Thermal Profile of a Physical Vapor Deposition Sputter Device

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ABSTRACT

Thermal Profile of a Physical Vapor Deposition Sputter Device. Sam Posen (Queen's University, Kingston, ON K7L 3N6) and Andrew Zwicker (Princeton Plasma Physics Laboratory, Princeton, NJ 08543).

Diamond thin films are extremely hard, thermally conductive, and resistant to chemical corrosion, making them ideal coatings for various industrial and high-tech applications. They are often chemically deposited, in a chamber containing a small concentration of methane in hydrogen and a substrate heated at least to approximately 700 degrees Celsius to ensure that the end product is not merely amorphous carbon. For this experiment, physical vapor deposition was used, in which argon plasma, heated with microwaves, sputtered carbon from a negatively biased graphite target onto a 3" diameter silicon wafer substrate sitting on a height-adjustable platform. In PVD, diamond growth can occur at lower substrate temperatures, but the temperature must still be controlled. In order to measure the bulk temperature, a thermocouple was placed in the substrate holder and measurements were taken at the extremes of platform height. The temperature was found to range from approximately 250 degrees Celsius at the lowest height to 550 at the highest. In addition, an optical spectrometer was used to determine the average electron temperature by measuring Ar II/Ar I intensity ratios. These temperature measurements, along with the installation of a new substrate handling system with heater, will improve future film quality by allowing for more precise control of temperature.

INTRODUCTION

Diamond thin films possess a combination of useful qualities that make them ideal for many advanced products. They are the hardest known substance and are inert to most chemicals, making them excellent coatings for instruments that are subject to heavy wear or harsh environments. They also possess the highest thermal conductivity at room temperature of any known substance, making them useful as channels to carry heat away from microchips when they are manufactured on such small scales that they would otherwise burn at high currents [1]. It is important to study the manufacture and formation of diamond films so that improvements can be made to their production and quality in these and other products.

In many cases, chemical vapor deposition (CVD) is used to create diamond thin films. In this process, a gas that usually consists of 1% methane and 99% hydrogen, but sometimes with some fraction of argon, is heated with microwaves or a filament such that it forms a plasma. This plasma can deposit carbon from the methane gas onto a substrate in the form of diamond if the conditions are right. The ratio of gases present and the total pressure must be within certain tolerances for this to happen, and the temperature of the substrate must be above about 700 degrees Celsius. If these conditions are not met, the deposited film will be merely amorphous carbon.

In this experiment, another method, physical vapor deposition (PVD) via sputtering, was used. Sputtering occurs when a negatively-biased carbon-containing target attracts positively-charged argon ions from the plasma, causing collisions that release carbon atoms from the target into the plasma where they eventually impact upon and coat a substrate. In PVD, the plasma gas does not need to contain carbon, so frequently the chosen gas is both inert so that it will not react with the substrate and of a high atomic weight so that collisions with the target are energetic enough to release carbon.

This experiment also takes advantage of Electron Cyclotron Resonance (ECR). ECR occurs as a result of the Lorentz force, F_L, which acts on charged particles in a magnetic field, and is described by

$$\boldsymbol{F_L} = q\boldsymbol{v} \text{ x } \mathbf{B}, \qquad (1)$$

where q is the charge of the particle, v is its velocity, and B is the magnetic field. This force will cause an electron in a static magnetic field to move in a circle perpendicular to the magnetic field in addition to its motion parallel to the field, confining it in the transverse direction. Furthermore, if electromagnetic radiation at the frequency of rotation ω interacts with the electron, it will transfer energy to the electron, heating it. This frequency is given by

$$\omega = eB/m. \qquad (2)$$

where e is the charge of the particle and m is its mass. In this experiment, coils with large DC currents through them created the confining magnetic field, and microwaves caused ECR heating, maintaining the plasma.

After creating a stable plasma, it was necessary to consider how to optimize conditions for diamond deposition. In PVD, which was used for this experiment, the temperature of the substrate does not have to be as high for diamond formation as it does in CVD, but it will not occur at low temperatures. To get an idea of the current deposition conditions, measurements were taken that allow for an estimate to be made of the temperature of the substrate at two locations in the plasma as well as the temperature of the plasma itself.

