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Effect of Adding Nitrogen to the Gas Mixture on Plasma Characteristics of a Closed-Field Unbalanced DC Magnetron Sputtering System

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In this work, the role of adding nitrogen gas to the discharge gas mixture containing argon was studied by introducing the electrical characteristics of plasma generated between two closed-field unbalanced magnetron electrodes. This role was also related to the presence and absence of magnetron at the electrodes in the fundamental design of such sputtering system. The role of nitrogen gas added to the gas mixture was reasonably observed by enhancing the electrical characteristics of the glow discharge plasma generated between the dual CFUBM electrodes. Adding nitrogen caused to increase the concentration of the charged particles produced by collisional ionization in discharge volume as the mean free path of primary discharge electrons was reduced. A relative reduction in electron temperature was observed as a result of adding nitrogen with increase in electron and ion densities while no observed difference was observed in the ion temperature due to their larger masses compared to those of electrons.

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1. Introduction

Since the first published work on the magnetron in 1960s, too many applications have based on this device. Amongst these applications, some of the most importance in industry and technology, such as microelectronics, materials processing and thin film deposition. Thin film deposition, have employed the magnetron to enhance and improve the characteristics of both operation and production. In sputtering deposition technique, employment of magnetrons makes this technique very efficient in micro- and nano-structure production [1-8].

Magnetron sputtering deposition techniques are widely applied both in industrial processes and in advanced material developments or treatment [9]. The first paper on the magnetron was reported in 1960s, but the physical basis originates back to the later [10]. Since then, magnetrons have known a continuous development in various industrial fields, especially microelectronic, surface processing and widely used for thin film deposition [11]. As well as, the field of applications is sputter deposition, reactive sputter deposition, reactive ion etching, and coating of thin films.

Taking the advantage of magnetic field, magnetron sputter operates at a low pressure and low voltage [12]. Basically magnetrons utilize an external magnetic field parallel to the cathode (target). The component of this field parallel to target traps energetic electrons in their travel from

the cathode to the anode leading to an amplification of gas ionization and form high density plasma near the cathode surface [13]. Ions produced by these electrons are accelerated toward cathode surface with high energy. This bombardment of ions not only sputters out target material, but also produces secondary electrons that maintain discharge [14].

Plasma nitriding is the most common method of surface treatment and now widely used for surface hardening of steel and non-ferrous materials (such as Ti and Al) in the manufacturing industry for surface modifications improving hardness, fatigue and wear resistance. Plasma nitriding is considered low cost method because it introduces faster nitrogen diffusion, which in turn allows for lower nitriding temperatures or shorter treatment times. This method is also environmentally friendly process, uniform treatment, and almost no distortion of the treated parts compared to conventional nitriding processes such as liquid or gas nitriding [15]. Plasma nitriding may replace hard chromium in applications on some small and complex components [16].

Nitriding is a lower-temperature process typically carried out at temperatures about 500°C for steels. Gas nitriding and plasma nitriding are the most popular methods, however, plasma nitriding is claimed to give improved control over the nature of

the surface layers and the processing time is shorter [17].

Gas additions to the main plasma gas provide to change the plasma parameters and can be used for plasma diagnostics. The abnormal glow discharge for plasma-based thermochemical surface treatment occurs at low pressures (0.1-10 mbar) and at relatively low voltages (300-800 V) between the anode and cathode in the transition zone of the negative glow light near the cathode [18].

The positively charged nitrogen ions accelerated toward the component provide nitrogen which is able to diffuse due to its high kinetic energy. It is incorporated into the surface and diffused into the surface zone of the component depending on the duration of the treatment and the temperature. Plasma nitriding process is regulated by precise specifications of the voltage, gas composition and temperature [18].

In this work, the role of adding nitrogen gas to the discharge gas mixture containing argon was studied by introducing the electrical characteristics of plasma generated between two closed-field unbalanced magnetron electrodes. This role was also related to the presence and absence of magnetron at the electrodes in the fundamental design of such sputtering system.

2. Experiment

The main parts of the plasma sputtering system are shown in Fig. (1) and the closed-field unbalanced magnetron (CFUBM) was employed at the cathode electrode.

