MAGNETRON SPUTTERING TECHNIQUE USED FOR COATINGS DEPOSITION; TECHNOLOGIES AND APPLICATIONS

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Abstract. The magnetron sputtering processes allow the deposition of metals, alloys, ceramic, and polymer thin films onto a wide range of substrate materials. Within the frame of this work, the recent developments of reactive magnetron sputtering technique are presented. The development, fundamental principles and applications of the magnetron sputtering process are discussed and commented. At the same time, the paper presents few examples of the use of this technique to develop advanced coatings for industrial applications, including corrosion resistant coatings, hard ceramic coatings, and coatings with novel thermal and chemical properties.

Keywords: magnetron sputtering, coatings, technological parameters, control, applications

1. Introduction

Deposition of thin films by physical vapour deposition (PVD) techniques has found widespread use in many industrial sectors [1]. Also, the technique it is used for a wide field of coating applications for, e.g., metal - working industry, biomedical applications, and optical or electrical components. There is an increasing demand for coatings with tailored and enhanced properties such as high hardness, wear and corrosion resistance, low friction, and specific optical or electrical properties as well as decorative colours and often complex combinations of those properties are requested [2, 3, 4]. For high - quality coating on temperature - sensitive substrates such as polymers, there is room for improvements using versatile PVD techniques [5]. Furthermore, magnetron sputtering offers the possibility to synthesize materials outside thermodynamic equilibrium. Thus, it enables the deposition of metastable phases. The field of applications includes integrated circuit (IC) manufacturing applications such as the formation of diffusion barriers, adhesion layers [6].

Magnetron sputtering has developed to the point where it has become established as the process of choice for the deposition of a wide range of industrially important coatings. The driving force has been the increasing demand for high-quality functional films in many diverse market sectors. In many cases, magnetron sputtered now outperform films deposited by other physical vapour deposition (PVD) processes, and can offer the same functionality as much thick films produced by other surface coating techniques. There is a general interest in developing the conventional magnetron sputtering processes to increase metal ionization, target utilization, avoid target poisoning in reactive sputtering increase deposition rates, especially for dielectric and ferromagnetic materials, and to minimize electrical instabilities such as arcs [7].

Surface - coating technologies now play a vital role in many manufacturing processes and in finished product protection. Currently, the most widespread applications of surface coatings are wear resistance and corrosion protection. For example, hard, wear - resistant coatings are now routinely applied to cutting tools to improve their performance and extend their service life. Corrosion - resistant coatings are also routinely applied to components, such as aircraft fasteners, again, to increase service life. Indeed, surface coatings are essential in enabling routine engineering materials to meet the demanding specifications of many current applications [8, 9].

In this paper, we presented the technology and some applications of the PVD magnetron sputtering technique. Subsequently, in first part, an introduction about magnetron sputtering is described in more detail, including the principle of this method. In second part are described some of the recent developments in the magnetron sputtering techniques (general aspects, ion poisoning, closed field unbalanced magnetron sputtering and pulsed magnetron sputtering). Applications of the sputtering techniques are presented third part.

2. Fundamentals of magnetron sputtering technique

2.1. General aspects

Within the sputtering process, gas ions out of plasma are accelerated towards a target consisting of the material to be deposited. Material is detached (sputtered) from the target and afterwards deposited on a substrate in the vicinity. The process is realized in a closed recipient, which is pumped down to a vacuum base pressure before deposition starts (figure 1). To enable the ignition of plasma usually argon is feed into the chamber up to a pressure between 0.5 Pa … 12 Pa. By natural cosmic radiation there is always some ionized $Ar^{\pm}$ ions available. In the dc - sputtering a negative potential U up to some hundred Volts is applied to the target. As a result, the Ar^{-} ions are accelerated towards the target and set material free; on the other hand, they produce secondary electrons. These electrons cause a further ionization of the gas. The gas pressure p and the electrode distance d determine a break through voltage UD. The bombardment of a non-conducting target with positive ions would lead to a charging of the surface and subsequently to a shielding of the electrical field. The ion current would die off. Therefore, the dc - sputtering is restricted to conducting materials like metals or doped semiconductors [10].

