Functional Inorganic Oxide Layers

by

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Summary of Ph.D. Thesis

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I. Introduction and objectives

In recent years, functional inorganic oxide layers have played a crucial role in research topics due to their unique properties and potential applications. Among these materials, aluminum oxide and vanadium oxides have been extensively studied for their high chemical stability [1-2], thermal resistance[3,4], good absorption ability [5-6], and excellent catalytic effect [7-8].

This research aims to contribute to the current understanding of the synthesis and characterization of transparent γ-Al_2O_3 and vanadium (IV, V) oxide thin films and their potential applications in environmental protection. The results of this study will provide valuable information for the development of environmentally friendly technologies that utilize these materials.

The purpose of the study is to investigate the synthesis techniques and methodologies to produce γ-Al_2O_3 and vanadium oxide (IV, V) thin films, as well as to characterize their physical and chemical properties. The task was to identify the optimal conditions for their production for environmental protection applications.

The synthesis of γ-Al_2O_3 and vanadium oxide (IV, V) thin films were realized by using various methods such as sol-gel, additive-assisted deposition, and dip coating in these experiments.

II. Motivation

The study of γ-Al_2O_3 and vanadium oxide (IV, V) thin films is significant due to their unique properties and potential applications in diverse fields such as environmental protection, energy conversion, and electronics. Thin films of these materials offer distinct advantages, such as high chemical stability, excellent catalytic activity, and efficient energy conversion and storage. Therefore, investigating the synthesis and characterization of these materials can help to develop new and improved methods to enhance their performance and application.

Furthermore, the synthesis and characterization of Al_2O_3 and vanadium oxide (IV, V) thin films are complex and challenging fields that require a deep understanding of underlying chemical and physical processes. Therefore, studying these materials provides an opportunity to gain insights into these processes and contribute to the development of new methods for synthesizing and characterizing these materials.

III. Material and methods

The first part of this study presents the synthesis of various layers from boehmite, Al_2O_3, Al nitrate, Al acetate, Al isopropoxide by sol-gel methods or additive-assisted deposition. The layers were deposited on quartz substrates via dip-coating and then heated. The properties of the layers were characterized using transmittance measurements, grazing incidence X-ray diffraction (GIXRD), and scanning electron microscopy (SEM).

In the second part of this study, sol-gel synthesis was used to prepare vanadium oxide thin films, with thermal decomposition and melting processes for comparison. Various precursors and chemical additives were tested to optimize layer quality. Dip-coating techniques were employed to fabricate the films on glass substrates at 400 °C. Characterization methods such as scanning electron microscopy, reflection optical microscopy, grazing incidence X-ray diffraction, UV-visible spectroscopy, and nuclear magnetic resonance spectroscopy were used to analyze the prepared films.

IV. Results and discussion

Transparent γ-Al_2O_3 thin layer [9]

Comparison of the colloidal suspensions (sol or slurry) with gel-like systems as precursors for layer creation has verified the application of gel-like systems results in better layers quality. The 3D network of the gel systems ensures the formation of a continuous film and allows the exact regulation of the layers thickness.

Boehmite and Al_2O_3 sol solutions were used as precursors for dip-coating techniques to produce thin layers. The research finds that boehmite sol-derived layers have better transparency and quality compared to Al_2O_3 sol-derived layers. Acetic acid (HAc) was identified as the most efficient acid for improving layer quality and resulting in 110-120 nm layer thickness. The optimal heat treatment temperature for boehmite transformation to crystalline γ-Al_2O_3 is 600 °C.

The best quality of layer (~90% transmittance, 50-60 nm thickness, perfect covering) has been achieved by the sol-gel technique starting from Al nitrate or Al acetate. The use of Al nitrate results in a nanolayer with an extremely smooth surface and the layer keeps its transmittance over 80% after 500 hours of application.