The temperature of the electrons in a plasma can be estimated given the intensity of photons emitted by gas particles relaxing from excited states. The wavelength of the photon emitted by a singly ionized gas particle relaxing from an exited state is unique and distinct from that of the photon emitted by a neutral gas atom in an excited state. For this experiment, which uses argon plasma, the electron temperature T_e can be found using I^+/I^0, which is the ratio of the intensity of the argon emission line at 480.6 nm, corresponding to a relaxation of Ar^+, to that at 750.3 nm, corresponding to a relaxation of Ar^0. This is accomplished using the relation given by Hope et al. [2] to be

$$I^+ / I^0 = \left(0.61eV \cdot T_e\right)^{0.75} \exp\left[-21.48eV / T_e\right]. \qquad (3)$$

The electron temperature should depend on the gas pressure. For a given amount of microwave heating power, if the pressure is increased, more plasma electrons will be available to absorb it, so each electron will receive less power. This should cause the average electron temperature to decrease. Gas pressure is an important parameter because it affects the deposition rate on the substrate by changing the frequency of ion collisions with the target and therefore the amount of carbon sputtered from the target. For maximum deposition rate, the gas pressure should be kept as high as possible without being in danger of the plasma becoming unstable and being extinguished, so it would be useful to know the relationship between electron temperature and gas pressure.

MATERIALS AND METHODS

The microwave system, shown in Figure 1, was created using ASTeX products. A 2.45 GHz A50RH microwave generator was closely impedance matched to the plasma load using an AX3060 SMARTMATCH, with a SA02WG4 Phase Sensor. The remaining reflected power was redirected into an AX3031 Dummy Load by an AX3021 Circulator.

The vacuum chamber is shown schematically in Figure 2. The chamber was stainless steel, pumped down to a normal base pressure of approximately 10^{-6} torr. Argon flowing into the chamber was regulated by an MKS type 250E Pressure Controller connected to a needle valve and an MKS Baratron Capacitance Manometer. Microwaves entered the chamber from the waveguide (1) through a quartz window (2) to heat the plasma. A pair of magnet coils (3) confined the plasma in the transverse direction, and allowed for ECR heating by the microwaves. The microwaves had a frequency of 2.45 GHz, corresponding (by equation 2) to a resonant magnetic field of 875 G. The current through the magnetic coils was adjusted until the magnetic field in the center of the coils was just above the resonant field. It was found that the best configuration for stability occurred when the coils generated fields through them that were slightly higher than the resonant field strength.

At the top of the chamber, under the quartz window was a short cylindrical graphite target (4) with a negative bias on it. The plasma was able to move parallel to the magnetic field, so after argon ions sputtered carbon from the target, transport along the field lines transferred the carbon to the 3” diameter silicon wafer substrate (5), at the bottom of the chamber. The substrate rested on an aluminum block on a height-adjustable platform (6), which was controlled remotely. At its lowest point, the substrate was 16.7

inches from the target and at its highest, it was 11.6 inches away. An Omega XCIB thermocouple was inserted into the aluminum block on the platform, and measured the bulk temperature at the extremes of platform height. The thermocouple was connected to an Omega HH506RA Digital Thermometer that converted the voltage produced by the thermocouple to a temperature reading. The temperatures over time were fitted with an exponential (see Appendix A) to determine the equilibrium temperature.

For the electron temperature measurements, a fiber optic cable viewed a chord through the bottom of the plasma in the area where the bulk temperature measurements were made. An Ocean Optics USB 2000 Spectrometer measured the spectrum of light emitted by the argon plasma. A fitting algorithm was used on the peaks at 480.6 nm and 750.3 nm to determine the ratio I^+/I^0, and equation 3 yielded the corresponding electron temperature.

RESULTS

Thermocouple measurements were taken over a period of about 20 minutes for two trials. The details of the runs are shown in Appendix A. The equilibrium physical temperature was found to be approximately 242 degrees Celsius at the lowest height of the platform, and 547 at the highest. This corresponds to a temperature change of over 300 degrees in 5.1 inches, a gradient of 59.8 degrees per inch. After the second trial, technical problems arose that prevented further data from being taken within the timeframe of this study.

The electron temperature was measured for three different argon pressures. These are shown in Table 1, and the derivation of these results is shown in Appendix B. From

Table 1, it seems that increasing the argon pressure decreases the electron temperature increases. These values were graphed in Figure 3 and a linear fit was performed. It was assumed that the data was linear in this small region. The data show that for every millitorr increase in gas pressure, the electron temperature decreases by 2.6 x 10^5 K.

DISCUSSION AND CONCLUSIONS

The temperature measurements will improve future film quality by allowing for more precise control of temperature. Even more precise control will be established with the installation of a new substrate handling system with heater. The system will also be capable of putting a bias on the substrate to increase nucleation and growth rate of diamond. The handling system that will be purchased will have to be able to work in temperatures up to at least 550 degrees Celsius, the temperature at the height deepest into the plasma that the handling system will go. This specification is an important outcome of this study.

Under the current setup, a wafer will be sputtered at the maximum height and the deposited film will be analyzed using Raman spectroscopy to evaluate the diamond content. Using the thermocouple measurements from this study, this content can be correlated to a deposition temperature of 550 degrees Celsius. If significant diamond growth is not seen at this temperature, then the heater will have to have a very high power output. If there is very good diamond growth, then the power output can be smaller. This specification is also very important.

