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OPTICAL EMISSION SPECTROSCOPY OF PLASMA OF MAGNETRON DC DISCHARGE IN ARGON WITH COPPER AND MOLYBDENUM VAPOURS ADMIXTURES

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Magnetron discharge plasma with copper and molybdenum vapours admixtures are investigated by means of optical emission spectroscopy. A copper disk target, which partially covered by molybdenum semicircle, was used to generate the plasma with Cu and Mo vapour admixtures in a magnetron sputtering system. The optical emission of such plasma was registered in the spectral range of 440…910 nm. The discharge was realized in an argon atmosphere at pressures of 1.3, 6.7, 13.3, and 53.3 Pa in currents range from 50 to 300 mA. Excitation temperatures of argon and metals' atoms were determined by Boltzmann plot technique based on emission intensities of Ar I, Cu I, and Mo I spectral lines.

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INTRODUCTION

Plasma-assisted processes such as sputtering, etching and deposition have attracted increasing interest in microelectronics and material research. Among the various types of discharges, magnetrons are widely used for these purposes. Magnetron sputtering has become a widely utilized method in the production of coatings for microelectronics, optics, hard coatings, solar cells, and nanoparticles generation owing to its ability to achieve high deposition rates, uniform coatings, and stable plasma operation under low-pressure conditions [1-3]. However, to further improve and control these processes, detailed investigations of the plasma parameters are essential.

In particular, the investigation of the process of deposition of composite thin films is of interest from the point of view of both fundamental and applied research.

It is known that copper is widely used in technologies that require high thermal and electrical conductivity, corrosion resistance, and ease of manufacturing. This material has good electrical properties and low cost, so it is used in such devices and components as microwave and vacuum devices; cooling components of integrated circuits with a high degree of integration, etc. Thin films based on copper are widely used in electronics [4, 5].

However, copper, depending on the technology and nature of applications, has some disadvantages: in particular, it is a relatively low-melting element, has a high coefficient of thermal expansion, low mechanical strength and wear resistance [6]. Therefore, in order to eliminate such shortcomings, the composite materials are used, in which the properties of copper and other components (e.g. chromium, tungsten, nickel, molybdenum, etc) are additively combined. Composite materials, particularly Cu-Mo, are widely used in cooling and heat-sink elements in electronic device components such as microwave integrated circuits, insulated gate bipolar transistors, diode lasers or light emitting diodes (see [7] and references therein).

It is worth noting that there is little work devoted to the deposition of the Cu-Mo thin films by the magnetron method [7-9]. Moreover the most of the works devoted to the deposition of Cu-Mo thin films focus on the study of the films directly and do not consider the processes in the plasma of magnetron discharges [10].

This work is the first part of a wider investigation of the properties of magnetron discharge plasma with copper and molybdenum vapour admixtures. Namely, this part is devoted to experimental studies of such plasma by means of optical emission spectroscopy. Results obtained in this work will be further used for numerical simulation of the ionization region of this discharge.

1. EXPERIMENTAL SETUP

Investigations were realized by magnetron sputtering deposition system (Fig. 1) built on the base of a 72 mm planar-type oil-cooled cathode (1) with two zones of erosion determined by built-in permanent samarium-cobalt magnets (2) and oil-cooled anode (3) made of copper tube, disposed at a distance of 15 mm from cathode (4).

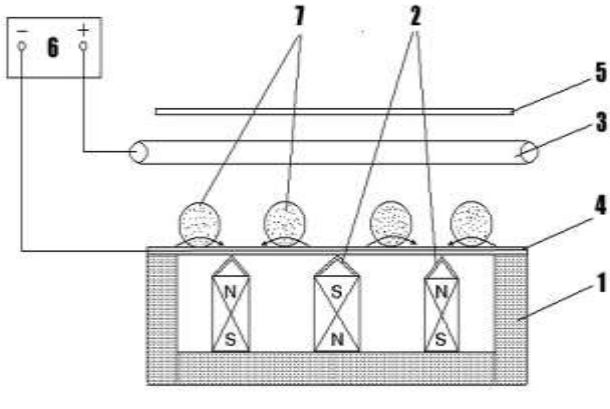

Fig. 1. Cross-section of the magnetron sputtering deposition system

Both, cathode and anode were installed in the chamber of the “VUP-5” industrial vacuum equipment. A 72 mm diameter disk made of copper was used as a target, on which a semicircle of the same diameter made of molybdenum was placed on top, were placed on the cathode surface and played a role of the sources of the sputtered materials. There also was special metallic screen (5) to reduce sputtering towards the glass walls of the chamber.

