„AL. I. CUZA" UNIVERSITY, IAŞI
FACULTY OF PHYSICS

Doctorate Thesis Summary

CONTRIBUTIONS TO THE STUDY OF CATHODE SPUTTERING PROCESSES IN STRUCTURES WITH ELECTRO-MAGNETIC CONFINEMENT

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This doctoral thesis was conducted over the course of several years (seven years), with an interruption for medical reasons, about two years. Preparing the thesis was developed successively in the Plasma Physics Laboratory of the Faculty of Physics in Iasi, in the Experimental Plasma Physics Group Laboratory of the Institute for Ion Physics and Applied Physics, University on Innsbruck, Austria and in the Plasma Chemistry Laboratory, Department of Surface and Plasma Science, Faculty of Mathematics and Physics, “Charles University” in Prague, Czech Republic.

The thesis is divided into seven chapters. The first two chapters form the monographic part, chapters III - VI contain the author's personal contributions, and the last chapter deals with general conclusions of the studies undertaken.

In this thesis have been studied mainly two cathode sputtering systems: the magnetron and the hollow cathode system. To produce plasma discharge was used several power supply sources, such as dc, RF and pulsed sources. The thesis main goal was the plasma diagnostics within the cathode sputtering zone in magnetically or electrically confined structures. As diagnostic methods were used: Langmuir probe and emissive probe, for magnetron discharge, optical emission spectroscopy, Langmuir probe and electrostatic analyzer for hollow cathode discharge.

Studies approach, in particular, the issue of emissive probe contamination exposed to the cathode sputtering and contributions have been made in defining how the phenomenon of sputtering in a magnetron argon discharge produced using tungsten, iron or stainless steel and titanium dioxide targets can modify the data obtained using a tungsten probe. The results obtained showed that if the electric probe is used for diagnostics of plasma from the cathode sputtering systems, such analyzes are necessary for any combination of target material, probe and working gas.

The manuscript begins with a brief **Introduction** setting out some considerations on the cathode sputtering process and the main reasons that led to approach such a theme in the thesis. First the *cathode sputtering* term is definied (the emission of particles from the surface of a solid material which plays role of a cathode due to energetic particles (atoms, ions, electrons or photons) bombardament). Sputtering occurs whenever any particle strikes a surface with enough energy to dislodge an atom from the surface.

Usually, the cathode sputtering process followed by deposition or condensation onto the substrate of sputtered material and / or its compounds, is characterized by several parameters such as sputtering rate, respectively, deposition rate of sputtered material, sputtering process *yield* and material deposition *yield* onto the substrate. Among these parameters, most significantly, especially in technological applications, is of course the *deposition rate* and the *deposition yield*, respectively. The *deposition rate* means the quantity of material deposited onto the substrate per unit time. The *deposition yield* can be defined as the ratio between the amount of sputtered material from the unit target area and the amount of material deposited upon the unit substrate area.[Chapman 1980].

To increase the efficiency of working gas ionization at low pressures, it can be used the magnetic field effects on electrons, resulting in so-called *magnetron discharge* [Lieberman & Lichtenberg (1994)].

Another option adopted for improving the cathode sputtering systems parameters is the so-called *double cathode effect* or, in another version, the *hollow cathode effect* "The hollow cathode effect" consists in increasing the discharge current intensity to much higher values than would result in a simple cathode discharge produced just at the same value of the gas pressure and anode-cathode voltage drop. At the same time it is found that in case of the hollow cathode effect, reducing the gas pressure up to a certain limit increases the current density, unlike the simple cathode discharge where the discharge current density decreases with decreasing gas pressure. Most properties of the hollow cathode effect results from more efficient use of fast electrons and ions compared to other discharge geometries [Francis (1956)]

In this thesis have been studied mainly two sputtering systems: the magnetron, , the modified hollow cathode discharge. The main difference between the two systems studied is that magnetron discharges operate at working gas pressures with one to two orders of magnitude smaller than to the discharges with electrostatic confinement. This leads to the fact that the deposited layers properties, using the two systems, to be different.

