International Science and Technology Journal
المجلة الدولية للعلوم والتقنية
Volume 33 العدد
October 2023 اكتوبر
المجلة الدولية للعلوم والتقنية
ISTJ

تم استلام الورقة بتاريخ: 28/ 9/2023م وتم نشرها على الموقع بتاريخ :31/ 10 /2023م

Review on the Effect of Deposition Time on Electrochemical Properties of Films Deposited by PECVD

Mustafa Imhmed Elshbo[1], Akram Albarouni[1], Muftah Aburgaiah [2], Azldin Alhaj Kozam.[3] and Omaima Akhubat[3]
[1]Libyan Authority for Scientific Research, Libyan Center for Plasma Researches Tripoli-Libya
[2]Libyan Authority for Scientific Research
[3]Libyan Advanced Occupational Center for Welding Technologies.

Email: elshbo@gmail.com

Abstract
Surface properties are among the most important properties that can affect the electrochemical behavior of materials. In this study, the contradictions in the results of the published researches that related to effect of deposition time were reviewed. The major area of interest discussed is the effect of deposition time on electrochemical properties of metal surfaces. The other parameters of plasma film deposition process were also highlighted in this study**.** The study concluded that the deposition time is important factor to improve the electrochemical properties of the deposited films. The other parameters of plasma film deposition process must be controlled to achieve the desired optimal time.
Key words: Plasma; Chemical Vapor Deposition; Electrochemical Properties; Deposition Time.

International Science and Technology Journal
المجلة الدولية للعلوم والتقنية
Volume 33 العدد
October 2023 اكتوبر
المجلة الدولية للعلوم والتقنية
ISTJ

تم استلام الورقة بتاريخ: 28/ 9/2023م وتم نشرها على الموقع بتاريخ :31/ 10 /2023م

مراجعة لتأثير زمن الترسيب على الخواص الكهروكيميائية للأفلام المترسبة بطريقة PECVD

مصطفى إمحمد الشبو[1] , أكرم الباروني[1] , مفتاح أبو رقيعة[2], عزالدين خزام[3], أميمة الخباط[3]

المركز الليبي لأبحاث البلازما[1] ; الهيئة الليبية للبحث العلمي[2] ; المركز الليبي المتقدم لتقنيات اللحام[3]

Email: elshbo@gmail.com

الملخص

تعد خواص السطح من أهم الخصائص التي يمكن أن تؤثر على السلوك الكهروكيميائي للمواد. في هذه الدراسة تمت مراجعة التناقضات في نتائج الأبحاث المنشورة المتعلقة بتأثير زمن الترسيب. مجال الاهتمام الرئيسي الذي تمت مناقشته هو تأثير وقت الترسيب على الخواص الكهروكيميائية لأسطح المواد. في هذه الدراسة تم أيضًا تسليط الضوء على العوامل الأخرى التي تؤثر في عملية ترسيب أفلام البلازما الرقيقة. خلصت الدراسة إلى أن وقت الترسيب عامل مهم لتحسين الخصائص الكهروكيميائية لهذه الأفلام المترسبة بطريقة البلازما. ولتحقيق الزمن الأمثل المطلوب يجب ضبط العوامل الأخرى المؤثرة في عملية الترسيب.

الكلمات الدالة: البلازما; ترسيب البخار الكيميائي ; الخواص الكهروكيميائية ; زمن الترسيب.

Introduction

Surface features composition is crucial for functionally designed materials, particularly in situations where surface contact behavior is critical. When in use, functionally developed components must demonstrate satisfactory performance for the intended purposes in hostile settings and under a variety of conditions without degrading or creating catastrophic disasters. The characteristics of the material's surface have a significant impact on its performance. Surface engineering of materials can be applied in several ways to produce altered surfaces. Surface-engineered materials have lowered costs, increased functionality, enhanced performance, and improved materials consumption efficiency.

