Optical Emission Spectroscopy Study of the Electron Temperature and Electron Density Dependence on the Pressure Chamber for the Carbon Deposition Produced by Argon Plasma Sputtering

D R S Pambudi¹, M A Hanif¹, D J D H Santjojo¹,², M C Padaga³ and Masruroh¹,²*

¹Department of Physics, Brawijaya University, Malang, Indonesia
²Collaborative Research Group for Advanced System and Material Technology (ASMAT), Brawijaya University, Malang, Indonesia
³Faculty of Animal Husbandry, Brawijaya University, Malang 65145, Indonesia

*Corresponding author: ruroh@ub.ac.id

Abstract. An investigation of the Optical Emission Spectroscopy (OES) to study the effect of the pressure chamber to the chemical species, electron temperature (Te) and electron density (Ne) was performed on RF 2 MHz plasma sputtering for carbon deposition. A carbon target and argon (Ar) gas were used to deposit carbon films. The carbon deposition was carried out at pressure chamber of 10, 15 and 20 Pa, and the RF voltage, flow rate and substrate temperature were kept at 120 volts, 60 ml/min, and 200°C, respectively. The emission spectrum of Ar plasma was monitored by OES in order to analyze the chemical species present in the plasma during the deposition process. The atomic spectroscopy data center (NIST) database was used to determine the species in the plasma and to calculate the Te and Ne. The OES emission shows the peak intensity which indicates the Ar I (Ar*) and Ar II (Ar⁺ ion). The electron temperature was calculated using the Boltzmann Plot while the electron density was calculated using Stark Broadening. The results show that both Te and Ne decreased on the increasing of the pressure chamber. The emission line measurements with Boltzmann Plot resulted in the electron temperature dependence of pressure is approximately 0.487±0.005, 0.481±0.006, and 0.474±0.011 eV, respectively. Moreover, the calculation of electron density resulted in approximately (5.495 ± 0.407) × 10¹⁸, (4.825 ± 0.384) × 10¹⁸, and (4.515 ± 1.037) × 10¹⁸ cm⁻³.

1. Introduction

QCM (Quartz Crystal Microbalance) is a device consisting of quartz crystals coated by electrodes [1]. QCM is very sensitive to the changes in mass and has a piezoelectric principle, i.e., to detect frequency shifts in quartz crystals due to changes in mass on the surface, making it widely used as a sensor [2]. QCM is commonly used as humidity sensor, biosensor, gas sensor, and other uses [3-5]. Coatings are needed on the surface of the QCM that matches its function, enabling the QCM to work optimally. The carbon layer is widely applied to the type of resonant sensor (QCM) as a gas sensor [6,7]. The methods used to form carbon into thin layers include spin coating, deep-coating, plasma chemical vapor deposition (CVD), and plasma sputtering. The plasma sputtering method is widely studied due to its resulting thin layer, homogeneity, and the ability to control the deposition process as needed by the requirements or the desired thin layer [8]. Sputtering is the process of colliding target materials using plasma. The atoms of the target material will be detached and deposited on the substrate, forming a thin
layer. The commonly used gas sputter is Argon (Ar), as Argon is an inert gas and has an ideal atomic weight. Argon, when compared to other noble gases like Krypton (Kr), Xenon (Xe), and Radon (Rn), has a lower sputter yield. However, they are hard to find and expensive. In addition, Rn is radioactive [9].

The atomic processes that may occur in plasma are as follows [10]:

\[ e + Ar \rightarrow e + Ar^+ (Excitation) \]  
\[ e + Ar \rightarrow 2e + Ar^+ (Ionization) \]  
\[ e + Ar^+ \rightarrow e + Ar (Deexcitation due to collision) \]  
\[ e + Ar^+ \rightarrow Ar^{++} (Ar II ion excitation) \]

Electrons have a crucial role in the plasma process, as most atomic processes require electrons. There are internal and external parameters in the plasma process. External parameters include chamber pressure, RF voltage, gas flow rate, substrate temperature, and deposition time. This work is a preliminary study focusing on the effect of the chamber pressure on the electron temperature and density.