In order to increase the collision frequency of argon ions with the target, and thus the deposition rate, the argon pressure must be increased. However, this decreases the overall electron temperature, which could become so low that the plasma cannot be sustained. For diamond deposition, the argon pressure should be kept as high as possible, but not so high that the plasma becomes unstable. It was found that the plasma became unstable very quickly when the gas pressure came close to approximately 0.50 millitorr, which indicates, according to the fit in Figure 3, that the minimum electron temperature for stability is 5.8 x 10^4 K. By continuously measuring the electron temperature using the spectrographic techniques in this experiment, the stability of the plasma can be monitored.

FUTURE WORK

In the future, it would be very useful to perform more trials of thermocouple measurements to determine the accuracy of the calculated temperatures. Multiple trials should be performed at several different heights to get the best estimate of the measurement uncertainty. It would also be interesting to see the effect of varying the target bias, gas pressure, and microwave power on readings both from the thermocouple and from the spectrometer. Such data may be utilised to improve substrate temperature control.

ACKNOWLEDGEMENTS

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APPENDIX A

The thermocouple was situated inside an aluminum block heated on one side by the plasma. To determine what type of function to fit the thermocouple data with, a highly simplified model of the situation was created. This model ignores many complexities involved in the real situation, treating the plasma as having a bulk temperature and greatly simplifying the heat flow in the aluminum block.

Consider one-dimensional, uniform heat flow with a linear temperature gradient for all time between one end of the block at a constant temperature T_{hot} and the other end where the thermocouple is located at a variable temperature T_{cold}. This is illustrated for three different times t_0, t_1, and t_2 in Figure A1. Note that the temperature scale is chosen such that $T_{cold} = 0$ at t_0.

The heat flow equation is

$$\dot{Q} = -\kappa A \frac{dT}{dx} \tag{4}$$

where κ is the thermal conductivity of the block, A is its cross-sectional area, T is the temperature distribution, and x is the distance along the path of heat flow. With a linear temperature gradient along the total length L between the end at constant temperature and the thermocouple junction, T is given by

$$\begin{aligned} T &= \frac{1}{2}\frac{T_{hot}(L-x)+T_{cold}x}{L} \\ T &= \frac{T_{hot}}{2} + (T_{cold} - T_{hot})\frac{x}{2L} \end{aligned} \tag{5}$$

Substituting this into the heat flow equation gives

$$\dot{Q} = \frac{\kappa A}{2L}(T_{hot} - T_{cold}) \tag{6}$$

To determine the heat flow, the total heat required to increase the temperature of the block must be calculated. In general, to raise the temperature of a mass *m* by an increment ΔT requires

$$Q = mc\Delta T \tag{7}$$

where *c* is the specific heat capacity of the material. The mass of the aluminum block is given by ρAL where ρ is the density. On average, since one end of the block is at a fixed temperature and the distribution is linear, the average increase in temperature ΔT will be $(T_{cold})/2$. This is clear from Figure 1. This gives

$$Q = \frac{1}{2}\rho ALcT_{cold} \tag{8}$$

Now a differential equation describing T_{cold} can be found.

$$\begin{aligned}
\dot{Q} &= \frac{dQ}{dt} \\
\frac{\kappa A}{2L}(T_{hot} - T_{cold}) &= \frac{d}{dt}\frac{1}{2}\rho ALcT_{cold} \\
\frac{\kappa}{L}(T_{hot} - T_{cold}) &= \rho Lc\frac{dT_{cold}}{dt} \\
\frac{dT_{cold}}{dt} &= \frac{\kappa}{\rho cL^2}(T_{hot} - T_{cold})
\end{aligned} \tag{9}$$

Assuming that $T_{cold} = 0$ at t = 0 and $T_{cold} = T_{hot}$ after a long time, the solution is

$$T_{cold} = T_{hot}\left[1 - \exp\left(-\frac{\kappa}{\rho cL^2}t\right)\right] \tag{10}$$

Since several approximations were made, the constant and the coefficient of the exponential were kept as two different constants and the equation used to fit the thermocouple data was

$$T_{TC} = T_{final} - C\exp\left(-t/\tau\right) \tag{11}$$

where T_{TC} is the thermocouple temperature, t is time, and the final temperature T_{final}, C, and τ are free variables to be fit. C should approximately be the difference between the final temperature and the initial. τ should be approximately $\rho c L^2/\kappa$. The data and fits are shown for both the lowest and highest platform heights in Figures A2 and A3.

Data was taken for as long as possible before the conditions would no longer sustain the plasma. Assuming that the data continued to follow the fitted trend, after a long time, the final temperature at the bottom height of the platform would be approximately 242 degrees Celsius and at the top it would be 547 degrees.