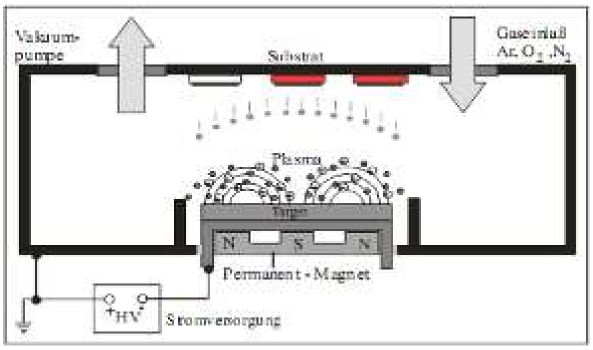

Figure 1. Principle of the magnetron sputtering process [10]

Magnetron sputtering deposition techniques are widely applied both in industrial processes and in advanced material development or treatment [11]. This eliminates the need for construction of expensive compound targets or the use of highly volatile gases.

2.2. Ion poisoning process

Sputtering in an inert environment yields no chemical reaction between sputtered species and ionic sputtering species. If a reactive gas is introduced into the sputtering environment, reactions between sputtered species and reactive gas molecules, or atoms, will occur. At relatively low partial pressures, the whole of the reactive gas will be consumed through reactions with sputtered species. According to [12], this process is synonymous with the getter pumping action of an ion pump and is referred to as the metallic mode of sputtering. As the partial pressure of reactive gas increases and the supply of reactive gas exceed the reaction rate with sputtered species, reactions will then occur at the surface of the target, resulting in compound formation on the surface of the target. If this material is electrically insulating, or the sputter yield of the compound is less than that of the pure metal, a decrease in deposition rate will occur. This is referred to as the non-metallic or poisoned mode of sputtering as the target is said to be "poisoned". The effect is generally described in terms of a hysteresis examining the deposition rate versus reactive gas concentration as seen in figure 2. Once poisoning of the target occurs, and the partial pressure of reactive gas is reduced, the deposition rate will not increase again until the reacted material on the surface of the cathode has been removed.

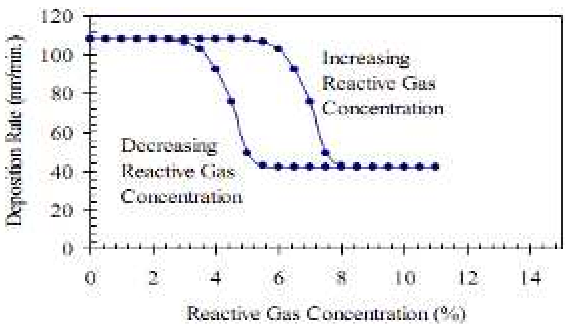

Figure 2. Reactive sputtering hysteresis [12]

2.3. Closed Field Unbalanced Magnetron Sputtering Technique (CFUBMS)

In the closed field configuration, the magnetic field lines between the magnetrons form a closed trap for electrons in the plasma. Few electrons are therefore lost to the chamber walls and dense plasma is maintained in the substrate region, leading to high levels of ion bombardment of the growing film. The magnetic fields in a conventional magnetron, an unbalanced magnetron and a dual - magnetron closed field system are compared schematically in figure 3. Various magnetron arrangements have been developed to suit specific applications. These systems have been used successfully to deposit a range of high quality novel materials, and materials with novel properties [13].

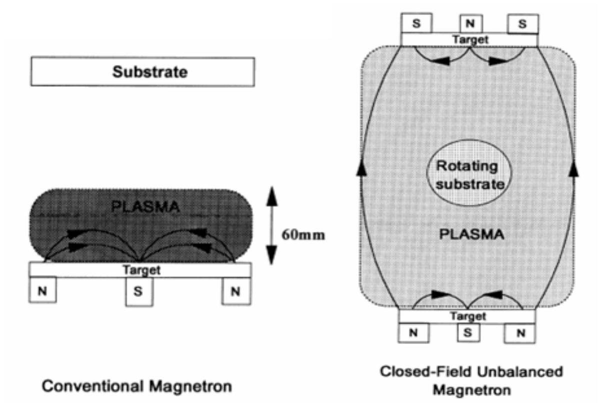

Figure 3. A comparison of the magnetic configuration and plasma confinement in conventional and dual-magnetron closed-field systems [13]

In addition to pure metal and alloy films, CFUBMS systems have been successfully used to deposit a wide range of reactively sputtered coatings onto various components. The reactive sputtering process can be controlled by plasma emission monitoring or by partial pressure control of the reactive gas, both processes offering control of the coating composition and properties.