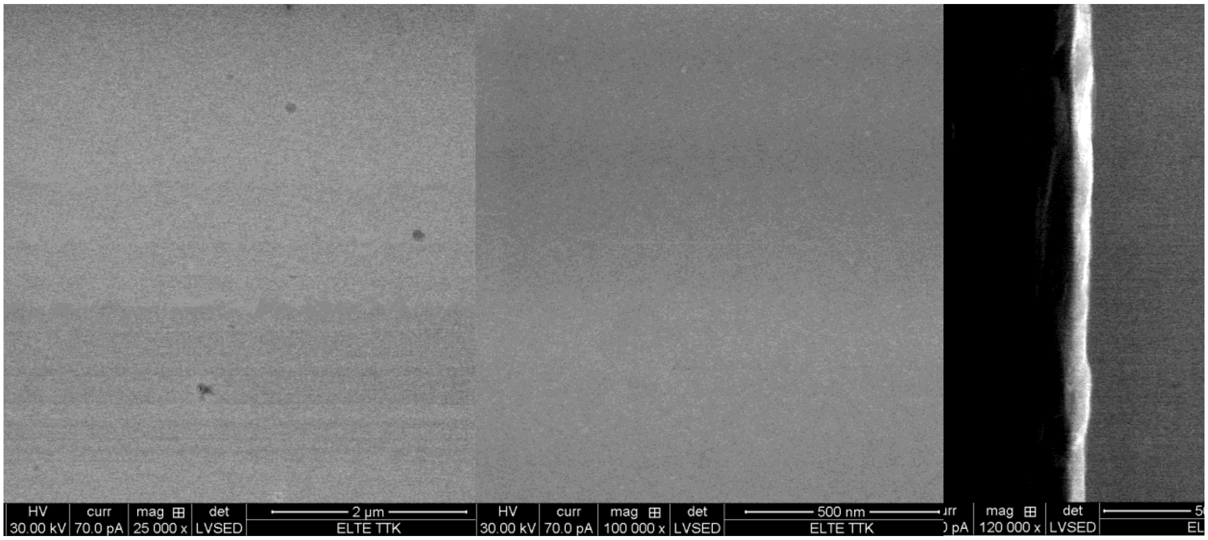

Figure 1. SEM of sol-gel derived layers prepared from Al nitrate.
Magnification: 25 000x; 100 000x, 120 000x. The layer thickness is 55-65 nm.[9]

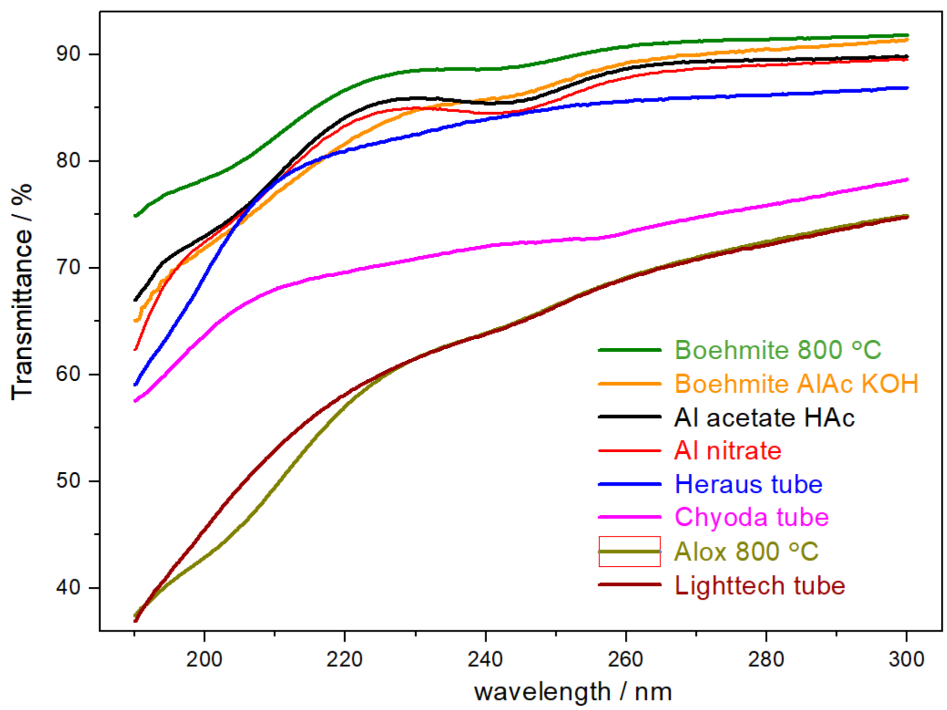

Figure 2. Comparison of the transmittance of γ-Al_2O_3 layers prepared by various techniques with commercial products (Heraus, Chyoda, and Lighttech)

Vanadium oxide (IV,V) thin layer [10]

This study investigates the synthesis of vanadium oxide thin films using the sol-gel method. Precursors such as ammonium metavanadate, ammonium decavanadate, VO_2, and vanadyl acetylacetonate were used, along with various additives (HNO_3, HCl, citric acid, oxalic acid, and ascorbic acids as a catalyst) and surfactants. Dip-coating was employed for film fabrication on glass substrates at 400°C.

The use of NH_4VO_3 and HNO_3 results in the best, complete and transparent layers. XRD results indicate that the thin films have orthorhombic structures with a preferred orientation along (101) direction. For thin films produced from oxalic acid, nitric acid, and ethyl acetate, the measured band gap values are 1.98 eV, 2.11 eV, and 2.17 eV, respectively.

