Spectrometric control of coatings deposition process

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Abstract. It is shown that one of the most important technological tasks for the process of reactive magnetron sputtering is to control the composition of a gas mix. Possibility of determining the composition of a gas mix using spectrometric equipment on example of argon–oxygen mix during deposition of tantalum pentoxide films is demonstrated. Results of experiments show that it is possible to control concentration of oxygen not only by change of intensity of oxygen lines, but also by relative change of intensity of argon lines.

1. Introduction
Magnetron sputtering is one of the most common technologies for deposition of films and coatings in opto-, micro- and nanoelectronics [1–3]. Compared to other methods of thin film deposition magnetron sputtering has several advantages, the main of which are:
– low temperature of the substrate;
– good adhesion of film to the substrate;
– high deposition rate;
– good uniformity of thickness.

In the discharge gap of magnetron systems simultaneously with the electric field a magnetic field that allows increasing the concentration of electrons to raise the density of the plasma is applied. In this case use of a magnetic field is equivalent to an increase of gas pressure.

In the magnetron sputtering system abnormal glow discharge in crossed electric and magnetic field is implemented. Discharge exists between cathode 1 and anode 2 (figure 1). Energy of the moving electrons is spent on ionization of the working gas atoms and maintaining of plasma discharge.

2. Analysis
When using a magnetron sputtering system electrons 3 beaten out from the cathode are accelerated in the field of cathode dark space with width d and with massive amounts of energy enter the plasma region 4, where they drift parallel to the surface of the cathode in closed cycloid trajectories h. The transition to a path more remote from the cathode surface is possible only after a collision in a field of plasma 4 of electron 3 with atom of plasma gas 6.

Fast free electrons are locked in the system in a kind of trap that is created, on one hand, by the magnetic field that returns electrons to the cathode, and on the other hand, by a surface of the target that repulses them. In this trap electrons move in complex trajectories and are located until and unless there are some ionizing or exciting collisions with atoms of a working gas, in which they lose energy received from the electric field. Prolonged circulation of electrons increases concentration of positive
Magnetron sputtering enables creation of thin films with a desirable composition free of impurities and defects with a high degree of repeatability [4–6]. Feature of reactive magnetron sputtering is the addition into the working chamber of a reactive gas (nitrogen, oxygen, methane, etc.) in supplement to the inert gas for directional changes in the composition of a coating. In reactive sputtering film is formed by interaction of reactive gas with atoms of the magnetron cathode material. Method of reactive magnetron sputtering is much more sensitive to the parameters of the technological process compared with conventional magnetron sputtering.

One of the main parameters requiring control is the partial pressure of reactive gas in the technological chamber. Minimum value of reactive gas pressure in the mix with the working gas is determined by the ratio of stoichiometric coefficients in the chemical formula of the coating material. The excess reactive gas in the technological chamber is undesirable, as in the case when oxygen is used as reactive gas it can lead to oxidation of the target and to changes in the dispersion parameters, and also to rapid failure of diffusion and preevacuation pumps. Since composition of the gas mix has a significant influence on the process of reactive sputtering and properties of the resulting films, maintaining a desired composition of the gas mix is an important task. Method of controlling the composition of the gas mix in the technological chamber carried out with the use of spectrometric equipment is perspective and finds greater application.

Spectrometric control is widely used in ion-plasma processes of etching and deposition of materials. Advantage of using spectrometric equipment for monitoring ion-plasma processes is not only simple integration of such systems into the technological process, but the lack of contact with the vacuum volume of the technological chamber, as well as possibility of diagnosing processes in real time. Depending on a task output of radiation can be made either integrally from the total volume of the technological chamber or selectively from a particular zone of interest for adjustment of the process. Optical fiber is most commonly used for light input to the spectrometer.

To conduct such research at the department of electronic devices and instruments of Saint-Petersburg State Electrotechnical University «LETI» was developed a universal spectrometric complex ISM3600 [7, 8], allowing control of ion-plasma processes, determination of coatings characteristics and properties of various substances, and to diagnose finished product of microelectronic production. Main characteristics of this complex are not inferior to similar device produced by leading companies such as «Avantes» and «Ocean Optics».

