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To cite this version:

Zdenek Hubicka, Martin Cada, Olexandr Churpita, Petr Virostko, Petr Adamek, et al.. Low pressure and atmospheric pressure plasma-jet systems and their application for deposition of thin films. 2004. hal-00002042

HAL Id: hal-00002042

https://hal.science/hal-00002042v1

Preprint submitted on 22 Oct 2004

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Low pressure and atmospheric pressure plasma-jet systems and their application for deposition of thin films

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Abstract
Two types of plasma jet systems were used for deposition of oxide layers on polymer substrates. The target was to deposit such kind of thin films with crystalline structure at low temperature in order to avoid polymer substrate damages. Both systems were excited by RF source working in pulse modulated mode. This modulation allowed exciting high density plasma in the active part of the duty cycle and simultaneously keeping the neutral gas in the plasma jets at the substrate cold thus protecting polymer substrate from thermal damages. The first system was the low pressure plasma jet system excited by RF hollow cathode. The hollow cathode works simultaneously as a nozzle. This system works in vacuum system which was continuously pumped. The low pressure plasma jet system was used for deposition of $PbZr_xTi_{1-x}O_3$ (PZT) perovskite thin films on kapton (polymer) foil with *Pt* electrode layer. The RF hollow cathode nozzle was fabricated from PZT ceramics and was reactively sputtered in Ar and O_2 high-density hollow cathode pulse modulated plasma. The substrate bias and ion flux current were monitored during the deposition process. Langmuir probe system was used for measurement of plasma parameters in different part of the modulation cycle in the location of the substrate. This measurement was combined with monitoring of RF voltage, current and their relative phase in the RF hollow cathode. The second system was the RF barrier torch atmospheric discharge plasma jet. This system works at open air without any vacuum system. This system was used for a low temperature deposition of thin conductive oxide thin films at atmospheric pressure on polymer substrates. Under certain condition in the atmospheric plasma jet, these films have crystalline structure. ZnO films deposited directly on polymer contained hexagonal crystalline phase, they were optically transparent and have electrical conductivity $\sigma \approx 10^{-1}$-10^{0} S/cm. As growth precursors for ZnO films, Zn-acetylacetonate vapors were used.

Introduction

The low pressure RF plasma jet sputtering system was already used for many PVD thin films deposition as for example TiN [1], TiO_2 [2], Cu_3N [3], CN_x [4] and ZnO thin films [5]. In these applications, usually metallic or semiconductor hollow cathode was reactively sputtered in a suitable working gas. An alternative approach will be presented in this paper where the RF hollow cathode was made of $PbZr_xTi_{1-x}O_3$ (PZT), i.e. of non-conducting material and reactively sputtered in Ar and O_2 gas mixture in order to form PZT films on polymer kapton substrate. PZT films have wide application as ferroelectric and piezo electric material. Many methods were used up to now for PZT films deposition [6,7]. Deposited PZT films were investigated by XRD and electron microprobe. This paper describes the first preliminary results of deposition experiments of this material by this method on polymer substrate.

The atmospheric plasma deposition of various thin films is a subject of great interest. Large number of systems for atmospheric PECVD deposition have been developed recently. Low temperature dielectric-barrier discharges [8,9,10,11,12,13] are very often applied for PECVD deposition of polymer and other kinds of thin films [14,15,16]. Other types of atmospheric plasma sources were developed as well [17,18,19], [20]. The atmospheric RF barrier-torch plasma jet described in [21] was already applied for the low temperature deposition of In_xO_y and SnO_x thin films on polymer substrates [22,23]. In this paper - apart from discussing the production of PZT layers - we describe also the deposition of crystalline transparent and conductive ZnO on polymer substrates at atmospheric pressure. ZnO films working as a transparent conductive oxide gained recently wide interest due their stability. They have applications e.g. in solar cell technology.