Power supply (6) of the magnetron discharge (7) was provided by the external setup (Fig. 2) consisted of adjustable voltage transformer (AT), step-up voltage transformer (T), set of variable ballast resistors (R1-R2-R3), rectifier circuit (BD-C) and AC/DC mode switch (X). There also were ammeter (mA) and voltmeter (V) to control discharge current and voltage drop, respectively.

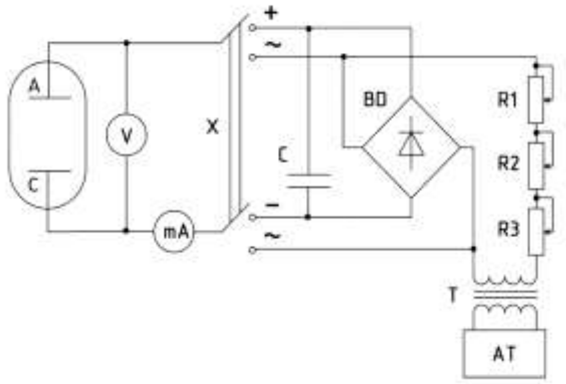

Fig. 2. Circuit diagram of the power supply setup for magnetron sputtering deposition

The magnetron discharge was studied in atmosphere of argon (Ar) at pressures of 1.3, 6.7, 13.3, and 53.3 Pa ($1\cdot10^{-2}$, $5\cdot10^{-2}$, $1\cdot10^{-1}$, $4\cdot10^{-1}$ Torr) in DC mode. Pressure of residual gases in the vacuum chamber was kept on the level of about $5\cdot10^{-5}$ Torr by pumping system of the vacuum device, consisted of backing vacuum pump and oil-diffusion pump, and controlled by ionization and thermocouple pressure gauges, the last one was also used to control Ar pressure during studies. Ar was introduced into the vacuum chamber using pressure reducer valve and inlet needle valve.

The studies of emission during magnetron discharge operation were carried out by optical emission spectroscopy. The Solar LS SDH-IV spectrometer was used to register the emission spectra of plasma. The excitation temperatures of metals’ and argon atoms were carried out by Boltzmann plot technique on the base of both metals and argon spectral lines [11].

2. RESULTS AND DISCUSSIONS

Typical emission spectrum of magnetron discharge plasma with copper and molybdenum vapour admixtures registered at 300 mA and 0.4 Torr is shown in Fig. 3. The data from the database of National Institute of Standards and Technology (NIST) [12] was used to identify the spectral lines of Cu I, Mo I, Ar I (see Fig. 3). One can see that the spectra consist predominantly of atomic argon lines. It is also seen that the spectral lines of both copper and molybdenum atoms also appear, which indicates a noticeable atomization of both materials in the discharge channel. Spectral lines of Cu I 465.1, 510.5, 515.3, 521.8, 578.2 nm; Mo I 473.1, 476.0, 550.7, 553.3, 557 nm; Ar I 687.1, 693.8, 696.5, 703.0, 706.7, 720.7, 727.3, 737.2, 738.4, 763.5 nm have been identified on the emission spectra and have been used in the excitation temperature determination by Boltzmann plot technique. It should be noted that other argon lines have been observed as well. But contours of observed lines with wavelengths more than 800 nm exhibited strong self-conversion. This behaviour indicates the presence of self-absorption, which in turn affects the determination of the intensity of spectral lines. Thus, all this lines were not used in the Boltzmann plots technique.

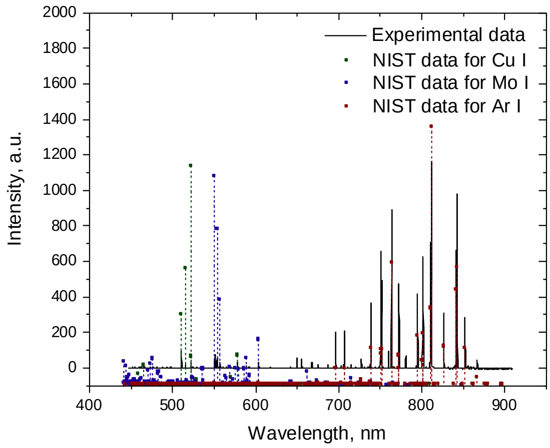

Fig. 3. Typical emission spectrum of magnetron discharge plasma with copper and molybdenum vapour admixtures registered at 300 mA and 0.4 Torr

