

DEPOSITION TECHNOLOGIES FOR OBTAINING THIN FILMS WITH SPECIAL PROPERTIES

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ABSTRACT

The properties of metallic materials can be improved by deposition of materials. The coating has a tear strength and better hydro-abrasive corrosion. The thin layer deposition has a thickness of less than 10 micrometers.

When speaking about deposition technologies, it is not just about deposited thin layers, but the whole assembly (layer / substrate), therefore the degree of adherence and the costs of making such a substrate have to be taken into account and the whole must be much more powerful than anything taken separately.

In this paper we presented several methods of thin film deposition. We also highlighted some of the advantages and disadvantages of several deposition methods.

Keywords: Deposition method, thin layers, substrate, SEM

1. Introduction

The surface is the most important part of all components, as the most defects appear here, especially those caused by corrosion.

The surface may also have important functional attributes, it is not limited to chemical and mechanical properties, but also features thermal, electronic, magnetic and optical characteristics, influencing the choice of the material.

Depositions of thin films are used worldwide in various technologies. These deposition technologies have been successfully applied for a long time, specifically since 1400 when their first use is registered [1].

Along with traditional technologies for obtaining thin layers, we witness the development, improvement and expansion of deposition, a modern technique of the physical and physico-chemical methods, which ensure high purity and strong adhesion through a wide variety of processes for coatings [1].

The involved technologies are based on vacuum processes, with a low environment impact.

Also, from the economic point of view, these technologies have an increased efficiency, compared to the traditional methods.

Therefore, in recent years there has been a dramatic increase in using these technologies in industrial applications.

2. Theoretical contributions

Thin layers can be produced by mechanical, chemical procedures, and by condensation of the gaseous phase. The work environment is one of the basic factors of depositing, which strongly influences the composition and structure of the deposited layers.

The environment necessary for the gas-phase condensation method is vacuum or pressure controlled atmosphere, reducing the average deployment submission process that ensures the achievement of reproducible layers unaffected by impurities.

Thin films vacuum deposition methods are classified as follows:

- Physical vapor deposition methods (PVD) by pulse laser deposition (PLD);
- Chemical vapor deposition method (CVD):

- CVD deposition method at high temperatures (HTCVD);
- CVD deposition method based on organo-metallic compounds (MOCVD);
- CVD deposition method of assisted plasma (PACVD).

2.1. Physical vapor deposition methods (PVD)

2.1.1. Pulsed laser deposition

Pulse laser deposition is the technique where a high power pulsed laser beam is focused inside a vacuum chamber in order to hit a target of the material that is to be deposited (Figure 1).

This material is vaporized from the target, in a plasma plume, which deposits it as a thin film on a substrate.

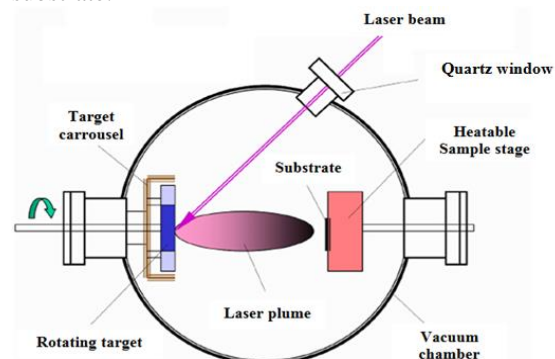


Fig. 1. Schematic diagram of the pulse laser deposition [2]

