

# Studies of Porosity in Ceramic Titanium Nitride Oxide PVD Coatings

Zhonghuai Wang, Michael Akkaoui  
Tanury Industries, 6 New England Way Lincoln RI 02865

## ABSTRACT

This paper summarizes a particular growth defect known as voids in physical vapor deposition (PVD) coatings. We focused on ceramic Titanium Nitride Oxide (TiNO<sub>x</sub>) coatings by conventional cathodic arc vaporization technology. Cathodic Arc deposition can sometimes produce large amounts of microdroplets and macroparticles. TiNO<sub>x</sub> exhibits many positive attributes:

1. A wide color pallet with different visible light wavelengths ranging from 400 nm (violet) to 700 nm (red).
2. High heat resistance for tools or sharp blades applications.
3. These films can be dielectric with high durability with improved scratch-resistance compared with pure metal.
4. Certain films have anti-bacterial properties and can be biocompatible for medical applications.

In our evaluation, cathodic arc deposition was utilized to deposit TiNO<sub>x</sub> coating on a polished brass substrate plated with nickel and chrome. While the films are typically very brilliant in color and appearance, we sometimes see white spots (or voids) the size of ~ 0.3 μm in diameter. These coating defects are caused by arc macro particles in the film and can be seen by the naked eye. While it may be difficult to understand the direct cause, our investigation has shown that the white voids had no coating present and or poor adhesion exposing the substrate layer. We utilized a scanning electron microscope (SEM) with Energy Dispersive X-ray analyzer (EDS) to evaluate the voids. The SEM showed that the poor coating area had a variety of foreign elements such as Fluorine, Aluminum, Silicon, Calcium, Potassium, Sodium or Chlorine from spot to spot instead of elements from plating process or the PVD coating process. In order to investigate this problem, we employed different types of plating or cleaning processes including Argon or oxygen plasma pretreatment. Further, several PVD coating parameters were modified to improve the coating quality. This paper will discuss these experiments and their results.

## INTRODUCTION

Titanium Nitride Oxide (TiNO<sub>x</sub>) coatings showed many interesting properties, such as low friction coefficient with about 30% lower compared with pure metal. Coatings have a

high melting temperature with applications for tools and sharp blades that extend the life cycle. Other benefits include a high degree of hardness and biological compatibility. Further, these films can have wide color choices for decorative coatings covering all visible light wavelengths ranging from 400 nm (violet) to 700 nm (red). PVD TiO<sub>x</sub> and TiNO<sub>x</sub> coatings have replaced certain precious metals with lower cost and increased scratch resistance to improve lifetime performance. Crystalline titanium dioxide (TiO<sub>2</sub>) thin films, especially films with an abundance of anatase phase show super-hydrophilic and photocatalytic activities after exposure to ultraviolet light. TiO<sub>2</sub> with high refractive index between 2.3 and 2.5 exhibit strong color effects based on thin film interference [1].

We, at Tanury, constantly conduct research to develop novel functional and decorative coatings with extremely high wear properties to satisfy our customer requirements and expand our business applications. Further our R&D teams are working to trouble improve our processes and coating quality.

## METHOD:CATHODIC ARC EVAPORATION TECHNOLOGY

**Problem:** The problem that we have visualized with these types of coatings is the appearance of these small white spots (or voids) in the film approximately ~ 0.3μm in diameter which can be seen with the naked eye. These macroparticles and/or macro droplets lead to a severe degradation in film quality resulting in film porosity.

**Question:** What are the potential causes of these white spots or voids in the film?

While there are many substrates used for PVD such as: stainless steel, steel, and nickel/ chrome plated materials. Here, the substrate utilized was brass. The brass substrate was polished and electroplated with copper, nickel, and chrome to create a hard-decorative film as a base for the PVD application. In order to improve adhesion, corrosion and scratch resistance, chrome was selected as the best interlayer or base for the PVD film. Our goal was to find the most effective chemical or mechanical method that would activate the substrate surface to create the best adhesion characteristics. Finally, we need to be able to form linkages between the coating layer and the substrate. All of these points mentioned above are necessary to achieve film

adhesion optimization. In this paper, SEM/EDX were utilized to diagnose and locate poor coating areas to provide deeper understanding of the film characterization in these white spot or void areas.