The chamber pressure is related to the mean free path, which is the average collision distance. Electron temperature is related to the average kinetic energy of electrons in the plasma, while electron density is related to the degree of ionization from plasma. They are crucial internal plasma parameter determining the deposition quality. The plasma was diagnosed with a spectroscopic technique (OES). The OES results showed a graph of the relationship between intensity vs wavelength. The electron temperature and density can be calculated from the Boltzmann plot [11], and Stark Broading [12,13]. The temperature and density of these electrons will affect the ion bombardment process in the plasma sputtering target material, which is related to the rate of deposition of thin-film formation. The internal parameters were studied against the variation of the chamber pressure.

2. Methods

2.1 Experimental Method

An RF plasma system with a frequency of 2 MHz was utilized for sputtering deposition of carbon on a QCM substrate. The target material was a carbon disk with a diameter of 25 mm and thickness of 6 mm. The disk was placed 1 cm above the substrate and enclosed with a stainless steel cathode as shown in Figure 1. The carbon deposition process was carried out under the following steps. First, the plasma was generated by introducing argon gas into the system. The argon flow rate was maintained at 60 mL/min during the process. Then the RF voltage was applied across the electrode. The voltage in this study was 120 volts ensuring a stable glow discharge. The temperature of the substrate was kept at 200 °C, while the chamber pressures were varied by 10, 15, and 20 Pa. Finally, the plasma was set off after 60 minutes of deposition. The experiment was repeated three times for each variation of pressure.

![Figure 1. Plasma reactor scheme for carbon deposition.](image-url)
2.2 Calculation Method
Intake of the Argon plasma spectrum was performed using OES Aurora 4000 in the wavelength range of 200-1000 nm. Determination of the electron temperature was done by plotting the Boltzmann equation:

\[ \ln \frac{I}{g A} = \text{Const} - \frac{E_i}{kT} \]  \hspace{1cm} (5)

Where \( I \) is the emission intensity, \( \lambda \) is the emission wavelength, \( g \) is the statistical weight, \( A \) is the transition probability, and \( E_i \) is the upper level of the transition energy. The related data for the specific wavelength and intensity were obtained from the atomic spectra database (NIST). The NIST database was also used to determine the species of Argon plasma. After obtaining the electron temperature value, the electron density is calculated using the Stark Broadening equation as follows:

\[ N_e = \left( \frac{\Delta \lambda_1}{2 \omega} \right) \]  \hspace{1cm} (6)

Where \( \Delta \lambda_1 \) is Stark Broadening (FWHM), \( \omega \) is the electron impact width parameter, and \( N_e \) is the electron density.

3. Results and Discussion
The emission spectrum in the plasma sputtering process is measured using OES. Spectrum wavelengths are then used to match with the NIST database to determine the type of Argon and Carbon species. The peak intensity vs wavelength shows the species Ar I and Ar II, while the C species does not appear, as shown in Figure 2. The Ar I species appears at wavelengths of 748.639, 762.044, 810.592 nm, whereas Ar II appeared at wavelengths of 309.429 and 736.036 nm. Ar I is an excited atom or Ar* [14] and emits photons like the mechanism in the process (1), while Ar II is an Ar atom which ionizes and produces Ar\(^+\) ions as a result in the process (2). Ar I has the highest peaks, indicating that excitation most often occurs in this process. Ar II has a peak that is quite low compared to Ar I as the energy to produce Ar II is high, which enables the ionization process. Ar II has a vital role in plasma sputtering as Ar\(^-\) ions are needed in the ion bombardment process of the target material.