تم استلام الورقة بتاريخ: 28/ 9/2023م وتم نشرها على الموقع بتاريخ :31/ 10 /2023م

Many functional coating materials for plasma enhanced chemical vapor deposition (PECVD) have been researched, explored, and found to be interesting for a wide range of technical applications. These materials are currently being used on an industrial scale. This work focuses on the influence of deposition duration in plasma accelerated chemical vapor deposition method to build polymerized thin films that shield the bulk of metal from the hostile surrounding situation, as there is already a large body of literature on this topic. (Martinu, L, 2010)

Many contradictions in the results of published researches about the effect of deposition time on the electrochemical properties of plasma polymerized thin films using pulsed Microwave (PECVD). The contradiction can be attributed to the complicity and sensitivity of the plasma process itself hence during deposition. So the published literature survey must be reviewed to determine the actual effect of this parameter and its interaction with other parameters and this study is intended to be a guide to highlight the role of this parameter.

Scope of the Study

Conducting critical theoretical study to the literature survey about the effect of deposition time on the electrochemical properties of plasma polymerized thin films using pulsed Microwave (PECVD). This study is intended to highlight the agreed results of the previous studies and remove the contradicted results, which confuse the engineers or anyone who is interested in plasma applications.

Statement of the Problem

Corrosion is a common and expensive problem for metallic alloys in industrial applications that cost billions of dollars. Applying a protective coating or paint is highly recommended as the most cost-effective and practical strategy to prevent corrosion. Organic coating technology has advanced dramatically during the previous decades. Organic coatings and anticorrosive paint mixes are

تم استلام الورقة بتاريخ: 28/ 9/2023م وتم نشرها على الموقع بتاريخ :31/ 10 /2023م

studied extensively to maximize their efficiency to prevent metals surfaces from corrosion. In addition, this study is an attempt in the context to reach this goal.

Objective of the Study

Reviewing and determining the influence of deposition time on the electrochemical properties of plasma polymerized thin films using pulsed Microwave (PECVD).

PECVD

New coated thin-film systems that offer consistently better performance in a variety of fields, from optics and optoelectronics to aerospace, biomedical, microelectronics, and other applications, have been made possible by scientific and technological advancements. In each case, a single layer or the entire thin-film system may simultaneously fulfill several functions (e.g., selective optical absorption and mechanical protection; optical transparency and gas barrier; antistatic). Numerous effective solutions in these fields have been identified, and they are typically based on a layered functional coating architecture. (Martinu, 2010)

The process of applying thin film layers to a surface is called surface coating. Vapor phase methods (physical and chemical vapor deposition), solution state processes, and fusion processes are a few examples of surface coating techniques. Thin layer deposition, plasma enhancement, ion bombardment, self-assembly, and vapor phase process are some methods for achieving this (Park, 2006; Voevodin, 1999). Surface deposition layers that are two-dimensional and have a thickness range of less than one-micron meter are typically referred to as thin films. Thick film, or coating, is the term used to describe the thicker layers that are greater than 1 micron in thickness. The resulting thin layer may be pure or impure, single crystal or amorphous.

تم استلام الورقة بتاريخ: 28/ 9/2023م وتم نشرها على الموقع بتاريخ :31/ 10 /2023م

Materials and Methods

Microwave Plasma Discharges:

Plasma generated by microwave discharges is frequently employed in a variety of settings. In the pulse and continuum wave regimes, at incident powers ranging from several Watts to hundreds of kW, the pressure range required to produce microwave plasma is broad and can range from 10-5 torr up to atmospheric pressure.

Up to 90% of the incident power can be reached by the plasma absorbed power. Microwave wavelengths span from millimeters to several tens of centimeters, and they should align with approved microwave frequencies for use in scientific, industrial, and medical applications. The most often utilized frequency is 2.45 GHz.

As a characteristic of microwaves, non-uniformity should be taken into account while designing microwave-to-plasma applicators for particular targets and performing diagnostics on plasma. Figure (1) shows the effects of external discharge parameters on plasma homogeneity. Lebedev (2010).

