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The low temperature plasma jet sputtering systems applied for the deposition of thin films

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Abstract

The low temperature, low pressure hollow cathode plasma jet systems were developed due to their high suitability for the functional TiO_2, $TiO_{2-x}N_x$ thin films preparation. Besides the conventional substrates, these methods allow coating of thermally sensitive materials like polymers.

The low pressure DC pulsed or RF pulsed modulated hollow cathode plasma jets work on the principle of the reactive sputtering of the hollow cathode usually in the gas mixture of Ar + O_2 or N_2. The DC pulsed power supplier was applied with combination of the RF source (13.56 MHz) for the plasma jets generation.

It was clearly demonstrated that the properties of TiO_2 and TiO_2:N films significantly depended on the plasma parameters.

The parameters of the chemically reactive plasma in the jets were determined using the time-resolved Langmuir probe system. The measurement of the ion energy distribution function was performed by means of the retarding field analyzer in the position of the substrate.

1. Introduction

Up to now a lot of effort was developed to create a reliable high density plasma source for PVD and PECVD depositions of various types of thin films. PVD methods utilize sputtering of the cathode material in the discharge due to ion bombardment. Thin films can be also deposited

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by PECVD (plasma enhanced chemical vapor deposition). Vapors of suitable precursors are added to the glow discharge plasma and are decomposed in the non equilibrium plasma in this technique. One disadvantage of the simple glow discharge plasma is relatively low electron and ion density and subsequent low deposition rate mainly in the case of PVD process. For this reason, many other types of low temperature plasma sources with higher plasma density were developed up to now. One possible simple way how to increase the plasma density is the application of hollow cathode discharges.

2. RF and DC hollow cathode plasma jet

The first RF hollow cathode system with the plasma jet was developed 1987 by Bardos [1, 2] as a high density low pressure plasma source. Since that time many papers [1, 2, 3, 4, 5, 6, 7, 8, 9, 10] were published by different authors about various modifications of this system and many experimental results were obtained. The RF plasma jet system was used for many applications of thin films deposition up to now. The plasma jet excited by the DC hollow cathode discharge was investigated as well in many papers for example in [10, 11, 12]. The review of hollow cathode plasma jet systems applied for dielectric and ferroelectric films can be found for example in [20].

The RF hollow cathode plasma jet originally developed by Bardoš, et. al. [2] is a tool for rapid plasma enhanced chemical vapor deposition (PECVD) of a-Si:H for example [1] and physical vapor deposition (PVD) of many types of thin films. Very fast (1μm/min) TiN deposition by sputtering of a Ti nozzle [13, 14] was obtained and the deposition of stoichiometric Ge_3N_4 [6] thin films, CN_x [15] films and Cu_3N [4, 7] thin films were done for example. A dc hollow cathode plasma jet source version with an applied magnetic field was also studied in several works [10, 12, 16, 17]. This dc version was similar to the RF jet except for the plasma excitation source. Recently, the hollow cathode plasma jet excitation was also done by a DC pulse power supplier with the high current density in the active pulse with the combination of RF excitation [17]. DC, DC pulse and RF hollow cathode plasma jet sputtering systems are very suitable tools for fast depositions of various oxide thin films as TiO_x and ZnO [17, 10]. The DC plasma jet sputtering system was successfully applied for Si:H electronic quality thin films deposition [12].

The basic schematic depiction of the rf and the dc plasma jet system is shown in Fig 1. The vacuum stainless steel chamber is continuously pumped by a high-speed turbomolecular pump. The working gas mixture