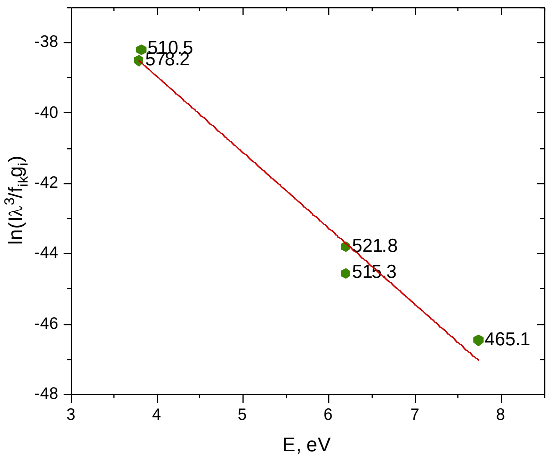

Fig. 4. Typical Boltzmann plots based on the obtained emission intensity of Cu I spectral lines registered at 300 mA and 0.4 Torr

The contours of each of the selected spectral lines have been approximated by the Voigt function [13] to obtain integrated observed emission intensity. The spectroscopic data (namely product of oscillator strength f_{ik} by statistical weight g_i) for the spectral lines of Cu I used in the temperature determination have been taken from a previous work [14]. Spectroscopic data of Mo I and Ar I spectral lines have been taken from NIST database [12]. Typical Boltzmann plots obtained based on the emission intensity of aforementioned Cu I, Mo I and Ar. I spectral lines are shown in Figs. 4, 5, and 6, respectively.

The excitation temperatures of different species were determined for each value of current and pressure. In this way, the current dependences of the excitation temperature at different values of working gas pressure in the chamber of the magnetron discharge are shown in Fig. 7.

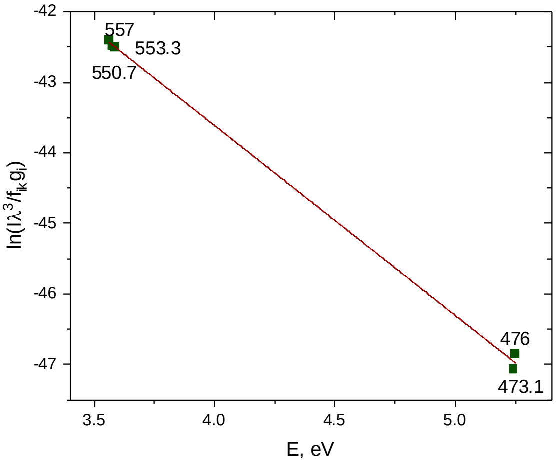

Fig. 5. Typical Boltzmann plots based on the obtained emission intensity of Mo I spectral lines registered at 300 mA and 0.4 Torr

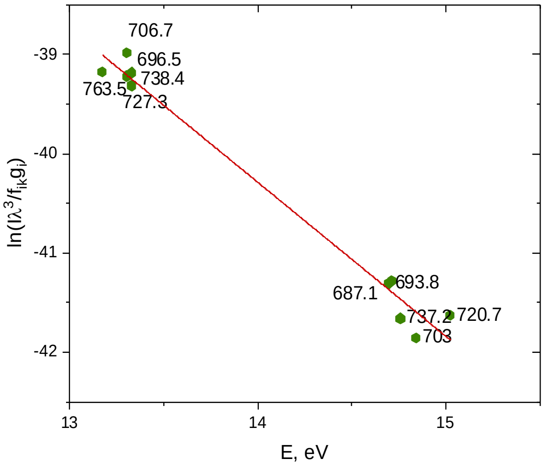

Fig. 6. Typical Boltzmann plots based on the obtained emission intensity of Ar I spectral lines registered at 300 mA and 0.4 Torr

One can see that the temperatures, obtained from the spectral lines of metals and argon, tend to decrease with increasing current. Moreover, the excitation temperature of copper and molybdenum atoms is lower than the temperature of argon atoms in all modes of discharge operation. Furthermore, a decrease in temperature with an increase in pressure is observed for all species (Fig. 8). It can also be seen from Fig. 7 that the difference between the excitation temperatures of atoms of both metals and argon atoms becomes smaller as the pressure of the surrounding gas increases.