### PVD Layer Deposition

The arc vapor deposition process was used to deposit the  $\text{TiNO}_x$  films. Figure 1 shows a photograph of the inside of a typical batch coater utilizing cathodic arc deposition[2]. Figure 2 illustrates the basic operating principle of the coating machine. Located at the top left of the picture is the Arc power supply. A high current is applied across the metallic target in order to vaporize the target material. The DC bias power supply at the top right adds a negative bias to the coated parts to increase adhesion, with increasing negative bias voltage the ion energy is increased to make the thin film denser and improving corrosion resistance. Process steps include [3]: (1) After loading, the deposition chamber was heated over  $100^\circ\text{C}$  to remove residual water molecules, inorganic or organic particles on the surface in order to assist adhesion. (2) Then, the pumping system remove the air from the chamber to achieve a base pressure less than  $5.0 \times 10^{-5}$  Torr. (3) Next, argon plasma treatment is used to clean the parts through ion bombardment to take out dust, oxides, and contaminants. This is necessary to improve the thin film layer that is adhering to the substrate; (4) In order to improve adhesion, this transition zone process or etch process will be applied before any metal coating process. Here, ions bombard the substrates in order to heat the substrate and dislodge any remaining impurities. Some of the ions are embedded in the surface of the substrate, creating an interlayer to enhance adhesion. Sometimes, chemical bonds will form at this layer. (5) A layer of pure metal is applied to adhere to the substrate to promote wear and corrosion resistance. (6) Finally, arc deposition of the Titanium Nitride Oxide layer (~1500 nm thick) in a mixed Argon, Nitrogen and Oxygen gas atmosphere occurs.

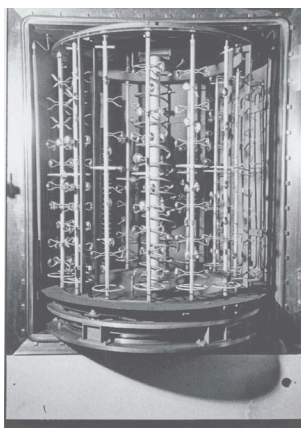


Figure 1. The inside of a batch coating system.

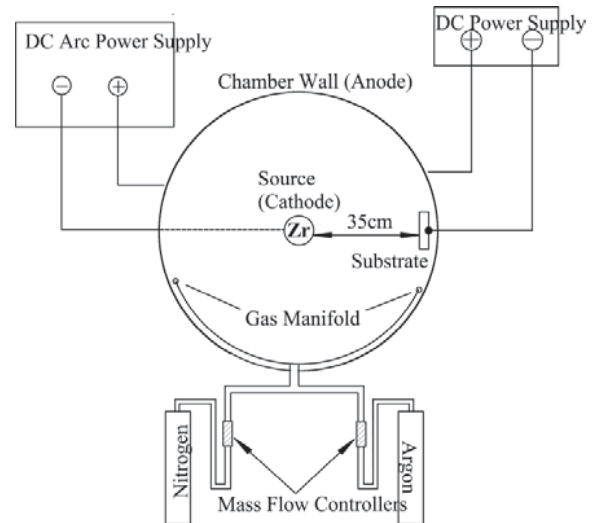
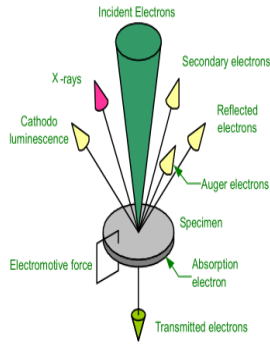


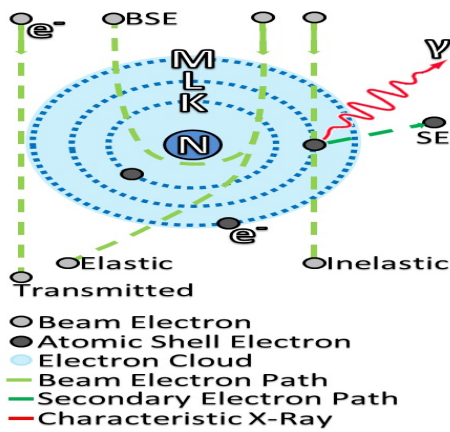
Figure 2. Schematic drawing for the basic operating principle of the coating machine. It includes Arc power supply that applies a current that vaporizes the metalized target, and the DC bias power supply that applies a negative charge to the coated parts to increase adhesion.

