

A Study of the Ion Flux During Deposition of Titanium Thin Films by Hollow Cathode Plasma Jet

Petr VIROSTKO, Zdenek HUBICKA, Martin CADA, Stepan KMENT, Lubomir JASTRABIK and Milan TICHY¹⁾

Institute of Physics of the Academy of Sciences of the Czech Republic, v. v. i., Prague, Czech Republic

¹⁾ *Charles University in Prague, Faculty of Mathematics and Physics, Czech Republic*

(Received: 1 September 2008 / Accepted: 4 December 2008)

Flux of positive ions to the substrate in the hollow cathode plasma jet system during deposition of titanium thin films was studied. The substrate was negatively biased by applying 50 kHz pulsed DC, or 0.50–1.25 MHz and 13.56 MHz high-frequency voltage to it. The ion flux determined in the DC hollow cathode discharge during the active high frequency bias was systematically higher than for the pulsed DC bias or determined right after the high frequency bias was turned off. On the other hand in the RF hollow cathode discharge, the ion fluxes determined for the active high frequency and 50 kHz low frequency bias were comparable. Possible explanations of this phenomenon are discussed.

Keywords: ion flux, plasma jet, hollow cathode, plasma diagnostics

1. Introduction

Bombardment of substrate with positive ions from plasma is often used in plasma deposition systems to modify the properties of deposited films. The films' structure and surface morphology can be influenced by the flux and energy of ions impinging on the substrate during deposition [1, 2, 3]. Therefore, it is important to measure these quantities to control and reproduce the deposition processes. The ion flux to the substrate can be obtained from relatively simple current and voltage measurements. The advantages of these measurements are that they can be done *in situ* during deposition and that they don't need any additional instrument added into the discharge. Additionally, the ion flux measurements can be combined with a model of the sheath around the substrate to obtain the energy distribution of ions impinging on the substrate [4, 5].

2. Experimental Setup

A schematic view of the low-temperature and low-pressure hollow cathode plasma jet deposition system [6, 7] can be seen in Fig. 1.

The main part of the deposition system is a nozzle made of material to be sputtered. The nozzle is connected to a power generator. A working gas flows through the nozzle and an intensive hollow cathode discharge is ignited at its outlet. The discharge is carried out into a grounded continuously pumped UHV reactor and a plasma jet is formed. Downstream from the nozzle a substrate is placed, on which a thin film is deposited. The discharge can be operated in a continuous DC, a pulsed DC, an RF, or a pulse-modulated RF mode [8]. Two discharge excitation modes were used: DC mode with discharge current $I_D = 600$ mA

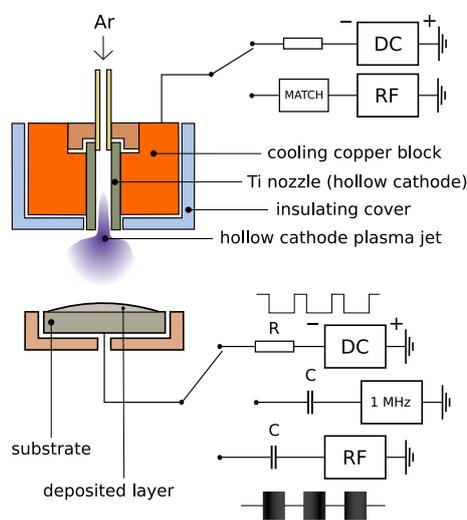


Fig. 1 The experimental setup of the hollow cathode plasma jet deposition system.

corresponding to power $P_D = 120$ W absorbed in the discharge, and 13.56 MHz RF excitation with absorbed power varied in the range $P_{RF} = 50$ –250 W. Titanium nozzle and argon as the working gas were used. The flow rate of argon was set to $Q_{Ar} = 120$ sccm and the pressure was held at $p = 2.7$ Pa during all reported experiments.