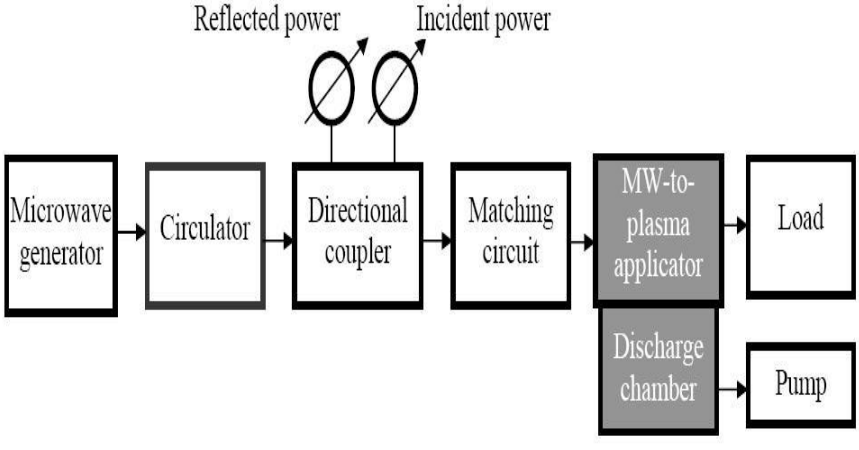

Figure 1: Typical structure of the microwave plasma stand. (Lebedev, 2010)

تم استلام الورقة بتاريخ: 28/ 9/2023م وتم نشرها على الموقع بتاريخ :31/ 10 /2023م

Discussion

It is important to mention that this study raised an issue of lacking previous researches that cover the core of this study which is the effect of deposition time under specific conditions of plasma enhanced chemical vapour using microwave as a media to create plasma state. It is not exaggerating to say that there are handful of researches published which directly dealt with this issue. In addition, this is considered one of the advantages of this study.

According to Sana Sebeta, the deposition time is a very important parameter that affects the water contact angle. In her study, she used the stainless steel grade 304 as substrate, benzene (C_6H_6) and Argon as precursor gas. The parameters used in that study is shown below in table **1**. (Sbeta, 2017)

TABLE 1. Deposition Time Have the Greater Impact on the Measured Contact Angle.

Samples No	Working pressure (m torr)	Time of deposition (minutes)	Contact angle degrees [θ°]
Bare metal			81
T1	50	5	71
T2	50	15	67
T3	50	30	44
T4	30	30	30
T5	10	30	33

The effect of deposition time on corrosion resistance was studied by using three different time intervals. The coated samples were immersed in 3.5% NaCl solution as corrosive media. The intervals were 5, 15, and 30 minutes of deposition time as illustrates in figure 2.

تم استلام الورقة بتاريخ: 28/ 9/2023م وتم نشرها على الموقع بتاريخ :31/ 10 /2023م

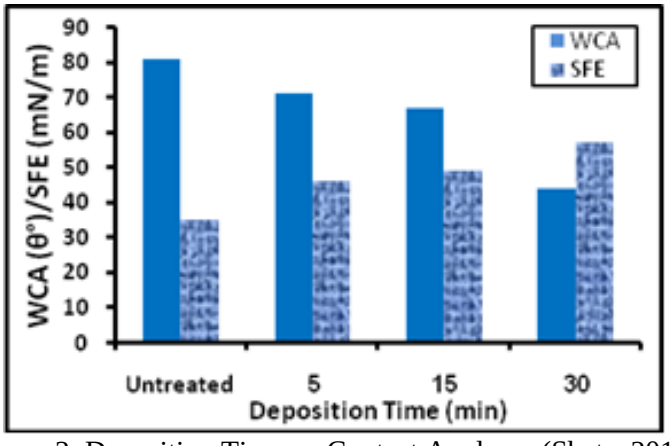

Figure 2: Deposition Time on Contact Angle. (Sbeta, 2017)

Although the linear relationship according to this study between the deposition time and physical properties of the film, it should be mentioned that Schaurer in his research stated that " it is not advisable to grow films for extended periods of time since this will lead to poor film adhesion to substrate due to the intrinsic stress caused by increasing film thickness due to increasing in deposition time and probably affect (in a negative way) other physical and mechanical properties. (Schauer, 2007).

Sbeta found that the deposition time was found to have had the greatest influence of all parameters on the rate of film deposition and the WCA measured. (Sbeta, 2021)

Zreiba`s &Lubnas research raised an issue of adhesion of the film deposited by MWPECVD. As after corrosion test was carried most of the films were broke down and showed that the films deposited were not durable to protect aluminum against corrosion. The study stated that the effect of deposition time is clear but not in harmonic relationship as the study showed that the samples over deposited within interval time 30 minutes and pressure 50 torr. The film did not last long time and peeled off the surface. While the samples deposited in the same pressure but in 45 minutes the film immediately separated off the surface. In many trying different deposition intervals and pressure the condition parameters that gave

تم استلام الورقة بتاريخ: 28/ 9/2023م وتم نشرها على الموقع بتاريخ :31/ 10 /2023م

reliable results were he conditions of 7, 9, and 30 m torr. With deposition times of 60 min and 90 min. (Zreiba, 2021). Table 2 shows the condition parameters used in the study by Zreiba.