Experimental

The low pressure plasma jet configuration for PZT thin films deposition can be seen in Fig 1. The reactor chamber was continuously pumped by combination of Roots and rotary vane pump. Many papers

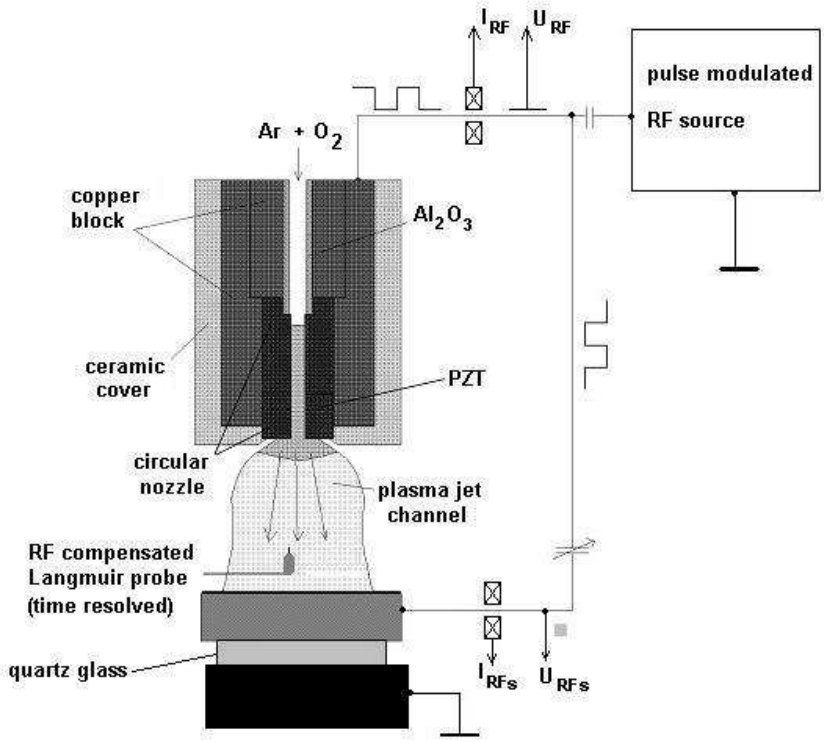

Figure 1. Low-pressure plasma-jet system for deposition of non-conducting PZT layers.

described such a system with metallic or semiconductor hollow cathodes reactively sputtered in several reactive gases [1,3,24]. Recently, reactive sputtering of $LiCoO_2$ RF hollow cathodes with zero electronic conductivity was reported in [25]. Also in our case the cylindrical nozzle was made of non-conducting PZT and acted as an RF hollow cathode. The internal diameter of the nozzle was 3 mm and its length 30 mm. In order to avoid overheating of the material with low thermal conductivity the PZT nozzle was clamped in between two copper blocks cooled by flowing water. By supplying sufficiently high RF power to the nozzle an intensive RF hollow cathode discharge [26] was generated inside the nozzle on the background of the primary capacitive RF discharge, which was excited in the volume of the reactor also at lower RF powers. The incoming working gas forced this RF hollow cathode discharge out of the nozzle into the reactor chamber and this supersonic plasma jet interacted with the substrate. The substrate was placed perpendicularly to the plasma jet axis in the distance range 10-40 mm from the hollow cathode outlet. The PZT thin films were deposited simultaneously on Si wafer and a kapton foil coated by Pt layer.

Parameters of deposited PZT films were measured by XRD diffraction in order to get information about the phase composition and by electron microprobe for chemical composition analysis.

RF generator in pulse modulated mode was used for plasma jet excitation. During the active part of the cycle, RF power P_{RF} = 500 W was applied on the electrode and P_{RF} = 0 W appeared on the electrode during non-active part of the cycle. The length of the active part was always set at T_w =500 μs and that of the non-active part at T_0 = 7 ms. The advantage of the pulse modulated mode was the enhancement of the plasma density during the active part of the cycle. Hence the sputtering process proceeded at higher applied RF power. On the other hand the

Figure 2. Running discharge in the low-pressure plasma-jet deposition system.