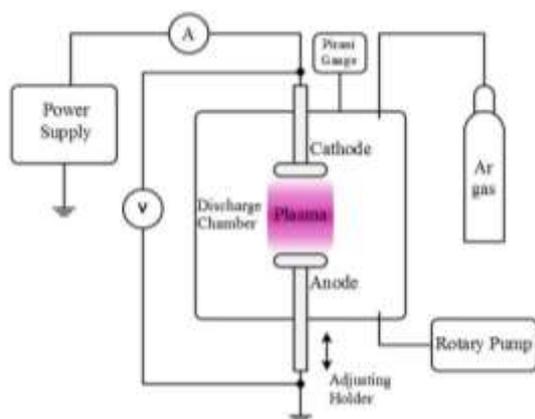


Fig. (1) Schematic diagram of the system used in this work

Electrodes (anode and cathode) were made of stainless steel and each was a disk of 8 cm in diameter and 4 mm in thickness. Two annular concentric magnets were placed behind each electrode to form the magnetron configuration. The outer diameters of the two magnets were 8 and 4 cm, while the inner diameters were 4 and 3.2 cm, respectively. The electrodes were connected to a DC

power supply to provide the electrical power required for discharge. The lower electrode (anode) could be move vertically with respect to the fixed upper electrode (cathode) to adjust the separation of the two electrodes from 1 to 8 cm.

Pure argon gas was used to produce the discharge plasma. A DC power supply up to 5 kV was used for electrical discharge between the electrodes and both breakdown voltage (up to 1 kV) and discharge current (up to 100 mA) were monitored by two digital voltmeter and ammeter, respectively. A current limiting resistor of 6.75 kW was connected in series to the discharge circuit in order to control the current flowing in the circuit.

The discharge chamber was evacuated by a two-stage Leybold-Heraeus rotary pump and the vacuum inside chamber was measured by Pirani gauge connected to a vacuum controller from Balzers VWS 120. Argon gas was supplied to the chamber through a fine-controlled needle valve (0 - 160 ccm) to control the gas pressure inside the chamber. High-purity nitrogen was mixed with argon to form the discharge gas mixture at different mixing ratios and then injected to the chamber at flow rate of 8 sccm.

3. Results and Discussion

For primary indication of the effect of adding nitrogen to the working gas mixture of the CFUBM sputtering system considered in this work, the discharge plasma was photographed, as shown in Fig. (2), and the deformation is clearly observed in case of adding nitrogen gas.

This may be attributed to the difference in electrical properties of argon and nitrogen, which reasonably determines how much discharge power transferred to each of them (Ar and N₂) before the breakdown occurs. Also, the discharge of only argon is clearly uniform due the homogeneity in size and properties, which is expected as well if only nitrogen is used.

Different mixtures were characterized, as shown in Fig. (3), to determine the optimum ratio at which the required silicon nitride will be prepared. When nitrogen gas was added to the argon with mixing ratio Ar:N₂ of 4:1, an increase in discharge current was observed, as shown in the Fig. (4), which may be attributed to the contribution to total current from the ionized nitrogen molecules [19].

Ionization of these molecules can occur by collisions with primary electrons under the effect of applied electric field and/or by the secondary electrons. The difference is very small at low discharge voltages (200-300V) because the major contribution of nitrogen molecules is due to the ionization by primary electrons. This difference is clearly observed at high discharge voltages (>300V) because the secondary electrons are accelerated by higher electric field (V/d) and then the ionization of nitrogen molecules by collisions with these electrons

is increased [20]. Therefore, the contributions of ionized molecules are added.

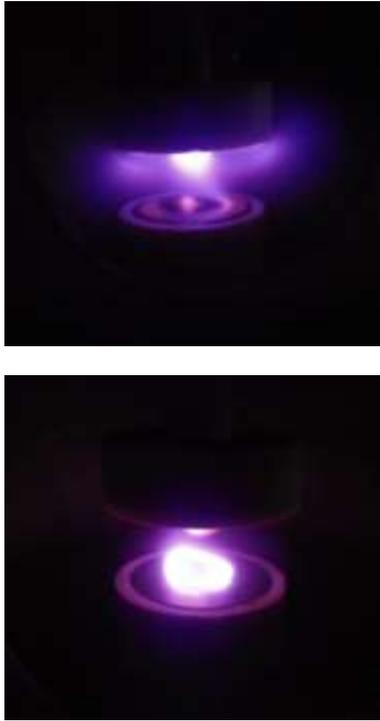


Fig. (2) The effect of adding nitrogen to the working gas mixture on the spatial distribution of the plasma formed between the two magnetron electrodes when using only argon (upper) and when using argon and nitrogen (lower)

