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Study of Plasma System by OES (Optical Emission Spectroscopy)

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Abstract. Low-temperature and low-pressure plasma was investigated by OES (optical emission spectroscopy) in the range 200–1100 nm. For displaying measured emission spectra and identification of spectrum lines the software Spectrum Analyzer was used. Two modes of glow discharge present in the DC cylindrical magnetron apparatus which were previously researched by a mass spectrometer were studied by OES. The changes in the spectral range 300–600 nm during the transition between discharge modes are contributed to the emission of metal particles sputtered from the cathode material.

Introduction

At the present time magnetron sputtering systems are widely used for deposition of thin films with unique physical or chemical characteristics in a variety of industry branches e.g. in microelectronics, cutting tools or reflecting layers manufacture. In the cylindrical magnetron the dc discharge is created by the radial electric field and discharge plasma is confined by a magnetic field applied parallel to the axis. Crossed electric and magnetic fields cause E×B drift of charged particles. Study of electron drift velocity was described in work [*Borah et al*., 2010]. High-energy electrons are confined in the vicinity of the cathode in E×B drift loops. These electrons help to ionize neutral noble gas atoms. Created positive ions are accelerated towards the cathode with high energy and they bombard of cathode causes secondary electron emission and sputtering atoms from the cathode. Sputtered material of the cathode deposits thin films on the substrate placed near the anode.

By injection reactive gas (e.g. oxygen, nitrogen) to the discharge chamber, it is possible to fabricate extremely hard layers of oxides and nitrides of the sputtered material for a various applications (e.g. solar cells, flat panel display). Reactive magnetron sputtering allows obtain a large composition range of layers by controlling the injected reactive gas.

The demand to create high quality thin films increases and it requires to make systematic experimental studies of the spatial and temporal plasma parameters and to investigate correlation between the properties of the processing plasma and the characteristics of the deposited films during the deposition in the magnetron sputtering system. The most common plasma diagnostic method is Langmuir probe [*Pfau et al*., 2000], which is widely used to estimate plasma parameters. This method is comparatively cheap and easily technically practicable. Optical emission spectroscopy can be used as a mutually complementary method to the probe diagnostic. The technique of the optical emission spectroscopy is non-invasive, easy to implement and measurements are fast. Method of OES is passive and based on recording light emitted from the plasma. Through collisions of plasma particles with electrons, plasma particles are excited to higher electronic states. Relaxation of excited particles, which are present in the chamber, to lower energy states is the origin of emitted photons of light. Energy of released photon is equal to the difference between excited and lower energy state and corresponding with wavelength of spectral line described by relation:

$$\lambda = \frac{hc}{E_p - E_k}.$$

where h is Planck's constant, c is the speed of light, E_p and E_k is upper and lower energy state, respectively. Since the energy of a transition is a characteristic of the particle species, the analysis of the photon energy can reveal the composition of the plasma. It is important to note, that when spectral lines of some particles are not observed by OES, these particles could be still present in discharge plasma but not excited. Basic information on plasma spectroscopy, but also often used population models: corona model (CM) and collisional radiative model (CRM), is reported in works [*Frantz*, 2006, *Frantz*, 2004] in detail.

In recent years different techniques of OES in combination with models or other diagnostic methods were developed for determination of plasma parameters. Combination of optical spectroscopy and Langmuire probe technique was used in work [*Kang et al.*, 2008]. Information about plasma obtained by OES was compared with measurements of Thomson scattering in work [*Crintea et al.,* 2008]. Trace rare gases optical emission spectroscopy (actinometry) was reviewed in work [*Donelly*, 2004]. This method was used to obtain plasma electron temperatures and electron energy distributions by tracing a small amount of rare gas (Ne, Ar, Kr, Xe) injected in observed discharge using OES. Plasma parameters were extracted from the best match between recorded and CR model calculated relative emission intensities. In efforts to obtain electron temperature and electron density, OES method based on the line-ratio technique is usually used. One creates a population model for two selected excited levels (lines) and from this model it is possible to obtain density ratio of these two chosen levels like a function of plasma and discharge parameters. From the best fit between measured intensity ratio and calculated density ratio the plasma parameters are obtained. Detailed study of the three kinds of line-ratio techniques for low-temperature plasmas containing argon and nitrogen is described in work [*Zhu et al.*, 2010].