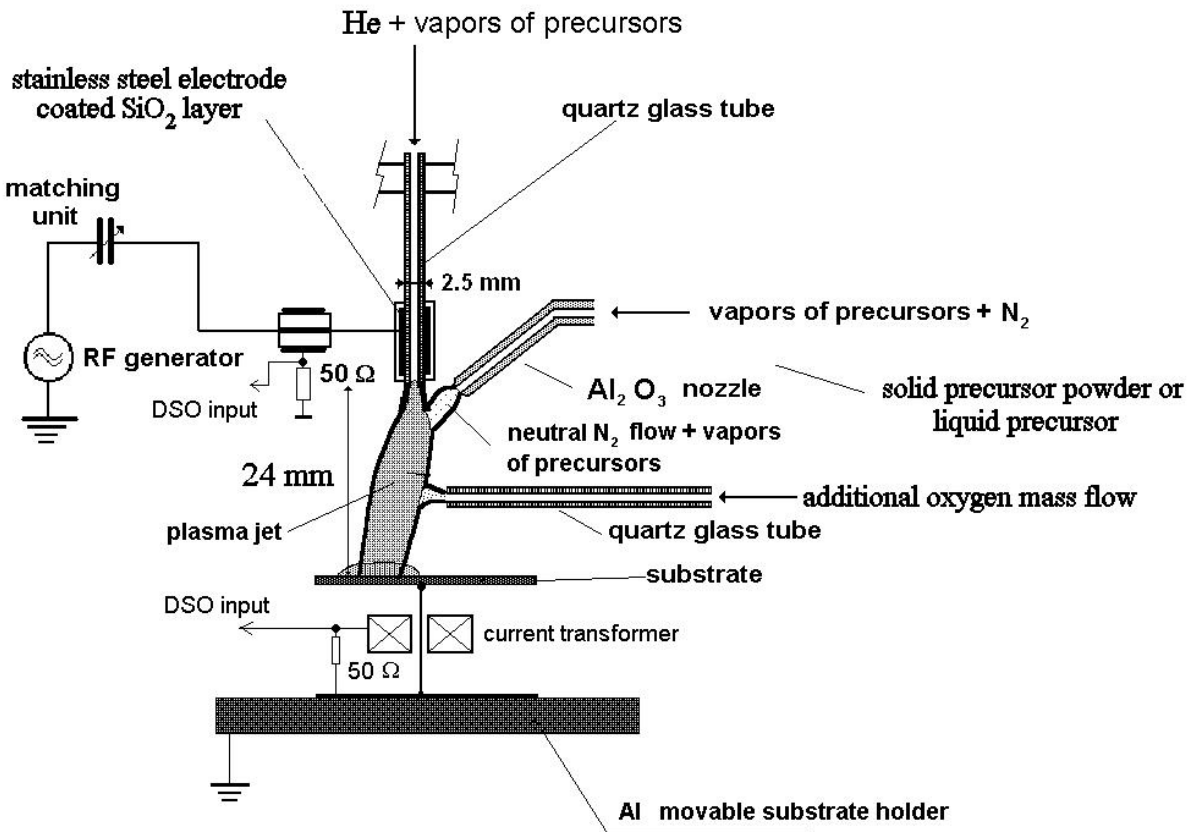

Figure 3. The barrier-torch atmospheric-pressure plasma-jet system used for deposition of ZnO thin films.

average applied RF power was low enough to avoid the (water-cooled) hollow cathode overheating and volatile Pb or PbO evaporation (which occurs at higher PZT temperatures). Simultaneously also the temperature of the kapton substrate was kept low in order to avoid thermal damage.

The fraction of the pulse-modulated RF power was fed over tunable capacitance on the substrate, see Fig. 1, in order to generate controllable pulse DC bias on the substrate. The current and voltage probes were capable to measure RF power, RF voltage and current on the nozzle and substrate. Furthermore, it was possible to get information from these RF measurements about the substrate ion current. The method developed by Sobolewski [27] was used for that purpose. The pulse-modulated plasma was further investigated by the time resolved Langmuir probe system in order to get information about plasma parameters in the position of the substrate (35 mm from the substrate). The photograph of the discharge in the described low pressure plasma jet system can be seen in Fig. 2.

The schematic diagram of the barrier-torch atmospheric-pressure plasma jet system can be seen in Fig. 3. The quartz glass tube with internal diameter 1.5 mm is surrounded by the stainless steel RF powered electrode. Helium with mass flow Q_{He} = 900-1500 sccm comes through the nozzle. Due to the high RF field at the edge of the electrode, RF barrier-torch discharge