![Figure 2. Argon plasma spectrum at 10 Pa pressure.](image-url)
Electron temperature calculations are performed using the Boltzmann plot. The spectral lines used are the three highest peaks of Ar I, namely 748.639, 762.044, 810.592 nm. The results of the electron temperature and electron density calculation are shown in Table 1.

**Table 1.** The calculated results of electron temperature and electron density at various pressure.

| Pressure (Pa) | Electron temperature (eV) | Electron density (cm$^{-3}$) |
|--------------|---------------------------|-------------------------------|
| 10           | 0.487±0.005               | $(5.495 \pm 0.407) \times 10^{18}$ |
| 15           | 0.481±0.006               | $(4.825 \pm 0.384) \times 10^{18}$ |
| 20           | 0.474±0.011               | $(4.515 \pm 1.037) \times 10^{18}$ |

The results show that the electron temperature decreases with increasing pressure. Pressure on the chamber affects the mean free path; the greater the pressure, the smaller the value of the mean free path. It means that the increasing of chamber pressure caused electron collision with neutral atoms also increases, resulting in by the mean free path between two successive collisions decrease, which shows that instead of getting energy by electrons from the electric field, more energy is transferred to neutral species as a result of the reduction in $T_e$. Electron density was calculated using stark Broadening. The peaks used for the calculation $N_e$ are selected from the three highest peaks of the Ar I, the same as the electron temperature calculation.

The increase of chamber pressure resulted in a decrease of both the electron temperature and electron density. The decrease is correlated to the distribution of energy in the plasma which is described using two mechanisms, namely Ohmic and stochastic heating. The former is the mechanism for channelling energy from the electric field to electrons. Energy is channeled through the collision of electrons with neutral atoms. In higher pressure, the collision intensity was increased, resulted in a decrease of the electron temperature. The decrease in the electron temperature allows for a decrease in the ionization process of neutral atoms, decreasing the number of electrons and hence the electron density. The latter mechanism was related to the process in the layer around the electrode called the sheath layer. The sheath layer is a layer that has a high electrical potential preventing electrons from passing. Only neutral ions and atoms can pass through the sheath. As the electrons are unable to pass through, electrons approaching the sheath layer will be reflected, thus creating a transfer of momentum from the sheath surface to the electrons. The more electrons reflected the more energy is given which in turn decrease the temperature electron.

4. Conclusion

Studies on the characterization of electron temperature and electron density in Argon plasma in carbon sputtering deposition at the various chamber pressure have been successfully carried out. The argon plasma species appeared in this study are only Ar I and Ar II. The decrease of the electron temperature and electron density due to the increase of chamber pressure were correlated and can be thought as the process controlled by two mechanisms, i.e. ohmic heating and stochastic heating.

References

[1] Vashist S K and Vashist P 2011 *J. Sensors* **2011** 1
[2] Jie H 2006 *Technical Background, Applications and Implementation of Quartz Crystal Microbalance Systems* (Finlandia: University of Jyväskylä)
[3] Li X, Chen X, Chen X, Ding X and Zhao X 2018 *Mater. Chem. Phys.* **207** 135–40
[4] Masruroh, Djoko D J D H, Didik L A, Rahmawati E, Pagaga M, Abdurrouf and Sakti S P 2014 *Appl. Mech. Mater.* **530–531** 54–7
[5] Van Quang V, Hung V N, Tuan L A, Phan V N, Huy T Q and Van Quy N 2014 *Thin Solid Films* **568** 6–12
[6] Nasir S, Hussein M Z, Zainal Z and Yusof N A 2018 *Materials (Basel)*. **11** 1–24
[7] Mazzocco R, Robinson B J, Dickinson J, Boxall C and Kolosov O V. 2012 *Tech. Proc. 2012 NSTI Nanotechnol. Conf. Expo, NSTI-Nanotech* **2012** 173–6
Acknowledgements
This work was partly supported by RISTEKDIKTI for Hibah Kompetensi Grants through LPPM University of Brawijaya.