Experimental apparatus

The experimental data presented in this study were obtained using the cylindrical magnetron apparatus, which is placed and studied at the Charles University in Prague and was developed at the University of Greifswald. The system of cylindrical magnetron is schematically shown in Figure 1.

The cylindrical magnetron consists of two cylindrical electrodes coaxially mounted in a stainless steel vacuum chamber. The inner electrode is negatively biased and placed at the axis of the discharge chamber. The cathode is 18 mm in diameter and is water-cooled to avoid its overheating. The grounded chamber serves as the outer electrode (anode) and its inner diameter is 58 mm. The length of discharge region is 300 mm. At both ends of the chamber limiters held on cathode potential are placed. The discharge was generated by a high voltage source, which works in regime of constant discharge current.

Magnetic field parallel to the chamber axis is created by six magnetic coils specially mounted around the discharge chamber to achieve best homogeneity. Magnetic field can vary from 0 to 40 mT. Experimental system contains eight vacuum ports to the discharge chamber placed between magnetic coils. Five of them are usually used for Langmuir probe or emissive probe measurements. Two ports with glass windows could be used as ports for viewing.

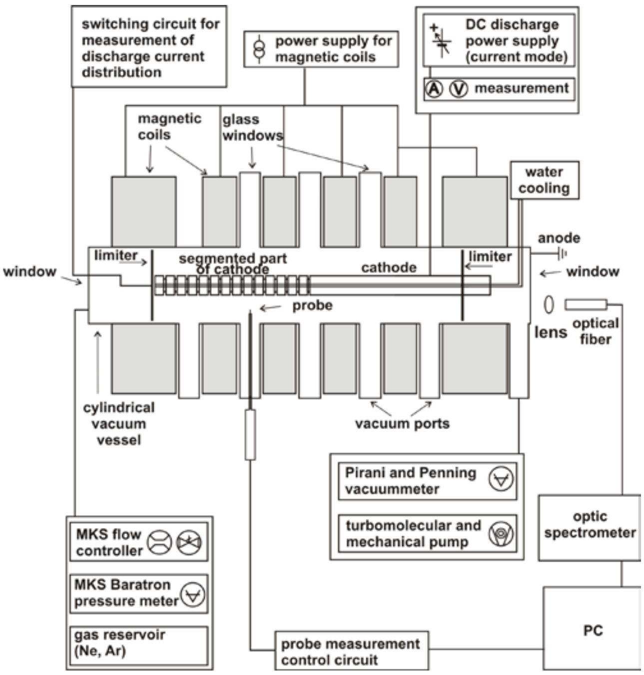

Figure 1. Schematic diagram of the cylindrical magnetron apparatus.

The vacuum system is pumped by the combination of oil free piston pump and turbomolecular pump. The ultimate pressure achieved in the system is in the order of 10^{-3} Pa. The discharge is usually produced in noble gases (Ne, Ar). The working pressure is possible to set up in the range from 1 to 10 Pa at typical discharge currents of 100–400 mA. Typical electron densities are in the order of 10^{16} m^{-3} and typical electron temperatures are in the range from 0.5 to 3 eV. The flow of the working gas is regulated by the MKS mass-flow controller. To achieve plasma homogeneity when the discharge burns the working gas is introduced in the chamber from both sides via limiters and vacuum system is evacuated in the middle of the chamber.

The light emitted from the discharge region goes through apertures in the limiter and then is collimated by a lens to an optical fiber with 600 nm in diameter. The optical fiber is placed parallel to the chamber axis in front of the window and connected to a detection device. The optical emission spectra were registered by an Ocean Optics spectrometer model HR4000CG-UV-NIR equipped with an entry slit of 5μm, grating of 300 grooves mm^{-1} and CCD detector (linear array of 3648 pixels). The measured emission spectra were obtained in the wavelength range 200–1100 nm. The optical resolution was 0.75 nm. For collecting data in real time and saving them the software SpectraSuite was used and for displaying measured spectra and identification of spectral lines the software Spectrum Analyzer [*Navrátil et al.*, 2006] was used.

