Analysis of ~~P~~pulsed ~~L~~laser ~~D~~deposited ~~A~~amorphous ~~C~~chalcogenide ~~F~~film ~~T~~thickness ~~D~~distribution: Plume ~~D~~deflection ~~A~~angle ~~D~~dependence

Martin Pavlišta~~1~~[a], *

martin.pavlista@upce.cz

Vít Zajac~~1~~[a]

Virginie Nazabal~~2~~[b], ~~3~~[c]

Jan Gutwirth~~2~~[b]

Francis Gouttefangeas~~4~~[d]

Petr Němec~~2~~[b]

~~1~~[a]Institute of Applied Physics and Mathematics, Faculty of Chemical Technology, University of Pardubice, Studentska 84, 53210 Pardubice, Czech Republic

~~2~~[b]Department of Graphic Arts and Photophysics, Faculty of Chemical Technology, University of Pardubice, Doubravice 41, Pardubice 533 53, Czech Republic

~~3~~[c]Institut des Sciences Chimiques de Rennes (UMR 6226) CNRS, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France

~~4~~[d]ScanMAT - CMEBA, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France

*Corresponding author.

Abstract

Pulsed laser deposition exploiting a KrF excimer laser was used to fabricate amorphous As-S thin films from bulk As_2S_3 glass target. Thickness profile of the film was extracted from variable angle spectroscopic ellipsometry data. The dependence of thickness distribution of prepared thin layer on laser beam plume deflection angle was evaluated and corresponding equations were suggested.

Keywords: Plume deflection; Thickness distribution; PLD; Chalcogenide; Thin film

~~1.~~1 Introduction

Amorphous chalcogenide thin films form very important group of inorganic materials that have a number of applications including optical waveguides, sensors, phase-change memories, etc. [1–3]. For their fabrication, different physical (vapour or plasma) deposition techniques such as radio-frequency magnetron sputtering [4,5], vacuum thermal evaporation [6] or electron beam deposition [7] are often used. A large variety of chalcogenide films was prepared by means of pulsed laser deposition (PLD) too [8–10]. This simple method has several advantages (i.e. relatively fast growth of the film, requirements of only small targets, often stoichiometric material transfer from the target to the film, etc.) but also some limitations such as possible presence of macroscopic/~~-~~microscopic particles ejected from the target, re-sputtering effect or non-uniformity of the film thickness that is partly caused due to the plume deflection. The plume deflection has also an influence on thickness distribution profile that is supposed to be radial, independent on azimuthal angle [11]. However, during preliminary PLD experiments dealing with the fabrication of amorphous chalcogenide thin films we obtained quite different thickness profiles in perpendicular directions. That is why we have studied in this work in detail the influence of plume deflection angle on thickness distribution of a prototypical amorphous chalcogenide material represented by As_2S_3 thin film. Real As-S film thickness distribution was extracted from spectroscopic ellipsometry data. Film thickness distribution was also modelled exploiting function describing plume deflection vs laser shot number dependence. Theoretical results based on the developed analytical model were found to be in a good agreement with experimental data.

~~2.~~2 Material and methods

Bulk chalcogenide glasses of As_2S_3 were synthesized in silica ampoules at a temperature of 850 °C from high-purity (typically 99.999%) elements by melt-quenching method and used for the deposition of amorphous layers. The

PLD set-up consisted of a laser system and a vacuum chamber. The KrF laser (Lambda Physik COMPex 102), operated at 248 nm with constant output energy of 300 mJ per pulse, pulse duration of 30 ns and repetition rate of 20 Hz, was used. The laser beam was focused by spherical lens with 0.61 m focal length onto 1" As_2S_3 target at incidence angle of 45° from the target surface normal. The target-to-substrate distance was 5 cm. The laser beam spot dimension was 1 × 3 mm^2 and the laser beam energy density was 2.5 J cm^{-2}. The thin film was deposited on 4" silicon wafer from plane-parallel target. The PLD experiment was performed at 2.9 × 10^{-4} Pa pressure. The deposition time was 2 min (2400 laser shots).

The chemical composition of PLD thin films was measured using a scanning electron microscope (SEM) with an energy-dispersive X-ray analyzer (EDS, JSM 6400-OXFORD Link INCA). Atomic percentage (± 1 %) of constituting elements (S, As) was extracted exploiting K and L line of S and As, respectively, working at 5 kV.

The thickness profile of the film was obtained from the analysis of variable angle spectroscopic ellipsometry (VASE) data measured using an ellipsometer with automatic rotating analyzer (J.A. Woollam Co., Inc.). The measurement parameters are as follows: spectral region 500–1700 nm with 10 nm steps, angle of incidence 70°. VASE data were recorded as x-y maps with 0.5 cm steps. Resulting data sets were analyzed with Cauchy dispersion formula.