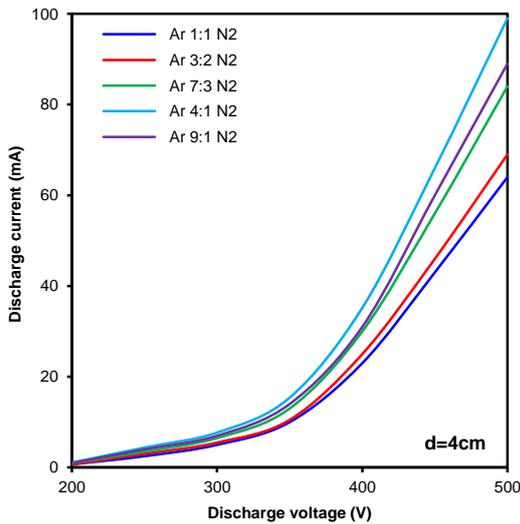


Fig. (3) Discharge current-voltage characteristics for different argon/nitrogen mixtures at total gas pressure of 0.7mbar and inter-electrode distance of 4cm

Higher current was measured as the production of the charged particles was increased due to the additional contributions from ionized nitrogen

molecules. As the density of particles (Ar atoms and N₂ molecules) in discharge volume is increased, mean free paths of electrons are reduced and their collisions with argon atoms and nitrogen molecules are accordingly increased. So, an electron in case of argon/nitrogen mixture may make more collisions than in case of argon only and hence produce more ions [21]. These ions may include argon and nitrogen ions, as the former are employed for sputtering while the latter are required for nitriding.

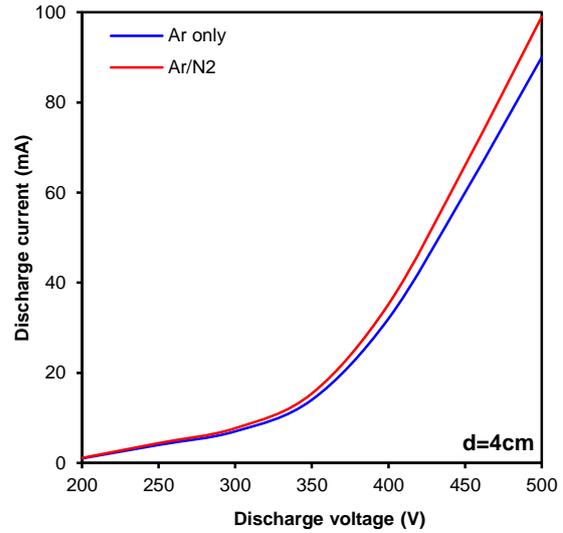


Fig. (4) Comparison of current-voltage characteristics of glow discharges in argon gas and argon/nitrogen (4:1) mixture at total pressure of 0.7mbar and inter-electrode distance of 4cm

At inter-electrode distance of 4cm and discharge voltage of 700V, the relation between discharge current and argon/nitrogen mixture (4:1) pressure was plotted and compared to that for only argon, as shown in Fig. (5).

The current-voltage characteristics of Langmuir probe diagnostics of unmagnetized glow-discharge plasma for two different cases (Ar gas and Ar/N₂ mixture) at working pressure of 0.7 mbar are shown in the Fig. (6). There was an increase in the probe current in case of Ar/N₂ mixture due to the increase in collisional ionization coefficients in presence of the nitrogen molecules added to argon.

In the negative biasing region (ion current region), shown in Fig. (7), the current is too small to be noted on the figures at the same scale of electron currents. At high negative bias voltages, the ion current can be considered equal to saturation ion current (I_{is}). The intersection of this curve with the horizontal axis (bias voltage) gives the value of floating potential ($V_f \approx 5V$), which seems to be stable for this range of working pressures. In Table (1), the summary of the obtained results are presented to explain the effect of using nitrogen in the working gas mixture.