A planar copper substrate of circular cross-section with diameter $d_S = 8.1$ mm was placed 30 mm downstream from the nozzle outlet, coaxially with the nozzle. The substrate was connected to a pulsed DC source through a resistor R, or through a blocking capacitor C to a 0.50–1.25 MHz generator, or to a pulse-modulated 13.56 MHz RF generator (see Fig. 1). In case of pulsed DC bias, the substrate voltage was square-modulated with repetition frequency 50 kHz.

author's e-mail: virostko@fzu.cz

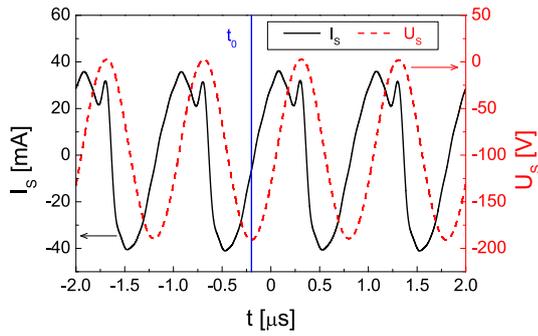


Fig. 2 Current $I_S(t)$ and voltage $U_S(t)$ waveforms on the substrate measured in the DC discharge for bias with frequency 1 MHz. Average bias voltage $U_{DC,S} = -100$ V.

The substrate was held on negative voltage $U_{DC,S}$ in the active part of modulation cycle, and it was grounded in the off-time. The pulsed DC voltage was used instead of continuous DC bias because of possibility to measure the ion current also for thin dielectric deposited layers. The current to the substrate was determined from the voltage drop measured by two oscilloscopic probes on the resistor R with resistivity 1235Ω . For the high frequency bias of the substrate, proprietary Rogowski coil and voltage sensor were installed on the feed line to the substrate to measure the current and voltage waveforms. The Rogowski coil and the voltage sensor were mounted on the feed line between the substrate and the capacitor C , outside of the reactor as close as possible to a vacuum feedthrough for the line. The sensors were calibrated for the frequency range 0.5–80.0 MHz. The voltage on the substrate was also measured by an oscilloscopic probe placed on the feed line between the sensors and the capacitor C with the capacitance $C = 11.8$ nF.

3. Results and Discussion

Average ion fluxes were determined as the ion currents to the substrate divided by the area of substrate. For the pulsed DC bias, the ion current was determined as the current flowing to the substrate when the DC bias was on. This is valid for bias voltages sufficiently negative to repel most of the plasma electrons from the substrate.

For the high frequency substrate bias, the ion current was determined from the measured current and voltage waveforms according to [9]. In this case, the ion current is determined from the current waveform on the substrate $I_S(t)$ as the current $I_S(t_0)$ at time t_0 when the simultaneously measured substrate voltage $U_S(t)$ reaches its minimal value. We will further refer to it as to the “ t_0 method”. An example of the measured current and voltage waveforms for the 1 MHz high frequency bias is depicted in Fig. 2.

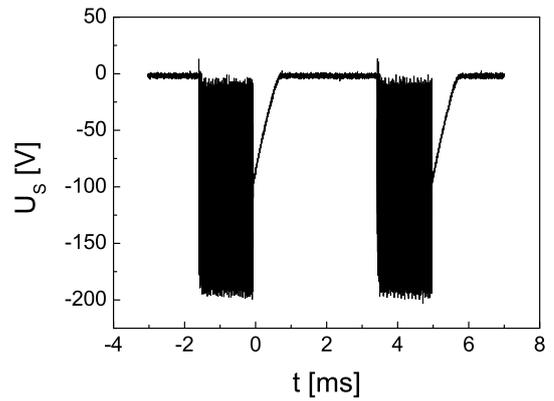


Fig. 3 Time evolution of voltage on the substrate U_S for pulse-modulated RF bias with frequency 13.56 MHz. Average bias voltage $U_{DC,S} = -100$ V.

Time t_0 , when the substrate voltage is minimal, is marked. A peak of the substrate current $I_S(t)$ caused by the electron part of the current can be seen at the times of maxima of substrate voltage $U_S(t)$ in Fig. 2.

