PhD in Information Technology and Electrical Engineering

Università degli Studi di Napoli Federico II

PhD Student: Shomnath Bhowmick

XXIX Cycle

Training and Research Activities Report – Second Year

Tutor: Giovanni Breglio – Co-Tutor: Giuseppe Coppola

Personal Information:

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Study and Training Activities:

Courses:

1) Euro Progettazione credits: 3 CFU
2) National Instrument training Credits : 3 CFU
3) Three core issues for the internet: things, security and economic Credits: 2 CFU
4) GE2015 PhD school Credits: 4 CFU
5) AFM/EFM specialist course (1 week) "South korea" Credits: 6 CFU
6) An introduction to physics of nanostructures Credits: 4 CFU
7) Integrated Photonics Credits: 9 CFU
8) A lung-on chip to measure oxygen affinity of single red blood cells Credits : 4 CFU

Seminars:

1) Luce e future Credits: 0.8 CFU total hours (7+1 hrs)
2) Horizon 2020 I progetti Europei nella prospettiva di Un valutatore Eu (CNR) credit: 0.4 CFU. Total hours: 4 hrs
3) Biotechnologie industriali Credit: 0.4 CFU total hours: 2 hrs
4) Secondo convegno nazionale sensori 2Credit: 2 CFU total hour: (7hr+7hr+7hr)
5) Engineering electromagnetic fields at the nanoscale credit: 0.4 CFU total hours (4 hrs)
6) Keys to getting your papers published credits: 0.2 CFU total hours (2hrs)
7) Label-free imaging and characterization of bovine sperm cells: a combined holographic and spectroscopic approach. Credits: 0.2 CFU total hours : 2 hrs
8) Laser emission devices and methods for CARS-based spectroscopy of electroporated biological cells. Credits:0.2 CFU total hours: 2 hrs
9) Sintesi e proprietà ottiche di nanocristalli di Si generati in plasma. Credits: 0.2CFU, total hours: 2hrs

Conference/ workshops:

1) Capri EOS tropical meeting 2015 17th September -19th September.
2) toriono fotonica conference 6th- 8th may 2015.
3) GE Siene Conference 22nd-24th June 2015
4) Rome nano-italy conference 23/09/2015 (8hrs)

Research Title: **Analyzing Pyroelectric Emission From –Z surface of $LiNbO_3$ by Integrating Microheaters**

Summary

Microheaters have been widely investigated for their sensor-based applications, such as gas sensor, flow rate sensor and other microsystems. Here, we investigate the pyroelectric effect, activate by microheaters fabricated on –Z surface of $LiNbO_3$ crystal. Pyroelectric effect is the capability of certain crystal to produce temporary voltage during heating or cooling transient. Fabrication of microheaters on $LiNbO_3$ crystals gives an advantage of confined temperature gradient, together with low power consumption for application-based sensors. In this paper, we study the electron emission from the –Z surface of a pyroelectric material ($LiNbO_3$), relevant to the microheaters fabricated on the +Z surface of crystal. Different geometries of microheaters, such as Fan, Meander, Double Spiral and S- Shape were fabricated on + Z surface of a single domain $LiNbO_3$ crystal [1]. Thermal behavior of these microheaters was analyzed using COMSOL^{TM} Multiphysics and compared with the experimental data obtained by FLIR SC7000 Series thermo camera. Static and time-dependent thermal analyses were performed using a voltage generator by applying DC and step voltage signals to the microheater. It was observed that the electric field resulting from the temperature induced by the microheater changes the spontaneous polarization of the $LiNbO_3$ crystal affecting the electron emission. This pyroelectric electron emission (PEE) from –Z surface of the $LiNbO_3$ crystal was investigated using two-probe point measurement. It was observed that the PEE from $LiNbO_3$ is due to the perturbation, by the temperature variation, of equilibrium between spontaneous polarizations P_S in the crystal and external screening charges (q_{SC}) on its surfaces. At equilibrium, all P_S are fully screened by q_{SC} and no external electric field exists. Any excess or lack of screening charges (q_{SC}) relatively to $P_{S,}$ leads to the appearance of an electrostatic state from the uncompensated charges (ρ) given by $\rho = \Delta\,(P_s - q_{sc})$ [2]. Furthermore, we verified the pyroelectric emission effect in a transient condition for all the microheaters. A voltage signal at 10mHz was applied to the microheater using signal generator. A tip (diameter~0.254mm) was positioned at distance ≤ 1mm from the –Z surface of $LiNbO_3$ crystal. The current peaks were acquired using oscilloscope that occurs due to the non-distribution of P_s on the –Z surface of $LiNbO_3$. It was observed that microheaters with complex structure have significantly higher number of current peaks compared to a simplest structure, because complex microheater leads to a non-uniform temperature gradient on the –Z surface of the $LiNbO_3$ crystal [3]. It was also noted that the temporal distances between adjacent electrical peaks exponentially increases during the application of the thermal transient, showing a dependency of the rate of heating and cooling on the PEE in a transient condition of the crystal. Finally, we demonstrate two pyroelectric effect based applications: Pyro-jetting of liquid droplet (oil, OIR 906, water and PDMS) [4,5] and pyro-emission lithography using microheater [6].