In Chapter I **Electric discharges at low pressure. The cathode sputtering** are presented general considerations for electric discharges at low pressure and cathode sputtering, considerations about the two types of discharges used as cathode sputtering systems: magnetron discharge and hollow cathode discharge.

In chapter II **Electrical, optical and spectral methods in plasma diagnostics**, which concludes the thesis monographic part, are presented the diagnostic methods used for investigating the plasma properties: Langmuir probe, emissive probe, electrostatic analyzer, optical diagnosis using Abel transform and optical emission spectroscopy.

In deposition processes of thin films by sputtering an important plasma parameter is the *plasma potentia*l.

Plasma potential can be determined by several experimental techniques. One of the fundamental and well established methods is determination of the plasma potential as a potential at which the zero cross of the second derivative of the Langmuir probe characteristic occurs [Auciello & Flamm (1989)].

Another diagnostic used for the plasma potential determination is an emissive probe diagnostic. Two base techniques for the plasma potential determination by the emissive probe are frequently used – the strongly emitting probe technique and the inflection point in the limit of zero emission technique. Both techniques are based on the effect of thermionic emission of electrons from a probe wire.

Thermionic emission of electrons from probe appears in emissive probe characteristic as an increase of ion saturation current in ion accelerating region, because the emission current superimposes on the ion saturation current. At increasing emission of electrons from the probe the floating potential of the probe moves towards the plasma potential. This fact is base of the plasma potential determination via strongly emitting probe. Electron saturation current is expected to remain unaffected by emission of electrons from the probe since the emitted electrons are attracted back to the probe when the probe voltage becomes positive with respect to the plasma potential. In first approximation it is also true in many cases. On the other hand, in some cases the variation of electron saturation current cannot be neglected [Mahdizadeh *et al*. (2005)]. Study of variations of the electron saturation current at varying probe heating is one of the goals of the this thesis [Madani *et al*. (2004)].

The current collected by Langmuir probe is the result of contribution of electronic and ionic plasma components Separating the contribution of these two components can be done using a grid electrode interposed between the collecting electrode and the plasma. The grid electrode can be polarized to a potential negative enough to reject electrons, either to a potential positive enough to reject ions [Popa & Sirghi (2000)]. This results in a device called the *electrostatic analyzer*. To characterize the hollow cathode discharge plasma in terms of ion energy was used a four grid electrostatic analyzer [Bohm & Perrin (1993)].

Optical measurements of plasma emissivity were carried out. For a homogeneous optically-thin plasma, the integral light intensity registered by the light receptor depends on: (a) the depth, x, of the measured plasma chord along the receptor's line of sight, (b) the distance, y, between the discharge axis and the chord, (c) local plasma emissivity, ε. The local emissivity at a distance r from the axis of symmetry can be expressed as:

$$\varepsilon(r) = -\frac{1}{\pi}\int_r^R \frac{\mathrm{d}I(y)}{\mathrm{d}y}\frac{\mathrm{d}y}{\left(y^2 - r^2\right)^{1/2}},$$

where R is the radius where $\varepsilon(r)$ vanishes [Lochte-Holtgreven (1968)].

The recorded light intensity curves, $I(y)$, were first fitted to Gaussian functions (correlation coefficients better than 0.99). Then an Abel inversion was applied to the fitted curves to obtain $\varepsilon(r)$ according to above equation.

The relative value of the electron plasma density was determined assuming an optically thin plasma, where excitations are produced by electron-atom collisions and de-excitations by spontaneous transitions. The radial distribution of the light intensity was measured at different positions along the distance between the two electrodes and between cathode and anode. After application of an Abel transformation to the radial distribution of the light intensity, the quantity proportional to the electron plasma density n_e was calculated

Chapter III describes the three **experimental devices** used throughout the research: cylindrical magnetron, the cavity hollow cathode discharge and the planar magnetron.

Cylindrical magnetron consists of two coaxially placed cylindrical electrodes. The outer discharge electrode with 58 mm in diameter is grounded and serves as anode. The inner coaxially placed water cooled electrode has diameter of 18 mm and serves as cathode. Plasma in the magnetron is confined by homogenous magnetic field parallel to the axis, created by six magnetic coils. Plasma parameters can be determined by means of electrical probes placed in vacuum ports equidistantly distributed along the discharge region. In the presented experiments, magnetron plasma was produced in argon; discharge conditions are: p = 4 Pa, B = 20 mT, I = 200 mA.