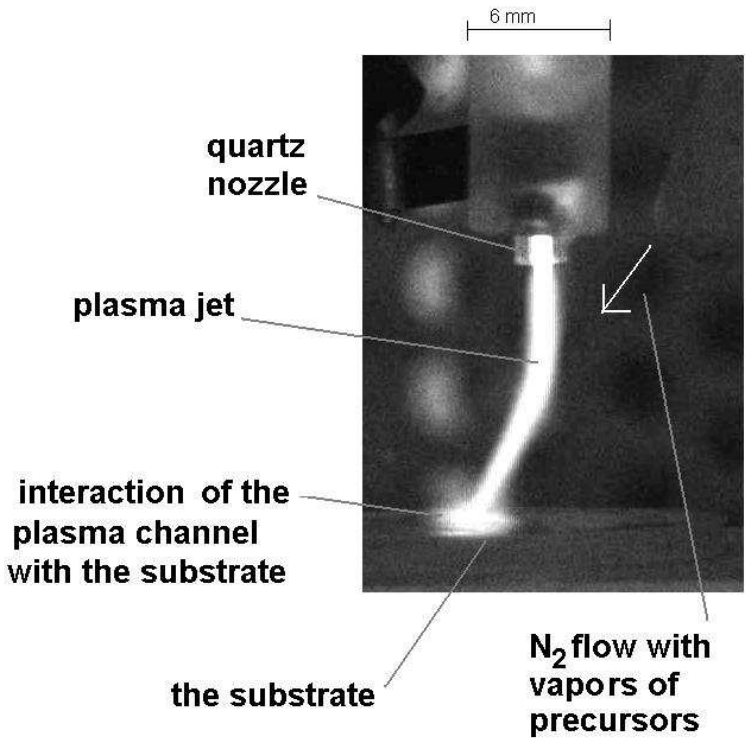

Figure 4. Running discharge in the barrier-torch deposition system.

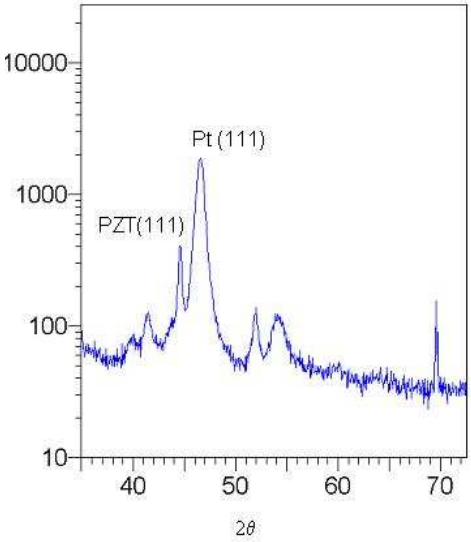

Figure 5. XRD diffraction analysis of selected sample of deposited PZT layer.

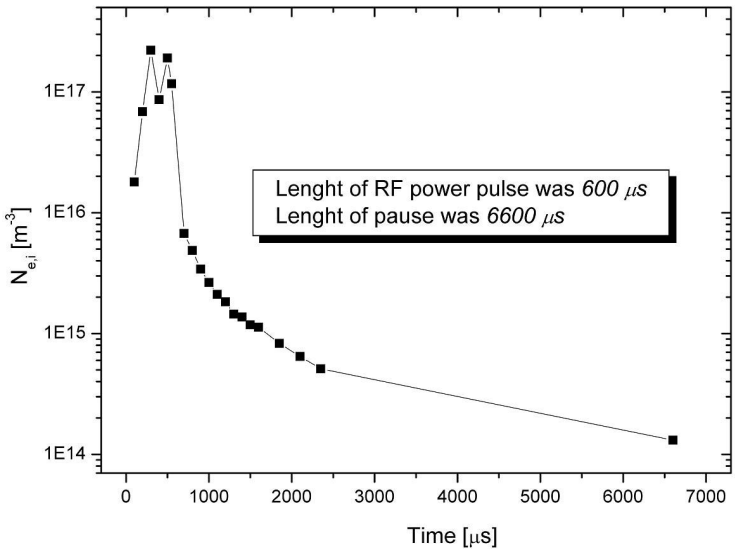

Figure 6. The electron/ion concentrations measured by Langmuir probe in the plasma jet during the modulation cycle.

is generated in He gas flow [21]. Helium plasma jet channel interacts with neutral nitrogen flow Q_{N2} = 90-300 sccm containing vapor of precursors. Alternatively, vapors of precursors were fed directly into the nozzle powered by RF electrode. As the growth precursors, vapors of Zn-acetylacetonate $Zn(C_5H_7O_2)_3$ were used for the deposition of ZnO thin films. These chemicals in the form of solid powders were placed into the heated container. Bare kapton foil, Si and quartz glass substrates were used. Coating of the larger area was provided by motor-driven *x-y* movement of the grounded Al substrate holder.