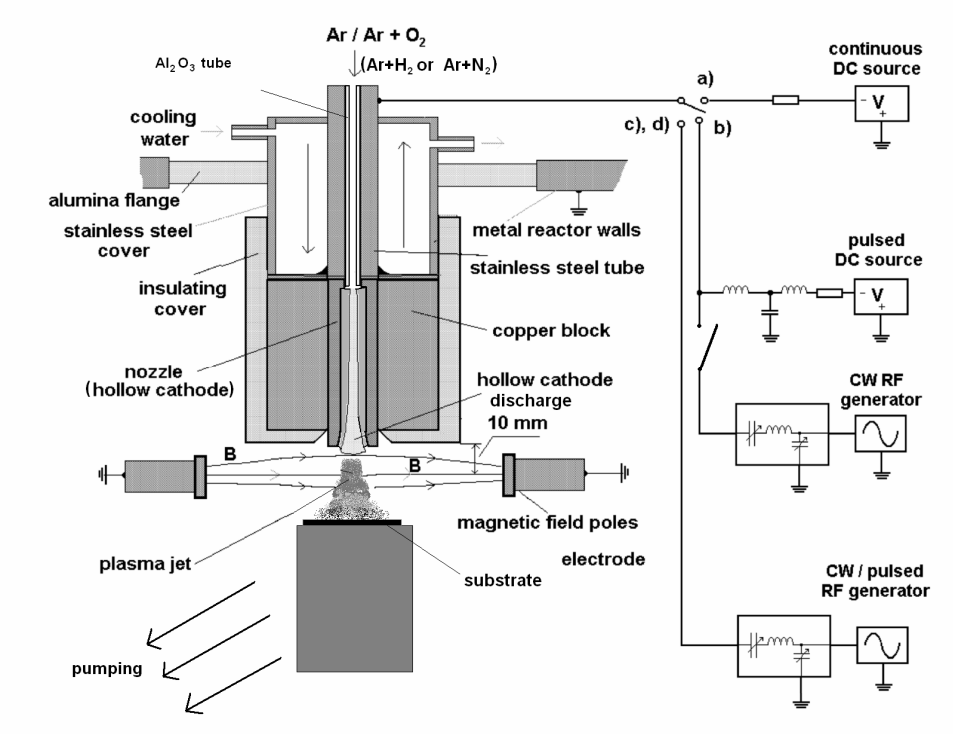

Figure 1 DC, DC pulse, RF and RF modulated deposition plasma jet system (taken from [17]) .

enters the feeding tube connected to the nozzle which is held by the water cooled electrode insulated from the grounded chamber. Typical used gas flow rates through the nozzle are in the range $\boldsymbol{Q}$=0.1-0.2 Pa m^3 s^{-1} (60-180 sccm). The nozzle can be connected to either the dc or

the rf power supplier. In the case of the rf generator, the high-density rf hollow cathode discharge is formed inside the nozzle. In the case of use the dc source, the dc hollow cathode discharge is formed in the nozzle. This nozzle acts as the DC hollow cathode and the grounded magnetic poles act as the grounded anode. Due to working gas flow through the nozzle, the high-density rf or dc hollow cathode plasma is blown out of the reactor chamber creating the plasma jet. The material of the nozzle is sputtered or reactively sputtered by ions in the high-density plasma and the sputtered species are carried by the plasma jet to the substrate. The

Figure 2 Photography of DC pulse plasma jet system during TiO_x sputtering.

inner diameter of the nozzle is usually 3-6 mm and the outer diameter 6-10 mm. The typical distance from the nozzle outlet to the substrate is usually $l_s \approx 50$ mm.

The DC plasma jet system is usually operated with magnetic field in order to create suitable anode for DC discharge circuit well separated from the substrate. Only cathodes fabricated from electrically conducting materials and semiconductors can be used. The DC plasma jet sputtering

system is optimal to operate in the range of pressures in the reactor from 0.2 Pa up to 20 Pa.

In case of application of the DC plasma jet for the deposition of oxides by reactive sputtering of metallic nozzles, the use of DC pulse plasma excitation is very useful. The hollow cathode is connected with the DC pulse power supplier eventually with the parallel RF source for more stable discharge operation (Fig1). The high current in the active pulse can be used but with low average current.

The photography of typical DC pulse hollow cathode plasma jet operation during TiO_2 deposition from the titanium nozzle can be seen in Fig 2. In this case, the pressure in the reactor chamber is $\boldsymbol{p_r}$ = 2 Pa and the argon gas flow through the nozzle is $\boldsymbol{Q_{Ar}}$ =0.16 Pa m^3 s^{-1} (100 sccm). The oxygen flow is applied directly to the reactor chamber and is not present inside the nozzle where only argon gas flows. In this way, it is possible to prevent TiO_2 formation on the sputtered nozzle surface and achieve the high deposition rate of transparent TiO_2 up to 0.4 μm/min.