The coefficient of t in the equation, α, should approximately be $\rho c L^2/\kappa$. Assume that these values are approximately constant for any temperature. For aluminum near room temperature, κ is 2.37 W/cmK, ρ 2.70 g/cm^3, and c is 0.9 J/gK [4]. The distance L between the thermocouple junction and the top of the aluminum block is 1.1 cm. This gives an α value of 1.2 s or 0.021 min. The observed values for α were 13 min and 16 min. This large discrepancy is likely due to the large number of assumptions made, which ignore the very complex heating and cooling situation that is really occurring. However, in spite of these simplifications, this analysis created an equation that fit the measured data very well.

APPENDIX B

Three different runs were performed to determine the average electron temperature. The resulting histograms of intensity versus wavelength shown in Figures B1, B2, and B3 (presented in order of increasing pressure) were fit to determine the intensity of light at the two relevant wavelengths so that the electron temperature could be determined using equation 3. Note that in the figures, the units of intensity are arbitrary since the ratio of the intensities of two lines was the only measurement made. The conditions during these runs and the result of the temperature analysis are shown in Table B1.

FIGURES

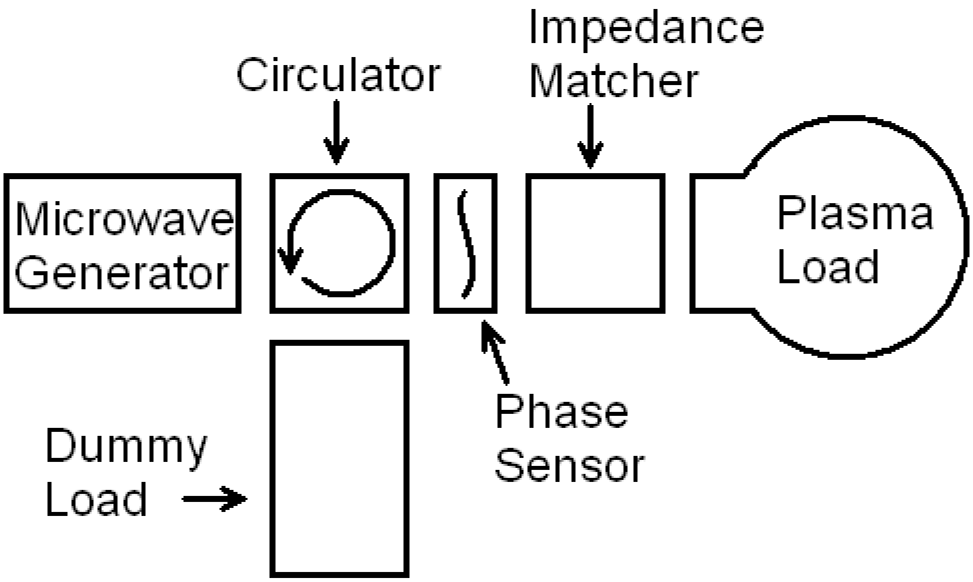

Figure 1: Block diagram of microwave system used to heat plasma.