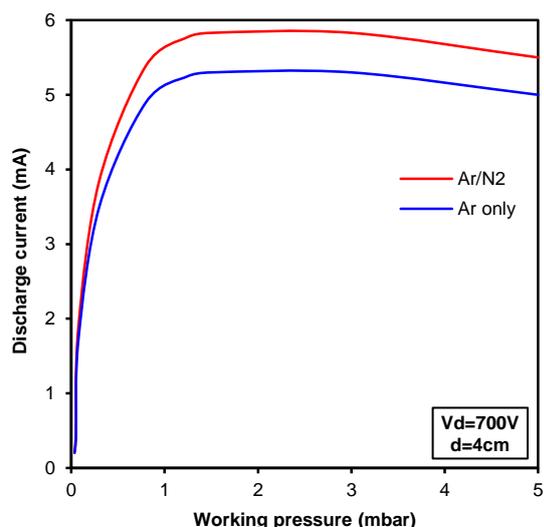


Fig. (5) Comparison between current-pressure curves for argon gas and argon/nitrogen mixture (4:1) at discharge voltage of 700V and inter-electrode distance of 4cm

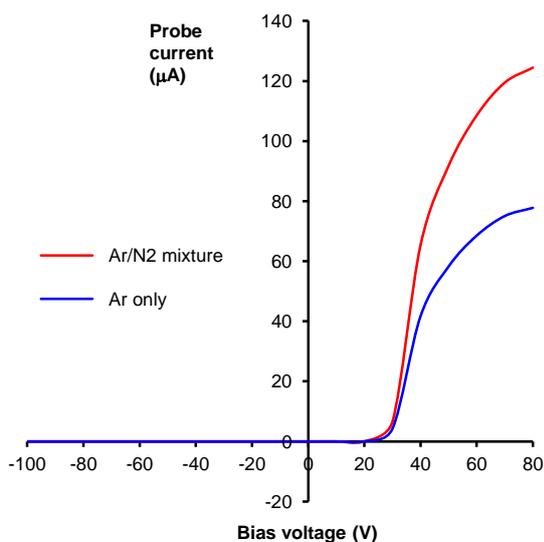


Fig. (6) Effect of mixing argon with nitrogen on the Langmuir probe characteristics at total working pressure of 0.7mbar and inter-electrode distance of 4cm

Table () Effect of using nitrogen in gas mixture on the plasma parameters

Dual magnetrons	Ar gas only	Ar/N ₂ mixture
Electron temperature (eV)	4.850	4.837
Electron density (x10 ²¹ m ⁻³)	1.130	1.811
Ion temperature (eV)	0.864-1.16	0.865-1.16
Ion density (x10 ²¹ m ⁻³)	1.130	1.329

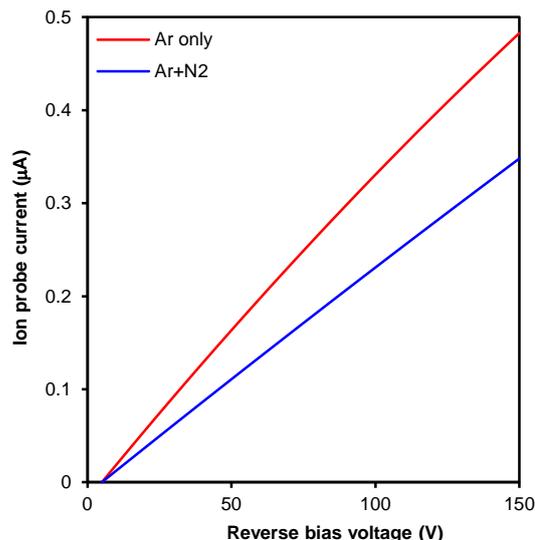


Fig. (7) Effect of mixing argon with nitrogen on the Langmuir probe characteristics of ions in negative biasing region at total working pressure of 0.7mbar and inter-electrode distance of 4cm

4. Conclusions

From the results obtained in this work, the role of nitrogen gas added to the gas mixture was reasonably observed by enhancing the electrical characteristics of the glow discharge plasma generated between the dual CFUBM electrodes. Adding nitrogen caused to increase the concentration of the charged particles produced by collisional ionization in discharge volume as the mean free path of primary discharge electrons was reduced. A relative reduction in electron temperature was observed as a result of adding nitrogen with increase in electron and ion densities while no observed difference was observed in the ion temperature due to their larger masses compared to those of electrons.

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