The photograph of the typical ignited atmospheric plasma jet stream can be seen in Fig. 4. The distance of the nozzle outlet from the substrate surface was always set at 10 mm. The RF power modulated by square pulses was used for plasma excitation. The length of the cycle was 50 ms. Length of the active part of the cycle was 5 ms when the maximum RF power was applied on the electrode. Since in this arrangement one has to expect large losses in the matching unit we measured directly the RF voltage applied on the discharge and the discharge current in order to get information about the real absorbed RF power in the plasma jet.

ZnO thin films deposited on silicon were analyzed by electron microprobe. Samples deposited on SiO_2 and kapton were investigated by XRD in Bragg-Brentano (BB) geometry. Electrical conductivity was measured on the films deposited on SiO_2 and polymer substrates by four points van der Pauw method [28].

Results and discussion

Low pressure plasma jet system

The low temperature plasma jet was capable to deposit PZT films on kapton coated by Pt and Si substrates. Chemical composition measured by electron microprobe has shown dependence on the magnitude of pulse DC bias induced around the substrate. Table 1 shows dependence of atomic concentration on negative substrate DC bias. It can be seen that the best attained composition appears for the DC bias in the range 30-70 V. For the lower bias magnitudes the films contain excess of *PbO* and for the higher magnitudes the films suffer from *Pb* deficit.

Table 1

Sample/at%	Pb	Ti	Zr	O	U_{DC} [V]
P5	21	8,4	5,6	65	0
P1	18	11	5,3	64	-30
P14	18,8	9,5	5	67	-75
P2	8,7	18,2	5,7	67,4	-151
P3	9,7	16,6	7,1	66,6	-141
P4	9	15,1	6,4	68,4	-217

The XRD diffraction analysis the sample of which is illustrated in Fig. 5 has shown that certain fraction of the films is perovskite ferroelectric phase. On the other hand XRD patterns have shown also presence of some fraction of undesirable pyrochlor phase. The samples presented in Fig. 5 contained minimum pyrochlor phase from all our deposited samples. The magnitude of negative DC bias on the substrate was 75V and the substrate ion current on the substrate was $I_0 = 400$ mA. It appeared that it was the maximum ion substrate current we have obtained in our system. Other samples deposited with the same DC bias but at lower ion substrate current contained much more of undesirable pyrochlor phase. Keeping all other deposition parameters constant it was possible to influence the substrate ion current by changing the distance l_s between the nozzle and the substrate. The maximum substrate ion current was achieved for $l_s = 10$ mm.

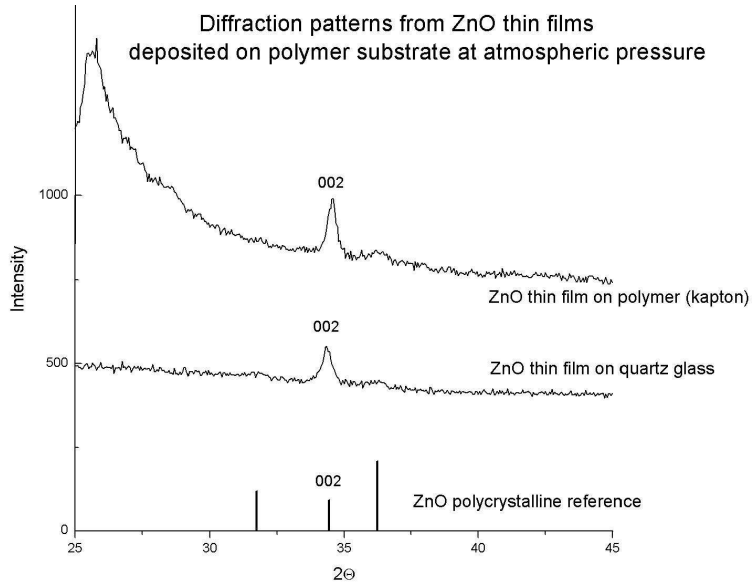

Figure 7. XRD patterns showing the presence of hexagonal crystalline phase on deposited ZnO samples.