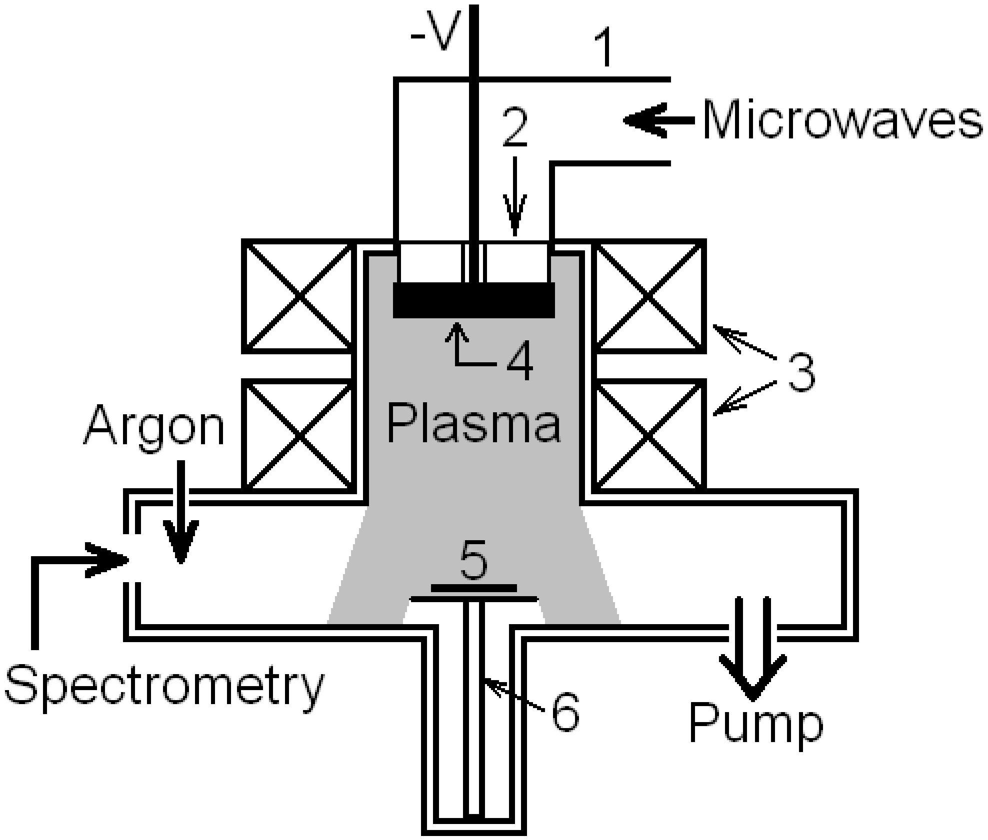

Figure 2: Cross-sectional view of ECR sputter device vacuum chamber. Drawing not to scale.

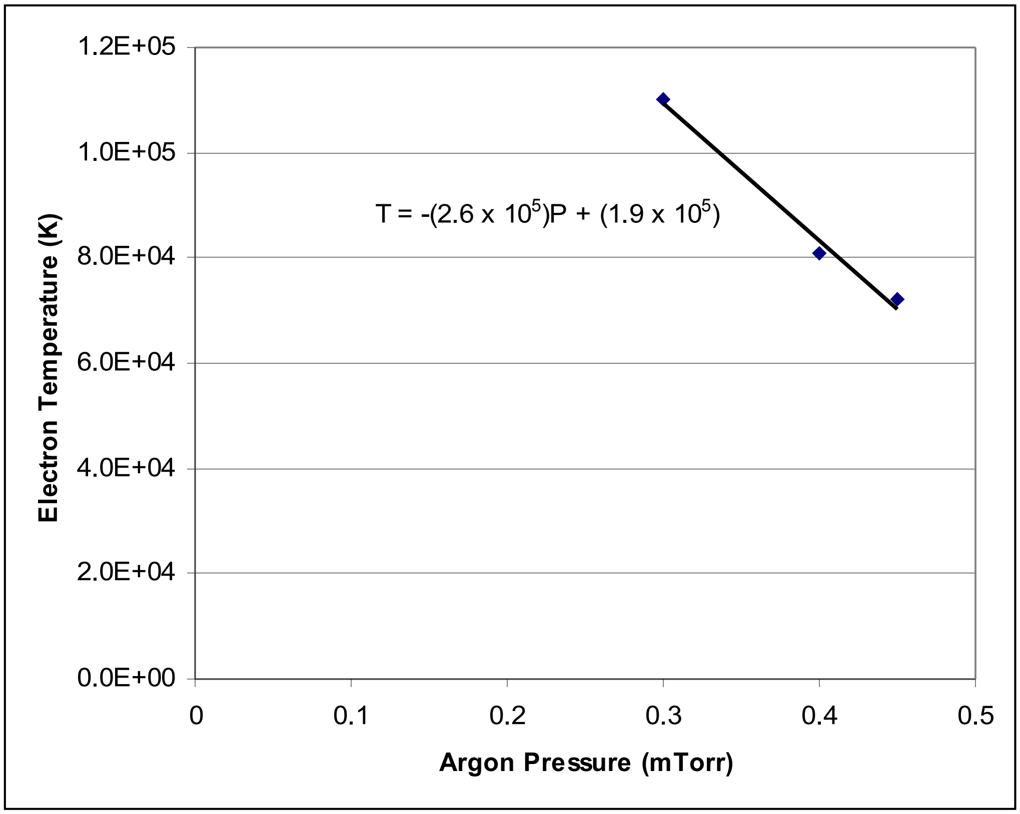

Figure 3: Relationship between electron temperature and argon pressure. The equation of best fit is displayed on the graph.

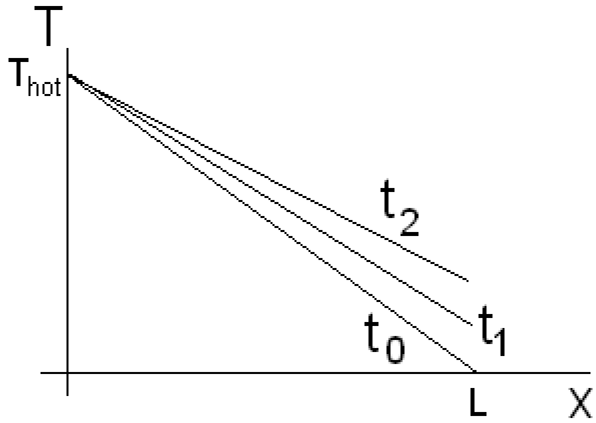

Figure A1: Modelled temperature gradients in the aluminum block. At any time, the gradient was assumed to be linear.