Use of the CFUBMS system also allows coatings with graded properties to be produced. Very recently, the introduction of grading of the coatings to form multilayer structured coatings using the CFUBMS technique has led to great improvement in adhesion of the DLC coatings to the substrate; this has made the successful practical application of such coatings possible. Many alloy systems have been studied using this technique, and a particularly successful application has been the deposition of highly corrosion resistant aluminium – magnesium alloy coatings as a potential replacement for cadmium in the aerospace industry [14].

2.4. Pulsed Magnetron Sputtering (PMS) technique

According [15], Pulsed Magnetron Sputtering (PMS) process is widely recognized as an enabling technology, particularly for the deposition of dielectric materials. Pulsing the magnetron discharge in the medium frequency range (20 ÷ 350 kHz) alleviates the chief problem associated with the continuous dc reactive sputtering of such materials, namely the occurrence of arc events at the target. This is achieved through the discharging of the poisoned regions on the target during the reverse voltage or 'pulse off' phase. The correct selection of pulse parameters (frequency, duty, reverse voltage) can result in extended arc free operating conditions, even during the deposition of highly insulating materials. The suppression of arcs stabilises the deposition process and reduces the incidence of defects in the film. Consequently, films of, for example, alumina, titanium and silica, can be produced by pulsed sputtering with very much enhanced structural, electrical and optical properties, in comparison with films produced by continuous dc processing. The pulsed sputtering technique is now being exploited commercially in large area multiple magnetron systems for many applications, including solar control and low emissivity coatings, barrier layers on packaging, flat panel displays and solar cells. Again, very long-term process stability, reduced defect densities, improved film properties and enhanced dynamic deposition rates have been reported for these systems [16].

The pulsed technique made its entry in vacuum coating techniques some years ago. A pulsed bias voltage was used successfully in the coating of temperature sensitive substrates. Overheating of crucial spots on intricate substrate configurations such as sharp cutting edges and pointed ends does not occur although the bias action needed for the layer growth is attained, be produced even at low pulse rates. For a series of applications, it is desirable to obtain layers with many phase boundaries. With higher pulse rates, this solution offers a true alternative to sputtering from an alloy target. First trials have shown that stable sputtering conditions can be achieved in reactive mode even with target materials that difference in exhibit a pronounced discharge voltage. Needed for these applications are high performance bipolar power supply units with an adjustable pulse duty factor. In the case of special coating configurations, it is often feasible to match the cathodes accordingly. When using different materials for the single targets, the layer composition can be varied within wide limits on the similar principle of pulse changing [17].

Recent studies have shown that pulsing the magnetron discharge also leads to hotter and more energetic plasmas in comparison with continuous dc discharges, with increased ion energy fluxes delivered to the substrate. As such, the PMS process offers benefits in the deposition of a wide range of materials.

3. Applications

In many applications, magnetron sputtered coatings now outperform coatings produced by other techniques. However, their market penetration is currently limited to certain "niche" sectors. Traditional surface engineering techniques still dominate the market place, and are likely to do so for several years to come [18]. Part of the reason for this is the perceived high cost of sputter (and other PVD) coated components. However, this is deceptive, as the cost of a component is more than compensated for when the subsequent increase in performance is considered. For example, data from Oerlikon Balzers Company suggests that coating a forming punch by magnetron sputtering processes can add 35% to the cost of the tool, compared to only 8% for a gas nitro-carburizing treatment. However, the PVD coated tool can offer an increase in life over an uncoated tool of up to 32 times, compared to the 1.5 to 4.5 times increase in life offered by the other technique [19]. A factor, which has limited the exploitation of advanced magnetron sputtering processes, is their unsuitability for use with many substrate materials such as low alloy steel and titanium alloys. For example, in the case of hard coatings, this is due to the lack of load bearing support provided by the substrate; whereas, in the case of corrosion resistant coatings, pin-hole defects have compromised the performance of the coating. To address these problems, and to extend the commercial viability of advanced magnetron sputtering processes, other reactive magnetron processes have been developed.