The cavity **hollow cathode** sputtering source consists of two specifically shaped equi-potential metallic disks, 25 mm in diameter, separated by a glass spacer, 18 mm in diameter, 6 mm high. The disks delimit a 1.4 cm^3 cylindrical cathode chamber, visible trough the glass spacer during optical and spectral measurements. The additional cylindrical chamber (5 mm in diameter) inside the lower disk is used to further enhance the ionization rate in the cathode cavity [Kazemeini *et al* (2000)]. The cathode ensemble was introduced into a cylindrical glass cover. The grounded wall of the 1 liter discharge chamber plays the role of the anode. In certain experiments, an additional 30-mm diameter ring anode, placed at 6-20 mm in front of the cathode nozzle was used; usually, the ring served as substrate holder.

After evacuation to a base pressure of 10^{-4} Pa, the Ar gas was admitted in front of the nozzle through three inlets. The average gas pressure was measured in the anode region.Under normal operation, a conical glowing plasma jet exits from the cathode conical nozzle, its shape being related to electrical and pressure gradients. In the pulsed regime, the d.c. power supply was substituted by either an *L-C* branch, with elements adjusted to ensure adequate current pulse repetition rate, in accordance with discharge parameters, or by an externally strobbed current source. A slight thermal drift due to the electrode heating, leading to run the discharge into an unstable regime was observed in the self-oscillatory regime. Therefore, a second configuration was tested to drive the source in pulsed regime. A current source using a transistor chopper, driven by an external pulse generator, was used to modulate the discharge current. With this arrangement, current pulses up to 200 mA with 1 ms duration (or shorter) and frequencies up to 1 kHz were obtained. These values are connected with limitations by the power supply and natural heat dissipation.

The device used to deposit thin films using sputtering **planar magnetron** consists of a stainless steel chamber with a volume of 30 liters, with 9 access ports. Inside chamber there is a Kurt J. Lesker planar magnetron ("Thorus magnetron", which allows sputtering metal and dielectric targets that have a diameter of 3 inches)Magnetron discharge was powered using either an RF generator or a pulsed current source. For thin film deposition have been used various types of substrates (glass, quartz, silicon, and / or conductive material) that are placed on a cylindrical sample holder containing a heating system and a samples temperature monitoring system.

In chapter IV **Considerations on the use of emissive probe subjected to cathode sputtering** are presented experimental results conducted on the influence of the sputtered material from target on the emissive probe material and thus on the probe characteristics. In thesis this issue was approached and contributions have been made in defining how the phenomenon of cathode sputtering in a magnetron discharge produced in argon, using targets of tungsten, iron or stainless steel and titanium dioxide, , can modify the data obtained using a tungsten probe. In case of using electric probe diagnostics of plasma in sputtering systems, such studies are necessary for any combination of target material, probes and working gas, . Experiments were performed both in pulsed magnetron and in dc or rf powered magnetrons. These studies have allowed specifying the precautions to be taken in this case. Emissive probe was placed near the deposition substrate to measure the plasma potential. The value of this potential is important for correlating the thin film features deposited on the substrate with the plasma parameters and it was found that this value is affected by errors due to probe contamination with the cathode sputtered material. Depending on the target material, we demonstrate that these errors are greater for targets whose materials react with the probe material (eg TiO2 target and probe of tungsten).

In chapter V **Floating potential and electronic saturation current of emissive probes in magnetized plasma** are presented considerations about variation of an emissive probe electronic saturation current. The cause of these variations was identified by studying the plasma evolution, the influence of probe material and probe size.

In papers published recently, has been shown that the use of hot probes and emissive probes, the electronic saturation current intensity may vary depending on the heating of the probe [Marek *et al* (2006)].