The gas pressure inside the hollow cathode is usually apparently higher than in the reactor chamber [22, 23]. Here we try to present a simple model of gas pressure inside the cathode for the case of very low pressure in the reactor chamber in the range $\boldsymbol{p_r} \approx 0.1 - 5$ Pa and for the sonic speed of the plasma flow inside of the nozzle near to outlet. According to Shih-I Pai [21], gas flow in a cylindrical tube with a constant inner diameter can only reach the maximal critical sonic speed at the outlet of the nozzle. This statement is valid for a one-dimensional model of gas flow of an ideal gas with friction and heat absorption. In our case it is reasonable to consider the gas flow with friction and due to the hollow cathode discharge the gas will absorb some heat from discharge energy. The critical sonic speed at the nozzle outlet and subsequent supersonic expansion into the reactor can be attained if the pressure in the reactor is lower than the pressure at the nozzle outlet. The mass flow of the working gas Ar, through the feeding tube and the nozzle, is constant in the stationary case and can be expressed according to the mass conservation law as [21]:

$$1) \qquad m' = \frac{dm}{dt} = \frac{Q}{R_M T_{300}} = \frac{p_N v_C S}{R_M T_N}$$

where $\boldsymbol{Q} = \boldsymbol{p\ dV/dt}$ is the volumetric flow rate measured by the flow controller [m^3 s^{-1} Pa]; $\boldsymbol{R_M} = \boldsymbol{R/M_{Ar}}$; $\boldsymbol{R}$= 8.31 $Jmol^{-1}K^{-1}$, is the universal gas constant; $\boldsymbol{M_{Ar}}$ = 4 x 10^{-2} kg mol^{-1}, is the molar weight of argon; $\boldsymbol{S}$ is

the cross sectional area of the nozzle; p_N is the pressure at the nozzle outlet; T_N is the thermodynamic temperature of the neutral gas flow at

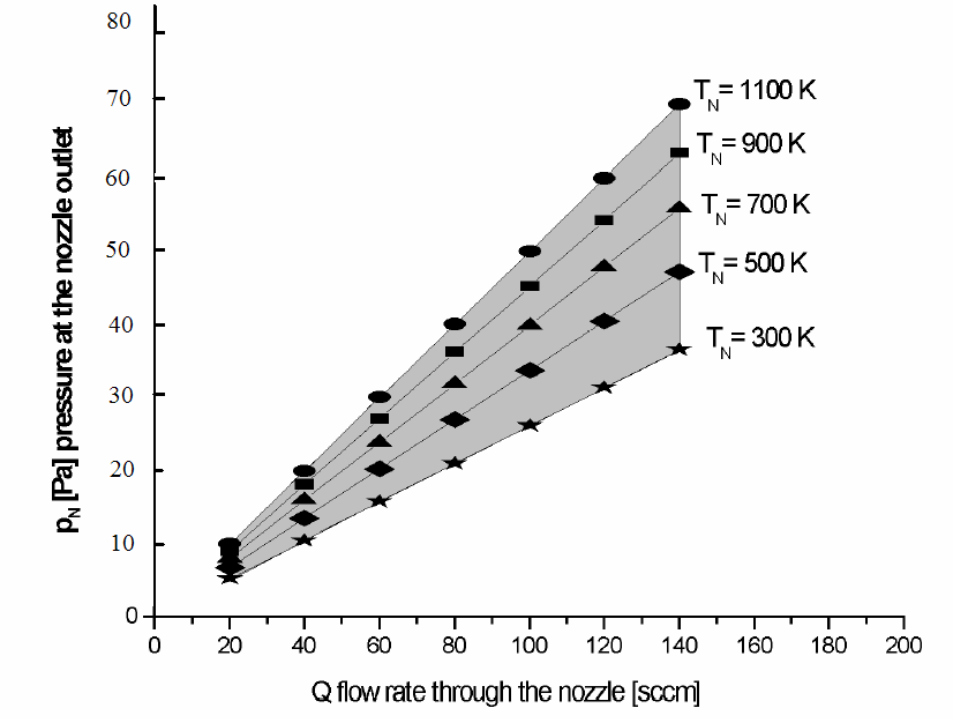

Figure 3 Dependence of pressure at the outlet of the nozzle on the flow rate of gas. (taken from [20])