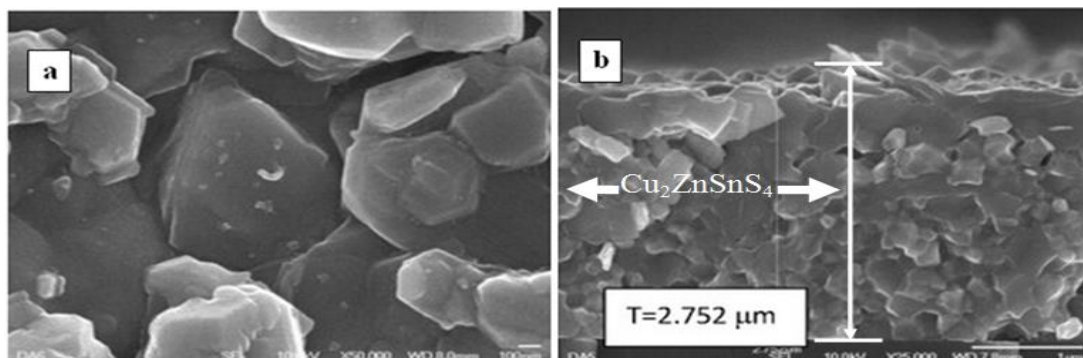


Fig. 2. SEM images of $\text{Cu}_2\text{ZnSnS}_4$ thin layers obtained by using the coated PLD method: a) surface image for the thin layer; b) cross sections through coating and substrate layer [3]

Figure 2(a) shows the SEM image of the annealed $\text{Cu}_2\text{ZnSnS}_4$ thin films for various deposition times. It is observed that, due to recrystallization with annealing, the resulting grain size is increased, compared to the as-deposited film.

Figure 2(b) shows the cross-sectional FE-SEM image of the annealed $\text{Cu}_2\text{ZnSnS}_4$ thin films.

The thickness of film is found to vary between 0.525 and 2.902 μm , which indicates that deposition time is a vital parameter to increase thickness indirectly, and to increase efficiency [2].

2.2. Chemical vapor deposition method (CVD)

2.2.1. High temperature chemical vapor deposition

The thin layer deposition methods work at high temperatures in the range of 2100-2300 $^\circ\text{C}$ and a schematic diagram of this method is shown in Figure 3. With HTCVD, crystals can be produced with high

quality, large SiC diameter and costly efficient, opening new markets and applications.

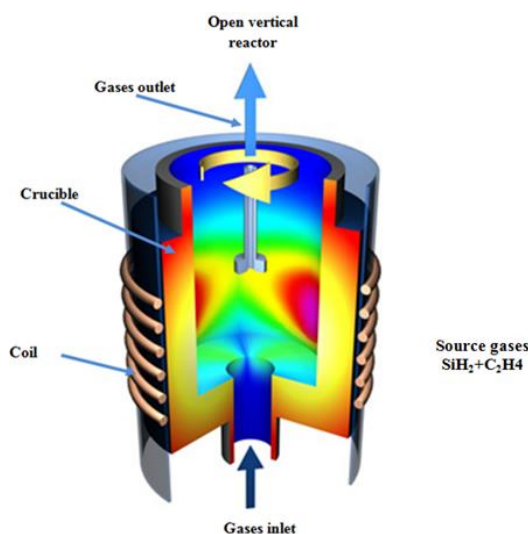


Fig. 3. Schematic diagram of the method of high temperature CVD (HTCVD)