The electron/ion concentrations measured by Langmuir probe in the plasma jet during the modulation cycle can be seen in Fig. 6. In this experiment the Langmuir probe was positioned at the distance 35 mm from the nozzle outlet. It can be seen that during the active part of the modulation cycle (500 μs) the concentration of charged particles was relatively high: $n_{e,i} \approx 10^{11}$ cm^{-3}. This took place despite the comparatively large distance from the end of the nozzle where the plasma was generated. After 500 μs the RF source was switched off for the remaining 7 ms of the cycle. However, 1000 μs after switching off the RF power we measured the electron/ion density in the afterglow plasma $n_{e,i} \approx 10^9$ cm^{-3}, which was probably still high enough to somewhat influence the layer growth process during the non-active part of the cycle.

High pressure plasma jet system

The atmospheric barrier-torch plasma jet in the configuration described above was capable of depositing ZnO films on kapton foil as well as on quartz substrates. Electron microprobe has proved presence of ZnO stoichiometry with several percent of carbon contamination. The XRD patterns the sample of which is illustrated in Fig. 7 have shown the presence of hexagonal crystalline phase on both quartz and kapton substrates. It can be seen from Fig. 7 that hexagonal crystallites have preferred orientation with 'c' axis perpendicular to the substrate surface. ZnO samples 500 nm thick on quartz and kapton substrates exhibited electrical conductivity in the range 10^{-1}-10^0 S/cm. The higher electrical conductivity was attained at lower sublimating temperature of solid powder used as growth precursor and hence at lower deposition rate. Nevertheless, accurate mechanism, how the deposition parameters influence the electrical conductivity of the layers is not clear yet. In Fig. 8 we depicted the RF voltage and current waveforms measured directly on the discharge during the active part of

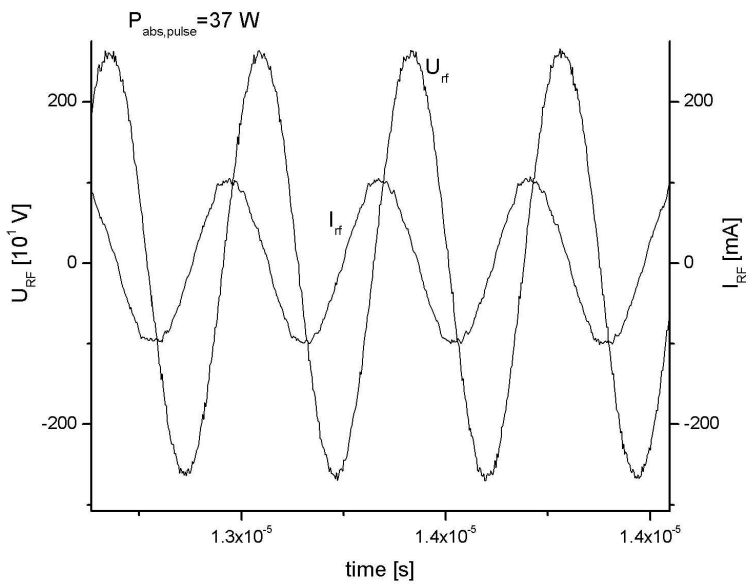

Figure 8. RF voltage and current waveforms measured directly on the discharge (for location of current and voltage oscilloscope probes see Fig. 3).

modulation cycle. From the phase shift between voltage and current it is evident that the barrier-torch discharge system has strong capacitive character. Relative high RF voltage $U_{RFm} = 2500$ V has to be generated in order to maintain the discharge. The discharge current amplitude was $I_{RFm} \approx 90$ mA. Real absorbed RF power in the atmospheric-pressure plasma jet during the active part of the modulation cycle (taking into account the phase shift between voltage and current) was $P_{RF} \approx 37$ W.

Conclusion

The low pressure plasma jet system was used for deposition of PZT thin films on polymer substrates. Certain fraction of deposited films was the perovskite ferroelectric PZT phase. The best PZT samples were deposited for the highest substrate ion current. On the other hand the deposited PZT films still contain certain fraction of pyrochlor phase and hence the deposition technology has to be improved.

The atmospheric barrier-torch discharge was used for deposition of conductive crystalline ZnO thin films on polymer kapton foil. It was possible to set up the conditions in the plasma jet in such a way that ZnO crystallization was possible even at high pressure and low substrate temperature.

5. Acknowledgment

This work was partially financially supported by Grant Agency of the AS CR, grants KJB1010302 and S1010203, by Czech Science Foundation, grant 202/03/0827 and by project COST, action 527.70.

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