the nozzle outlet; and T_{300} = 300 K is the temperature of the gas flow immediately behind the flow controller. v_c is the critical sonic speed of gas flow near the nozzle outlet. According to Shih-I Pai [21] this can be expressed as:

$$v_c = \sqrt{\frac{dp}{d\rho}} \qquad 2)$$

where p is the pressure and ρ is the density of the gas. According [21] we can write:

$$v_c = (\gamma R_M T_N)^{1/2} \qquad 3)$$

where γ is adiabatic constant and when the values for argon are placed in the equation we get:

$$v_C = 19\sqrt{T_N} \qquad 4)$$

From 1) and 4) we get

$$p_N = \frac{Q\sqrt{T_N}}{T_{300}19 \cdot S} \quad 5)$$

for the pressure near the nozzle outlet where the speed of gas is sonic. The values for argon were used in this model. The plot of the calculated pressure p_N at the nozzle outlet as a function of flow rate is shown in Fig. 3. Since we usually do not have exact information about $\boldsymbol{T_N}$, we set it as a free parameter. For our range of flow rates, 40-140 sccm, the pressure in the nozzle is always higher than 25 Pa in the region where the flow speed has critical sonic value. At our typical conditions, the pressure in the reactor was lower than ≈ 5 Pa. This means that the assumption of critical sonic velocity at the nozzle outlet was reasonable. The main result of this model is the fact that even for the low gas flow rate through the nozzle $\boldsymbol{p_N}$ inside the nozzle, where the sputtering process takes place, is relatively high. On the other hand at the substrate surface, the pressure can be much lower.

3. Characterization of DC and RF hollow cathode characterization during PVD thin films deposition

DC and RF plasma jet hollow cathode systems were subjected to experimental investigation during the deposition of various thin films [17, 18]. Langmuir probe measurement was one of the possible methods. We will describe here experiments where the RF cylindrical compensated Langmuir probe (LG) [10, 17, 18] was placed in the position of the substrate and was in parallel with the plasma jet axis. As an example of this experiment, we will present here typical results of LG measurement in DC, DC pulse, RF and RF pulse modulated hollow cathode plasma jet systems during the sputtering of titanium nozzle. In the case of RF pulse modulated excitation the RF power applied into the plasma jet was modulated by square pulses with the length of active part of modulation cycle $\boldsymbol{T_A}$=750 μs and non-active part with zero RF power $\boldsymbol{T_M}$=3ms. The DC pulse plasma jet system was operated together with the auxiliary RF source connected in parallel operated with very low CW RF power ≈ 10 W. $\boldsymbol{P_D}$ was the instant electrical power absorbed in the plasma jet system in the active period. The working gas pressure in the reactor was held on

p_R = 6 Pa during all these measurements. The inner diameter of the titanium nozzle was 4 mm and the length was 30 mm.