TABLE 2. The Condition Parameters Used In the Study by Zreiba. (Zreiba, 2021).

Base Pressure (P_o, mtorr)	Power (Watt)	Time (Min)	Film Weight (mg)	Film Thickness (μm) ± 5%
1.7	540	60	1.1	1.0416
1.7	540	60	1.7	1.6098
1.7	540	60	3.7	3.5037
1.7	540	90	1.5	1.4204
1.7	540	90	1.9	1.7992
1.7	540	90	4.1	3.8825

In general, Table 3 indicates that the deposited films on Al hardly improve corrosion resistance, and hardly decrease the corrosion rate of Al alloy substrate (only 165 mV improvements in E_{corr}, and about 0.06 μA/cm^2 decreases in i_{corr} for highest η). The maximum η of 55.4% is for deposited film at 30 mtorr and 90 min. After corrosion test most benzene films detached from Al alloy substrate and the only film that partly remained on sample was of 30 mtorr for 90 minutes. Although the efficiency calculations remains questionable as it was measured based on the change of i_{corr} and not on the change in corrosion rate.

TABLE 3. Corrosion Properties of Aluminum Alloys Bare and Covered With Benzene. (Zreiba, 2021).

	E_{corr} (mV)	i_{corr} (mA/cm^2)	η (%)
Bar Al	-726.5	0.0001	
7 mtorr, 60 min.	-612.5	0.0000794	20.6
9 mtorr, 60 min.	-578.7	0.0000630	36.91
30 mtorr, 60 min.	-571.0	0.0000501	49.88
7 mtorr, 90 min.	-595.0	0.0000616	38.35
9 mtorr, 90 min.	-574.5	0.0000562	43.77
30 mtorr, 90 min.	-561.5	0.0000446	55.4

تم استلام الورقة بتاريخ: 28/ 9/2023م وتم نشرها على الموقع بتاريخ :31/ 10 /2023م

One of the notes on this study is the metal samples coated were not first exposed to a nitriding or carburizing plasma in order to sputter-clean the surface, and to harden the near-surface region by implementing a hardness gradient due to the diffusion of nitrogen or carbon and this is probably the main cause of creating the adhesion problems and consequently affected the results of the study.

Delim stated in a study carried out under title "Corrosion protection performance of silicon-based coatings on carbon steel in NaCl solution: a theoretical and experimental assessment of the effect of plasma-enhanced chemical vapor deposition pretreatment" it was assumed that the presence of N_2O during deposition was responsible for the oxide film's strong adherence to the noble metal interface and Argon effect extended to decrease the contact surface. (Amel Delimi, 2022).

A study titled `Corrosion protection by microwave plasma-polymerized organic films` by Suliman Hemali showed the importance of plasma enhanced chemical vapor deposition as a potential anti-corrosion coating method. Although the study did not focused on the deposition time, it proved the parameters effect on the electrochemical properties of the films deposited by (PECVD) process. It showed that by changing the percentage weight of precursor gas with Argon could dramatically improve the corrosion resistance of the films and found the highest protective efficiency was 65% at a 15% toluene ratio. Table (4) shows the corrosion rate of samples as received. Table (5) shows the effect of deposited films on corrosion rate. (Elhamali, 2022).

TABLE 4. Corrosion Rate of As- Received Obtained From Potentiodynamic Experiment.

E_{corr} (mV)	I^0_{corr} ($\mu A / cm^2$)	Corrosion Rate (mm / year)
-747	11.65±0.05	0.13

تم استلام الورقة بتاريخ: 28/ 9/2023م وتم نشرها على الموقع بتاريخ :31/ 10 /2023م

TABLE 5. Corrosion Properties of Films With Different Toluene/Argon Ratios Obtained From Potentiodynamic Experiment. (Elhamali, 2022)

Toluene Ratio	E_{corr} (mV)	I_{corr} (± 0.05μA/cm^2)	P_i %	Corrosion Rate (mm / year)
15 %	-850	4.20	65.00	0.040
30 %	-745	4.22	63.80	0.046
60 %	-725	7.49	35.70	0.079

The study carried out by Abourayana stated that the results indicate that the benzene and HMDSO deposited films are suitable for protection of the aluminum substrate against corrosion. The changes in the processing parameters seem to have a strong influence on the film protective ability and the highest protective efficiency was 60.22 %. Although the study neglected the effect of the deposition time the experiment carried out in different times 150 & 90 minutes without mentioning the reason of using two different deposition times. However, the procedure of the study implies that many experiments were carried out with different deposition times and the best time was chosen in compatible with the other plasma process parameters. (Abourayana, 2011).

