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Optical emission spectra of Zn and Bi in pulsed magnetron plasma

***Abstract**. This study aimed at determining the relations between technological parameters of sputtering process - power discharge, the target-substrate distance, working gas pressure and the chemical composition of pulsed magnetron plasma by means of optical spectrophotometry. Planar 0.90Zn-0.10Bi target was sputtered in Ar, O_2 and in the atmosphere of the both gases mixture. Optical emission spectra were measured in 200-800 nm wavelength range.*

***Streszczenie**. Za pomocą spektroskopii optycznej określono korelacje pomiędzy parametrami procesu rozpylania - moc wyładowania, odległość target-podłoże, ciśnienie gazu, a składem chemicznym plazmy magnetronowego wyładowania jarzeniowego. W badaniach zastosowano stop 0,90Zn-0,10Bi. Target rozpylano w atmosferze argonu (Ar), tlenu (O_2) oraz mieszaninie obu tych gazów. Widma emisyjne rejestrowano w zakresie długości fal od 200-800 nm. (**Spektroskopia emisyjna plazmy zasilanej impulsowo w trakcie magnetronowego rozpylania stopu Zn-Bi**).*

Keywords: magnetron sputtering, optical spectroscopy, emission lines, pulsed plasma.
Słowa kluczowe: rozpylanie magnetronowe, spektroskopia optyczna, linie emisyjne, plazma zasilana impulsowo.

Introduction

A current development of microelectronics and optoelectronics forced the search for new materials with strictly defined electrical and optical properties. Recently, one of the most explored materials has been thin film of zinc oxide (**ZnO**). It has been extensively studied because of its present and potential application in various areas [1-8]. Other works also show structural and optoelectrical characteristic of **ZnO** that can be modified by doping with other elements [9-12]. In the last year investigations on doping with **Bi** started [13].

There are varieties of methods in preparing thin films as zinc oxide [14-19]. One of the most commonly applied methods is magnetron sputtering [20, 21]. **ZnO** thin layer can be obtained by sputtering a metallic target in the reactive (O_2) atmosphere [22, 23]. This method is characterized by a high rate of deposition, approaching several hundred nanometers a minute and it is now one of the versatile deposition processes for the industrial production of *ZnO* films [24].

In sputtering techniques there is a number of ways to apply the voltage to the cathode depending on the nature of the discharge: AC, DC, Pulse DC, radio frequency etc. In producing thin films the applying of high power pulses to a magnetron constitutes a relatively new method [25]. Depending on the type of the supply unit applied and technological parameters, physical and chemical processes occurring in the plasma undergo a change. It has a crucial effect on the stoichiometry, structural, optical and electrical properties of the obtained layers. By modification of the basic parameters of magnetron sputtering it is possible to obtain dielectric, semiconducting and conducting thin oxide layers. Additionally, the processes in the interelectrode space of excitation, ionization and recombination take place randomly. It makes the process very complex. Unambiguous determination of the relations between technological parameters of the magnetron sputtering process and chemical composition of plasma would be very vital. It would enable better control of sputtering processes and repeatability of electro-optical characteristics of deposited layers.

In the paper, the results of investigations of the magnetron plasma chemical composition by means of an optical spectrophotometry method are presented. Thin films were deposited by the pulse magnetron sputtering method. The influence of sputtering process parameters like target-substrate distance, power dissipated in the target and composition of working gas on the intensity of characteristic optical lines of bismuth I_{Bi} and zinc I_{Zn} (concentration of **Zn** and **Bi** atoms) were studied.

Experiment

Thin films were deposited by means of the pulse magnetron sputtering method. High-purity **Zn-Bi** (with wt% 0.90 **Zn**-0.10 **Bi**) target with a diameter of 50 mm and thickness of 6 mm was used. The sputtering processes were performed on the vacuum system equipped with a turbo molecular pump with the pumping speed of 312 l/s. The final pressure of the deposition chamber was 0.003 Pa. The deposition of **Zn-Bi** was carried out in the atmospheres of pure argon, pure oxygen and the mixture of both gases at the room temperature. Investigations in *Ar* and O_2 atmosphere were conducted under the same pressure 1.5 Pa. In the mixture of both gases the partial pressure of oxygen was changed in the range $0 < p_{O2}/p_{(O2+Ar)} < 1$. The magnetron cathode was powered by DPS Power Supply (medium frequency power supply) unit [25]. The power dissipated in the target was controlled by the pulses with the frequency of 2 kHz. The target - substrate distance was changed from 10 to 80 cm.