### SEM/EDS TECHNOLOGY

JSM-6010 LA (JEOL) SEM was utilized to analyze our coated samples. Figure 3 exemplifies the interactions between electrons and specimens. It should be noted that the SEM/EDS spectra process generates three types of physical phenomena: 1. Secondary electrons, 2. reflected electrons and 3. X-rays. Here, one of the more important phenomena is called characteristic X-ray. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray spectrum. To stimulate the emission of characteristic X-rays from a specimen, a high-energy beam of charged particles such as electrons is focused into the sample being studied. At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron once existed. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell will be released in the form of an X-ray. Figure 4 represents the physics diagram for interaction between the energized electron and atom. The number and energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. The energy of the X-ray is characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted, allows the elemental composition of the specimen to be measured.



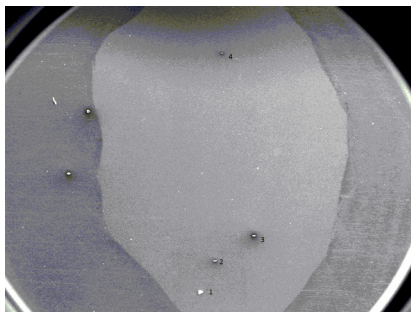
**Figure 3.** Interactions between electrons and the specimen to produce a variety of physical phenomena that can be measured.



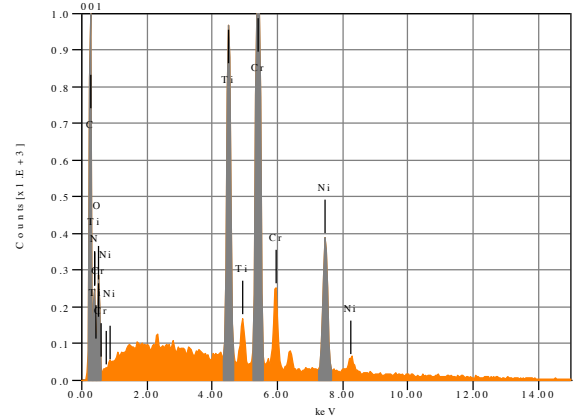
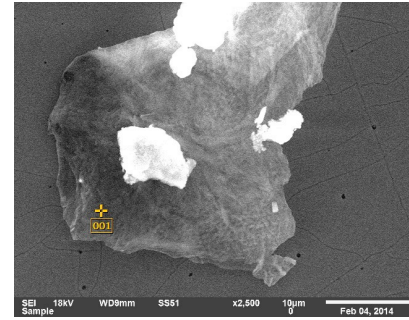
**Figure 4.** Physics diagram for electron beam and specimen interactions.

## RESULTS AND DISCUSSIONS

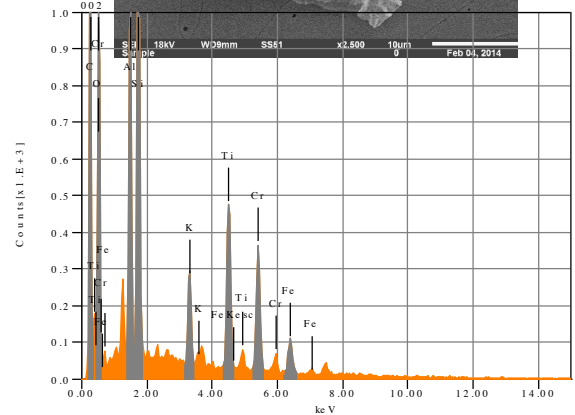
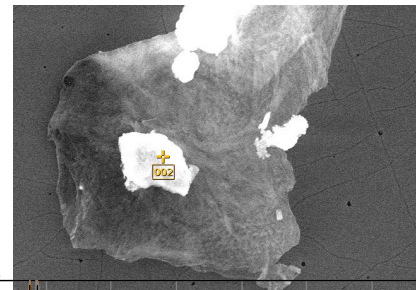
Figure 5 displayed the general SEM view of the coated surface by marking with 1, 2, 3 and 4. This showed typical image of white spots /voids.