The method [10] was used to measure the ion current for substrate bias with frequency 13.56 MHz. In this method, the RF bias is periodically turned off and the ion current is determined from the discharging of the capacitor C after the turn off as: $I_i = C \frac{dU_S}{dt}$. An example of measured voltage waveform of pulse-modulated 13.56 MHz bias can be seen in Fig. 3.

The dependence of ion flux j_i on the value of substrate bias $U_{DC,S}$ measured in the DC discharge is depicted in Fig. 4. The values of ion flux measured for 50 kHz and pulsed 13.56 MHz bias were similar or the same within the experimental error while the ion flux determined by the t_0 method for 1 MHz bias frequency was systematically higher. The higher values of ion flux determined by the t_0 method have been measured in the DC hollow cathode plasma jet before for 500 kHz [11] and also for 13.56 MHz bias [12]. Possible explanations were given as the relatively high error of measurements in the t_0 method (especially for the 13.56 MHz bias), the failure to fulfill the assumptions of the t_0 method, or the influence of the high frequency bias on the plasma around the substrate by heating the electrons and increasing the ionization. To shed light on this effect, measurements of ion flux in the 13.56 MHz RF hollow cathode plasma jet were performed, with results depicted in Fig. 5.

A dependence of ion flux on the power P_{RF} absorbed in the discharge was measured. The substrate bias voltage $U_{DC,S} = -50$ V was used for 50 kHz and 1 MHz bias. For 50 kHz, substrate bias of $U_{DC,S} = -100$ V was also used. The 13.56 MHz bias could not be used because of interference with the RF source for the discharge excitation using the same frequency. In the RF discharge, the difference between

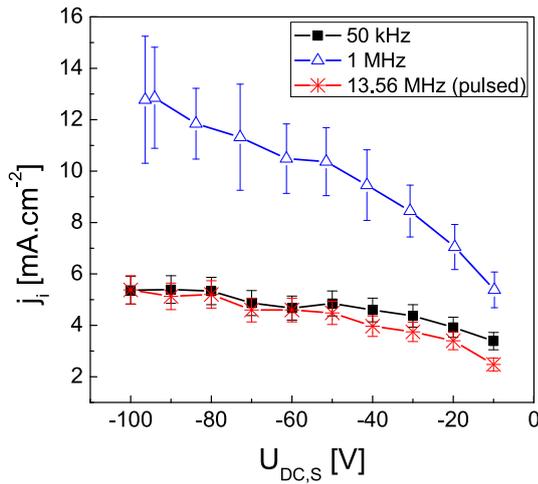


Fig. 4 Ion flux j_i to the substrate in the DC discharge for different substrate bias values $U_{DC,S}$. 50 kHz — for pulsed DC bias of substrate, 1 MHz — ion flux determined by the t_0 method for bias frequency 1 MHz, 13.56 MHz (pulsed) — ion flux determined from discharging of blocking capacitor for bias frequency 13.56 MHz.

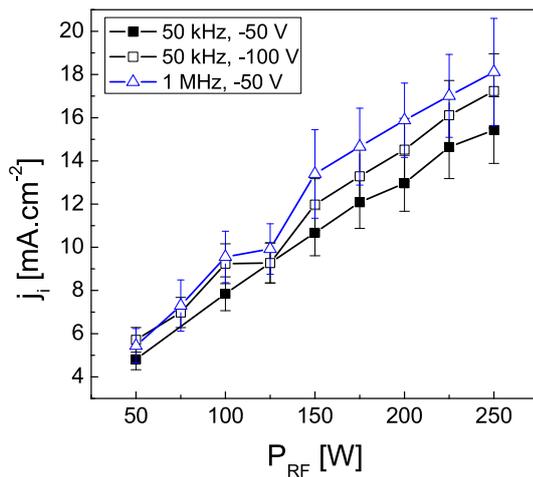


Fig. 5 Ion flux j_i to the substrate in the RF discharge for different power absorbed in the discharge. 50 kHz, -50 V — for pulsed DC bias with $U_{DC,S} = -50$ V; 50 kHz, -100 V — for pulsed DC bias with $U_{DC,S} = -100$ V; 1 MHz, -50 V — for 1 MHz bias with $U_{DC,S} = -50$ V.