For the analysis of the chemical composition of magnetron plasma, M250 optical spectrophotometer in Czerny-Turner arrangement, equipped with Hamamatsu photomultiplier of R995 type was used. The optical system was made of pipe waveguides, located in the vacuum chamber, quartz viewfinder and quartz waveguide connected with a monochromator [26]. The system enabled the measurements of spectrum in the wavelength range from 200 nm to 800 nm with the resolution of 0.05 nm.

Results and discussion

A simultaneous analysis of **Zn** and **Bi** transmission lines is difficult to study due to their high coincidence. Additional complication is the fact that the intensity of emission lines depends on the method of atoms excitation. To distinguish between the two metals, their lines should be analyzed at two different wavelengths. In our investigation λ_{Bi} = 306.77 nm and λ_{Zn} = 636.23 nm were chosen.

The dependence of emission lines intensity I_{Zn} and I_{Bi} for selected wavelengths versus power dissipated in the target, sputtered in 1.5 Pa Ar atmosphere and target-substrate distance d = 20 mm is shown in figure 1a. Comparative studies were carried out in the atmosphere of pure oxygen at the same pressure 1.5 Pa (Fig.1b). The power dissipated in the target was changed in the range from 120 W to 500 W. As previous studies proved, the application of the power exceeding 500 W causes excessive heat on the target and its local melting. This leads to replacing the process of sputtering with the process of vaporization. As a consequence, the target can be destroyed. The obtained results of the plasma composition show that the absolute values of the optical spectrum are not constant.

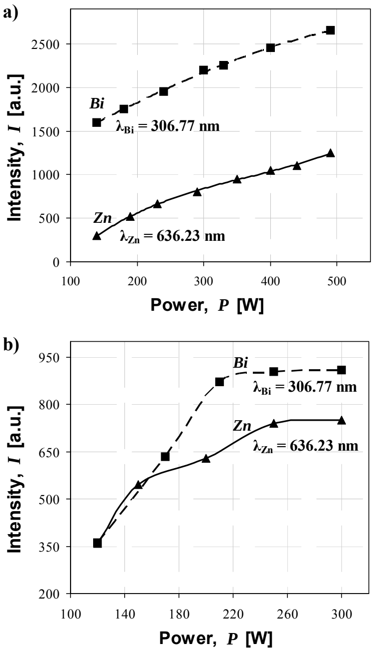

Fig.1. The effect of power dissipated in target on I_{Bi} and I_{Zn} intensity in: a) argon atmosphere p_{Ar}=1.5 Pa, d=20 mm, b) oxygen atmosphere: p_{O2}=1.5 Pa, d=30 mm

The intensity of the zinc and bismuth optical lines have a saturation tendency. In the process of reactive **Zn-Bi** sputtering, this takes place already at 200 W (Fig.1b). Additionally, the values of intensity of I_{Zn} and I_{Bi} emission lines in the atmosphere of oxygen are lower than in argon. This is due to oxidation processes which take place on the surface of the sputtered material. The target is covered by a sub-thin dielectric layer of oxide, which slows down the sputtering process and, as a consequence, the amount of ions of the sputtered material is lowered. Therefore, a further increase of power does not contribute to the increase in the absolute value of the lines intensity. In the case of argon, the greater value of power makes the amount of ions greater and at the same time the intensity increases. It is connected with the fact the sputtering process is becoming quicker. The ratio of the **Zn** and **Bi** lines intensity in argon for the power over 300 W is constant. This means that the material is sputtered steichiometrically. Below this value, the concentration of bismuth atoms is greater in comparison with its content in the target. For oxygen, this ratio is visible when the power exceeds the value of 200 W.

Figure 2 shows the effect of target–substrate distance on I_{Bi} and I_{Zn} intensity in argon p_{Ar}=1.5 Pa (a) and oxygen p_{O2}=1,5 Pa atmosphere (b). The distance was changed from 10 to 80 mm. In both cases there is a decrease in the absolute value of the optical lines intensity in the distance function from the target. For argon we can notice that zinc lines above 40 mm are practically constant. The intensity of lines I_{Zn} is lower than I_{Bi}. In the reactive process, this situation is reversed (Fig.2b). Moreover, in the process with the presence of oxygen we can observe a gradual disappearance of I_{Zn} and I_{Bi} lines. Similar dependencies were observed in previous studies [27].