1. Introduction

Pyroelectric effect based sensor applications has gained a lot of interest in past few decades, due to its property of generating electrical charges for a small variation of temperature. Recently, a lot of new functionalities have been generated using the pyroelectric effect on biosensor such as: aligning CNT and carbon based nano-particle using electrode free approach, electro-hydrodynamic lithography for 3D polymer structures, micro-needles formation under pyro-electro-hydrodynamic effect using PDMS, nano-droplet drawing under the action of electric field generated using pyroelectric effect, and many more [4-8]. In these approaches, macroscopic thermal stimulation tools (such as LASER, soldering iron rod or hot plate) were used to create a variation in temperature, so generate pyroelectric effect that induces a spatial charge distribution on the surface of driving ferroelectric crystal. However, these techniques were limited due to: the complex heat generation control; the large thermal distributions; and their macroscopic dimensions, that don't fulfill the demand for cheap and miniaturized devices.

In this work, we propose a method for applying the pyroelectric effect using microheaters, to overcome the limitations of traditional way of heating a pyroelectric crystal. Moreover, using microheaters, we are able to easily control the temperature gradient and thus PEE in the region of interest from the pyroelectric crystal. We report on four-microheater designs (meander, fan, double-spiral and S shape) that are fabricated on +Z face of (10mm*10mm*500µm) $LiNbO_3$ crystal using photolithography and thin film deposition techniques [1].

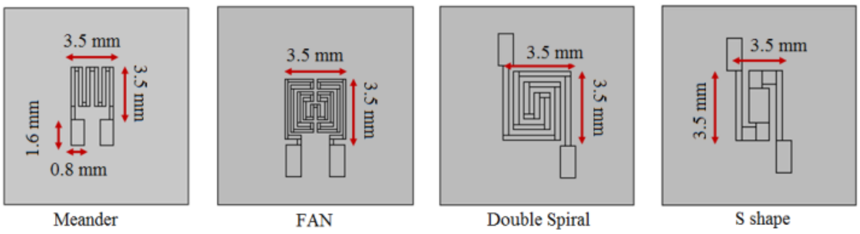


Fig1: Four design of the Microheater.

Titanium (Ti) of 300nm-thick films was the choice for heater materials. Ti has a low density and remains resistant to the corrosion in various conditions due to the thin layer of oxide which forms on its surface and makes it particularly suitable for MEMS devices [9]. Titanium was deposited using electron beam.

2. Thermal analysis of microheater designs

Thermal analyses of titanium microheater designs were performed both theoretically and experimentally, using COMSOL™ Multiphysics package and FLIR SC7000 series thermo camera. Steady state and transient state regime were investigated to better understand the thermal behavior of different heater designs. In figure 2, the temperature attained by the individual microheater designs with respect to the power applied is demonstrated. The 3D simulations were performed by coupling the power generation, due to the joule heating, with the heat conduction and dissipation into the device and with surrounding medium. The Multiphysics simulation uses the electric current module in combination with the heat transfer module. The Figure 2 shows the temperature with respect to electric power applied for the simulated and experimentally obtained result. A well agreement between the experimental and theoretical model considered for the simulation can be observed in the plots for different microheater designs.

