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REVIEW

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Magnetron sputtering: A recent review on types and application for advanced coating

Chintan Morsiya[1], Vandan Vyas[2], Kamlesh Chauhan[2] and Sushant Rawal[3]

[1]Department of Mechanical Engineering, L.J Institute of Engineering and Technology, Ahmedabad, 382210, India
[2]CHAMOS Matrusanstha Department of Mechanical Engineering, Chandubhai S. Patel Institute of Technology, Charotar University of Science and Technology (CHARUSAT), Changa, 388421, India.
[3]McMaster Manufacturing Research Institute (MMRI), Department of Mechanical Engineering, McMaster University, 1280 Main Street West, Hamilton, ON L8S4L7, Canada

ABSTRACT

Magnetron sputtering is a physical vapor deposition (PVD) process which is a type of vacuum deposition method used for development of thin films. In PVD, vapor of material is mainly produced by two methods, which is heating and sputtering. This vapor material gets deposited on to the substrate material in the presence of vacuum. As magnetron sputtering, having different configurations, is widely used in different research areas, attempts have been made to provide detailed review of recent advancement in magnetron sputtering methods and its applications. Different configurations of magnetron sputtering process such as closed field unbalanced magnetron sputtering (CFUBMS), pulsed closed field magnetron sputtering (P-CFUBMS), high power impulse magnetron sputtering (HiPIMS) and Deep oscillation magnetron sputtering (DOMS) are discussed. HiPIMS and DOMS are the most researched techniques for deposition of high quality and well adhered coatings in recent trends. Process parameters affecting film deposition are also listed in this paper. Majorly, this paper will outline recent applications of magnetron sputtering in Micro electro mechanical systems (MEMS), lithium sulfur batteries, biomedical implants and instruments, supercapacitors, tribology and many more for improvement of mechanical, optical, biomedical and electrical properties

KEYWORDS

Magnetron sputtering; Types; Closed field; Impulse; Plasma; Parameters; Recent applications

ARTICLE HISTORY

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Introduction

Sputtering is the process in which material is deposited on the substrate by vaporizing material from the target. It is the process in which momentum exchange takes place due to collisions between the energetic ions and atoms. In this, vacuum is required which extends formation time for oxides and reduces impurities contamination. For the purpose of thin film deposition, various sputtering techniques are available, among these dc diodes sputtering systems is the basic model. Remaining systems are improvements on the dc diode sputtering system. In the dc diode sputtering system one of the electrodes is an anode and the other is cathode covered with metal target material. If the target material is insulator, the dc power supply is replaced by a radio frequency (RF) power supply to sustain sputtering glow discharge [1]. Many materials have been deposited by the basic sputtering process, but it has limitations like low deposition rate, high substrate heating temperature and low ionization efficiency in the plasma. The term plasma is composed of particles such as electrons and ionized atoms, where a particle's electric charge becomes neutral. Based on temperature plasma can be divided in two types, one is low temperature plasma, generated at low pressure environment by the providing electric energy to a gas, and the other is high temperature plasma, which evolves in an environment greater than 10,000 °C. Plasma is important as it provides the environment for deposition and also used for etching, ion implantation and epitaxy [2]. During sputtering, to extend the lifespan of electrons escaping from cathode, Penning had suggested the use of magnetic fields in the 1930s [3]. Later, advancement in this concept led to the method known as magnetron sputtering. Magnetron sputtering method is being developed rapidly in the last three decades where it has become an important technique for the deposition of thin film for various purposes. In this method, an electromagnet and permanent magnet or combination of both can be used to create a magnetic field [4,5]. Limitation of the basic sputtering process is improved by the magnetron sputtering process and its different configurations.

Plasma confinement is the main factor that makes a difference among all the processes. In conventional magnetrons, the magnetic core is the end point for magnetic flux generated from a cathode which is called a balanced magnetron as shown in figure 1(a). Whereas, unbalanced magnetrons have different degrees of plasma confinement in which an additional magnetic field is applied to the balanced magnetron as shown in figure 1(b) [1]. In a balanced magnetron, the target region is the place where plasma is confined, which extends dense plasma about 60 mm in front of the target. In this process substrate inside this region gets deposited which results in modification of properties and microstructure of thin film, whereas substrate outside this region lacks sufficient ion bombardment to alter the

*Correspondence: Dr. Sushant Rawal, McMaster Manufacturing Research Institute (MMRI), Department of Mechanical Engineering, McMaster University, 1280 Main Street West, Hamilton, ON L8S4L7, Canada, e-mail: sushant@mcmaster.ca

properties and microstructure of thin film. An unbalanced magnetron is the solution for this problem. The second limitation of sputtering technique is the inability to deposit dense and defect free coating such as oxides and medical implant coating. This advantage is obtained by the method known as pulsed closed field magnetron sputtering technique [6]. So now, in the next topic we will continue our discussion regarding recent configurations of magnetron sputtering and their advantages.