Results and discussion

We investigated the low temperature weakly magnetized neon plasma of the cylindrical magnetron device. During previous experiments in cylindrical magnetron we often observed two different modes of the glow discharge with different discharge voltage and color. This phenomenon was mentioned in works [*Rusz*, 2003, *Holík et al.*, 2004]. The discharge burns in the first mode just after switching on. For the first mode lower and unstable discharge voltage with decreasing trend (during regime of the constant discharge current) is typical. For the second mode higher and stable discharge voltage is specific. The transition between these two modes proceeds after several tens of minutes from switching on the discharge and takes approximately 1–2 minutes. During the transition process the discharge voltage rapidly increases and discharge color changes to color characteristic for the working gas but pressure in the chamber was constant. Observed transition was spontaneous and nonreversible process.

Figure 2 shows volt-ampere characteristics measured in the first and second mode of the discharge and in the moment of the spontaneous transition. The reason for this behavior is not completely known. Mass spectra, obtained using quadrupole mass spectrometer to analyze working gas purity as a reason of different modes of the discharge, are depicted in Figure 3 and 4.

An example of the recorded emission spectra in the first mode in neon is depicted in Figure 5. In the right part of the spectra (550–800 nm) we can see spectral lines of the working gas, i.e. Neon (Ne I; 576.4, 585.2, 588.2, 594.5, 597.5, 603, 607.4, 609.6, 614.3, 616.4, 621.7, 626.6, 630.5, 633.4, 638.3, 640.2 ,650.7, 653.3, 660, 667.8, 671.7, 692.9, 703.2, 717.4, 724.5 and 753.6 nm). Considerable

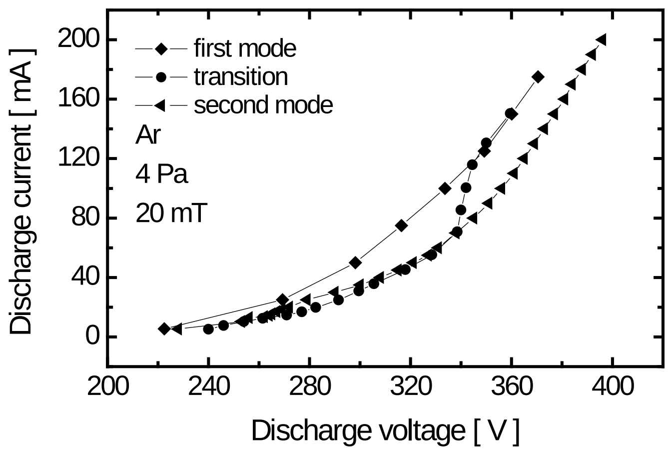

Figure 2. Volt-ampere characteristics of discharge in the magnetron apparatus. From [*Rusz*, 2003].

change of spectral lines intensity in this wavelength range for both modes was not observed. Left part of the emission spectra (300-600 nm) is better to see in next figures. We can see different value of the intensity of spectral lines in the first mode, transition and second mode shown in Figure 6, 7 and 8, respectively. Measurements were performed in neon at pressure 10 Pa. Discharge current was 250 mA. For each spectroscopic measurement the background noise was reduced by averaging of 50 individual optical spectra integrated 0.75 second.

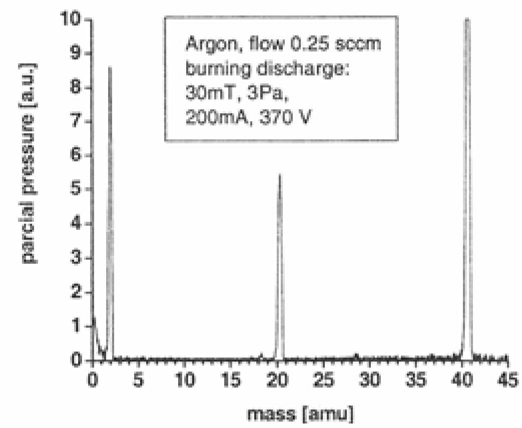

Figure 3. Mass spectrum measured in the first mode of argon discharge. From **[***Holík*, 2004].

