"Optical characterization of thin films deposited on Ti-6Al-4V substrate by spectroscopic ellipsometry"

Vladimir Petkov, Stancho Yordanov*, Bojidar Jivov, Shaban Uzun, Mihaela Aleksandrova,

Institute of Metal Science, Equipment, and Technologies “Acad. A. Balevski” with Center for Hydro- and Aerodynamics at the Bulgarian Academy of Sciences, 67 "Shipchenski prohod" str., 1574 Sofia, Bulgaria
e-mail: stancho14@abv.bg

Abstract: *Spectroscopic ellipsometry was applied to study the optical properties of Ti–6Al–4V alloy before and after anodization in acetic acid electrolyte. The main findings can be summarized as follows: The ellipsometric spectra of the uncoated alloy were successfully modeled using a multi-Lorentz oscillator approach with MSE values of 20–26, and surface roughness ranging from 17 to 52 nm. Anodized surfaces exhibited distinct interference features, confirming the formation of a transparent oxide layer. The optical modeling revealed increased surface roughness and modified optical constants due to the formation of a* TiO_2 *-based film with amorphous–anatase character. The applied ellipsometric methodology proved reliable for evaluating the thickness and optical properties of anodic oxide films on titanium alloys. These results form the basis for future quantitative analysis of anodic oxide thickness and refractive index as functions of anodizing parameters, which is important for optimizing the surface properties of titanium alloys in biomedical, protective, and optical applications.*

Keywords: ELLIPSOMETRY, ANODIZATION, TI–6AL–4V, LORENTZ OSCILLATOR

1. Introduction

In recent decades, titanium and its alloys (Ti-6Al-4V and others) have gained significant importance as high-quality metallic materials, applicable in various fields [1-6]: chemical production, oil refining industry, medicine, energy, automotive engineering, shipbuilding, aerospace engineering and many others. This trend is due to the presence of a number of suitable basic characteristics: high specific strength, low density, high ratio strength/weight, excellent corrosion resistance, good biocompatibility, etc. [1,3,6]. At the same time, when compared with some traditional metals for modern mechanical engineering (aluminum, steel or others), titanium alloys exhibit a tendency to thermal softening (at high temperatures), low plastic shear resistance and a specific and complex deformation mechanism in extreme and dynamic environments [1-4]. These main disadvantages, as well as the presence of low volume specific heat and low thermal conductivity, complicate the conditions of machining and cutting (of titanium alloys) and cause the risk of accelerated depreciation of the standard metal-cutting tools used [1,4]. A significant critical operational disadvantage of titanium alloys is their tribological characteristics, which limit their wear resistance and the possibilities for application in the production of machine parts exposed to intense sliding, abrasive or impact [3,6]. Strong adhesion wear, high frictional coefficient and low abrasion resistance are unfavorable characteristics observed in titanium alloys [4,6].

In this aspect, the application of alternative innovative production methods for effective and cost-effective processing of titanium alloys is of significant interest. The development of various technological solutions based on the concept of additive manufacturing (AM) is considered a current and promising approach [2,7-10].

Titanium alloys are characterized by a lower elastic modulus (compared to a number of traditional alloys), which favors their successful application in modern orthopedics [3,6]. Using AM technological approaches, methods have been developed for obtaining high-quality biocompatible and non-toxic personalized implants, applicable as suitable substitutes for supporting hard tissues [11-14]. The resulting diverse products are suitable for fracture therapy and osteoplasty. Various modifications of titanium alloy implants (mainly Ti-6Al-4V and others), prepared by selective laser melting (SLM), favor effective osseointegration between the implant and the adjacent bone tissue [15-17].

Improving the surface characteristics of titanium alloys is a top priority, ensuring a significant increase in their service life and long-lasting and enhanced functionality of the products, especially in aggressive and intensive working environments (with the presence of high-stress settings and high-wear) [1,4]. Effective options for targeted change and modification of the surface properties of technical details made of titanium alloys are the application of appropriate surface coatings (ceramic, amorphous and others), alloying as well as various lubrication techniques [6].