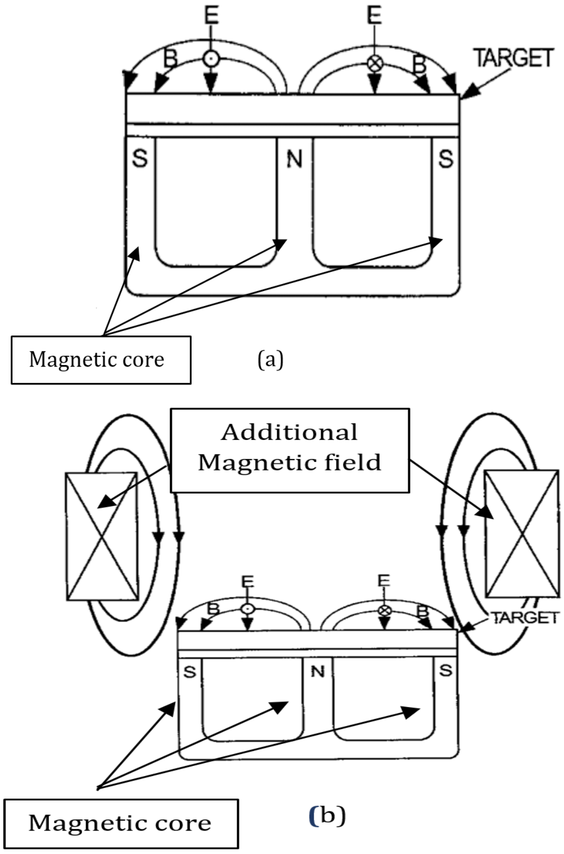

Figure 1. (a) Balanced Magnetron (b) Unbalanced Magnetron [1]

Different Magnetron Sputtering Processes and Their Advantages

Initially, magnetron is applied for coating of metal and its alloys but now with the development, this technique can be used for fiber, ceramic and also for functionally graded material to enhance its microstructural, mechanical, optical, electrical and biomedical properties. The basic principle used by magnetrons is that secondary electrons are constrained towards the target by means of a parallel magnetic field. Which will result in dense plasma generation and more ion bombardment on the substrate enabling higher sputtering rate and thus high deposition rate at the substrate surface. The configuration of magnetrons with a flat, cone, and cylindrical target were designed for extended magnetron sputtering systems (MSS). It has different names based on different power sources used such as DC, Radio frequency (RF), Pulsed magnetron sputtering. Schematic diagram for magnetron sputtering is shown in (Figure 2). Basic requirements for magnetrons are high vacuum in the range of 10^{-6} to 10^{-8} of an atmospheres, controlled flow of gas like argon (inert gas) and oxygen (reactive gas) which raises the pressure to the prerequisite level, the power in the form of DC or RF (13.56 MHz) which provides voltage about 300V to operate the magnetrons. It uses magnets behind the negatively charged target material to control ion bombardment which results in faster deposition rates[7,8].

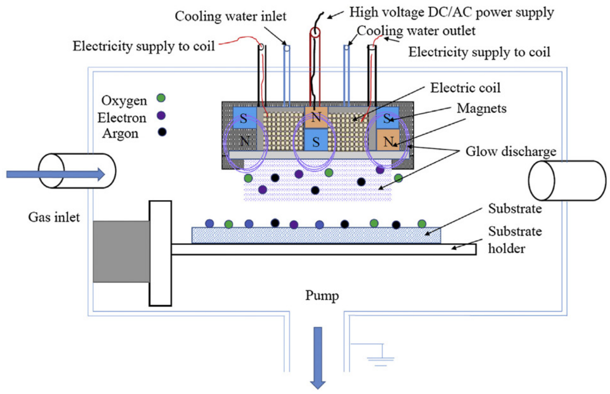

Figure 2. Schematic diagram of Magnetron sputtering Machine [11]