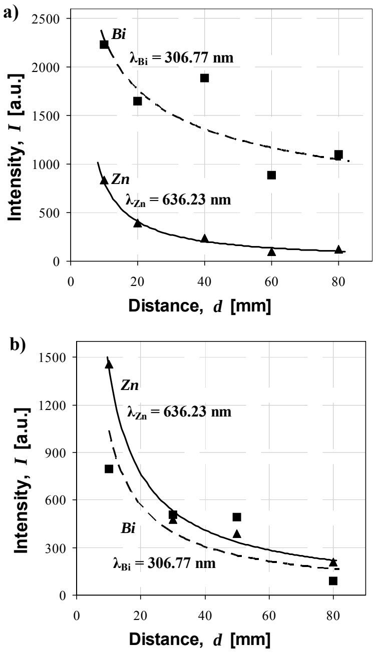

Fig.2. The effect of target-substrate distance on I_{Bi} and I_{Zn} intensity in: a) argon atmosphere: p_{Ar} = 1.5 Pa, b) oxygen atmosphere: p_{O2} = 1.5 Pa

Both diagrams in figure 2 present various ratios of the intensity of I_{Zn}:I_{Bi} lines in the target-substrate distance function, i.e. a different ratio of concentration of zinc ions to bismuth ions. This brings about the condition in which the obtained layers are characterized by a various chemical composition for each distance. Therefore, this composition can be regulated by means of the target-substrate distance.

The values of intensity of I_{Bi} and I_{Zn} emission lines depend also on oxygen partial pressure (Fig.3). It was stated that the relative lines intensities are a function decreasing with the increase in the oxygen concentration. In the range $0 < p_{O2}/p_{(O2+Ar)} < 0.5$, oxygen partial pressure practically does not affect the intensity of I_{Bi} and I_{Zn}, and consequently, the rate of target sputtering. Above this range, as far as up to 0.7, we can observe a rapid decrease of the intensity in the case of both lines.

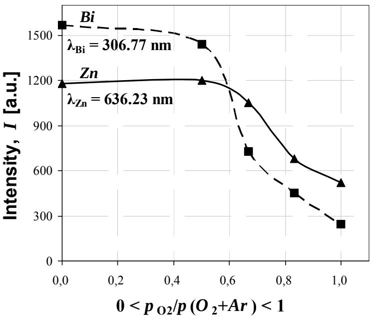

Fig.3. The influence of oxygen partial pressure on the value of I_{Bi} and I_{Zn}. Target-substrate distance d = 30 mm, power dissipated in target P =150 W

The studies prove that the thin layers obtained in the range of partial oxygen pressure 0-0.5 are composed mainly of metallic ***Zn*** and **Bi**. In the second segment the metallic **Zn-Bi** additionally contains bismuth and zinc oxide (**Zn-Bi-O**). Above the value of 0.7 for the partial oxygen pressure, there is only pure **Zn-Bi-O**. The conducted experiment proves that it is possible to change the chemical composition of the deposited layers by means of regulating the pressure.

Conclusions

The paper describes the results of studies on the influence of basic impulse magnetron sputtering parameters on the chemical composition of plasma. In the described method, the relative intensity of optical lines for **Zn** and **Bi** ions as well as for the working gases is different in comparison with other methods of the plasma excitation. There are no model lines for the impulse glow discharge. Therefore, it is difficult to conduct further studies.

When analyzing the obtained spectra, it was noticed that for **Zn** ions there are no maximum lines in the range of 200 to 250 nm. The maximum line was registered at the wavelength of 307.58 nm. Similarly, for bismuth ions – there are no strong lines in the ranges 220-240 nm, 360-430 nm and 510-530 nm. The maximum I_{Bi} reflex was obtained for the wavelength of 359.61 nm.

The conducted studies proved that stoichiometry of the obtained layers depends both on the target chemical composition and the technical parameters of sputtering (power dissipated in the target, the target-substrate distance, working gas pressure). The conducted optical studies have shown that the plasma chemical composition is also a function of these parameters. Consequently, this method can be employed in control systems and automation of magnetron sputtering.

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