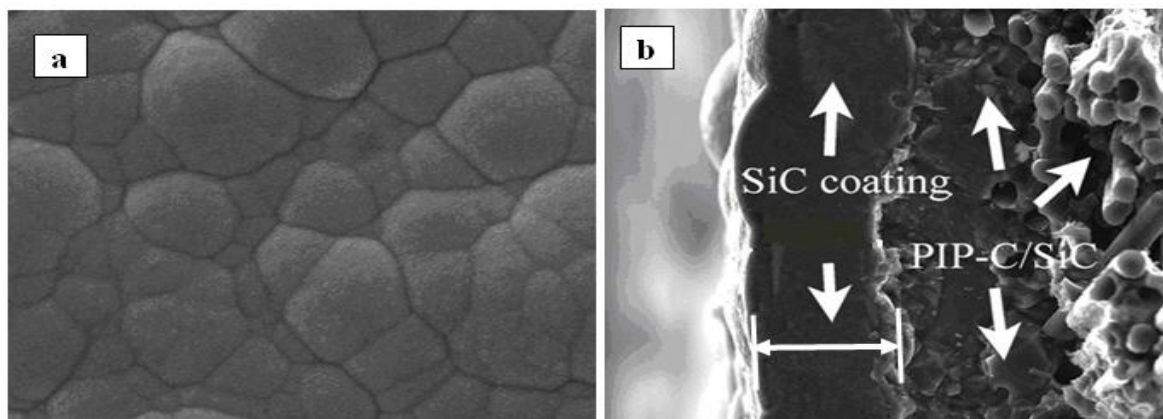


Fig. 4. SEM images of SiC thin layers obtained by using the coated HTCVD method: a) surface image for the thin layer; b) cross sections through coating and substrate layer [4]

Figure 4 shows the cross-section and surface morphology of HTCVD coated samples. The SiC coating has a thickness of about 30 μm and a good adhesion to C/SiC composites, Figure 4(a).

No obvious interlinear or impenetrable cracks can be observed.

The high magnification image in Figure 4(b) shows that the surface is closely stacked by spherical grains, with grain size in a range of 10-30 μm .

The coating shows a dense surface with no visible micro cracks. The SiC layer can improve the compactness of the coating and provide good oxidation protection for C/SiC composites at high-temperature [3].

High temperature, specific to HTCVD process, is a major drawback, it adversely affects the structure of the substrate, especially when it is steel. To eliminate the negative effects, both prior and subsequent heat treatments are required to reduce the negative effects of overheating [4].

2.2.2. Metalorganic chemical vapor deposition

The MOCVD method is quite simple and it consists in dissolving the organic metal compound in an organic solvent. Fig. 5 shows the diagram of the principle of this method.

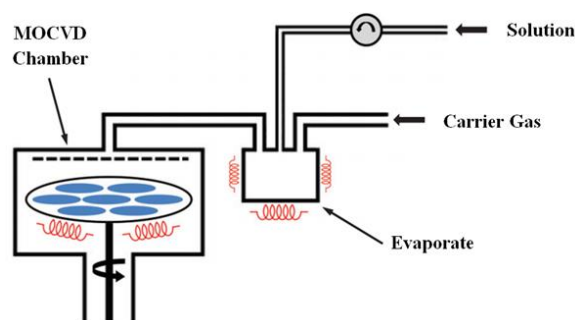


Fig. 5. Schematic diagram of MOCVD deposition method [5]

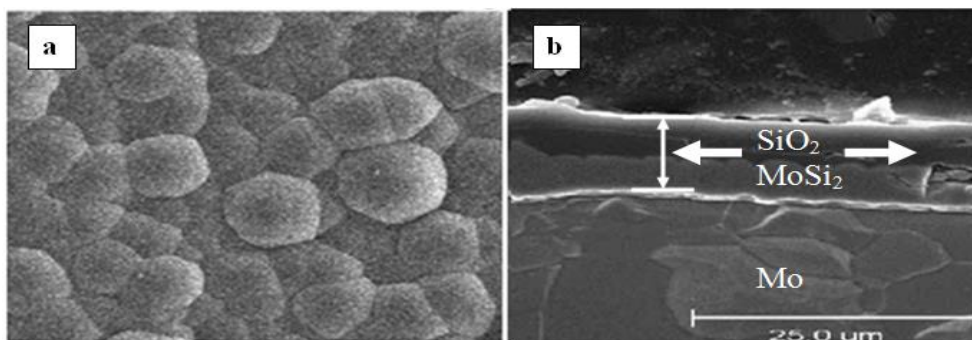


Fig. 6. SEM images of MoSi₂ thin layers obtained by using the coated MOCVD method: a) surface image for the thin layer; b) cross sections through coating and substrate layer [6]

The micrographs were obtained by a scanning electron microscope (SEM).