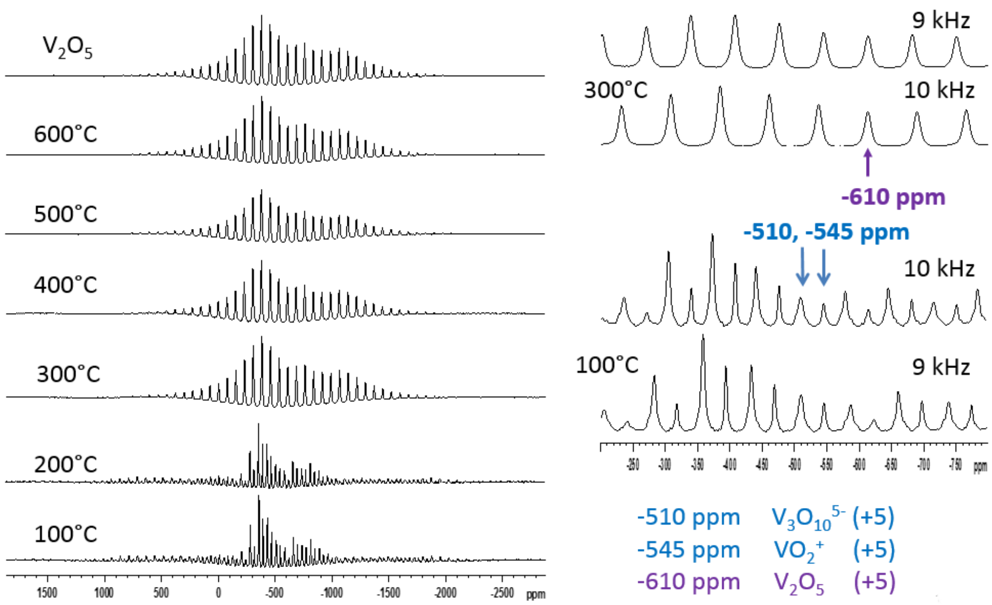

Figure 3: ^{51}V NMR spectra of layer synthesized from NH_4VO_3 and catalysed with HNO_3 vs temperature. [10]

The other aim was to adjust various V^{IV}/V^{V} ratios. The ratio of V^{IV} and V^{V} possesses a substantial role in the electric properties. The complete and homogeneous layers can be prepared from VO_2 and vanadyl (IV) acetylacetonate in the presence or absence of reducing agents. The V^{IV} oxidation state could be retained only in N_2 atmosphere at higher temperatures.