Most of spectrometric research methods need a panoramic observation of a spectrum. In mentioned device when using a diffraction grating with 300 lines per mm maximum observed wavelength range is limited to the region of 200...1000 nm, determined by the optical properties of the used silicon CCD.
photosensor. Optical resolution of the used device is determined by a diffraction grating and has a value about 1.0 nm. In terms of a tuned technological process it is not required to have a high optical resolution due to the presence of weak and strong lines in the spectrum of each substance; and if the focus is on the latter to monitor the presence of the most important technology components above mentioned optical resolution is sufficient.

Let us consider control process of reactive magnetron sputtering on example of depositing tantalum pentoxide (Ta$_2$O$_5$) coatings, applicable in various fields of technology, particularly in electronics when creating components operating in extreme conditions [9, 10]. This material has several properties that distinguish it from other compounds, namely high dielectric permittivity, density and melting point.

With the help of developed spectrometric complex, experiments were conducted on the study of plasma radiation of argon and oxygen mix in a reactive magnetron sputtering installation. Figure 2a shows a panoramic emission spectrum of the gas mix. This spectrum contains a number of lines of oxygen, argon and other substances involved in the process, which significantly complicates its analysis.

![Figure 2a](image)  ![Figure 2b](image)

Figure 2. Emission spectrums of plasma during deposition of tantalum pentoxide films:
(a) – panoramic spectrum; b – fragment of spectrum at different concentrations of oxygen.

To control the composition of the gas mix it is efficient to proceed to consideration of spectrum fragment that contains the most intense lines. Figure 2b shows a portion of plasma radiation spectrum for a fixed value of a discharge current during deposition of Ta$_2$O$_5$ films at different volumetric oxygen concentrations.

In the considered range of wavelengths argon is characterized by a number of intense spectral lines (738.4, 751.5, 763.5, 772.4 nm), and many of them are close in wavelength to the emission lines of oxygen. Taking into account low resolution of the spectrometer these lines will merge with each other. For atomic oxygen the greatest intensity has a triplet of lines, which is perceived as one line with a maximum at wavelength of about 777.5 nm. A distinctive feature of this oxygen line is its remoteness from the spectral lines of argon, which significantly increases its value in spectral analysis.

Experimental results show that emission line of oxygen 777.5 nm when the volumetric concentration of oxygen is less than 10–15 % is very weak compared with the lines of argon, and to judge the dependence of its intensity on the pressure of oxygen is not possible. With increasing concentration of oxygen there is an increase in the intensity of this line, also there is a significant decrease of intensity of argon lines, especially for the most intensive line of argon with wavelength 751.5 nm.

Volumetric concentration of oxygen during Ta$_2$O$_5$ film deposition in the majority of cases is low and is not more than 20 %. Experimental results show that control of oxygen concentrations should be
performed not so much by the change of oxygen lines intensity, how many on the relative change of the intensity of argon lines (figure 3).

![Figure 3. Dependence of the intensity of spectral lines of argon and oxygen from the volumetric concentration of oxygen.](image)

Decrease in the intensity of emission lines of argon with a simultaneous increase in the intensity of the oxygen lines is explained by a transfer of excitation from the metastable energy levels of argon to oxygen according to the following scheme:

\[
\text{Ar} + \text{O}^*(3P) \rightarrow \text{Ar}^* + \text{O}^+(3p^5).
\]

Energy of the first metastable level of argon is approximately 11.6 eV, excitation energy of the oxygen line 777.5 nm is 10.74 eV. In addition the creation of excited states of oxygen can occur via dissociation:

\[
\text{Ar}^* + \text{O}_2 \rightarrow \text{Ar} + \text{O}^*(3P) + \text{O}^+(3p^5).
\]

3. Conclusion
This study demonstrates the effectiveness of optical spectroscopy for monitoring composition of gas mix in the process of reactive magnetron sputtering, which allows controlling parameters of the obtained coatings. This method of control is not only simple in implementation, but also allows producing diagnostics in real time without any impact on the technological process.

4. References
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