In this aspect, various technological approaches are used: chemical vapor deposition (CVD), physical vapor deposition (PVD), plasma spraying technique, sol-gel method and a number of others [18-26]. Experimental developments have been implemented for the deposition (on titanium alloys) of various thin coatings (with a diverse structure) [6,18,21,23,26]: oxides (Al_2O_3, SiO_2, TiO_2 and others), TiN, SiC, diamond-like carbon (DLC), smooth diamond coatings and others.

The functional characteristics of thin films (SiO_2, TiO_2 and others) obtained by the sol-gel method on Ti-6Al-4V surfaces have been studied. The role of the used technological regime, the specificity of the compositions and the preliminary preparation of the metal surface on the morphology, thickness and homogeneity of the obtained coatings and their physicochemical, strength, adhesion and tribological properties has been analyzed [27,28].

To study the phase composition, structure, micromorphology, optical and other indicators of experimental samples (obtained by various technological methods), various laboratory techniques for analysis are used. Of particular interest are the analytical capabilities of some laboratory methods for studying thin films and multilayer coatings deposited on various materials [29-33].

Modern spectral ellipsometry is considered a particularly promising method, allowing optical characterization of thin and ultra-thin films [34]. Ellipsometry is a highly sensitive non-destructive optical method for studying the properties of surfaces by determining the change in the polarization of light upon interaction with various systems [35,36]. The ellipsometric method does not require the provision of a vacuum environment and special preliminary preparation of the samples, unlike other techniques (for laboratory analysis) of surfaces.

The method is widely used for studying various systems and processes in carrying out fundamental and applied research in various scientific fields [37-42]: materials science, physics, chemistry, microelectronics, biology, medicine and a number of others. At the same time, ellipsometry is applicable as a standard routine method for technological control in modern industry (microelectronics, optoelectronics and a number of others) [35,43].

Ellipsometry is not a direct experimental method. The results obtained are based on the technical capabilities of the equipment and the formalisms and algorithms used for the interpretation of the primary ellipsometric data [34,36]. The physical characteristics of the studied objects are established from the experimental data by solving the inverse ellipsometric problem by determining some basic parameters of the model system (approximating the real system), when the optical response of the real system is registered [43].

The main objective of the present work is to study, using spectral ellipsometry methods, the optical characteristics of thin functional coatings deposited on titanium alloy (Ti-6Al-4V) metal samples.

2. Experimental procedure

2.1. Sample preparation

The investigated samples were cylindrical specimens made of Ti–6Al–4V alloy (grade 5 titanium) with dimensions of 10 × 15 mm. The nominal chemical composition of the alloy was Ti – 88.6 wt.%, Al – 6 wt.%, V – 4 wt.%, Fe – 0.25 wt.%, O – 0.20 wt.%, C – 0.08 wt.%, N – 0.05 wt.%, and H – 0.025 wt.%.

Prior to anodization, the samples were mechanically polished to obtain a mirror-like surface. Grinding was performed sequentially using SiC abrasive papers of grades P600, P800, P1000 and P1200. The polished specimens were ultrasonically cleaned in a 2% aqueous solution of Decon 90 detergent for 5 min, rinsed with distilled water, degreased with organic solvents (1,2-dichloroethane and acetone), rinsed again with ethanol, and air-dried. Immediately before anodization, the samples were slightly etched to remove residual surface oxides and to ensure uniform surface activity.

2.2. Anodization process

The anodization of the titanium alloy was carried out in an acetic acid electrolyte (0.4–1.0 M CH_3 COOH) at a temperature of 20–30 °C. A stainless-steel plate (304L) was used as the cathode. The anodizing voltage was varied from 15 to 100 V, with the current density controlled in the range 0–5 A. The anodization parameters were selected to achieve oxide films of various thicknesses and interference colors. The electrochemical process resulted in the formation of a compact TiO_2 -based oxide layer on the Ti–6Al–4V surface, improving its corrosion resistance, wear resistance, and biocompatibility.