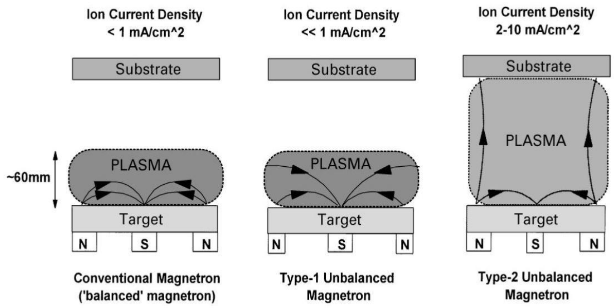

Figure 3. Plasma Confinement observed in conventional and unbalanced magnetron [6]

In an unbalanced magnetron sputtering arrangement of the outer ring of magnet is such that it provides strength relative to the central pole. Here, all the field lines are directed towards the central and outer poles in magnetron as well as directed towards substrate. So, plasma is not restricted only near to the target region but it also expands outwards of the substrate, which will cover the entire substrate material that gives accurate and uniform thin film over the substrate material increasing its mechanical and other required properties. Additionally, the target current is directly proportional to the ion current drawn at the substrate. Different magnetron modes are shown in (Figure 3), which have different plasma confinement regions. Above discussed design is termed as Type-2 by Savvides and Window. However, lines are concentrating towards chamber walls and result in lower plasma generation. This type is not used due to lower ion bombardment but some researchers have used this technique for the development of the novel structure zone model [9,10].

Unbalanced magnetron sputtering has greater advantages over conventional magnetron sputtering but has certain limitations such as it is difficult to uniformly coat complex shapes using a single source. So to overcome this problem, use of multiple sources were suggested at different angles to coat

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complex shapes [12]. In multiple magnetron systems different polarities are set to obtain different configurations such as “mirrored” and “closed field”. Both the configurations are shown in (Figure 4). As shown in mirror-field configuration, field lines are moving towards the chamber wall and result in loss of plasma. However closed field configuration field lines are moving towards target materials or magnetrons which will result in dense plasma generation and losses to the chamber are less. The effectiveness of closed field (CFUBMS) configuration compared to Unbalanced (UBMS) and Mirror field (MFUBMS) is shown in (Figure 5) [13,14]. For large cylindrical targets, rotating magnetrons are used for coating. In this configuration, the rotating tube is a cathode target and inside the cylinder magnetic assembly is available[15].

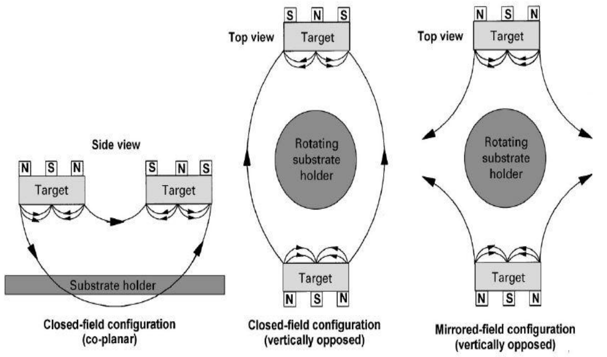

Figure 4. Different Configuration of Unbalanced magnetron sputtering [9]

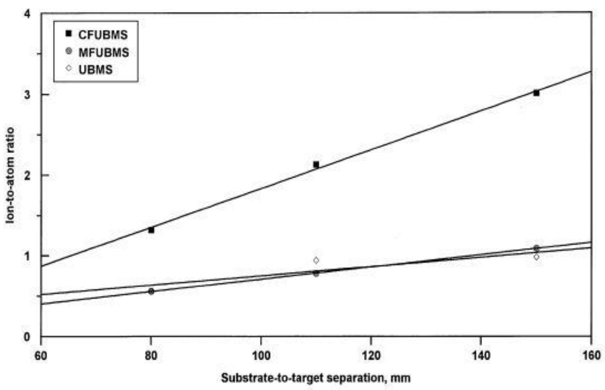

Figure 5. Variation of substrate to target separation in the ion to atom ratio incident at the substrate for CFUBMS, MFUBMS and UBMS [9]