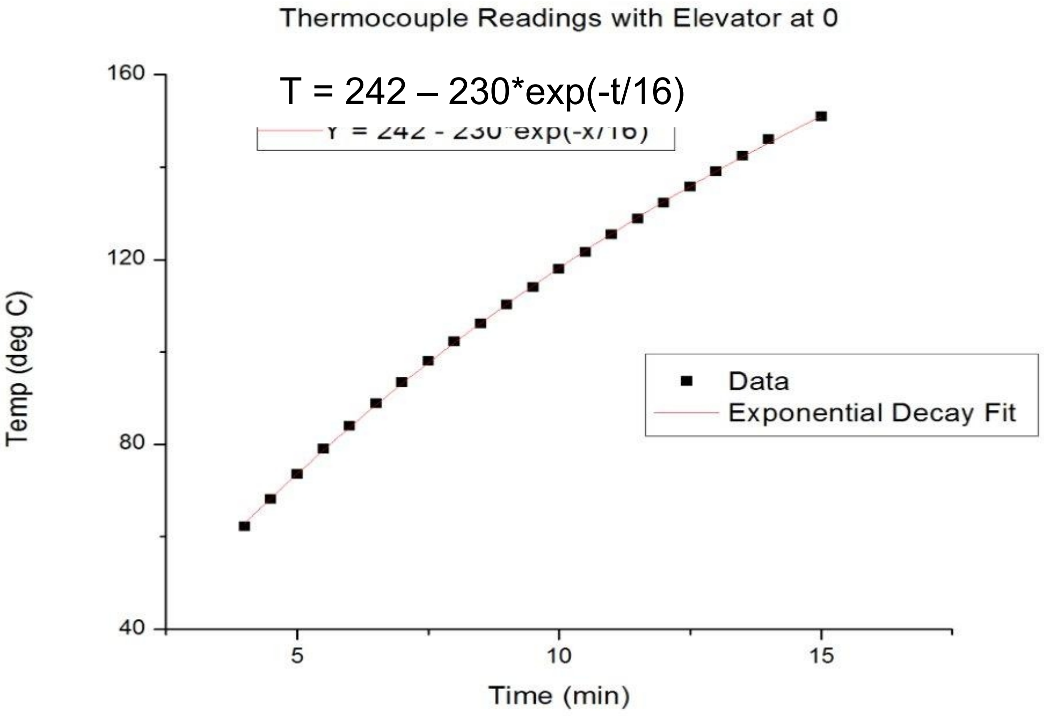

Figure A2: Thermocouple readings over time as the aluminum block is heated by the plasma at the lowest platform height, 16.7 inches from the target. After a long time, the fit indicates that the temperature will reach 242 degrees Celsius.

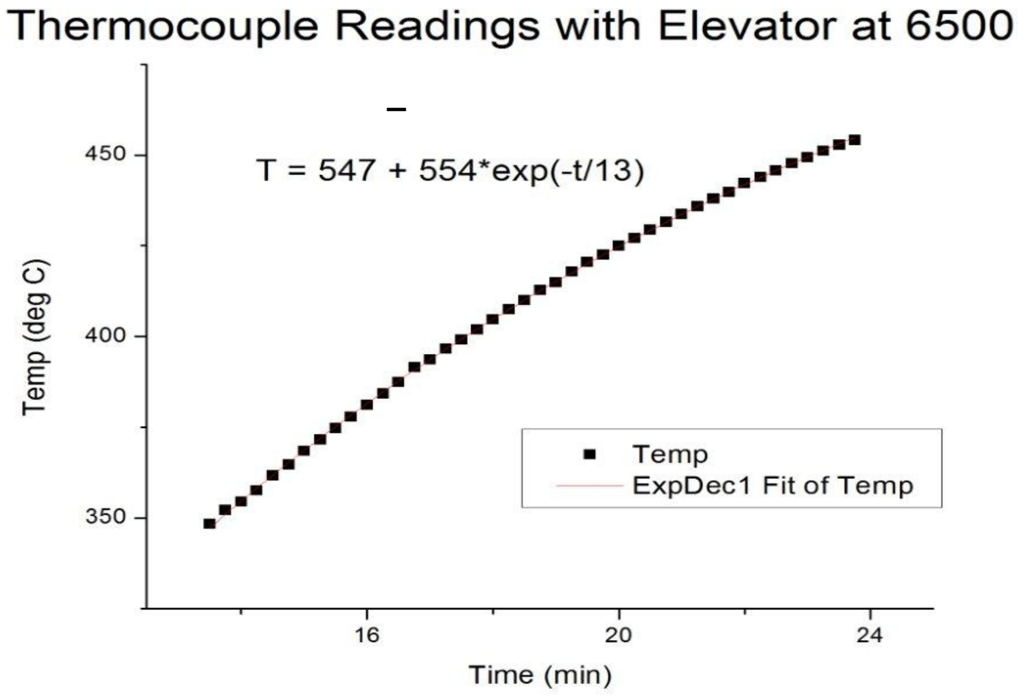

Figure A3: Thermocouple readings over time as the aluminum block is heated by the plasma at the highest platform height, 15.6 inches from the target. After a long time, the fit indicates that the temperature will reach 547 degrees Celsius.