the ion flux for the 1 MHz bias and the ion flux for the 50 kHz bias was smaller than in the DC discharge. Since the ion plasma frequency for Ar^+ ions calculated from Langmuir probe measurements [11] is comparable to the angular frequency of the 1 MHz bias, the ions respond to the instantaneous electric field around the substrate, rather than to an average DC bias. And since the ion flux by the t_0 method is determined at the instantaneous voltage $U_S(t_0) = -100$ V for 1 MHz bias in Fig. 5 (for average bias $U_{DC,S} = -50$ V the peak-to-peak voltage is 100 V — compare with

Fig. 2 for $U_{DC,S} = -100$ V and peak-to-peak voltage 200 V) the values of ion flux determined for DC bias $U_{DC,S} = -100$ V for 50 kHz are more appropriate to compare with values of ion flux determined for DC bias $U_{DC,S} = -50$ V for 1 MHz. Ion fluxes for these two cases are the same within the error of measurements for the RF discharge (Fig. 5), while they are different for the DC discharge (compare the points for 50 kHz and $U_{DC,S} = -100$ V and for 1 MHz and $U_{DC,S} = -50$ V in Fig. 4. This agreement of values of ion flux in the RF discharge means that the error in measurements is probably not the main source of the disagreement in the DC discharge.

By using the t_0 method one assumes the displacement current flowing through the sheath around the substrate is zero at time t_0 [9]. This is not true for ion plasma frequency comparable to the angular frequency of the bias as was discussed by [13] and what is mostly the case of experiments reported here. According to [13] the non-zero displacement current at time t_0 can lead to higher determined ion currents in the t_0 method, but the differences between the high frequency bias and pulsed DC bias for similar low-temperature plasma reported there were smaller than in Fig. 4; this effect could be possibly attributed only to the difference of ion flux for 1 MHz ($U_{DC,S} = -50$ V) and 50 kHz ($U_{DC,S} = -100$ V) bias in Fig. 5.

Another method-related explanation of the difference of ion flux in the DC discharge is that the time t_0 is determined for minimum of voltage on the sheath, but the voltage $U_S(t)$ is measured on the substrate with respect to the ground and not to the plasma. The measured voltage $U_S(t)$ is the substrate sheath voltage plus the voltage on the plasma and on the sheath around the grounded surfaces. If the voltage drop on the plasma and on the ground sheath are significantly time-varying with the bias on the substrate, the minimum of measured voltage $U_S(t)$ will occur at different time than the minimum of voltage on the sheath around the substrate and this could lead to incorrect ion flux determination by the t_0 method. The effect of time-varying voltage drop on the plasma is more likely to be present in the DC hollow cathode plasma jet than in the RF hollow cathode plasma jet, because in the DC discharge the plasma is visually more localized near the central axis than in the RF discharge where a spread RF glow discharge can be seen in the whole volume of the chamber. For a more localized plasma, the impedance between the plasma and farther grounded surfaces could have a more resistive character, resulting in a high-frequency voltage on the plasma with different phase than voltage on the substrate sheath, which has more capacitive impedance.

To study this effect, we performed measurements

of voltage between the plasma and the grounded chamber with a copper belt with planar surface of dimensions approximately 10×100 mm encircling the substrate in a distance of approximately 10 mm. A low-capacitance high-impedance oscilloscopic probe was mounted on the vacuum electrical feedthrough to which the belt probe was connected. The high-impedance probe in combination with large probe surface area were used to minimize the voltage drop on the sheath around the belt probe. The principle of the belt probe measurement was the same as the loop probe measurement described in [14]. The voltage between the plasma and the grounded reactor measured with the belt probe consisted of a DC drop with only a negligible time-varying component both in the DC and in the RF hollow cathode discharge with 1 MHz bias on the substrate. When this voltage was subtracted from the measured voltage of substrate with respect to ground $U_S(t)$, only the value of the minimum voltage was changed, but the minimum occurred at the same time t_0 as the minimum of the $U_S(t)$ waveform for both the DC and the RF discharge. The same behavior was also observed by [9]. This means that the effect of shift of time t_0 when the substrate voltage is measured between the substrate and ground instead of between the substrate and plasma is not the source of the discussed difference of ion flux in the DC discharge.