The study of the electron saturation current variations collected by the emissive probe at varying probe heating was presented and discussed here for a weakly magnetized low temperature argon plasma in the cylindrical magnetron It was found that electron saturation current variations can be divided into non-reversible and into reversible changes. The non-reversible variations were dominant and were connected with change of the emissive probe properties. Reversible variations – variations connected with thermionic emission from the probe – were less pronounced. Possible processes responsible for variations were discussed here. It was found, that variations were more pronounced in case of the shorter probes and for those with higher work function. The variations were less pronounced in case of thinner probes. It was concluded that it was due to the temperature induced non-reversible changes since the heat transport to the ceramic probe shaft was higher in all described cases with more pronounced electron saturation current variations.

In the second part of this chapter overestimation of the plasma potential by the strongly emitting probe in the low temperature plasma was studied and compared with analytical model. It was shown, that experimental data overestimate the plasma potential somewhat more than was the model prediction.

In chapter VI **Plasma diagnostics of a hollow cathode discharge in the cathode sputtering regime,** a low-cost, high-efficiency sputtering source, based on the cavity hollow cathode post-discharge (CHCPD) operated in both dc and pulsed regimes was investigated [Apetrei[1] *et al* (2006)], [Apetrei[2] *et al* (2006)], [Bălan *et al* (2005)].

Diagnosis based on Langmuir probe and OES measurements was performed to characterize the post-discharge. Good correlations between local plasma parameters as the electron temperature, density, or electron velocity distribution function and the total light emissivity have been found. This fact is useful since light emissivity is easier to be measured. By monitoring certain spectral lines of both buffer gas and sputtered metal, the distribution of the atomic species both inside the hollow cathode and in the anode-cathode interval data for the design of a adequate geometry for film deposition were gathered. Time-resolved measurements on optical emission spectra and Langmuir probe characteristics allowed us to find appropriate values of the circuit elements, gas pressure, and discharge current for pulse operation regime.

The current results demonstrate that this device can be used, either in dc or pulse operation, with beneficial effects of substrate bombardment with energetic particles during deposition. Due to its simplicity and small dimensions, the source can be easily used in a low-temperature aggregation cluster source for basic and applied research. Investigations are in progress to characterize metal clustering.

At the end of the manuscript are summarized the main **Conclusions** drawn from chapters III - VI:

1) Heated probes can be used to measure plasma parameters, and mainly the plasma potential, in the case of tungsten probes used in magnetron discharges with target made from wolfram or from metals that either don't modify the surface potential values, or don't interfere with the probe composition. Emissive probe floating potential values approximate well enough, error below one volt, the local plasma potential.

2) Measuring local plasma potential allows to establish the potential to be applied to the substart to control the ions energy bombarding deposited layer and, to some extent, their flow.

3) Using tungsten probes for magnetron discharge plasma diagnostic with titanium dioxide targets is not recommended due to rapid diffusion processes of titanium and its oxides in tungsten probe volume. This process leads to a continuous change of the probe surface properties leading to a large and cuasicontinuos variation of floating potential values, obtained from one measurement to another. Furthermore, heating the probe does not lead to clean it, but rather to increase the process of diffusion and depth tungsten probe contamination with titanium and their compounds. Floating potential values obtained in this case may deviate by more than 10 V to the plasma potential.

4) The study of the electron saturation current variations collected by the emissive probe at varying probe heating for a weakly magnetized low temperature argon plasma showed that the variations can be divided into non-reversible and into reversible changes. The non-reversible variations were dominant and were connected with change of the emissive probe properties. Reversible variations – variations connected with thermionic emission from the probe – were less pronounced.

5) Possible processes responsible for electron saturation current variations collected by the emissive probe at varying probe heating for a weakly magnetized low temperature argon plasma were discussed. It was concluded that:

i) the variations were more pronounced in case of the shorter probes and for those with higher work function.

ii) the variations were less pronounced in case of thinner probes.

iii) it was concluded that it was due to the temperature induced non-reversible changes since the heat transport to the ceramic probe shaft was higher in all described cases with more pronounced electron saturation current variations.

6) Also, overestimation of the plasma potential by the strongly emitting probe in the low temperature plasma was studied and compared with analytical model. It was shown, that experimental data overestimate the plasma potential somewhat more than was the model prediction.

