve 1 to curve 2 with evaporation time increasing, in other words, with thickness increasing. If we suppose that voids of the porous film are filled by the transparent substance, we can state that location of experimental points of samples 6–14 corresponds to the refraction index of the substance that fills the pores, increasing approximately from 1.5 (sample 6) to 2.2 (sample 14).

The parameters of film 5 (see Tab. 1) aged for 1 year in the air (curve 3 in Fig. 1) differ not much from the values obtained for this film immediately after preparation (curve 2 in Fig. 1). This proves a weak interaction between substance and air.

Then, an increase in the refraction index of the other component with film thickness increasing can be explained by the oxidation of the host substance by the oxygen which escapes from the CdTe charge during its decomposition and is evaporated by the source. Since a fine-dispersed charge has a large free surface area and was kept in the open air before its loading in the chamber, it is highly oxidized and emanates oxygen during heating in the source. Refraction index of 2.2 is close to the refraction index of the oxide compounds CdO and TeO_2.

Volume fraction of inclusions in the Maxwell–Garnett approximation equals from 0.4 (sample 6) to 0.2 (sample 14). In the Bruggeman approximation, the region of volume fraction fluctuation is slightly smaller – from 0.3 to 0.2, which can be more probable.

At the same time, the experimental points obtained in [7] on the films with the time of evaporation of 8 minutes locate in that region of the diagram where extinction indices of the other component are considerably greater than those for CdTe.

As was noted in [14], the column structure of the films is complicated by the coexistence of different crystalline phases and can change during evaporation when film thickness increases. Because of the porosity, the substance has well developed equivalent surface which can capture water vapor and contain different defects. Particularly in [1, 4, 5], the presence of free Te atoms in the samples was detected. An increase in refractive index in the films that contain Te in appreciable quantity can result in stronger absorption of this substance in the visible region of the spectrum. Thus, an increase in extinction coefficient of the films studied in [7] can be explained by the presence of telluride atoms on the porous surface.

5. Conclusions

Deviation of CdTe film optical constants from the bulk CdTe optical constants can be explained by the porous structure of the film. If one assumes that cavities between separate grains of the host substance (CdTe) are filled with a transparent substance, then volume fraction of this substance in the film changes from 0.3–0.4 to 0.2. In just-prepared films obtained during different times of evaporation, the host substance volume concentration is approximately equal, but refractive index increases from 1.5 (films with short time of evaporation) to 2.0 (films with evaporation time of 14 minutes). Some films, which were exposed to the air over a long period of time (more than a year), have such values of optical parameters which corresponds to the cavities in the films, which are filled with a relatively strongly absorbing substance. This kind of substance can be a mixture of oxide and underoxidized substance.

Acknowledgements – The authors wish to acknowledge Prof. Fedir F. Sizov, whose advise and research were invaluable in the preparation of this paper.

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Received July 21, 2011
in revised form January 12, 2012