The last possible explanation of higher ion flux for high-frequency bias in the DC discharge is the influence of the high frequency bias on the plasma. This hypothesis is supported by the dependence of the 1 MHz bias in Fig. 4 on the bias voltage. According to the theory of a planar Langmuir probe, the ion saturation current has to be independent on the probe voltage as is the case of ion flux for low frequency 50 kHz bias and pulse-modulated 13.56 MHz bias determined by discharging of the blocking capacitor. On the other hand, the rise of the ion flux determined in the active 1 MHz bias with the amplitude of bias voltage is expected when the influence of the plasma depends on the magnitude of the high frequency substrate voltage. This influence can be stochastic heating and ohmic heating of plasma around the substrate, which both depend on the amplitude of high frequency voltage as well as on the bias frequency according to [15]. The dependence of ion flux to the substrate on the bias frequency f measured in the DC and in the RF hollow cathode discharge is depicted in Fig. 6.

The ion flux was determined by the t_0 method for all frequencies except for the 50 kHz bias. To obtain the ion flux for 13.56 MHz bias for the DC discharge, the parasitic impedance between the substrate and the measuring point was accounted for according to [12]. The frequency dependence is bigger in the DC discharge than in the RF discharge as is also visible in

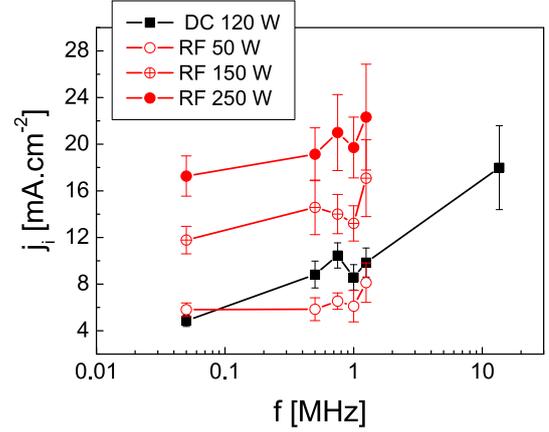


Fig. 6 Ion flux to the substrate j_i for different frequencies f of substrate bias. The DC hollow cathode plasma jet with discharge current $I_D = 600$ mA corresponding to power $P_D = 120$ W and the RF hollow cathode plasma jet with three different power P_{RF} absorbed in the discharge are compared.

Figs. 4, 5.

According to the preceding discussion, we can expect that the plasma around the substrate is heated when there is a high frequency bias present on the substrate. The electron temperature measured in the DC hollow cathode discharge (without any substrate bias) is according to [11] $T_e \approx 0.2$ eV, while the electron temperature determined in the 13.56 RF hollow cathode discharge is higher $T_e \approx 4-5$ eV. The difference in the electron temperature between the DC and the RF hollow cathode plasma jet can explain the bigger influence of high frequency bias on the ion flux in the DC discharge than in the RF discharge, since the electrons in the DC discharge with the significantly lower temperature can be more easily heated up. The rise of the electron temperature caused by the high frequency bias leads to the rise of ion flux because the ion velocity end hence the ion flux is determined by the Bohm criterion, which includes the dependence on the electron temperature: $j_i = n_i e \bar{v}_i \approx n_i e \sqrt{\frac{k_B T_e}{M_i}}$, where n_i is the ion density, e is the elementary charge, \bar{v}_i is the mean ion velocity, k_B is the Boltzmann constant, and M_i is the ion mass. Thus, the rising of electron temperature around the substrate by the high frequency bias can explain the observed phenomena. However, the electron temperature was not measured during the reported experiments and the hypothesis should be confirmed by further measurements.