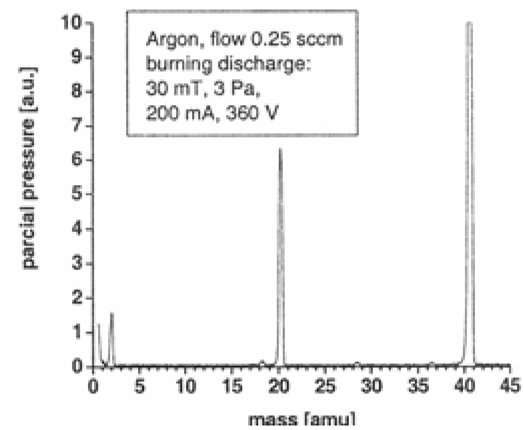

Figure 4. Mass **spectrum** measured in the second mode of discharge**.** From [*Holík*, 2004].

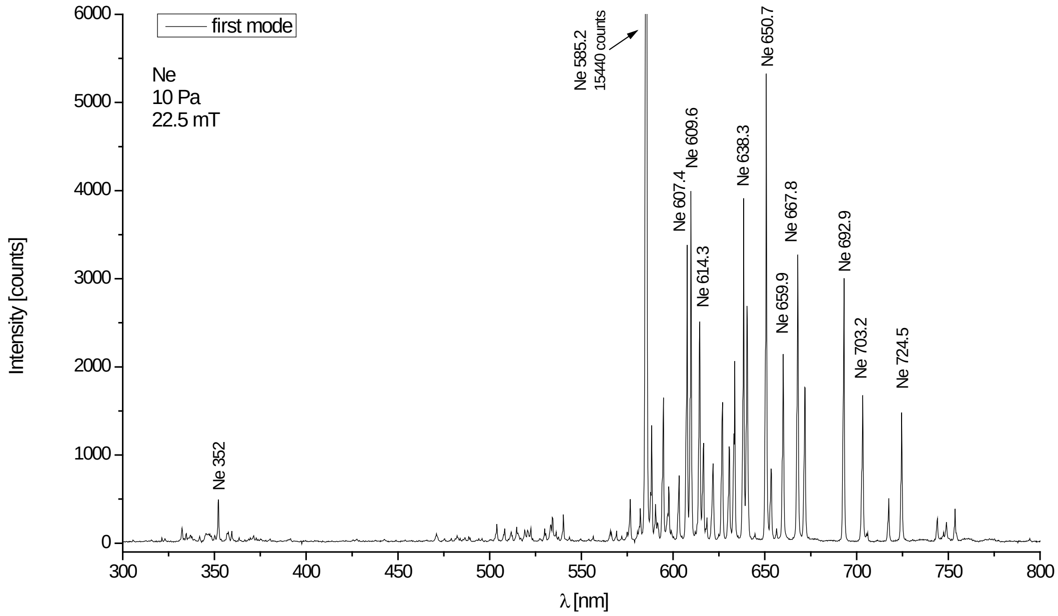

Figure 5. Emission spectra measured in neon plasma in the first mode of discharge at pressure 10 Pa.

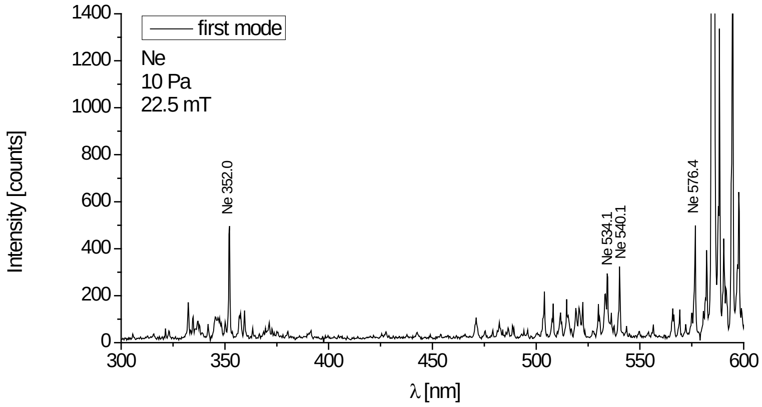

Figure 6. Optical emission spectra of magnetron plasma in the first mode of the discharge performed in neon at pressure 10 Pa.