According to research published in Royal Society of The Chemistry in 2020, the deposition rate in electron-beam evaporation is not a linear function of deposition time. ZrN coatings were prepared using hollow cathode discharge ion-plating.167. The same duration was used for all samples, but the coating thickness had large variation from 0.47 to 1.17 mm. Nitridation of the Zr source occurs during deposition, which lowers the vapor pressure of Zr and the deposition rate. Low vapor pressure targets require use of higher temperature or greater power for deposition. (Ul-hamid, 2020).

Note_as Michel More said that " although the mechanisms of polymer growth have been well characterised , the growth of plasma polymers is less well understood because many random process occur in plasma phase and species which contribute to film

تم استلام الورقة بتاريخ: 28/ 9/2023م وتم نشرها على الموقع بتاريخ :31/ 10 /2023م

growth may be neutral, radical, ionic, or even metastable". (More, 2016).

The contradiction can be attributed to the complicity and sensitivity of the plasma process itself is the main responsible for the contradiction in results of the experiments. Hence During deposition, the bulk plasma parameters generally control the rate at which chemically active precursor species (molecular fragments – free radicals) and energetic species (electrons, ions, photons) are created. Even for relatively simple gas mixtures involving two or three gases, many plasma reactions are taking place and many new species are created.

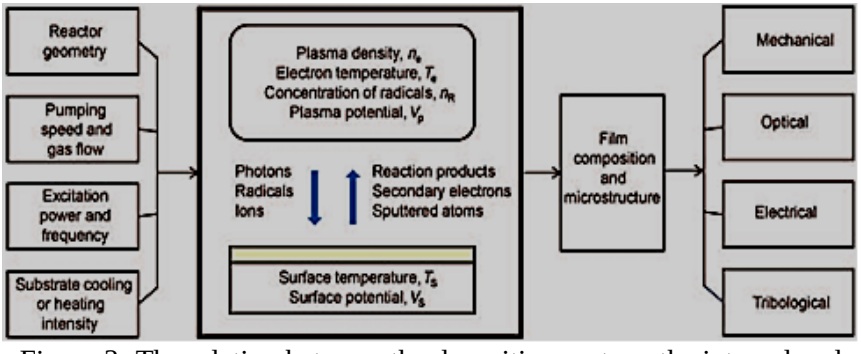

Figure 3**:** The relation between the deposition system, the internal and external process parameters, and the film characteristics**.** (L.Martinu, 2010).

In addition, the interface is considered one of the most important factors that affect the characteristic of the deposited film. Figure 3 showed the relation between the deposition system, the internal and external process parameters, and the film characteristics**.** Interfaces in coating technology ensure compatibility and adhesion between the coating and the substrate and between the individual coatings and to ensure the thickness of the interfacial region. (L.Martinu, 2010).

A study carried out by Lee looked at plasma polymerizing acrylic acid in a pulsed microwave PECVD reactor on stainless steel substrates. They tested deposition times from 5-30 minutes and found the film deposited for 15 minutes provided the best

تم استلام الورقة بتاريخ: 28/ 9/2023م وتم نشرها على الموقع بتاريخ :31/ 10 /2023م

corrosion protection, with corrosion current densities an order of magnitude lower than the uncoated substrate. Longer times did not further improve the protection. (Lee, 2011)

Jeong studied depositing hexamethyldisiloxane films on aluminum in a similar PECVD system. They tested 5, 10 and 20 minute deposition times and found the 10 minute films had the highest impedance after salt spray and cyclic corrosion testing, indicating they were most protective. (Jeong, 2006).

Researchers and engineers should be aware of the interacted controlling processes before starting the film deposition experiment. Surface hardness and control roughness, and/or to add specific surface functions providing wettability, biocompatibility, etc. These processes can be considered in competition, and the prevalence of one of them can be controllably adjusted by the choice of the external plasma parameters. As mentioned before the plasma thin film deposition is sensitive and complicated processes. Therefore the comprehensive understanding of the role of the influencing parameters is important factor in achieving the final product with the desired properties and decreasing the contradictions of the results.