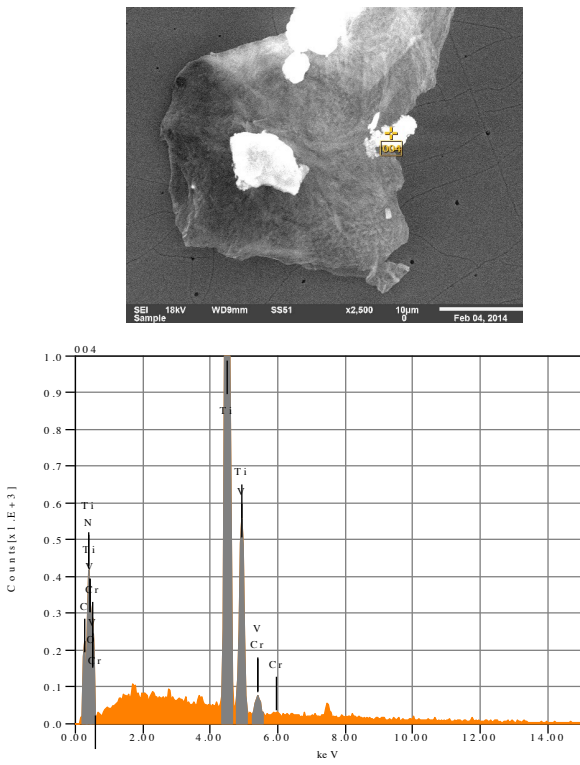
**Figure 5.** Low magnification SEM image showing the Ni/Cr plated base and Ti based coating. Porosity points or voids are marked by 1, 2, 3, 4.



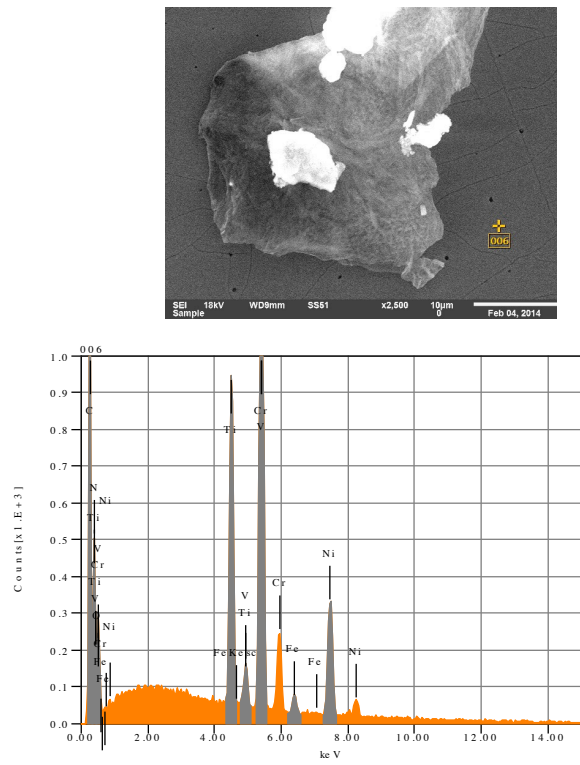
**Figure 6.** SEM image and EDS spectra for point (1) showing that Ni/Cr plated base and Titanium based coating. In this area there is no evidence of any foreign contaminants.



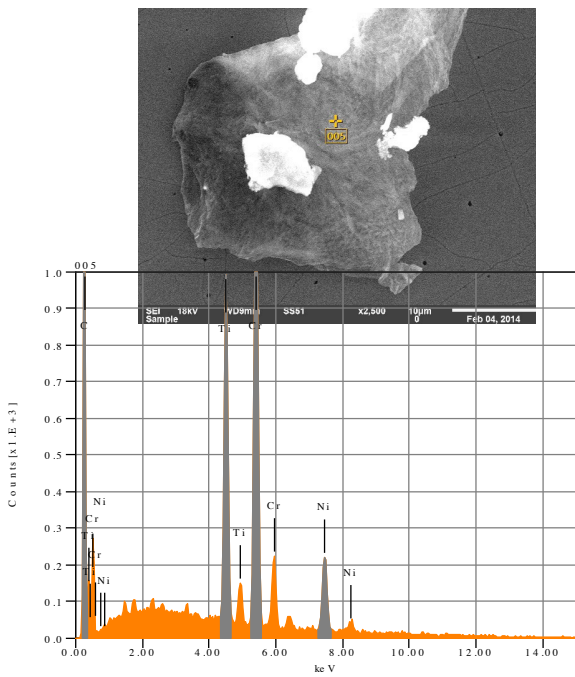
**Figure 7.** SEM image and EDS spectra for point (2) showing that Ni/Cr plated base and Ti based coating. Al, Si, K could be found in this area. Fe was picked up as well. Evidence of contamination could be a primary cause of the void defect.



