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Pulsed plasma applications in material science and space propulsion

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Summary of Habilitation Thesis

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This habilitation thesis presents the most important scientific results obtained by the author in implementation, development and optimization of new technologies for plasma processing materials and electric propulsion in space. The scientific results presented in this thesis are structured in two main sections. In the first section, comprehensive studies on **development of High Power Impulse Magnetron Sputtering (HiPIMS) technique for applications in the field of plasma processing materials** are presented. The main characteristics and strategies for controlling plasma parameters using different operating modes or pulse configurations, as well as the main applications of HiPIMS in material processing in the form of thin films are described. Different strategies to improve process efficiency and stability, and the properties of thin films are presented.

High power impulse magnetron sputtering (HiPIMS) is an emerging physical vapour deposition technique which provides a substantially ionization of the depositing flux, allowing the synthesis of advanced materials. The driving force behind the fast development of HiPIMS technology has been the increasing demand of high quality functional thin films in widespread application areas, including hard and wear-resistant coatings, and coatings with specific characteristics for nuclear fusion and solar energy applications. However, due to particular behaviours of HiPIMS process, such as *very high power density, high ionization degree of sputtered material, self-sputtering, side-way ion transport and gas rarefaction effect*, there are two main drawbacks associated to this deposition technique: *reduction of deposition rate* and *transition to arc discharge*.

My scientific research activity has mainly focused to find solutions to overcome the main drawbacks of HiPIMS technology and to find optimal conditions for the synthesis of advanced materials. Therefore, the aim of my and co-workers research studies has been to make the HiPIMS process an industrially viable deposition technique for the efficient synthesis of high-quality metal and composite thin films. This was achieved by developing and understanding of the processes related to HiPIMS discharge operating in different modes, (*e.g.* short monopolar, bipolar and multi-pulse), and by employing both metal and compound materials such as oxides, nitrides, oxinitrides and carbides. A compressive understanding of the HiPIMS process has been achieved by studying the influence of the discharge parameters, such as pulse and magnetic field configuration, gas pressure, composition of gas mixture, on the plasma behaviour and properties of the deposited thin films. A lot of plasma diagnosis and material characterization techniques have been employed to control plasma parameters and consequently, thin film properties.

The strategies adopted by the author of the thesis to overcome the loss deposition rate without compromising one of the most important advantages of HiPIMS, namely the high ionization degree of sputtered material, were to find the optimal pulsing and magnetic field configurations by using short pulses, low peak current, additional magnetic field or different magnetic balance degrees. The experimental results showed that the use of short-pulse duration, low peak current, additional magnetic field or different magnetic unbalance degrees of the magnetron cathode facilitates the increase of the deposition rate and allows obtaining high quality thin films. In the case of HiPIMS assisted by external magnetic field, the deposition rate values for some materials (*e.g.* Al, Ti, Mn, Ni, Cu, Zn) were almost the same or even higher as compared to those measured in dcMS, at the same average power. The advantages of multi-pulse HiPIMS techniques were further exploited to deposit hard and wear-resistant coatings (pure metals, DLC, carbides and nitrides). It was shown that multi-pulse operating mode in HiPIMS together with the addition of an external magnetic field is an excellent solution for growing thin films with enhanced topological, structural, mechanical and tribological properties.

The thesis presents also a strategy to suppress arcing and to achieve controllable deposition processes in the compound-sputtering mode by limiting the energy per pulse using ultra-short pulse duration. It was shown that a proper selection of pulse configuration allows to minimize the probability for the occurrence of arcing during the reactive HiPIMS process and facilitates the growth of thin films with improved optical and mechanical performances.

The author of the thesis brought important contributions for better understand ion acceleration mechanism, highlighting the advantage of bipolar HiPIMS technique in controlling ion energy and thin film's properties without using substrate bias. It was proved that fast BP-HiPIMS technique allows excellent control over the ion energy and flux towards the substrate by proper choosing of pulse configuration. It was found that the high ionization degree of HiPIMS plasma, combined with an efficient ion acceleration process, may control and enhance the structural and mechanical properties of the growing film, regardless of the nature of the substrate (electrically conductive or insulator). Bipolar HiPIMS process can be compared to a conventional HiPIMS with a synchronized pulsed bias, which has the same timing as the applied positive pulse, and can be successfully used for selective ion acceleration. To further prove the ability of bipolar HiPIMS technique to grow advanced coatings onto nonconductive substrates, the ion-assisted deposition technology related to bipolar HiPIMS was used for the synthesis of high-quality diamond-like carbon (*DLC*) and CrN.