~~3.~~3 Results and discussion

~~3.1.~~3.1 Model

A theoretical approach based on a geometry concept was chosen for the description of the dependence of thickness distribution of prepared thin layer on laser beam plume deflection angle. In analogy with one dimensional thickness profile $D(x)$ for ablated material [12] expressed

$$D(x) = K\left[1 + \left(\frac{x}{h}\right)^2\right]^{-(p+3)/2} \tag{1}$$

it is possible to derive two dimensional thickness profile $D(x, y)$ in the following form

$$D(x, y) = \frac{Kab(p+1)}{2\pi h^2}\left(1 + \frac{a^2x^2 + b^2y^2}{h^2}\right)^{-(p+3)/2}, \tag{2}$$

where h is target-to-substrate distance, x is the distance from the center of the distribution curve. The laser beam projection onto the target surface plane coincides with y axis. The constant K reflects growth rate of deposited material. Constants a, b, p are related to the shape of the distribution, which is influenced by different parameters, for example laser spot dimensions, laser energy fluence and wavelength [11].

Since Eq. (2) represents film thickness deposited on the plane $z \equiv h$, it can be generalized for any plane at a distance z from target surface plane:

$$D(x, y, z) = \frac{Kab(p+1)}{2\pi z^2}\left(1 + \frac{a^2x^2 + b^2y^2}{z^2}\right)^{-(p+3)/2}. \tag{3}$$

One laser shot with plume deflection of angle Ψ (i.e. angle measured from the target surface normal either in positive or negative directions of y axis) generates thickness distribution expressed in its own coordinate system as follows:

$$D_\Psi\left(x_\Psi, y_\Psi, z_\Psi\right) = \frac{Kab(p+1)}{2\pi z_\Psi^2}\left(1 + \frac{a^2x_\Psi^2 + b^2y_\Psi^2}{z_\Psi^2}\right)^{-(p+3)/2}. \tag{4}$$

Using transformation

$$\begin{pmatrix} x_\Psi \\ y_\Psi \\ z_\Psi \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\Psi & -\sin\Psi \\ 0 & \sin\Psi & \cos\Psi \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix}, \tag{5}$$

one obtains distribution given by Eq. (4) in original coordinate system as

$$D_\Psi(x, y, z) = \frac{Kab(p+1)}{2\pi(y\sin\Psi + z\cos\Psi)^2}\left(1 + \frac{a^2x^2 + b^2(y\cos\Psi - z\sin\Psi)^2}{(y\sin\Psi + z\cos\Psi)^2}\right)^{-(p+3)/2}. \tag{6}$$

Considering that $z \equiv h$, one can derive ~~obtain~~ the following relation for one laser shot

$$D_{\Psi}(x,y) = \frac{Kab(p+1)}{2\pi(y\sin\Psi + h\cos\Psi)^2}\left(1 + \frac{a^2x^2 + b^2(y\cos\Psi - h\sin\Psi)^2}{(y\sin\Psi + h\cos\Psi)^2}\right)^{-(p+3)/2}. \quad (7)$$

Then, the total thickness distribution deposited by N laser shots is given as

$$D_N(x,y) = \frac{Kab(p+1)}{2\pi}\sum_{n=1}^{N}\frac{1}{\left(y\sin\Psi_n + h\cos\Psi_n\right)^2}\left(1 + \frac{a^2x^2 + b^2\left(y\cos\Psi_n - h\sin\Psi_n\right)^2}{\left(y\sin\Psi_n + h\cos\Psi_n\right)^2}\right)^{-(p+3)/2}, \quad (8)$$

where Ψ_n is function describing plume deflection of n-th laser shot.

~~3.2.~~3.2 The case of As_2S_3 thin film

Using the previous relations, the thickness profile of As_2S_3 amorphous film was ~~analysed~~analyzed. This film was deposited during custom PLD experiment setup that is commonly used for most applications.~~-~~ The irradiated target was rotating and each point of the resulting spot circle was in average hit by 70 laser pulses during this experiment. In order to obtain approximate values of the parameters K, b, and p, the measured thickness values extracted from VASE data were firstly fitted using Eq. (2) that does not include plume deflection angle dependence. The parameter value $a = 1$ was set in this and subsequently derived equations because the mutual dependence between a and b parameters exists. The a parameter value is consistent with Eq. (1) describing one-dimensional thickness profile in x axis and it was exclusively considered for determination of thickness profile distributions of various materials [11].

The plume deflection phenomenon was observed for silicon targets [13,14]. During described experiment with As_2S_3 glass target the plume deflection has been also observed. The plume deflection could be also deduced visually from the interference patterns of the film. Since the experimentally found function describing plume deflection angle of n-th laser shot Ψ_n can be partly either convex or concave depending on laser fluence value [13,14], the exponential function $\Psi_n = C(e^{\alpha n} - 1)$ was chosen. Here, the C and α are non-zero parameters (C, $\alpha \neq 0$).~~-~~ The resulting convex Ψ_n function describing plume deflection of n-th laser shot for deposited As_2S_3 film is depicted in Fig. 1. This Ψ_n function cannot be compared with previously found experimental functions due to the fact that different experimental conditions (laser type, pulse duration, laser fluence) and different materials (Si, Cu, Ti) were used.