It can be concluded, that the local thermodynamic equilibrium is not realised in such plasma. It is known that atoms of both metals (copper and molybdenum) and argon under room temperature conditions of the gas are predominantly in the ground state.

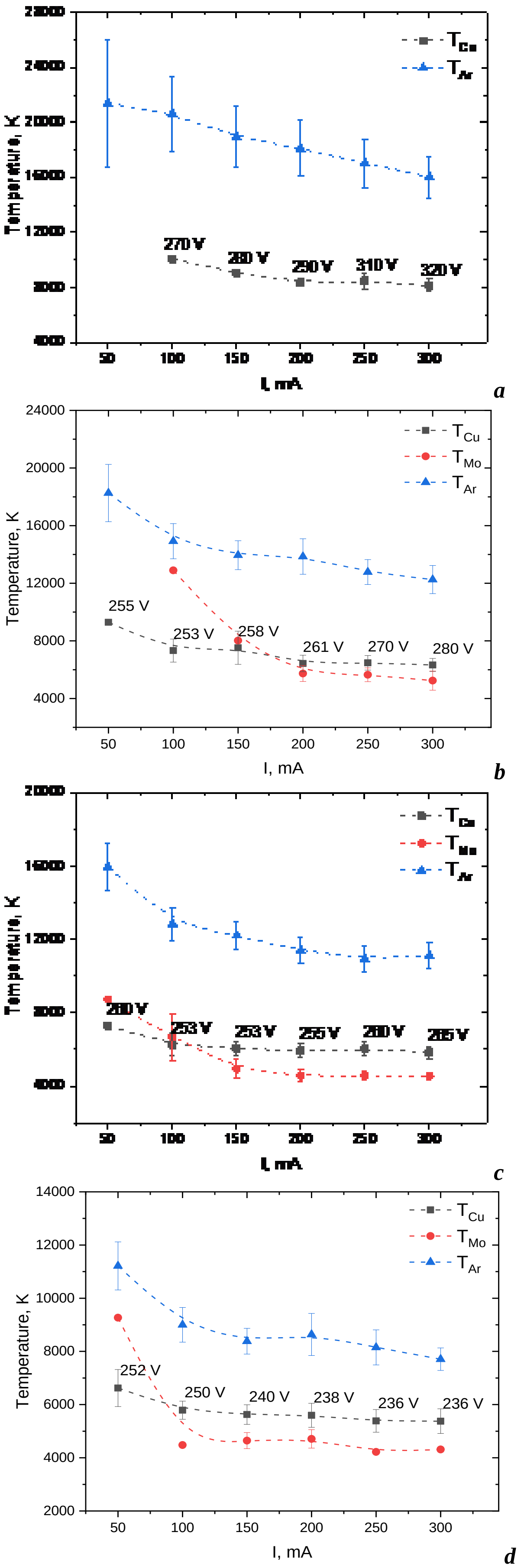

Fig. 7. Current dependences of the excitation temperatures of copper, molybdenum and argon atoms at pressure of 0.01 Torr (a), 0.05 Torr (b), 0.1 Torr (c), and 0.4 Torr (d)