It was demonstrated the capability of reactive HiPIMS technique for narrowing the energy band-gap of metal oxide semiconductors, as ZnO and TiO_2, by doping with nitrogen atoms. It was shown that a key factor in controlling the nitrogen content in the reactive HiPIMS deposition of oxynitride films is the low content of oxygen in the working gas mixture. The low amount of oxygen injected into the discharge leads to an insufficient incorporation of oxygen atoms into the coating, allowing the un-oxidized metal atoms to bond with the less reactive nitrogen atoms. Furthermore, by using short HiPIMS pulses, both hysteresis effect and arcing could be drastically suppressed, ensuring good process stability without using any particular approaches or feedback control systems. The results pointed out the important role of crystalline order for improving of the photocatalytic activity of semiconductors in visible light, besides the role of a narrow energy band gap.

In addition to the well-known applications in thin films deposition, the magnetron discharge, operated in high power pulse mode, was used to mimic critical aspects of the plasma-wall-interaction under nuclear fusion relevant conditions, the instantaneous power density applied on the magnetron cathode being comparable to the steady-state heat fluxes in the ITER divertor region (~10 MW/m^2). For nuclear applications the gas entrapment in the HiPIMS deposition of thin film allows to mimic critical aspects of the plasma-wall-interaction under fusion relevant conditions. The high ionization degree of the HiPIMS plasma combined with efficient ion acceleration during the positive pulse recommend the bipolar HiPIMS technique to reproduce reference samples for re-deposited W layers in fusion devices after discharges with Ar, and Ne gas seeding. The experimental results showed that the process of enclosing Ne and Ar into co-deposited W thin layers can be optimized using low gas pressure, high negative and positive target voltages, short negative pulses and relatively long positive pulses.

In the second section, operating principle and **applications of thermionic vacuum arc (TVA) discharge in material processing and electric propulsion in space** are presented. It was also emphasises the successful implementation and development of pulsed TVA within the IPARC group. An important feature of the thermionic vacuum arc is that the plasma bulk's potential is highly positive, and under appropriate conditions, the anodic plasma is surrounded by a well-defined potential structure indicating the formation of a strong double layer (DL). The occurrence of a strong DL in TVA discharge and the fact that the metal ions gain kinetic energy corresponding to the DL potential fall were first reported by our group. One of the most important applications of plasma with DLs, stemmed from the capability to accelerate ions, and the production of energetic metal ion beam without using acceleration grids or substrate bias. These benefits allow TVA technique to be employed for the deposition of coatings for nuclear fusion and solar energy applications, as well for space propulsion applications.

Apart from the fact that the TVA-deposition method is an environmentally friendly, time-saving, cost-effective and facile PVD technology, the definite advantages are the high deposition rates, high purity of the thin films and good adhesion of the coating to the substrate. In this thesis it was shown that the thermionic vacuum arc is a powerful technique for deposition of thin films with improved topological, structural and mechanical properties for nuclear fusion applications. Furthermore, pulsed TVA technique (PTVA) was developed and reported in literature for the first time by our group. Preliminary studies have shown that operating the TVA discharge in high power pulsed regime significantly increases the ionization degree of the metal vapours (up to 20%), as well as ion energy (up to 2 keV), improving thus the ion beam flux. The benefits of pulsed TVA were further explored to synthesize nanostructured ZnO with applications in fotocatalytic degradation of organic pollutants. It was shown that the pulsed TVA deposition technique is a favourable and facile method for fabrication of one-dimensional (1-D) ZnO nanorods structures, with outstanding photocatalytic performance towards UV photo-degradation of organic contaminants. The superior photocatalytic activity of flower-like nanostructured ZnO synthesized by pulsed TVA might be attributed to the high crystalline order, high specific surface area and better separation of photo-excited electrons and holes on different crystal facets. Moreover, nanostructured ZnO coatings shynthesized by PTVA seem to be an excellent candidate for other solar energy applications, such as solar cells and H_2 generation via solar water splitting.

Besides implementation in plasma processing material applications, the PTVA technology was for the first time proposed by our group for space propulsion applications, as metal ion thruster. The invention refers to an innovative approach for the development of a new electric propulsion system, capable of independently controlling, in a wide range of values, the thrust and the specific impulse, without using expensive propellants or acceleration grids. By operating the TVA in pulsed regime both plasma ionization degree and ion energy are significantly improved leading to performance parameters (thrust, specific impulse, and overall efficiency) comparable or even superior to those of other classical electric propulsion systems.

At the end of the thesis, future work and perspectives in the studied research field are presented. The future scientific research activity will be mainly focused on the development and optimization of the bipolar HiPIMS and pulsed TVA for plasma processing materials and space propulsion applications. A careful attention will be paid for the strengthening the collaborations, human resources and laboratory infrastructure within the group by engaging young researchers and PhD students in the research activities related to the proposed topics, and by attracting financial resources from national and international programs.