2.3. Ellipsometric measurements

Spectroscopic ellipsometry was performed in the wavelength range of 0.2–1.0 µm, corresponding to the operating spectral range of the ellipsometer. Measurements were taken at several angles of incidence on two arbitrary regions of each cylindrical sample, denoted as “Side 1” and “Side 2.” Since the surfaces were not pre-marked, the exact same positions could not be re-measured.

The ellipsometric parameters Ψ (Psi) and Δ (Delta) were recorded for both uncoated (clear) and anodized samples. The experimental data were analyzed using Lorentz-type dispersion models available in the instrument software. The optical response of the Ti–6Al–4V alloy was modeled using a multilayer structure consisting of an ambient/roughness layer (effective medium approximation) and a bulk metallic substrate represented by several Lorentz oscillators.

Reference optical constants of pure titanium were taken from literature sources [Palm *et al.*, ACS Photonics **5**, 4677 (2018); Johnson & Christy, Phys. Rev. B **9**, 5056 (1974); Werner *et al.*, J. Phys. Chem. Ref. Data **38**, 1013 (2009)]. Significant discrepancies were observed between the datasets, attributed to differences in material purity, crystal structure, and measurement techniques. For comparison, optical constants of aluminum reported by McPeak *et al.* (2015), Rakić (1995), and Cheng *et al.* (2016) were also analyzed, showing more consistent spectral trends / Figureя 1, 2/.

2.4. Data modeling and fitting

The fitting of the ellipsometric data was performed by minimizing the mean squared error (MSE) between the experimental and model-generated Ψ and Δ spectra. For the uncoated Ti–6Al–4V surfaces, MSE values of 20–26 were obtained, indicating reasonable agreement between experiment and model. The surface roughness, derived from the effective medium approximation, ranged between 17 and 52 nm depending on the analyzed region.

The optical model included up to five Lorentz oscillators representing interband transitions, with parameters such as amplitude (A), broadening (Br), and resonance energy (En). A small angular offset correction (0.7–2.5°) was applied during fitting. A reference silicon wafer was used for calibration, yielding MSE = 1.1 and a native oxide thickness of 1.73 nm, confirming the high accuracy of the instrument and reliability of the measurement procedure.

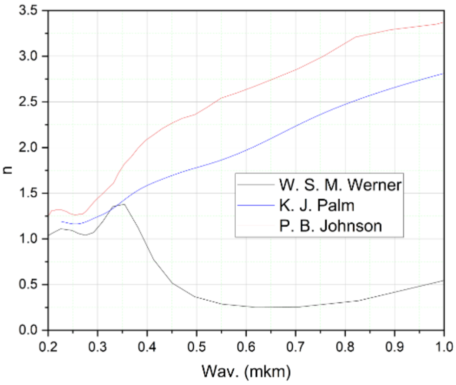

Figure 1. Optical constants of titanium (Ti) in the range 0.2 – 1.0 µm (the working range of the ellipsometer)

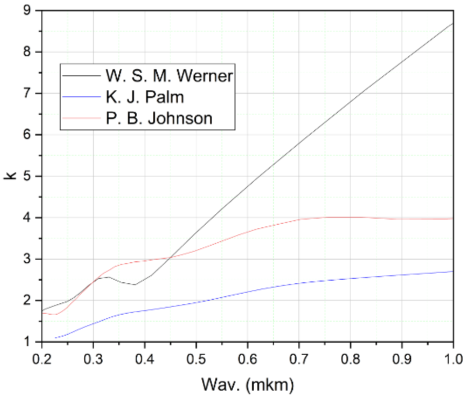

Figure 2. Optical constants of titanium (Ti) in the range 0.2 – 1.0 µm (the working range of the ellipsometer)

3. Results and discussion

3.1. Optical constants of Ti–6Al–4V alloy

To interpret the ellipsometric data properly, a comparison with literature values for pure titanium was made. Figure 1 shows the spectral dependence of the refractive index (*n*) and extinction coefficient (*k*) in the 0.2–1.0 µm range, based on different sources. As can be seen, the datasets vary considerably in magnitude and shape due to differences in material purity, phase composition (α or β-Ti), and measurement methodology. Since the studied alloy contains aluminum and vanadium, deviations from the optical response of pure titanium are expected.