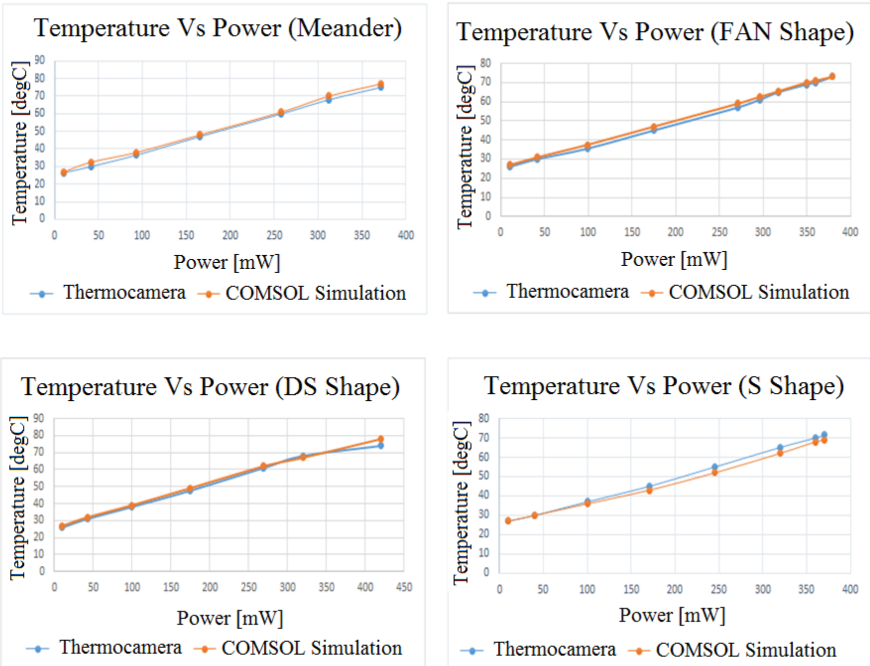


Fig2: The temperature vs. power plot for the titanium microheater estimated using simulator and observed by Thermo-camera.

In addition to the steady state analysis, transient study was also analysis (both experimentally and by simulation) by applying a step triggering voltage with a heater-on-off-time of 8sec with 50% duty cycle using a voltage pulse generator. In figure 3, we can observed that the rate of heating was stepper and the cooling was faster in experimental analysis compared to the simulation model. This effect or behavior could be attributed to the heat dissipation in the experimental analysis from various condition such as: environment condition, silver adhesion layer and contact resistance which were neglected in the theoretical model.

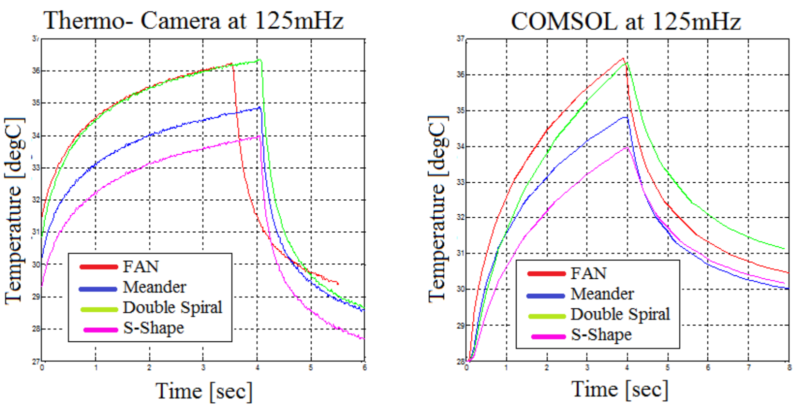


Fig3: Experimental and simulated transient analysis of Microheater designs with heater on-time of 4sec.

The maximum temperature reaches in transient condition for each microheater shows similar result for both simulated and experimentally analyses.

3. Pyroelectric electron emission analysis

Pyroelectric electron emission (PEE) effect from –Z surface of $LiNbO_3$ was further investigated for different titanium microheater designs using two-point probe method at ambient conditions. In two-probe point measurement, a metallic tip is bought near the –Z surface of $LiNbO_3$, while the other probe is used for grounding same surface that can be observed in figure 4. When a temperature variation occurs, due to the electrical power dissipated by the microheater, a strong electric field is generated on the –Z surface of the $LiNbO_3$ due to the uncompensated charges.

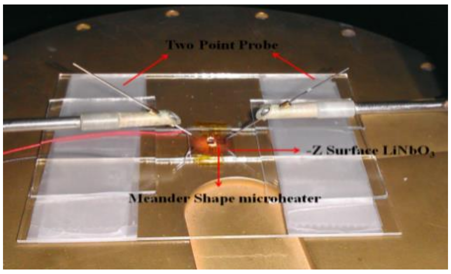


Fig4: Two -point probe measurement set-up.