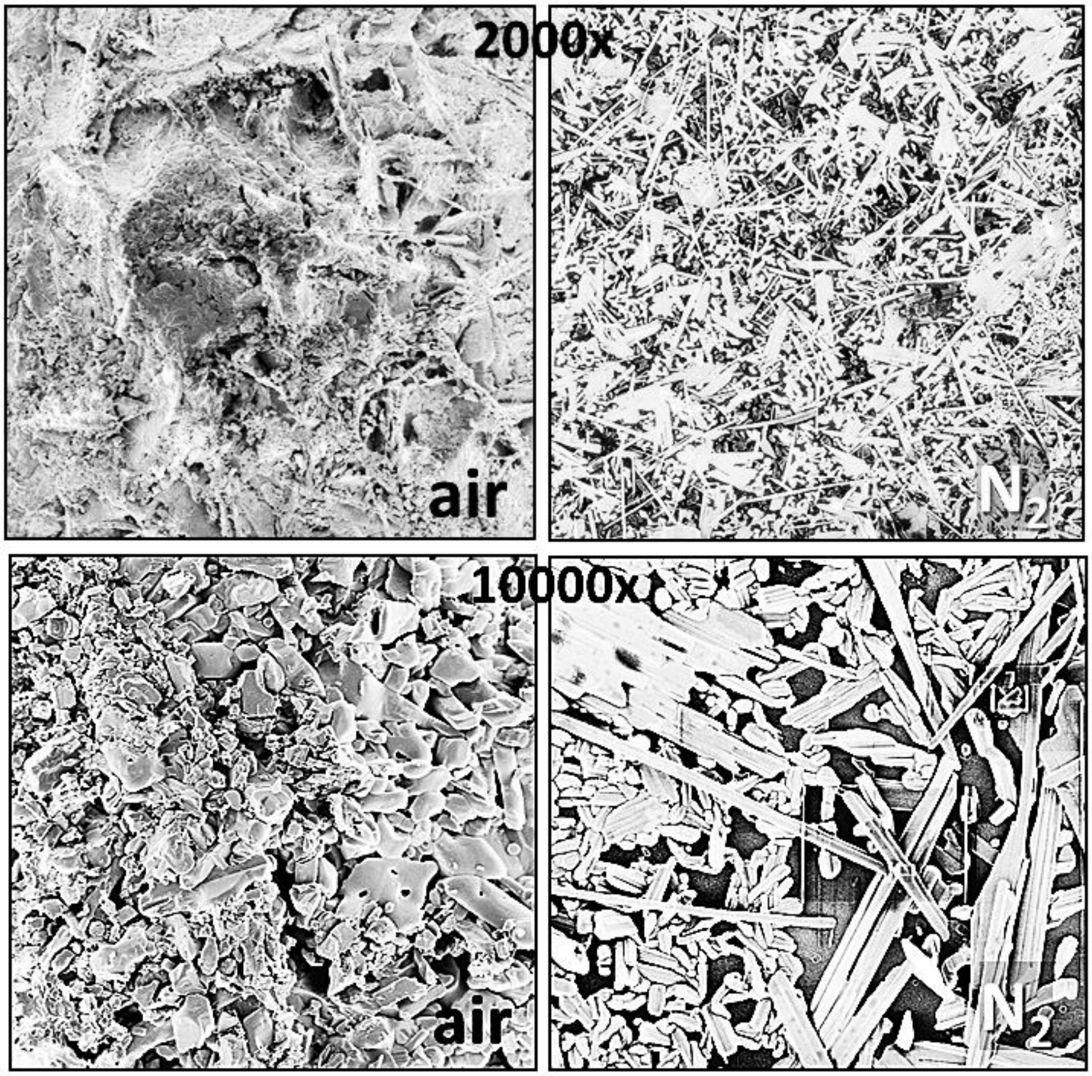

Figure 4. SEM images. The samples were prepared from $VO(acac)_2$ and heated in air and N_2 atmosphere[10]

V. Thesis points

- Two synthesis routes were successfully developed to synthesize a transparent **γ-Al_2O_3 thin layer** as a protective or absorbent layer in environmental protection.
- A uniform and well-distributed nanolayer with exceptional transparency, including in the ultraviolet range, can be fabricated using boehmite sol in the presence of acetic acid.
- The best quality layers (~90% transmittance, 50-60 nm thickness) could be achieved using sol-gel techniques with Al nitrate or Al acetate. Application of Al nitrate yields extremely smooth surfaces and maintaining over 80% transmittance after 500 hours of industrial application.
- Our newly developed technique has already been implemented as a protective layer in LightTech Kft in spot amalgam lamps on quartz bulbs.

- We successfully identified the optimal chemical conditions for preparing **V^V-containing layers** using the sol-gel technique from NH_4VO_3 as the V precursor and HNO_3 as the catalyst.
- Fully transparent layers featuring orthorhombic structures and a preferred orientation along the (101) direction can be successfully fabricated.
- Complete and homogeneous layers with various V^{IV} and V^V ratios could be prepared from VO_2 and vanadyl (IV) acetylacetonate in the presence or absence of reducing agents.
- The application of ^{51}V MAS NMR spectroscopy could be solved in monitoring and controlling the oxidation state of vanadium.

VI. References

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[10] M. Bouzbib, J. Rohonczy, and K. Sinkó, “Effect of vanadium precursor on dip-coated vanadium oxide thin films,” *J. Sol-Gel Sci. Technol.*, vol. 105, no. 1, pp. 278–290, 2023, doi: 10.1007/s10971-022-05965-z.

VII. Publications related to the PhD thesis

- **M. Bouzbib**, A. Pogonyi, T. Kolonits, Á. Vida, Z. Dankházi, and K. Sinkó, "Sol – gel alumina coating on quartz substrate for environmental protection," *J. Sol-Gel Sci. Technol.*, pp. 262–272, 2020, doi: 10.1007/s10971-019-05193-y.

- **M. Bouzbib**, M. El Marouani, and K. Sinkó, "Effect of various additives on aluminum oxide thin films prepared by dip coating, thermal behavior, kinetics and optical properties," *J. Eur. Opt. Soc. Publ.*, vol. 17, no. 1, 2021, doi: 10.1186/s41476-021-00170-x.

- **M. Bouzbib**, J. Rohonczy, and K. Sinkó, "Effect of vanadium precursor on dip-coated vanadium oxide thin films," *J. Sol-Gel Sci. Technol.*, vol. 105, no. 1, pp. 278–290, 2023, doi: 10.1007/s10971-022-05965-z.

Selected conference

- **M. Bouzbib** and K. Sinkó , Transparent Gamma Al_2O_3 Layer for Environmental Protection, Mai 2018, Eger (Hungary), 11th Conference on Colloid Chemistry 11CCC.

- **M. Bouzbib** and K. Sinkó, Aluminum oxide thin films synthesis prepared by dip coating, Jully 2018, Budapest (Hungary), FEMS Junior EROMAT.