3.2. Ellipsometric spectra of uncoated surfaces

Figure 3 presents the Ψ and Δ spectra for the uncoated Ti–6Al–4V alloy. Both examined regions (Side 1 and Side 2) show similar trends, with minor quantitative differences attributed to surface inhomogeneity and polishing-induced microtexture variations. The Lorentz model provided acceptable fits with MSE values between 20 and 26. The estimated roughness (17–52 nm) corresponds to mechanically polished metallic surfaces, consistent with the surface morphology observed visually.

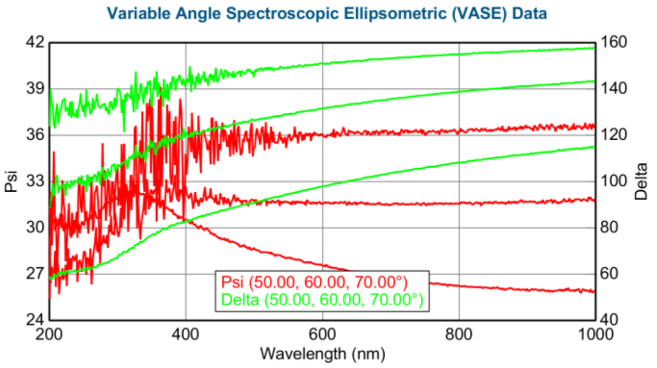

Figure 3. Ellipsometric angle spectra (Psi and Delta) of the "pure" (Ti64) sample

3.3. Ellipsometric spectra of anodized surfaces

After anodization, the Ψ and Δ spectra exhibit pronounced interference fringes (Fig. 4), typical of thin dielectric films. These oscillations indicate the formation of a transparent TiO_2 -based oxide layer. Increasing the anodizing voltage led to a red-shift of the interference extrema, corresponding to an increase in film thickness. This effect also correlates with the visually observed color changes of the anodized samples—from yellowish to blue-violet—caused by optical interference in the oxide film.

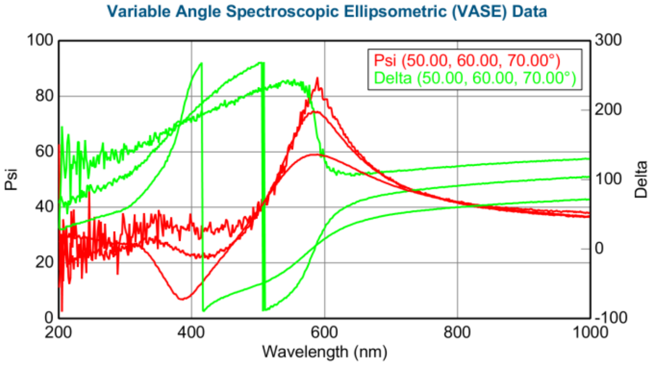

Figure 4. Spectra of the ellipsometric angles (Psi and Delta) of the anodized sample

3.4. Modeling and interpretation

The anodized surfaces were modeled using a four-layer structure consisting of:

1. ambient (air),
2. surface roughness layer (effective medium approximation),
3. oxide layer (TiO_2),
4. metallic substrate (Ti–6Al–4V).

The best fits were obtained using 4–5 Lorentz oscillators describing interband transitions at energies between 1.7 and 6.0 eV. The obtained angular offset (0.7–2.5°) indicates good consistency between the measured and simulated data. The roughness values for anodized surfaces were higher than for the uncoated alloy, which is consistent with the porous microstructure of the anodic oxide.

The spectral behavior and model parameters suggest that the anodic film possesses an amorphous–anatase structure with an estimated thickness ranging from tens to several hundred nanometers, depending on the applied anodizing voltage.

3.5. Reference measurement and comparison

A reference measurement on a Si wafer with a native oxide layer confirmed the accuracy of the ellipsometric method (MSE = 1.1; oxide thickness = 1.73 nm). Comparison of the obtained optical parameters with literature data for pure titanium and aluminum showed that, although the absolute values differ, the overall spectral behavior and characteristic trends are consistent. This supports the validity of the measured data and the applied modeling approach.