7) In studies on a sputtering source, used especially for sputtering magnetic materials with high efficiency, whose active part is a hollow cathode, good correlations were found between the local plasma parameters: electron temperature, density, energy distribution function of electrons and ions measured by Langmuir probe and by electrostatic analyzer, , and optical data obtained, such as plasma emissivity.

8) By measuring the intensity of spectral lines both of the working gas and of the sputtered metal, we were able to obtain information on the spatial distribution of atomic species, both inside the hollow cathode and within anode-cathode.

9) Experimental results show that the hollow cathode device can be used both in dc and in pulsed regime, in the second case resulting higher quality metal deposited layers due to substrate bombardment with higher energetic particles during the process.

Selective references

Apetrei[1], R., Alexandroaei, D., Luca, D., Bălan, P., Ioniță, C., Schrittwieser, R. & Popa, G. (2006), Optical Emission Spectroscopy Diagnostic of Discharge Plasma in a Hollow-Cathode Sputtering Source, *Japanese Journal of Applied Physics* **45** (10B), 8128–8131.

Apetrei[2], R., Alexandroaei, D., Luca, D., Bălan, P., Ioniță, C., Schrittwieser, R. & Popa, G. (2006), Pulsed Regime of a Hollow-Cathode Discharge Used in a Sputter Source, *Japanese Journal of Applied Physics,* **45** (10B), 8132 – 8136.

Auciello, O. & Flamm, D.L. (1989). *Discharge Parameters and Chemistry*, vol. 1 of *Plasma Diagnostics*. Academic Press, San Diego, London.

Bălan, P.C., Apetrei, R.P., Luca, D., Ioniță, C., Schrittwieser, R., Popa, G (2005), Electrical and optical diagnosis of a cavity-hollow cathode post-discharge used as a sputtering source, *Journal of Optoelectronics and Advanced Materials* **7** (5), 2459-2464.

Bohm, C. & Perrin, J. (1993), Retarding-field analyzer for measurements of ion energy distributions and secondary electron emission coefficients in ion low-pressure radio frequency discharges, *Rev. Sci. Instrum.* **64** (1), 31-44.

Chapman, B.N. (1980) *Glow Discharge Processes*, John Wiley & Sons, New York.

Francis, G. (1956), *The Glow Discharge at Low Pressure, Encyclopedia of Physics vol. XXII* ed. by S. Flugge, Springer-Verlag, Berlin.

Kazemeini, M.H., Berezin, A.A. & Fukuhara, N. (2000), Formation of thin TiN_xO_y films using a hollow cathode reactive DC spputering system, *Thin Solid Films* **372**, 70-77.

Lieberman, M.A.& Lichtenberg, A.J. (1994), *Principles of Plasma Discharges and Materials Processing*, Wiley & Sons, Inc, New York, USA.

Lochte-Holtgreven, W. (1968), *Plasma Diagnostic*, North-Holland, Amsterdam, p 134.

Madani, R., Ionita, C., Schrittwieser, R., Amarandei, G., Balan, P. & Klinger, T. (2004). A Laser-Heated Emissive Probe for Fusion Applications. *Proceedings of 31st EPS 2004 in London, ECA Vol.28G, P-5.127* , 1–4.

Mahdizadeh, N., Greiner, F., Ramisch, M., Stroth, U., Guttenfelder, W., Lechte, C. & Rahbarnia, K. (2005). Comparison of Langmuir and Emissive Probes as Diagnostics for Turbulence Studies in the Low-Temperature Plasma of the Torsatron TJ-K. *Plasma Phys. Control. Fusion*, **47**, 569579.

Marek, A., Pickova, I., Kudrna, P., Tichy, M., Apetrei, R.P., Olenici, S.B., Gstrein, R., Schrittwieser, R. & Ionita, I. (2006). Experimental investigation of the change of the electron saturation current of a dc-heated emissive probe. *Czech. Jour. Phys., Suppl B*, **56**, B932–B937.

Popa, Gh. & Sîrghi, L. (2000) *Bazele Fizicii Plasmei*, Ed. Univ. „ Al. I. Cuza”, Iaşi.