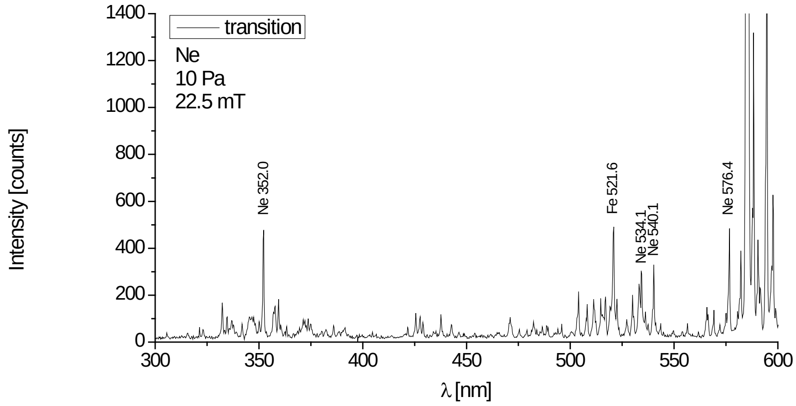

Figure 7. Optical emission spectra of magnetron plasma in the transition between two modes of the discharge performed in neon at pressure 10 Pa.

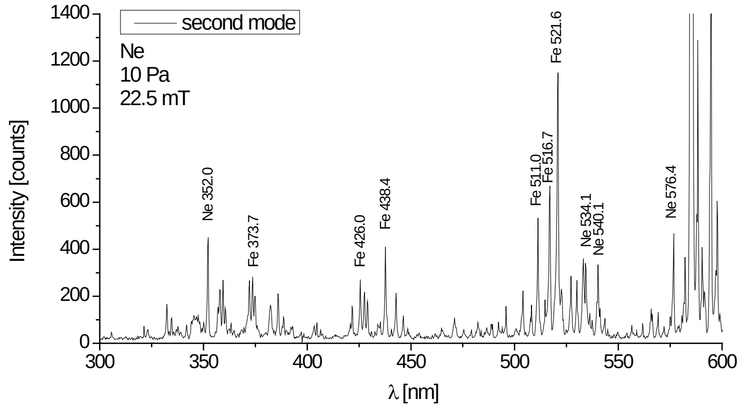

Figure 8. Optical emission spectra of magnetron plasma in the second mode of the discharge performed in neon at pressure 10 Pa.

After transition process, we can see in Figure 8 increasing intensity of the spectral lines in range 350–550 nm. We associate these wavelengths with particle species sputtered from the cathode surface, mainly iron (Fe I, 373.7, 386, 426, 438.4, 511, 516.7 and 521.6 nm). Precise identification of the observed lines is difficult because of the spectrometer resolution and it will be the subject of our further study. Increase of the intensity of spectral lines correlates with increase of the concentration of the particles emitting the light from the plasma volume. From mass spectroscopy measurements published in work [*Holík et al.*, 2004] it is known that the amount of impurities decreases immediately after switching on the discharge and the presence of impurities is probably the reason of these two modes. The time period of burning discharge in the first mode probably depends on the quality of vacuum before the measurement. The ultimate pressure is in the order of 10^{-3} Pa. After several experiments, time period of the first mode was shorter (but still several tens of minutes). Figure 4 shows decrease in amount of hydrogen in the second mode. From the emission spectra the presence of hydrogen was not observed but these particles could be still present in discharge plasma but not excited. In the “cleaner” discharge the surface of the cathode is more intensively sputtered by the positive ions of working gas and therefore the concentration of iron increases and we can observe higher intensity of emitted light in Figure 8. This observation confirms that the second mode correlates with cleaner plasma and stable discharge. For technological applications it is therefore important to sputter thin layers in the second mode. This also applies to plasma diagnostics. The study of plasma in the apparatus of the cylindrical magnetron using OES is complementary method for mass spectroscopy and probe diagnostic. Langmuir probe is during waiting for the stable second mode in the vessel coated by the layer of the cathode material and it causes a depreciation of the probe.

Conclusion

We installed and tested the OES diagnostic for the measurements in the cylindrical magnetron apparatus. Using OES emission spectra of the low temperature weakly magnetized neon plasma were recorded. We observed, studied and described two different modes of the glow discharge and the transition process between them. The measured data confirm results published in work [*Holík et al.*, 2004].

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