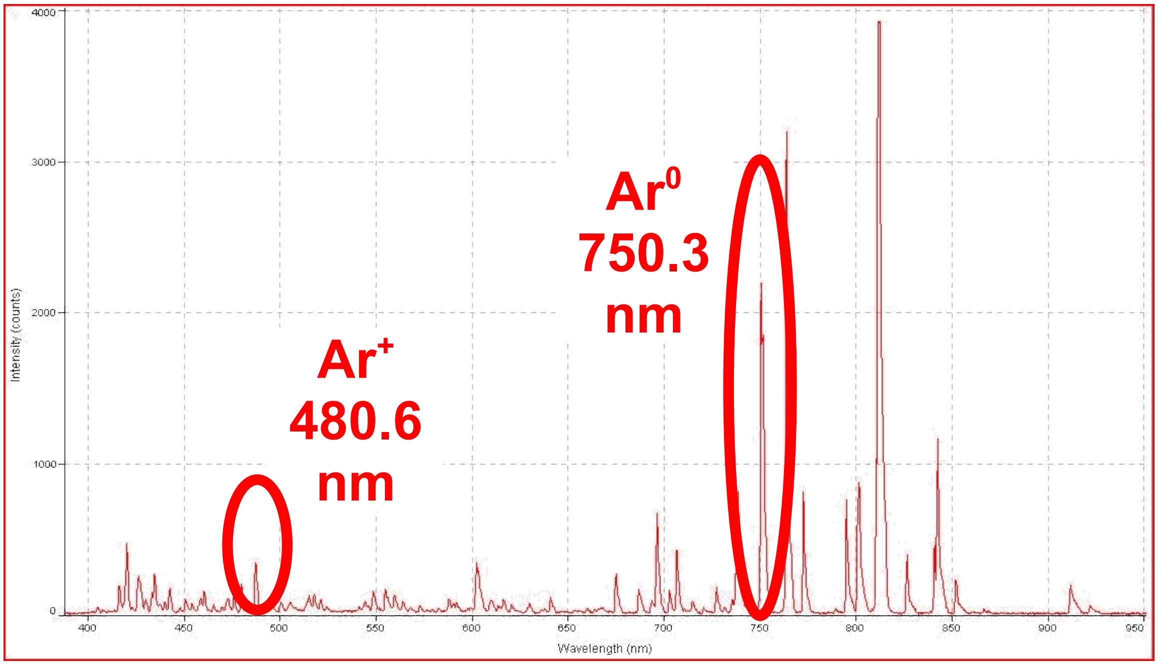

Figure B1: Spectrum of emission intensities at a gas pressure of 0.30 mTorr. Intensity is in arbitrary units. The line at 480.6 nm, corresponding to Ar^+ and that at 750.3 nm, corresponding to Ar^0 are highlighted. The ratio of the intensities of these two lines were used to find the electron temperature.