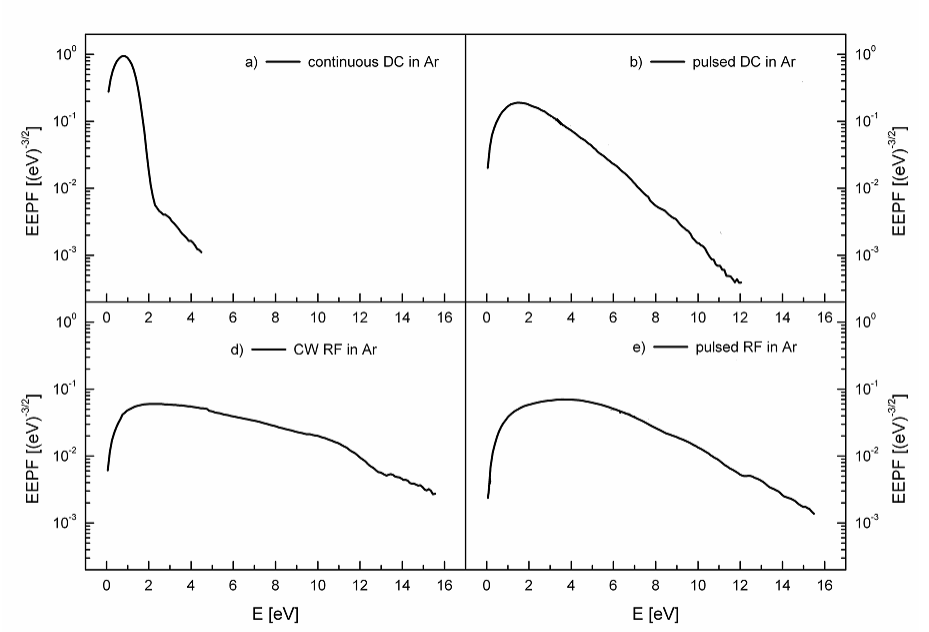

Figure 4 Electron energy probability functions(EEPFs) measured in the position of substrate for different used plasma jet excitation modes . EEPFs and power absorbed in the plasma are measured in the middle of the active pulse in pulsed DC and pulsed RF modes . a) Continuous DC mode Q_{Ar}=0.3 Pa m^3 s^{-1} (180 sccm) P_D= 250 W b) Pulsed DC mode ; O_{Ar}=0.3 Pa m^3 s^{-1} (180 sccm) P_D= 750 W . T_M=3 ms. T_A=750

The samples of electron energy probability function (EEPF) measured in the position of the substrate in these four plasma jet excitation modes (continuous DC, pulsed DC, CW RF, and pulsed RF) are depicted in Fig 4. It was found that the EEPF for the continuous DC excitation mode was bi-Maxwellian-like, i.e. composed of two linear parts in semi-logarithmic scale (see Fig. 3). The electron temperature of the colder one

of the two electron groups was $T_{ec} \approx 0.2$ eV. This electron temperature was calculated from the slope of the steeper linear part of the bi-Maxwellian EEPF in semi-logarithmic scale. The electron temperature of the other, hot electron group was $T_{ec} \approx 2$ eV. In the pulsed DC as well as in both CW, and pulsed RF excitation modes the EEPFs were approximately Maxwellian or slightly different from Maxwellian. The value of effective electron temperature calculated by use of integration method of EEPF was $T_{eff} \approx 2\text{-}6$ *eV*.

4. Deposition of TiO_2 and TiO_2:N thin films by double DC pulsed plasma jet with additive RF plasma excitation.

TiO_2 films doped with nitrogen were prepared by the pulsed double hollow Ti cathodes plasma jet sputtering (Fig. 5). The DC pulsed double

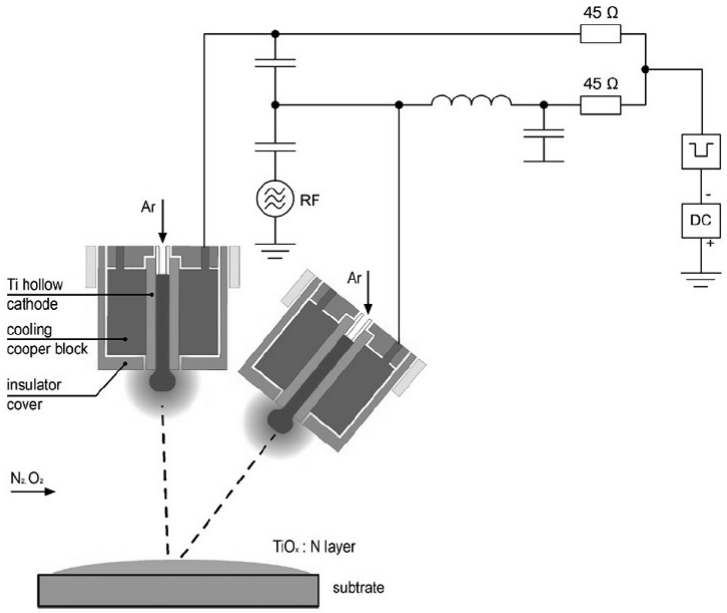

Figure 5 DC pulsed double hollow cathode plasma jet system.

hollow cathode system was already described in [19]. The cathodes were placed in the ultra-high vacuum chamber (10^{-6} Pa) and the operating pressure level was set at 3.5 Pa. Argon with the flow rate of 80 sccm (standard cubic centimeter per minute) was used as a carrier gas passing

through both jets with the same velocity. Oxygen (80 sccm) and nitrogen (80 sccm) streams were supplied to the reactor via a lateral entry. Cylindrical nozzles (hollow cathodes) were made of pure Ti (internal