The magnetron sputtering technique can be used in biomedicine, in order to improve the wear resistance, together with biocompatibility enhancement polyurethane for special implants for cardio surgery, orthopaedics and ophthalmology [20]. Artificial substances are very important group of materials used in biomedicine. Among the most important purposes to attend by the applied polymer modifications are change of the cell adhesion (e.g. peptides), change of the wetting angle, biocompatibility improvement, surface functionality, friction coefficient reduction. The polymer is characterized by many very good properties; however, application of polyurethane onto elements, which have the contact with flowing blood, especially for long-term use implants, can bring a risk of degradation and surface damage. The most important limitation of those methods is the necessity of keeping a low temperature during the modification process. From the other side application of low temperature, processes can unfavourably affect the adhesion strength to the substrate surface. Until now, existing literature data shows that the most promising polyurethane surface modification results were obtained using the PLD (Pulsed Laser Deposition) method [21].

Magnetron sputtering at low temperatures is used to deposit gate, source, and drain metals for thin film transistors and contacts for PIN diodes for the semiconductor industry. Furthermore, highly unbalanced magnetrons for the deposition of hard coating types such as titanium nitride (TiN), zirconium nitride (ZrN), titanium carbonitride (TiCN), titanium aluminium nitride (TiAlN), chromium nitride (CrN) etc., which are used in machining and cutting tool applications [22]. Highly balanced magnetrons with high magnetic field strength are used for low voltage sputtering of indium tin oxide (ITO) coatings for a wide range of visual display applications. Double magnetrons (sometimes called dual magnetrons or dual cathodes) could be employed for high rate reactive deposition of oxides for display or plastic web coating (typically titanium dioxide (TiO_2), silicon dioxide (SiO_2), tantalum pentoxide (Ta_2O_5)).

The application of magnetron sputtering offers a flexible approach to surface improvement of metal implants [23]. This technique facilitates to producing of dense and well adhered films with controlled elemental composition. Various methods have been used to deposit bioactive ceramic coatings such as plasma spraying, electrostatic spray deposition, pulsed laser deposition, micro-arc oxidation, sol–gel deposition and magnetron sputtering [24]. An additional advantage when coating a metallic implant with ceramics is the reduction in ion release from the metal alloy, consequently increasing corrosion resistance [25]. Magnetron sputtering of calcium phosphate coating is a promising method for forming a biocompatible ceramic coating. It is possible to deposit a desired Ca–P coating or its composite coatings by choosing the appropriate deposition parameters. Therefore, the coated implants have an outstanding potential for supporting bone material in growth and remodelling in orthopaedic and dental applications [26]. Implants made of titanium or its alloys are frequently used as permanent implants after dental or bone injury.

4. Conclusions

In recent years, there have been numerous exciting developments in the field of the magnetron sputtering techniques. Several recent developments made in the magnetron-sputtering field have been discussed in this paper. These include closed field unbalanced magnetron sputtering and pulsed magnetron sputtering. The coatings obtained by this process are rather unique and designed or formulated to work under certain application conditions. Together, these developments have transformed the capabilities of magnetron sputtering, and helped to establish it as the process of choice for the production of many industrially important coating/substrate systems. The PMS process is a major development in the reactive sputtering field. The high rate deposition of defect - free ceramic coatings onto complex components is now achievable using this technique, in conjunction with the CFUBMS process.

The results of a number of recent fundamental studies in this field have also been included and several industrial applications are discussed. Overall, therefore, this paper provides a review of the status of the magnetron sputtering process and considers future areas of exploitation for this technique.

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