**Figure 8.** SEM image and EDS spectra for point (4) showing that Ni/Cr plated base and Ti based coatings. There is no evidence of contamination.



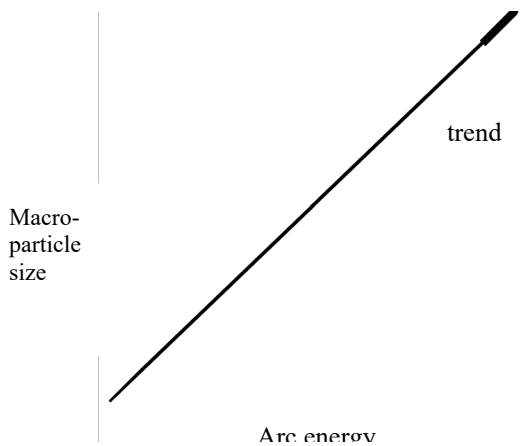
**Figure 10.** SEM image and EDS spectra for coating area (point 6) showing that Ni/Cr plated base and Ti based coatings. Ti, Cr Ni could be seen from the spectra. Vanadium (V) and Iron (Fe) were observed as well, these elements might come from target material.



**Figure 9.** SEM image and EDS spectra for point (5) showing that Ni/Cr plated base and Ti based coatings. There is no evidence of contamination.

Figures 6 to 10 represent points with EDS spectra. From area to area, Ti, Cr and Ni base elements could be found from spectra. Most important to our study are some abnormal elements such as Vanadium (Fig.8), Potassium, Calcium, Aluminum, Silicon, and Iron (Fig.7) are present in the suspect areas. Al and Si elements could be the by-product of surface polishing. V and Fe most probably come from the impurities of the Ti target. Potassium, Calcium or sometimes Chlorine are most definitely from wet plating process. Prior to the PVD layer the plated Cr layer is exposed to air and the surface could be oxidized and hence forming a  $\text{CrO}_x$  layer. Even during the coating process,  $\text{CrO}_x$  might be produced due to titanium-based oxide coating. These will not only reduce the adhesion force between these two layers, but also  $\text{CrO}_x$  itself has more stress or delamination. This explains why some areas showed Oxygen content by EDS spectra. In order to diminish these abnormal elements, different types of plating processes and more effective cleaning and drying processes have been employed with improved results.

Further, from a PVD coating process perspective, macro particles produced by cathodic arc technology could be diminished by changing the stoichiometric structure of coating by adjusting the bias power. Also, experimentation has been conducted using other critical process factors such as gas ratios (Ar and  $\text{O}_2$  ratio) and coating temperatures with limited positive results.



**Figure 11.** Expected trend of macro-particle size with arc energy

The expected result is larger target material particles (macro-particles) generated by the arc as arc energy increases, as shown in Figure 11. This suggests that for large-area coating, there is a greater importance of minimizing arc energy. Stated another way, arc energy could be reduced to minimize arc induced macro-particle size. Arc frequency (rate) could also be dropped to minimize the quantity of arc-induced macro-particles [4] to

improve corrosion resistance. Furthermore, the substrate temperature could be reduced by lowering the heating power and also minimizing energy transferred from the deposited particles using low power in order to achieve more dense amorphous coating with less columnar structure. Another advantage for lowering temperature deposition is to avoid surface oxidation by minimizing arc energy. The question we pose is : “Is the PVD layer compatible with the plated Cr layer?” This can be answered and/or investigated through laying down a PVD Cr layer over plated Cr and then deposit a  $\text{TiO}_x$  or  $\text{TiNO}_x$  layer. The general idea is to grow the coating layer finely, gradually producing a nano-sized ion in the coating stack to obtain a thin film that is denser and has less stress to improve hardness, corrosion, and stress.