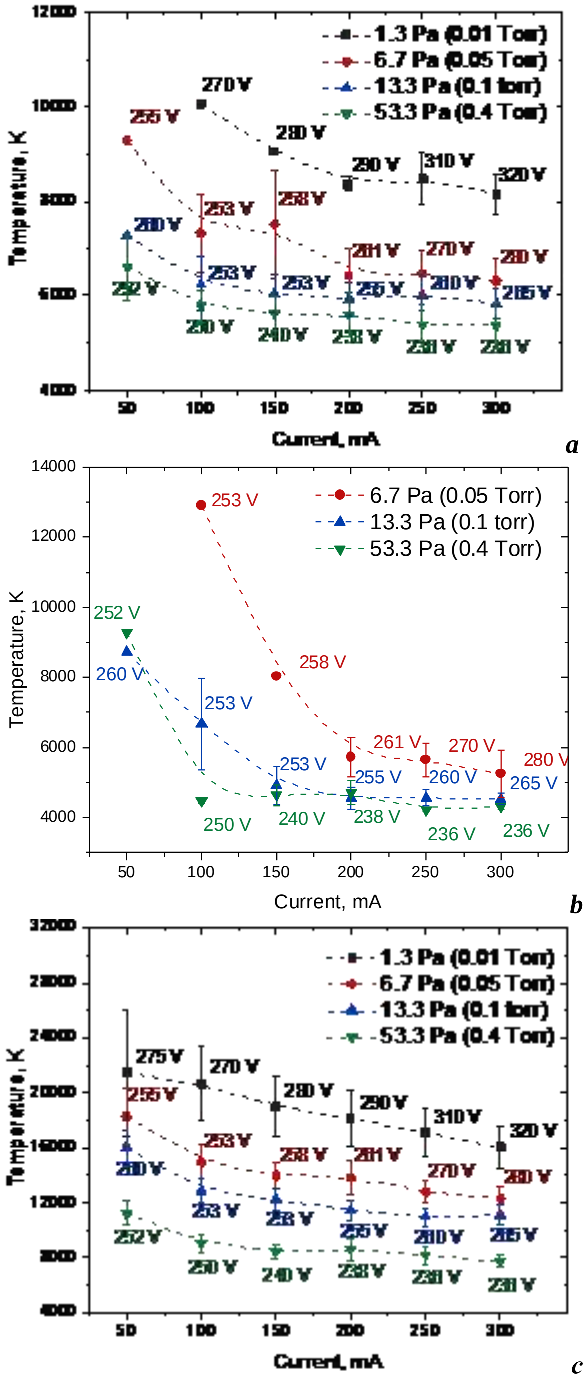

Fig. 8. Current dependences of the excitation temperatures of copper (a), molybdenum (b) and argon atoms at different pressures (c)

It is worth noting that the excitation energy values, at least of the resonance levels, differ significantly (approximately 4 eV for metals and 12 eV for argon [12]). It can be concluded that during inelastic collisions, the levels of atoms of these metals and argon are excited by groups of electrons with quite different energies, which, in turn, determines the different values of excitation temperatures obtained in the experiment.

As the pressure increased the collision frequency (both elastic and inelastic) between particles in the plasma increases. This leads to more energy redistribution through collisions, causing the energy to be spread across a larger number of particles, thereby lowering the excitation temperature.

CONCLUSIONS

The magnetron discharge plasma with copper and molybdenum vapour admixtures was investigated using optical emission spectroscopy. The investigations were carried out in atmosphere of argon at pressures of 1.3, 6.7, 13.3, and 53.3 Pa ($1\cdot10^{-2}$, $5\cdot10^{-2}$, $1\cdot10^{-1}$, $4\cdot10^{-1}$ Torr) in DC mode.

The emission spectra of the magnetron discharge plasma demonstrated the presence of spectral lines of copper (Cu I), molybdenum (Mo I), and argon (Ar I) atoms. The spectra were predominantly composed of argon lines, with visible contributions from copper and molybdenum, confirming the sputtering of both metals. Boltzmann plot technique based on the emission intensities of Cu I, Mo I and Ar I spectral lines was used to determine current dependences of the excitation temperatures of different kind of atoms at various pressures.

It has been found that the excitation temperatures of copper and molybdenum atoms are lower than those of argon atoms in all discharge modes. The results indicate that local thermodynamic equilibrium is not realised in the investigated plasma. This is due to significant difference between the excitation energy, at least of resonance levels, of metal and argon atoms which, in turn, leads to excitation these atoms by groups of electrons with quite different energies.

The experimental data gathered in this work will serve as a basis for future numerical simulations of the ionization region of magnetron discharges, contributing to improved control and precision in composite thin-film manufacturing processes.

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ОПТИЧНА ЕМІСІЙНА СПЕКТРОСКОПІЯ ПЛАЗМИ МАГНЕТРОННОГО РОЗРЯДУ ПОСТІЙНОГО СТРУМУ В АРГОНІ З ДОМІШКАМИ ПАРІВ МІДІ ТА МОЛІБДЕНУ

О. Мурманцев, А. Веклич, О. Костюкевич, О. Недибалюк

Методом оптичної емісійної спектроскопії досліджено плазму магнетронного розряду з домішками парів міді та молібдену. Для генерації плазми з домішками парів Cu і Mo в системі магнетронного розпилення використовували мідну мішень у формі диска, частково покриту молібденовим півколом. Оптичне випромінювання такої плазми реєстрували в спектральному діапазоні 440…910 нм. Розряд запалювали в атмосфері аргону при тиску 1,3; 6,7; 13,3 і 53,3 Па в діапазоні струму від 50 до 300 мА. Температури збудження атомів аргону та металів визначали методом діаграм Больцмана із залученням інтенсивностей випромінювання спектральних ліній Ar I, Cu I та Mo I.