Figures 6(a) and (b) show the surface morphology of the specimens before and after the different stages of coatings.

The original surface of the substrate appeared to be smooth. Several cracks on the surface of the MoSi₂ coating were observed from high magnification SEM. The observation was not unusual as MoSi₂ films produced by CVD of Si on a Mo substrate are often characterized by cracks and voids [7, 8].

On further coating with silica, the surface adopted equiaxed grain morphology. Cross-sections of the coating after 3 h at 620 °C were analyzed by SEM.

As shown in figure 6(b), this micrograph reveals that the coating thickness was about 7.5 µm at 620 °C [6].

An advantage of this method is the replacement of some donors using metal organic metal compounds.

By this replacement with metal organic compounds, the deposition temperature will be greatly decreased, reaching 400 °C.

2.2.3. Plasma assisted chemical vapor deposition

In this method, gas phase reactions are catalyzed by the CVD process specific to the presence in the reactor of cold plasma, produced by the glow discharge luminescence similar to the luminescence produced by the ion nitriding.

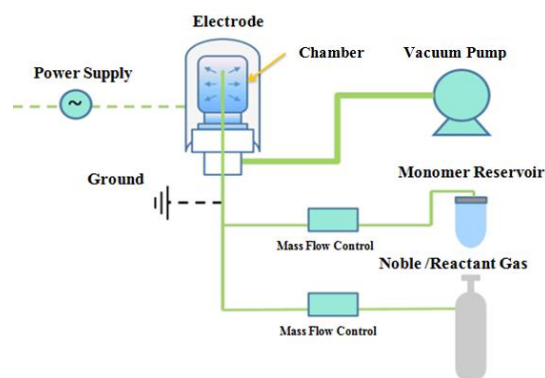


Fig. 7. Schematic diagram of deposition method [9]

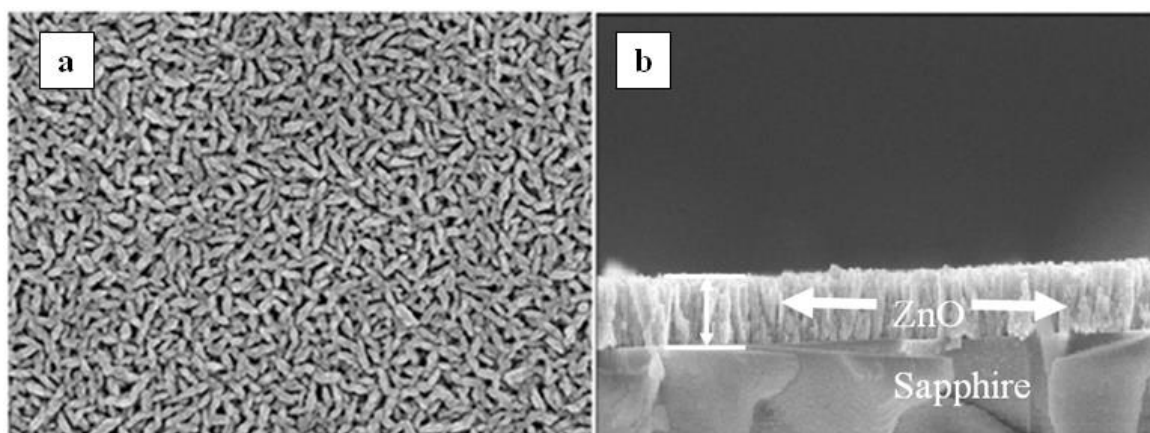


Fig. 8. SEM images of ZnO thin layers obtained by using the coated PACVD method: a) surface image for the thin layer; b) cross sections through coating and substrate layer [10]

Figure 8(a) represents the cross-section of the scanning electron microscopy (SEM) image for ZnO thin film grown at 185 °C.