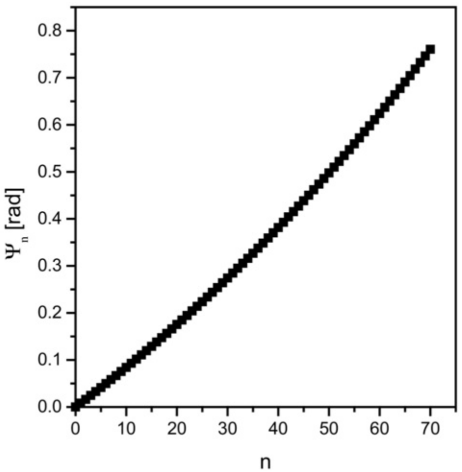

Fig. 1 Plume deflection versus number of pulses dependence obtained from experimental data fit.

alt-text: Fig. 1

K, b, and p parameter values calculated for distribution via Eq. (2) were taken as initial parameter values for measured data fitting when using the Eq. (8). Then, K, b, p, C and α parameters from the best-fit scenario are listed in Table 1. Finally, the resulting distribution $D_N(x, y)$ fit is presented in Fig. 2 together with thickness data obtained from VASE data analysis. One can see a good agreement between the model and the experimental data. Some differences > 25% between fitting function and measured thickness data can be observed in the central part of the film around the thickness peak. Here, the discrepancies might be connected with changes in chemical composition identified by EDS which are depicted in Fig. 3. The central part of the film is clearly enriched by As element due to possible re-sputtering of sulfur caused by laser generated particle bombardment of the deposited material. During this effect, the most volatile component, i.e. component with the lowest mass (sulfur in our case), is being depleted [15]. This effect would be possibly limited by the decrease of kinetic energy of plasma plume particles. The content of lighter elements in the films fabricated by PLD can be also moderated for example by the presence of background gas [11]. This effect will be studied within PLD of amorphous chalcogenide thin films in our future work.

Table 1 The characteristics of the thickness distribution profile (Eq. (8)) for prepared As-S film.

alt-text: Table 1

N	K	a	b	p	C	α
70	614.7 ± 19.6	1	8.8 ± 0.6	3.7 ± 0.1	1 ± 0.2	$(8.1 \pm 1.4) \times 10^{-3}$

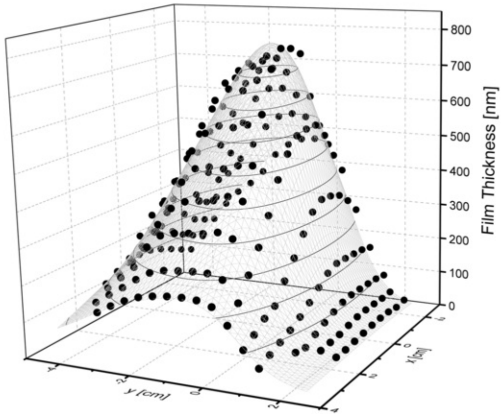

Fig. 2 Thickness distribution and fit of As_2S_3 film.

alt-text: Fig. 2

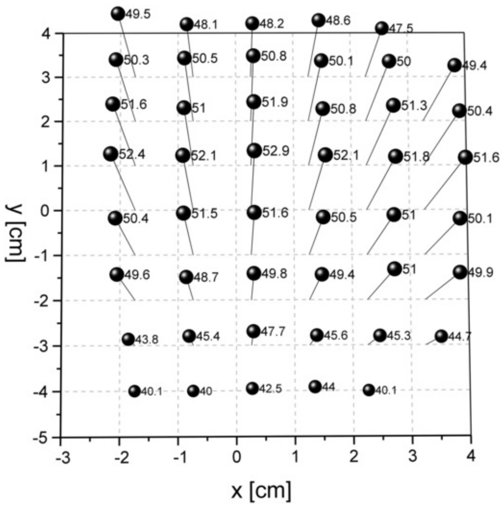

Fig. 3 The composition of As_2S_3 film obtained from EDS. The numbers indicate amount of As (at.%) in the film.

alt-text: Fig. 3

~~4.~~4 Conclusions

The amorphous As-S thin film was prepared by typical pulsed laser deposition experiment used for most applications. The analytical model predicting non-radial thickness distribution of the film depending on plume deflection angle was developed. The theoretical results for studied As_2S_3 thin film based on the analytical model are in a good accordance with experimental data. Future work will be dealing with the effect of background gas on the thickness and chemical composition profiles of amorphous chalcogenide layers deposited by PLD.

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Highlights

- 3D Thickness profile of As-S film was extracted from VASE data.
- Dependence of thickness distribution on laser plume deflection angle was evaluated.
- Analytical model predicting non-radial thickness distribution was developed.

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