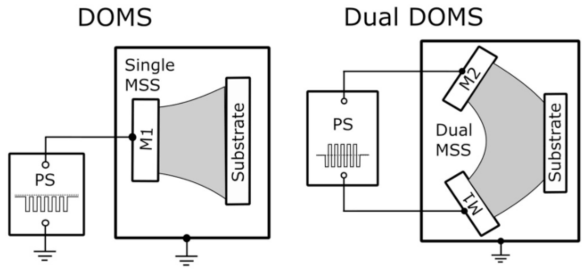

Figure 6. Schematic of DOMS and dual DOMS modes with voltage impulse curves [21]

To overcome problems faced during deposition of insulating film using reactive sputtering, pulsed magnetron sputtering is used. A pulsed magnetron system has different configurations such as a symmetric bi-polar pulsed, unipolar pulsed and high-power impulse magnetron system. High power impulse magnetron sputtering (HiPIMS) prevents arcing, provides more stable discharge ignition and also reduces the working gas pressure in vacuum chamber [16]. Detailed comparison between cathodic arc and HiPIMS technique was given by Andre Anders in his published work [17]. In the pulsed closed field unbalanced magnetron sputtering (P-CFUBMS) method, electrons are confined in the plasma by magnetic field lines between magnetrons and increase ion density which leads to high level of ion bombardment. This process can also be used to deposit alloy nitrides, oxides and carbides with the required composition and multilayer deposition by controlling the power density on multiple targets and partial pressure of reactive gas. However, a limited amount of research has been conducted on P-CFUBMS in reactive sputtering [18,19]. According to Avino et al., densification in the coating of objects can be improved using HiPIMS compared to direct current magnetron sputtering [20]. Recently, a new method is developed named the dual mode of deep oscillation magnetron sputtering (DOMS). The dual mode magnetron sputtering system solves the problem of disappearing anode, which arises in reactive sputtering of dielectric coating. A bipolar power source can be implemented in Dual DOMS to avoid long intervals between micropulses. V.O. Oskirko et al. provided schematic of DOMS and dual DOMS modes with voltage impulse curves as shown in (Figure 6) [21].

If we summarize, it can be written as dual target mode of deep oscillation magnetron sputtering provides advantages over high power impulse magnetron sputtering and high-power impulse magnetron sputtering provides advantages over direct current magnetron sputtering.

Parameters Affecting Magnetron Sputtering

Main parameters affecting the sputtering process are: Sputtering power, vacuum, sputtering gas, pressure inside chamber, distance between substrate and target material, temperature of substrate, target composition and magnets configuration [22,23]. According to P. Chelvanathan and his colleagues, during deposition of Mo thin film, growth rate was higher for higher RF Power and operating pressure. Higher kinetic energy of incident Mo atoms during deposition improves the crystallinity property [24]. M. Zhijun et al. has considered different sputtering parameters such as power, pressure, time, thickness and deposition rate. From his results it was observed that keeping power and deposition time constant, pressure and thickness obtained after deposition decreases. While keeping pressure and deposition constant, as power decreases there is slight increment and decrement in the thickness achieved by this process [25]. Energy is the main factor responsible for mechanical and physical properties of sputter films including their behavior to resist the crack and to enable their useful production [26]. Let us limit the discussion regarding the effect of process parameters on film deposition as it is a very wide area which depends on application of magnetron sputtering.

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Recent Development and Applications

Most recent applications of magnetron sputtering are in the field of Micro electro mechanical systems (MEMS), lithium sulfur batteries, super capacitors, tribology, solar cell, textile industries, biomedical implants and instruments. Most of the processes related with water need to have proper pH monitoring. Most of the chemical materials including blood in our body requires pH controlling in the range of 7.35 to 7.45. Exceeding pH, results in serious problems. Typically, Metal oxide-based pH sensors have found their applications in chemical and biological fields. They consist of attractive features such as insolubility, better sensing range, stability and mechanical strength. Metal oxides deposited by RF magnetron sputtering provides better PH sensitivity, fast response, good resolution and it also provides perspective for measuring pH which cannot be measured by glass electrode based pH sensors [27]. Mwema published a detailed review on application of Aluminium Nitride (AlN) thin films for harsh operating conditions, such as operating components under extreme shock loads, high temperature, corrosive environment and high pressure and forces. To measure above parameters different MEMS are available such as acoustic sensors, transducers, resonators and energy harvesters. Ceramic materials AlN have been deposited on various metallic and nonmetallic substrates for various sensing applications using RF magnetron sputtering [28]. Research was also carried out by depositing titanium nitride (TiN) thin films onto Si and Si/SiO_2 substrate by reactive pulsed DC magnetron sputtering for localized heating applications in MEMS devices [29]. Structural and optical properties were also improved by this process [30]. As nowadays we are using multi colored glasses, these can be obtained by multilayer coating of glasses. According to Yuan, it is possible to develop super hydrophobic film on glass which provides contact angle neary168.9°, which provides low surface energy, good stability under outdoor and ambient environments [31]. Zr-Cu-Ag thin film provides antibacterial coating for biomedical instruments which is amorphous, uniformly thick, and chemically homogeneous [32]. NiAl and NiAlN thin film was also obtained using closed field unbalanced magnetron sputtering which were deposited on glass and SS 316L material which improves biological properties of material such as corrosion resistance, friction and hardness [33]. Properties of material can also be changed by this method such as orientation of Cr was changed from (110) to (200) by the power density which results in non-cracking behavior less than 15N [34]. Recently target poisoning evolution is done by the magnetron sputtering process [35]. Rare earth material such as terbium is deposited on Si material which is investigated for optical properties and composition of terbium doped silicon oxide thin films [36].