4. Conclusion

Spectroscopic ellipsometry was applied to study the optical properties of Ti–6Al–4V alloy before and after anodization in acetic acid electrolyte.

The main findings can be summarized as follows:

- The ellipsometric spectra of the uncoated alloy were successfully modeled using a multi-Lorentz oscillator approach with MSE values of 20–26, and surface roughness ranging from 17 to 52 nm.
- Anodized surfaces exhibited distinct interference features, confirming the formation of a transparent oxide layer.
- The optical modeling revealed increased surface roughness and modified optical constants due to the formation of a TiO_2 -based film with amorphous–anatase character.
- The applied ellipsometric methodology proved reliable for evaluating the thickness and optical properties of anodic oxide films on titanium alloys.

These results form the basis for future quantitative analysis of anodic oxide thickness and refractive index as functions of anodizing parameters, which is important for optimizing the surface properties of titanium alloys in biomedical, protective, and optical applications.

References

1. H. D. Nguyen, A. Pramanik, A. K. Basak b , Y. Dong, C. Prakash, S. Debnath, S. Shankar, I.S. Jawahir f , Saurav Dixit, Dharam Buddhi, A critical review on additive manufacturing of Ti-6Al-4V alloy: microstructure and mechanical properties, Review Article, Journal of Materials Research and Technology, 18, 2022, 4641-4661.

2. B. Dutta, F. H. Froes, Additive manufacturing of titanium alloys: state of the art, challenges and opportunities, 2016, 1-84.

3. C. Leyens, M. Peters, Titanium and titanium alloys: fundamentals and applications. 2003. https://doi.org/ 10.1002/3527602119.

4. A. Pramanik, Problems and solutions in machining of titanium alloys. Int J Adv Manuf Technol, 70(5), 2014, 919-28.

5. L. Parry, I.A. Ashcroft, R. D. Wildman, Understanding the effect of laser scan strategy on residual stress in selective laser melting through thermo-mechanical simulation. Addit Manuf, 2016,12,1-15.

6. N. Senthilkumar, G. Perumal, K. Palanikumar, B. Deepanraj, M. Shameer Basha, Wear and mechanical characteristics of coated Ti-6Al-4 V alloy with an alumina-13 wt.% titania -40 wt.% yitrium stabilized zirconia ceramic composite via plasma spraying technique, Results in Engineering 25, 2025, 103777.

7. X.-Y. Zhang, G. Fang, S. Leeflang, A.J. Böttger, A.A. Zadpoor, J. Zhou, Effect of subtransus heat treatment on the microstructure and mechanical properties of additively manufactured Ti-6Al-4V alloy, J. Alloy. Compd. 735, 2018, 1562–1575,

8. S. Ghods, E. Schultz, C. Wisdom, R. Schur, R. Pahuja, A. Montelione, D. Arola, M. Ramulu, Electron beam additive manufacturing of Ti6Al4V: Evolution of powder morphology and part microstructure with powder reuse, Materialia 9 (2020) 100631.

9. M.-W. Wu, J.-K. Chen, B.-H. Lin, P.-H. Chiang, M.-K. Tsai, Compressive fatigue properties of additive-manufactured Ti-6Al-4V cellular material with different porosities, Mater. Sci. Eng. A 790, 2020, 139695.

10. S. Kamara, K.S. Faggiani, Moving into Additive Manufacturing. Fundamentals of Additive Manufacturing for the Practitioner, books, John Wiley & Sons; 2021.