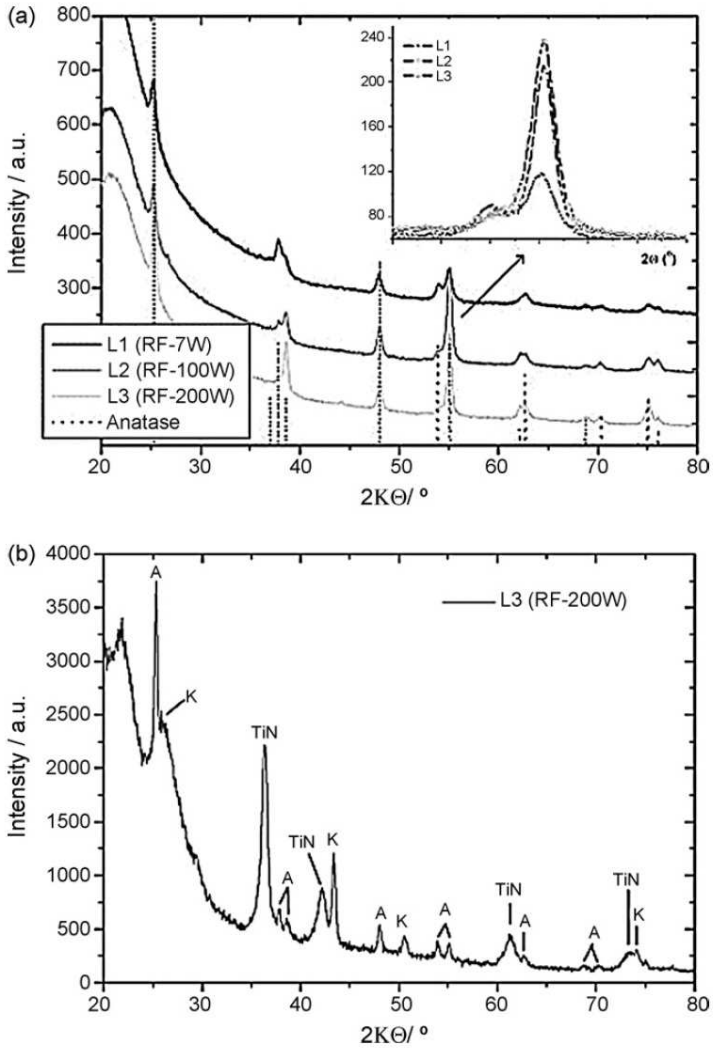

Figure 6 XRD diffractograms: (a) films prepared on a quartz substrate and (b) Kapton foil as a substrate (taken from [19].

diameter 5mm) and their distance from the surface was exactly 30mm. The hollow cathodes were connected to the DC pulse source with

frequency 2.5 kHz. The “ON” time of the pulse was 100 μs when the DC hollow cathode discharge was active and “OFF” time was 300 μs. The DC pulsed power supplier with the hollow cathode were also connected with the additional RF power source. All films were simultaneously deposited on electrically conductive ITO (indium tin oxide) coated glass substrates, quartz discs and Kapton polymer foil. Three different values of additional RF power were used for the deposition. Deposited films are coded: the type L1 – prepared with the additional RF power of 7W, L2 – 100 W, L3 – 200 W. The average DC current in both hollow cathodes was held constant for all the samples and has the magnitude 500 mA per each cathode. The maximum pulse DC current was ≈ 2A per each cathode.

Phase composition of the films was evaluated by XRD. Fig. 6a shows the XRD patterns of the films deposited on the quartz substrates with the additional RF power added to DC pulse plasma excitation. All these samples were polycrystalline with anatase phase. The extent of crystallization slightly varied with the increased RF power. Some variations in the XRD patterns were observed for films coated on the Kapton® foils (Fig. 6b). First, surprisingly the high extent of the anatase phase was achieved only at RF 200 W, at lower RF magnitudes the films were almost amorphous. It seems that the polymer substrate may play a certain role in terms of the TiO_2 crystallization. Besides the anatase phase the TiN related diffraction peaks were also detected.