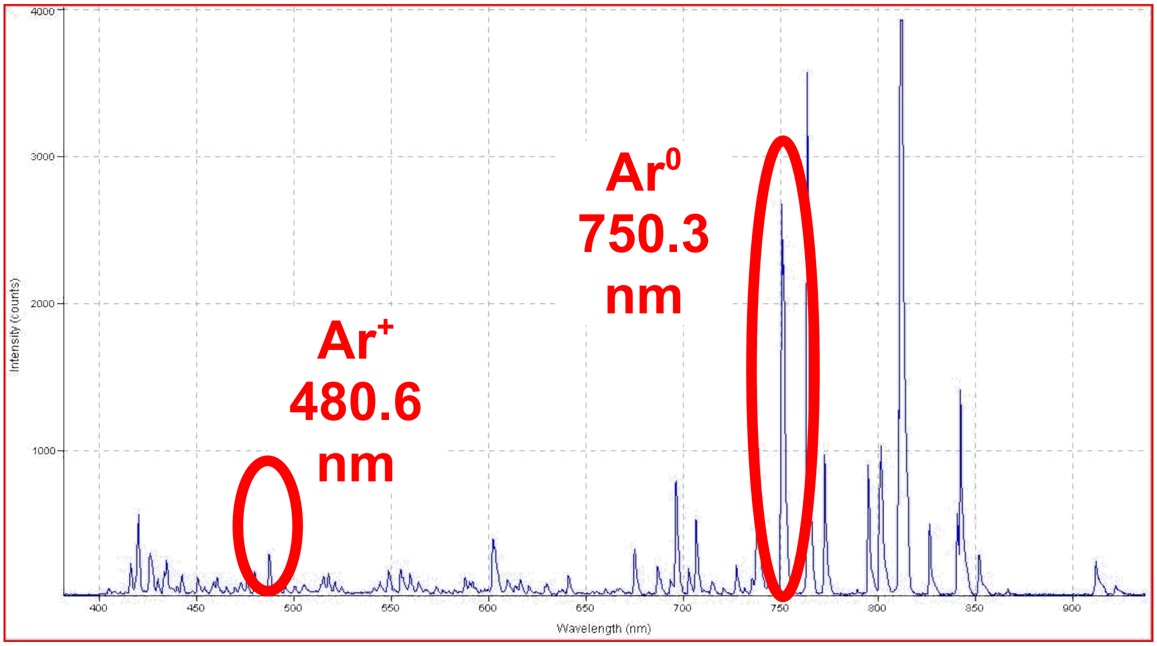

Figure B2: Spectrum of emission intensities at a gas pressure of 0.40 mTorr. Intensity is in arbitrary units. The line at 480.6 nm, corresponding to Ar^+ and that at 750.3 nm, corresponding to Ar^0 are highlighted. The ratio of the intensities of these two lines were used to find the electron temperature.

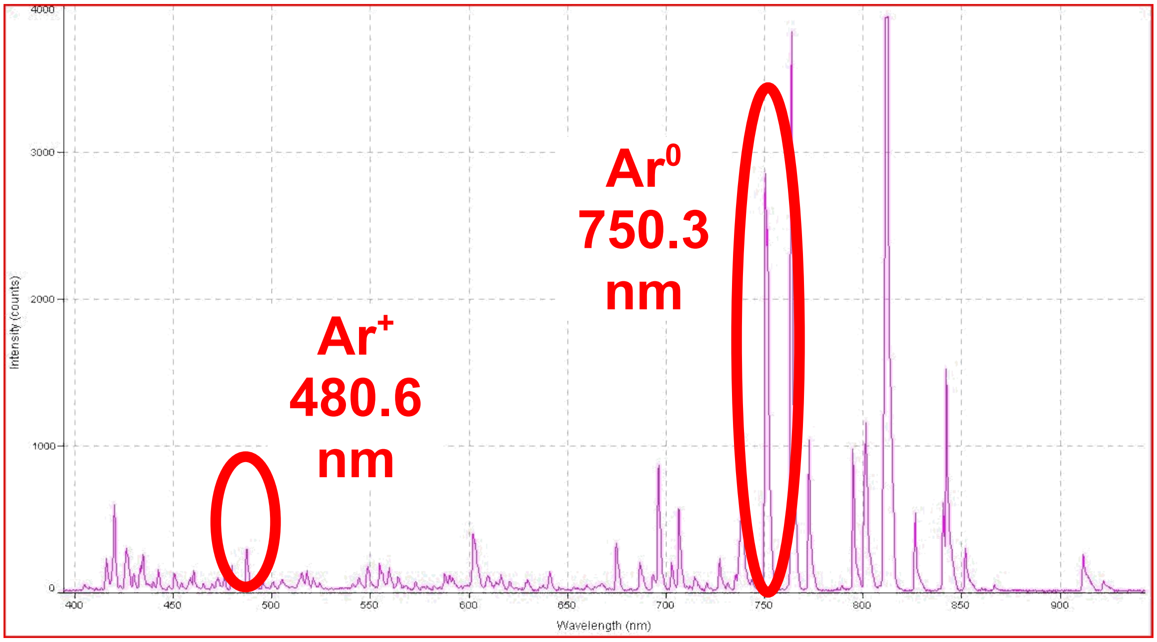

Figure B3: Spectrum of emission intensities at a gas pressure of 0.45 mTorr. Intensity is in arbitrary units. The line at 480.6 nm, corresponding to Ar^+ and that at 750.3 nm, corresponding to Ar^0 are highlighted. The ratio of the intensities of these two lines were used to find the electron temperature.

TABLES

Argon Pressure (mTorr)	Electron Temperature (K)
0.30	1.1×10^5
0.40	8.1×10^4
0.45	7.2×10^4

Table 1: Measured electron temperature at various argon pressures. Values calculated using intensity ratios of argon excitation lines measured with spectrometer.

Pressure (mTorr)	Target Bias (V)	Target Current (A)	Electron Temperature (eV)
0.30	200	0.57	9.1
0.40	150	0.71	7.0
0.45	150	0.81	6.2

Table B1: Measured electron temperatures at various argon pressures with other system parameters shown. The current through the target is an indication of the frequency of ion collisions.