11. V.S. Cheong, P. Fromme, M.J. Coathup, A. Mumith, G.W. Blunn, Partial bone formation in additive manufactured porous implants reduces predicted stress and danger of fatigue failure, Ann. Biomed. Eng., 48, 2020, 502–514,

12. J. Li, X. Cui, G. J. Hooper, K. S. Lim, T. B. F. Woodfield, Rational design, bio-functionalization and biological performance of hybrid additive manufactured titanium implants for orthopaedic applications: a review, J. Mech. Behav. Biomed. Mater. 105, 2020, 103671,

13. A. N. Aufa, M.Z. Hassan, Z. Ismail, The fabrication of titanium alloy biomedical implants using additive manufacturing: a way forward, J. Met. Mater. Min. 7, 2021, 39–48,

14. A. N. Aufa , M. Z. Hassan, Z. Ismail, Recent advances in Ti-6Al-4V additively manufactured by selective laser melting for biomedical implants: Prospect development, Review, Journal of Alloys and Compounds 896, 2022, 163072.

15. M. Elsayed, M. Ghazy, Y. Youssef, K. Essa, Optimization of SLM process parameters for Ti6Al4V medical implants, Rapid Prototyp. J. 25, 2019, 433–447,

16. M. F. Sadali, Effect of hatching distance on surface morphology and surface roughness of the Ti6Al4V for biomedical implant using SLM process, Malays. J. Microsc. 15, 2019, 72–82.

17. Aufa A.N., Hassan M.Z., Ismail Z, Harun N, Ren J, Sadali MF, Surface enhancement of Ti–6Al–4V fabricated by selective laser melting on bone-like apatite formation. J Market Res, 19, 2022, 4018–4030.

18. D. Barros, l. Vandenbulcke, Plasma assisted chemical vapor deposition process for depositing smooth diamond coatings on titanium alloys at moderate temperature, Diamond Relat. Mater. 9, 2000, 1862–1866,

19. D. Nolan, S.W. Huang, L. Leskovsek, S. Braun, Sliding wear of titanium and thin films deposited on Ti-6Al-4V alloy by PVD and plasma nitriding process, Surf. Coat. Technol. 200, 2006, 5698–5705,

20. L. Ceschini, E. Lanzoni, C. Martini, D. Prandstraller, G. Sambogna, Comparison of dry sliding friction and wear of Ti6Al4V alloy treated by plasma electrolytic oxidation and PVD coating, Wear 264 (1–2), 2008, 86–95,

21. G. Perumal, M. Geetha, R. Asokamani, N. Alagumurthi, A comparative study on the wear behaviour of Al_2O_3 and SiC coated Ti-6Al-4V alloy developed using plasma spraying technique, Trans. Ind. Inst. Met., 66, 2013, 109–115.

22. K.O. Cooke, M.A. Shar, S. Hussain, Micro-alloying and surface texturing of Ti-6Al4V alloy by embedding nanoparticles using gas tungsten arc welding, Manuf. Mater. Process 4 (2), 2020, 29, https://doi.org/10.3390/jmmp4020029.

23. L. C. Zhang, L. Y. Chen, L. Wang, Surface modification of titanium and titanium alloys: technologies, developments, and future interests, Adv. Eng. Mater. 22, 2020, 1–37,

24. U. Karakılınç, B. Ergene, B. Yalçın, K. Aslanta¸S, A. Erçetin, Comparative analysis of minimum chip thickness, surface quality and burr formation in micro-milling of wrought and selective laser melted Ti64, Micromachines (Basel), 14 (6), 2023, 1160, https://doi.org/10.3390/mi14061160.

25. X. Han, J. Ma, A. Tian, Y. Wang, Y. Li, B. Dong, X. Tong, X. Ma, Surface modification techniques of titanium and titanium alloys for biomedical orthopaedics applications: a review, Colloids Surf. B Biointerfaces 227, 2023, 113339.

26. I. P. Okokpujie, L. K. Tartibu, H. O. Musa-Basheer, Effect of coatings on mechanical, corrosion and tribological properties of industrial materials: a comprehensive review, J. Bio. Tribo Corros. 10, 2024, 2, https://doi.org/10.1007/s40735-023- 00805-1.

27. N. Kaczmarczyk, J. Szczurek, B. Babiarczuk, P. Gronowicz, M. Paszkowski, M. Kowalski, B. Borak, W. Jones, J. Detyna, J. Krzak, Thin flm quality of sol–gel SiO_2 coatings prepared on Ti6Al4V depending on their composition and titanium substrate preparation, J Mater Sci, 2025, 60:13974–14004.