An ion velocity distribution function IVDF was measured by the retarding field analyzer SEMION Impedance, inc. in the position of the substrate at similar conditions of TiO_2:N depositions. Time averaged measured IVDF functions can be seen in Fig 7. This type of diagnostic with this specific device is very approximate, it can provide neither mass resolution of ions hitting the substrate nor provide any information about angular ion distribution. This diagnostics requires for accurate IVDF measurement ideal non-isotropic distribution function, it means ions should form one-dimensional beam. Since this is not true in our case, this measurement carries only rough information about IVDF. However, we can see from Fig 7 that for the higher additional RF power applied to the plasma, the high energetic tail of IVDF is stronger. This behavior can be explained as follows. The additional RF power increases ionization of sputtered and gas particles in the plasma jets and simultaneously the plasma potential is increased as well due to the existence of capacitive RF plasma around the substrate. We suppose that the higher energetic

bombardment of the substrate for the high RF power improves crystallization of TiO_2 at lower temperatures.

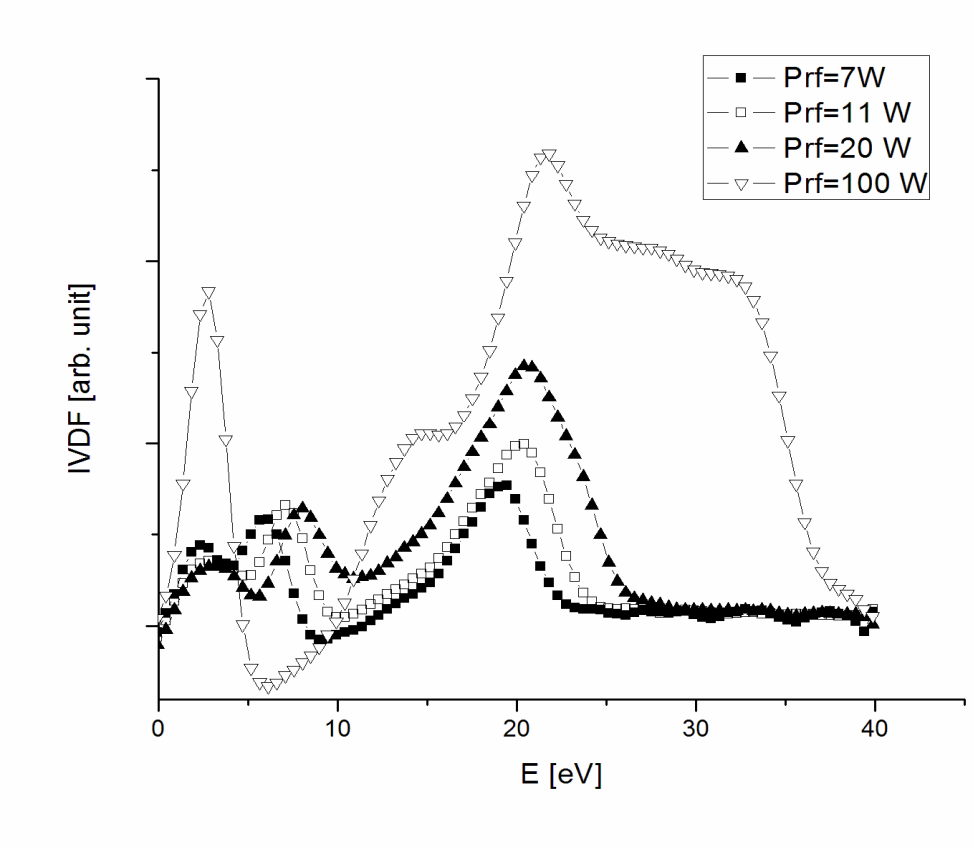

Figure 7 Measured IVDF at the position of the substrate for different additional RF power.

5. Conclusion

The low temperature plasma jet system is very efficient source for the reactive fast PVD deposition of various oxide thin films. TiO_2:N thin films with anatase structure were deposited on ITO coated glass and polymer substrates. The effect of the RF additional power applied to the cathodes was clearly demonstrated. This RF power effected crystallization of the deposited films and IVDF (ion velocity distribution function) measured at the position of the substrate. XRD has shown that although the temperature of the substrate did not exceed the temperature level of 423K the TiO_2:N films were clearly crystalline with the predominant anatase phase.

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