DC power supplies, MD frequency power supplies and also filtered Arc deposition technologies have the potential application to alter the stoichiometric structure of the coating. Filtered Arc deposition can make a more superior coating by achieving an amorphous or ultra-microcrystalline structure without any pinholes or voids in the coating [5]. Adding nitrogen to  $\text{TiO}_x$  could change the properties of the thin film significantly [6]. Furthermore, plasma modification of the surface using oxygen could remove of organic materials. Oxygen plasma can be very reactive and forms numerous active components, it can produce  $\text{O}^+$ ,  $\text{O}^-$ ,  $\text{O}_2^+$ ,  $\text{O}_2^-$ ,  $\text{O}$ ,  $\text{O}_3$ , ionized ozone,  $\text{O}_2$  and free electrons changing the surface energy. For example, plasma induced oxidation of polypropylene increase the surface energy of 29 dynes/cm to 73 dynes/cm in just a few seconds. At 73 dynes/cm, the polypropylene surface is completely water wettable [7-8]. The ionized particles deposited on the substrate seem to move freely on the surface, sometimes called “liquid state deposition.”

## CONCLUSIONS

Functional and decorative  $\text{TiO}_x$  or  $\text{TiNO}_x$  coatings are used in many applications. SEM/EDS is a valuable tool for locating and diagnosing the porosity of the coating. Other deposition techniques such as magnetron sputtering or filtered cathodic arc might solve the coating defects with this type of material. This paper illustrates the usefulness of SEM/EDS technology in identifying various types of contamination that can cause spots or voids in the coating. Once the contaminant is identified, the team can work to find the source and eliminate the material from the process. Cathodic arc technologies with improved processing techniques and methods evaluated and tested from start to finish can yield the results desired without spotting or voids.

## ACKNOWLEDGEMENTS

The authors would like to thank our Tanury PVD team for making contributions to this paper.

## REFERENCES

- [1] C. Metzner, B. Scheffel and H. Morgner and O. Zywitzk, “Functional and Decorative Coatings onto Metal Strips Deposited by Plasma-Activated High Rate Electron Beam Physical Vapor Deposition (EBPVD)”, 55<sup>th</sup> Annual Technical SVC Conference Proceedings, p.663-668(Santa Clara, 2012).
- [2] W.K.Grant and B. Mishra, “Corrosion Characterization of Arc Deposited Zirconium Nitride Coating by DC Electrochemical Techniques”, 43<sup>rd</sup> Annual Technical SVC Conference Proceedings, p.41-45(Denver, 2000).
- [3] D.C. McIntyre, G.G Chen, E.C. Sprague, D.B. Humenik and J.A. Kubinski, “Arc-Deposited, Pearl Nickel Finishes for Interior Trim Applications in Automobiles”, 44<sup>th</sup> Annual Technical SVC Conference Proceedings, p.51-56(Philadelphia, 2001).
- [4] David Christie, “Making Magnetron Sputtering Work: Reversing the Glow to Arc Transition”, SVC Bulletin Spring 2014 p.32-35.
- [5] D. Molenda, J.T. Grembowicz, A. Ginovker and O. Popow, “ Filter Arc Deposition – Fast and Superior Coating”, 40<sup>th</sup> Annual Technical SVC Conference Proceedings, p. 143-144 (New Orelans, 1997).
- [6] K. Hukari, R. Dannenberg and E.A. Stach, “Effects of Increasing Nitrogen on Amorphous  $TiO_xN_y$  Thin Films”, 45<sup>th</sup> Annual Technical SVC Conference Proceedings, p.286-291 (Lake Buena Vista, 2002).
- [7] F.D. Egitto and L.J. Matienzo, “Plasma Modification of Polymer Surfaces”, 36<sup>th</sup> Annual Technical SVC Conference Proceedings, p.10-21 (1993).
- [8] E. Finson, S. Kaplan and L. Wood, “Plasma Treatment of Webs and Films”, <sup>th</sup> Annual Technical SVC Conference Proceedings, p.53-57(Lake Buena Vista, 2002).
- [9] Peter Panjan et al. , “ Review of Growth Defects in Thin Films Prepared by PVD Techniques” , Coatings 2020, 10, 447. P 1-40
- [10] A Borrás, A. Barranco, A. R. Gonzalez-Elipse, “Design and Control of Porosity in Oxide Thin Films Grown by PECVD”, J. Mater. Sci. (2006) 41: p 5220-5226