Biomedical implants made from Ti, SS 316L and CoCrMo alloys require hydroxyapatite coating to improve biocompatibility and osseointegration. RF magnetron sputtering provides uniform coating thickness between 0.2-1 µm on flat surfaces result into better osseointegration with bones. It has also certain disadvantages like this is line of sight technique, time consuming, cannot coat complex substrates and produces amorphous coatings [37-39]. AISI 316L austenitic stainless steel is widely used for manufacturing of medical implants due to low cost, corrosion resistance and good fatigue strength [40]. However, these steels are prone to attack due to aggressive biological effects. To overcome this problem Ti coating is done on to the material in order to get good mechanical and corrosion resistance properties. This process is also useful for material which require harder surface on outer side but softer from inside. So, this can be achieved by depositing thin film of hard material such as titanium on the surface of the substrate. Presently there is eminent interest for the development of coating of transition metal nitride owing to its properties such as intrinsic biocompatibility, wear resistance and chemical stability. As the deposition of TiN coating requires low level of impurities and control of deposition rate, this can be achieved by magnetron sputtering by varying morphology and various crystallographic structure[41]. DLC (Diamond like carbon) coatings provides higher hardness, better wear resistance and low friction on Cr3C2-NiCr this can be achieved by Closed Field Unbalanced Magnetron Sputtering (CFUBMS). The duplex coating using this technique maintains a stable coefficient of friction and improves tribological performance [42]. Nowadays, conventional coating is replaced by use of composite coating, allowing combination of required properties. Lenis et al., deposited multilayer hydroxyapatite-Ag/TiN-Ti coating on Ti_6Al_4V to make it usable for manufacturing of surgical instruments. Schematic architecture of developed multilayer coating is shown in figure 7 [43]. Research on TiAlN (Ag,Cu) coating on AISI 420 steel was also carried out to make it suitable for applications in surgical and dental instrumentation by improving wear and corrosion resistance. According to Hernan et al., the lowest wear volume of 7.7 × 10-5 mm3 was exhibited by coating AISI 420 steel with 17 at.% Ag-Cu [44,45].

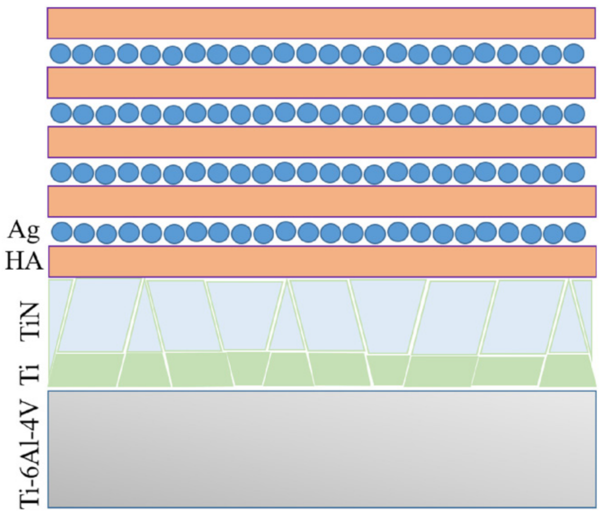

Figure 7. Schematic of multilayer coating [43].