Conclusion

Deposition time is important factor to improve the electrochemical properties of the deposited film by increasing thickness. However, there seems to be an optimal time where further increases do not significantly improve performance due to intrinsic stress caused by increasing film thickness and consequently affect the adhesion. In addition, the optimal time is a function of other parameters such as working pressure and precursor gas.

Study Recommendations

It is highly recommended to carry out many studies and researches as there is a lack of efforts which cover the core of this study to determine the effect of deposition time on electrochemical properties of deposited films and the give a comprehensive

تم استلام الورقة بتاريخ: 28/ 9/2023م وتم نشرها على الموقع بتاريخ :31/ 10 /2023م

knowledge about the effect of the parameters interaction on the deposited films characteristics.

Study Limitations

Lack of the sources that cover the core of the study which is the the Effect of Deposition Time on Electrochemical Properties of Plasma Polymerized Thin Films Using Pulsed Microwave (PECVD) it is not exaggerating to say there is handful of studies that dealt this issue since the most of studies give importance to the other parameters rather deposition time. So the study dealt with these few resources as a reference to determine the conclusion.

Acknowledgement

We would like to express my deepest appreciation to Libyan Centre for Plasma Research, and a special gratitude we give to the project team members. Finally, we would like to thank my family – Father Soul, Mother and Wife- who always support me and stand behind me for all success we achieve.

References

2024-T3 by Plasma Polymerized Hexamethyldisiloxane Thin

Abourayana, (2011). Synthesis and Characterization of Plasma Polymerized Thin Films Deposited from Benzene and examethyldisiloxane using (PECVD) Method. International Journal of Materials and Metallurgical Engineering.

Amel Delimi, (2022). Corrosion Protection Performance Of Silicon-Based Coatings On Carbon Steel In Nacl Solution: A Theoretical And Experimental Assessment Of The Effect Of Plasma-Enhanced Chemical Vapor Deposition Pretreatment . Royal Society of Chemistry.

Elhamali S., (2022). Corrosion protection by microwave plasma-polymerized organic films.

Films. Surface and Coatings Technology.

Jeong S., (2006). Corrosion Protection of Aluminum Alloy

تم استلام الورقة بتاريخ: 28/ 9/2023م وتم نشرها على الموقع بتاريخ :31/ 10 /2023م

L. Martinu, (2010). Plasma-Enhanced Chemical Vapor Deposition of Functional Coatings. William Andrew.

Lebedev Y., (2010). Microwave Discharges: Generation and Diagnostics. Belgrad.

Lee, J., (2011). Effect Of Deposition Time On The Corrosion Protection Performance Of Plasma Polymerized Acrylic Acid Thin Films. Surface and Coatings Technology.

Martinu, (2010). Plasma¬Enhanced Chemical Vapor. Elsevier Inc.

More, M. (2016). Thin Film Coatings for Biomaterials and Biomedical Applications.

Park S., (2006). Structure and Properties of Transparent Conductive Doped ZnO Films by Pulsed Laser Deposition.

Sbeta S., (2017). Thin Film of Benzene Deposited on 304L Stainless Steel Using Pulsed Microwaves Plasma Enhanced Chemical Vapor Deposition. Journal of Basic and Applied Science.

Sbeta, S., (2021). Synthesis and Characterization of Plasma Polymerized Thin Films on stainless Steel Using Microwave (PECVD) Method for Medical Applications. Second Libyan Conference on Metal Casting and Processing Technologies.

Schauer, (2007). PECVD-Deposition and Characterisation of C-Si Thin Film Systems on Metals. der Ruhr-Universit¨at Bochum.

Ul-Hamid A., (2020). The effect of deposition conditions on the properties of Zr-carbide, Zr-nitride and Zr-carbonitride coatings – a review. Royal Socity of Chemistry.

Voevodin A., (1999). Nanocrystalline WC and WC/a-C Composite Coatings Produced From Intersected Plasma Fluxes At Low Deposition Temperatures.

Zreiba E., (2021). Characterization of Thin Films Deposited from Benzene Using Microwave Plasma Polymerization. World Journal of Applied Physics.