The heating of plasma around the high frequency biased substrate can also lead to higher electron (and ion) density as was studied in [16]. This could also be a cause of higher ion flux for high frequency substrate bias. However, the ion flux is not higher in a short time of the order of microseconds after the 13.56 MHz

bias is turned off, as observed by the method using the discharging of capacitor. Since the electron density decay on longer time scales, of the order of tens to hundreds of microseconds according to [8], also the ion flux determined from the discharging of capacitor should have been higher if the ion density around the substrate would be increased by the high frequency bias.

4. Conclusion

Ion flux to the deposition substrate in the DC and 13.56 MHz-driven RF hollow cathode plasma jet system during deposition of titanium thin films was studied. Different frequencies of time-varying voltage were used to obtain the negative DC bias of substrate. Systematically higher values of ion flux were determined in the DC discharge by the t_0 method when a high frequency (0.50–1.25 MHz, 13.56 MHz) substrate bias was on. According to the presented results and discussion, this is not predominantly caused by an error in measurements of current and voltage waveforms on the substrate, as well as not by a failure to fulfill the assumptions of the t_0 method. The increase of electron temperature in the vicinity of substrate is the most probable cause for the higher ion flux to the substrate with the high frequency bias in the DC discharge. This effect can be used to control the flux of ions to the deposition substrate by changing the frequency of the bias, while keeping the ion energy, determined predominantly by the bias voltage, constant.

5. Acknowledgments

This work was supported by projects KJB100100707 and KJB100100805 of the Academy of Sciences of the Czech Republic and by projects 1M06002 and MSM0021620834 of the Ministry of Education, Youth, and Sports of the Czech Republic.

- [1] J. Musil and S. Kadlec, *Vacuum* **40**, 435 (1990).
- [2] N. Phinichka, R. Chandra and Z.H. Barber, *J. Vac. Sci. Technol. A* **22**, 477 (2004).
- [3] J.J. Olaya, S.E. Rodil, S. Muhl and L. Huerta, *Surf. Coat. Tech.* **200**, 5743 (2006).
- [4] M.A. Sobolewski, Y. Wang and A. Goyette, *J. Appl. Phys.* **91**, 6303 (2002).
- [5] M.A. Sobolewski, *J. Appl. Phys.* **95**, 4593 (2004).
- [6] L. Bardos, S. Berg and H. Barankova, *J. Vac. Sci. Technol. A* **11**, 1486 (1993).
- [7] Z. Hubicka, M. Cada, I. Jakubec, J. Bludska, Z. Malkova, B. Trunda, P. Ptacek, J. Pridal and L. Jastrabik, *Surf. Coat. Tech.* **174**, 632 (2003).
- [8] P. Virostko, Z. Hubicka, P. Adamek, M. Cada, J. Olejnicek, M. Tichy and M. Sicha, *Contrib. Plasm. Phys.* **46**, 445 (2006).
- [9] M.A. Sobolewski, *Appl. Phys. Lett.* **72**, 1146 (1998).
- [10] N.S.J. Braithwaite, J.P. Booth and G. Cunge, *Plasma Sources Sci. T.* **5**, 677 (1996).
- [11] P. Virostko, Z. Hubicka, M. Cada, P. Adamek, S. Kment, M. Tichy and L. Jastrabik, *Contrib. Plasm. Phys.* **48**, 527 (2008).
- [12] P. Virostko, M. Tichy, Z. Hubicka, M. Cada and P. Adamek, *WDS'07 Proceedings of Contributed Papers: Part II - Physics of Plasmas and Ionized Media* (eds. J. Safrankova and J. Pavlu, Matfyzpress, Prague, 2007) p. 212.
- [13] M.A. Sobolewski, *J. Appl. Phys.* **90**, 2660 (2001).
- [14] V.A. Godyak and R.B. Piejak, *J. Appl. Phys.* **68**, 3157 (1990).
- [15] M.A. Lieberman and M.J. Lichtenberg, *Principles of Plasma Discharges and Materials Processing* (Wiley, New York, 1994) p. 327.
- [16] M.A. Sobolewski and J.-H. Kim, *J. Appl. Phys.* **102**, 113302 (2007).