28. A. Knaislova´, D. Horkavcov´, E. Jablonska´, D. Vojtech, Sol-gel TiO_2-based coatings in 3D printed porous Ti-6Al-4V alloy structures as efficient antibacterial drug delivery systems: Thorough structural and biological characterization, Applied Surface Science Advances, 29, 2025, 100816.

29. P. Bulkin, D. Daineka, D. Kouznetsov, B. Drevillon, Deposition of optical coatings with real time control by the spectroellipsometry, Eur. Phys. J. Appl. Phys. 28, 2004, 235-242.

30. Kotlikov E. N., Lavrovskaya N. P., Tenev T. K., Milushev I. K., Aluminum oxide (Al_2O_3) optical films and their applications in the ultraviolet region of the spectrum. Journal of Optical Technology, 89, 12, 2022, DOI:10.1364/JOT.89.000752, 752-756.

31. E. Stoyanova, P. Levicharov, K. Antonova, I. Miloushev, T. Tenev. Design and elaboration of various multilayer beam splitters. Journal of Physics: Conference Series, 2436, 2023, ISSN:1742-6596, DOI:10.1088/1742-6596/2436/1/012006.

32. Christova K., Maslyanitsyn I. A., Miloushev I., Shigorin V. D., Tenev T., Voronov V.. Second Harmonic Generation in Thin Zinc Sulfide Films. Physics of Wave Phenomena, 26, 1, Allerton Press, Inc., 2018, ISSN:ISSN 1541-308X, DOI:10.3103/S1541308X18010028, 9-15.

33. Tenev T. K., Miloushev I. K., Peyeva R. A., Mirror coatings for eye-safe laser generation. Journal of Physics: Conference Series, 223, IOP, 2010, DOI:10.1088/1742-6596/223/1/012021, 012021.

34. H. Fujiwara, Spectroscopic ellipsometry, Principles and applications, John Wiley &Sons Ltd., 2007.

35. M. Canepa, "A surface scientist's view on spectroscopic ellipsometry, Springer Series in Surface Sciences, 2013, 99-135.

36. C. Cobet, Ellipsometry: A Survey of Concept, Springer Series in Surface Sciences, 2014, 1-26.

37. M. Losurdo, and K. Hingerl, Ellipsometry at the Nanoscale (Springer Berlin Heidelberg, 2013). 11. H. Arwin, "Spectroscopic ellipsometry and biology: Recent developments and challenges," Thin Solid Films 313-314, 764-774 (1998).

38. J. A. Woollam, B. Johs, C. M. Herzinger, J. Hilfiker, R. Synowicki, and C. L. Bungay, Overwiew of variable angle spectroscopic ellipsometry, Part I. Basic theory and typical applications, Proceeding of the 44th SPIE meeting CR72, 1999, 3-28.

39. J. A. Woollam, B. Johs, C. M. Herzinger, J. Hilfiker, R. Synowicki, and C. L. Bungay, Overwiew of variable angle spectroscopic ellipsometry, Part II. Advanced applications, Proceeding of the 44th SPIE meeting CR72, 1999, 29-58.

40. H. Arwin, Ellipsometry on thin organic layers of biological interest: characterization and applications, Thin Solid Films 377-378, 2000, 48-56.

41. S. Dligatch, R. P.Netterfield, and B. Martin, Application of in-situ ellipsometry to the fabrication of multi-layer optical coatings with sub-nanometre accuracy, Thin Solid Films 455-456, 2004, 376-379.

42. J. Li, N. J. Podraza, and R. W. Collins, Real time spectroscopic ellipsometry of sputtered CdTe, CdS, and CdTe1-xSx thin films for photovoltaic applications, Physica status solidi (a), 205, 2008, 901-904.

43. St. Rusev, Ellipsometry-apparatus, inverse problem and some applications, Dissertation for the degree of Doctor of Science, Sofia, 2014.

The article was completed with the support of the Project - No. KP-06-N57/5, 2021