Current research trends also show the interest of researchers to improve performance of lithium sulfur batteries using magnetron sputtering. Lithium sulfur batteries are of importance due to its low material cost and high energy density. But poor electro chemical performance limits its applications. Jin Li et al., attempted to deposit MoS_2 on carbon nanotubes

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paper through magnetron sputtering and used that to fabricate interlayers for lithium sulfur batteries to improve performance [46]. Recently, Shijian Yan suggested use of magnetron sputtering to fabricate cathode plates by reducing sulfur particle size for lithium sulfur batteries. This approach simplified the process and provided good results compared to traditional technologies as sulfur and carbon particles combined well without addition of binders. Schematic illustration to prepare cathode plate is given in (Figure 8) [47]. Sunlight is the most reliable and clean energy source available in the world which could be converted into useful energy. Solar cells are one of the devices which converts solar energy into electrical energy. Many researchers have experimented to improve the performance of solar cells by providing thin film of Mo, metal oxides such as TiO_2, ZnO, Fe-Ga doped ZnO, reduce graphene oxide TiO_2 (rgo-TiO_2) etc. In 1995, Scofield et al. suggested Mo as leading choice for the Copper Indium diselenide (CIS) and Copper Indium Gallium diselenide (CIGS) solar cells. Rashid et al. also deposited Mo on top of soda lime glass (SLG) using DC magnetron sputtering and proposed that 100W is optimized power to grow thin films on SLG as back contact material for fabrication of CIS and CIGS based solar cell devices [48]. Zheng et al. deposited Fe-Ga doped ZnO (FGZO) on glass substrates using RF magnetron sputtering to improve power conversion efficiency of solar cells. According to him, FGZO thin film formed at substrate temperature of 440 °C resulted in the increase in power conversion efficiency of 15.32% [49]. Another important device are the energy storage devices such as capacitors. Magnetron sputtering again finds its application in this field also. Zhang et al. proposed a new method to prepare 3D porous electrode materials based on graphene for application in supercapacitors. High conductivity and high contact interaction was observed between Co_3O_4 array and graphene after depositing by magnetron sputtering on Ni foam [50]. Mohd. Arif et al. also suggested thin film coating of TiN using DC magnetron sputtering on 304L steel substrate to make it suitable for super capacitor devices [51]. In addition to above all fields, magnetron sputtering is also researched in the textile industries to develop antimicrobial textiles. Y.H. Chen et al. deposited antimicrobial brass coating on PET (Poly ethylene terephthalate) textile by HiPIMS [52].

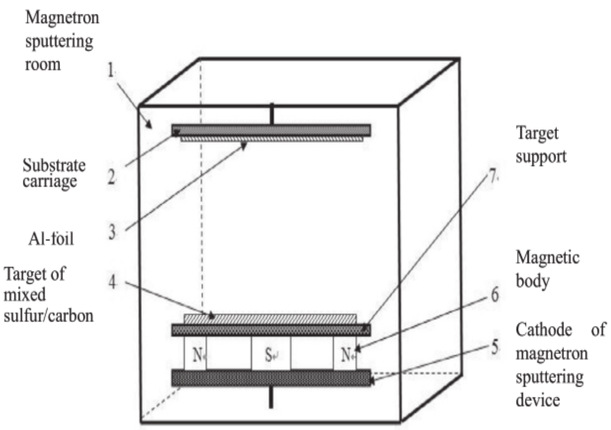

Figure 8. Schematic illustration to prepare cathode plate using proposed magnetron sputtering [47].

Conclusions

Magnetron sputtering is a physical deposition technique which helps to deposit thin film of required materials such as metal, nonmetals, carbide, nitride, oxide and ceramic such as hydroxyapatite. From all different magnetron sputtering configurations, HiPIMS and DOMS are widely used methods as it provides high density plasma and generates strongly adherent film at low substrate temperature. By controlling different parameters affecting the sputtering process one can change morphology and properties of material which are beneficial for mechanical, optical, electrical and biomedical applications. The most important parameter is selection of power source which may be DC or RF depending on material. RF power source is useful when material to be deposited is insulating material. Discussion of most recent applications in the field of MEMS, lithium sulfur batteries, supercapacitors, biomedical implants and instruments, tribology and textile industries in the current study will help researchers to understand current research areas and to select future research directions as per their requirement.

Disclosure statement

No potential conflict of interest was reported by the authors.

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