Figure 8 (b) shows the top view of SEM image for ZnO thin films grown at 160 °C. The thickness of ZnO thin film is about 200 nm and a pillar-like structure can be found [11] in Figure 8(a).

During deposition, the atomic kinetic energy is primarily determined by the deposition temperature. Figure 8(b) exhibits a collapsed pillar structure due to the low kinetic energy and weak intensity.

3. Conclusions

From this study of layers, which presents different methods for obtaining thin films and some surfaces and depth morphology, we can conclude the following:

1. By the PLD method, high quality coatings with a wide variety of properties can be obtained.
2. The quality of ZnO thin layers is improved when increasing the sputtering power.

3. The HTCVD deposition method is not much used as high temperature affects the substrate.
4. The MOCVD method is used for the deposition of thin films when the deposition temperature is low so it affects the layer.
5. The PACVD deposition method is an advanced and widely used method.

Therefore, the choice of the method of submission shall consider both the nature of the deposited layer and the base material.

Acknowledgements

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References

- [1]. G. Vermeesan, E. Vermeesan, *Introducere in ingineria suprafetelor (Introduction to surface engineering)*, Ed. Dacia Cluj-Napoca, 1999.
- [2]. G. Subramanyam, M. W. Cole, N. X. Sun, T. S. Kalkur, N. M. Sbrockey, G. S. Tompa, X. Guo, C. Chen, S. P. Alpay, G. A.

Rossetti Jr., K. Dayal, L. Q. Chen, D. G. Schlom, *Challenges and opportunities for multi-functional oxide thin films for voltage tunable radio frequency/ microwave components*, Journal of Applied Physics 114, 191301, 2013.

[3]. A. V. Moholkar, S. S. Shinde, A. R. Babar, Kyu-Ung Sim, H. K. Lee, K. Y. Rajpure, P. S. Patil, C. H. Bhosale, J. H. Kimb, *Synthesis and characterization of Cu₂ZnSnS₄ thin films grown by PLD: Solar cells*, Journal of Alloys and Compounds, 509, 2011.

[4]. X. Yang, L. Wei, W. Song, Z. Bi-feng, C. Zhao-hui, *Microstructures and mechanical properties of CVD-SiC coated PIP-C/SiC composites under high temperatur*, Surface & Coatings Technology, 209, p. 197-202, 2012.

[5]. G. Subramanyam, M. W. Cole, N. X. Sun, T. S. Kalkur, N. M. Sbrockey, G. S. Tompa, X. Guo, C. Chen, S. P. Alpay, G. A. Rossetti Jr., K. Dayal, L.Q.Chen, and D. G. Schlom, *Challenges and opportunities for multi-functional oxide thin films for voltage tunable radio frequency/ microwave components*, Journal of Applied Physics 114, 191301, 2013.

[6]. E. K. Nyutua, M. A. Kmetzc, S. L. Suiba, *Formation of MoSi₂-SiO₂ coatings on molybdenum substrates by CVD/MOCVD*, Surface & Coatings Technology 200, p. 3980-3986, 2006.

[7]. H. O. Pierson, *Handbook of Chemical Deposition*, Noyes publications, Park Ridge, NJ, 1999.

[8]. J.-K. Yoon, J.-K. Jee, J.-Y. Byun, G.-H. Kim, Y.-H. Paik, J. S. Kim, *Surf. Coat. Technol.*, 160, 2002.

[9]. ***, <http://www.sio2med.com/technology-plasma-deposition.html>.

[10]. P.-H. Lei, H. M. Wu, C.-M. Hsu, *Zinc oxide (ZnO) grown on flexible substrate using dual-plasma-enhanced metalorganic vapor deposition (DPEMOCVD)*, Surface & Coatings Technology, 206, p. 3258-3263, 2012.

[11]. I. Volintiru, M. Creatore, B. J. Kniknie, C. I. M. A. Spee, M. C. M. van de Sanden, *J. Appl. Phys.*, 102, 043709, 2007.