In fact, the PEE from a pyroelectric crystal is generally due to the perturbation, by the temperature variation, of equilibrium between spontaneous polarization P_s in the crystal and external screening charges (q_{sc}) on its surface. At equilibrium, all P_s are fully screened by q_{sc} and no external electric field exists. Any excess or lack of screening charges q_{sc} relatively to P_s leads to the appearance of an electrostatic state from the uncompensated charges (ρ) given by $\rho = \Delta\,(P_s - q_{sc})$, which generates a high electric field at the crystal surface (10^6-10^8 V/cm) [10]. The generated electric field is intense enough to cause the pyroelectric electron emission (PEE) by field emission (FE) and/or field ionization effect. PEE measurements were performed at ambient conditions, where the charges generated (due to spontaneous polarization effect) near the polar surfaces are localized at the boundary between the crystal and dielectric layer (air). The generated electric field, due to the thermal variation of crystal created using microheater, results in the dielectric breakdown of air (3×10^6 V/m) between the metallic tip and crystal surface. The dielectric breakdown of air makes it partially conducting and enables the metallic tip to collect the emitted electron from the –Z $LiNbO_3$ surface.

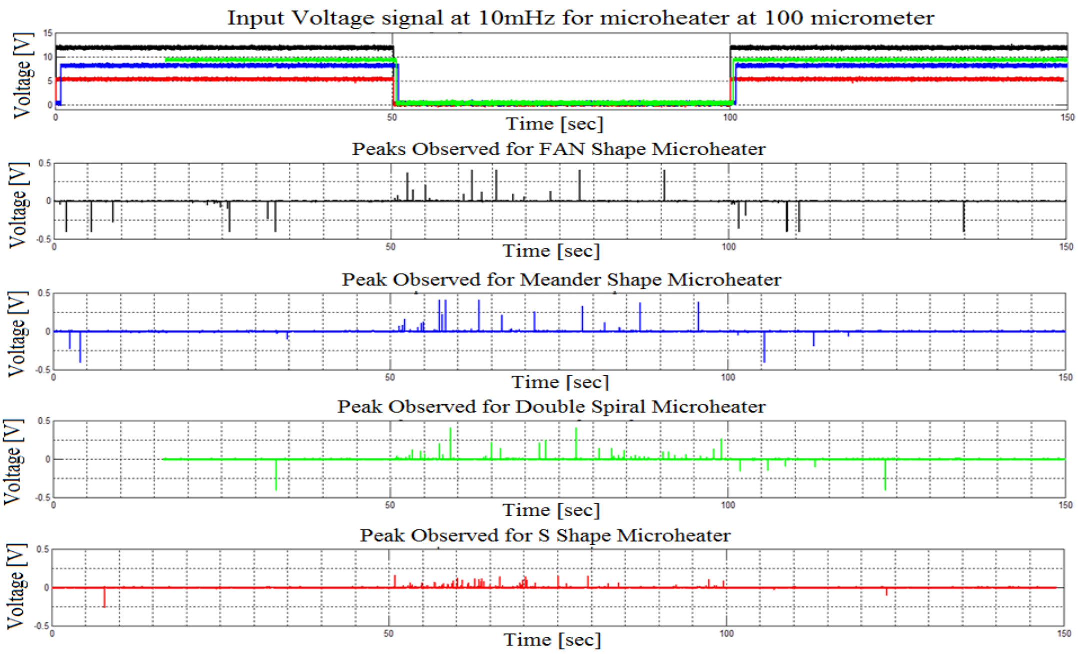


Fig 5: a) Voltage Vs. time (s) (~290mW power) at 10mHz applied (S, Meander, FAN, Double Spiral); b)- e) PEE detected from the surface of LN at a gap ~100[μm] (S [red], Meander [blue], FAN[Black], Double Spiral [Green].

Significantly, the probe detected higher current peaks from the fan shape compare to the simple S- shape microheater as observed in figure 5. The basic reason for detecting higher current peaks is attributed to the temperature distribution due to different shape, spacing between the heater track and the thickness of the $LiNbO_3$ crystal. S- shape being the planar structure produces lower current peaks. It was observed that as the temperature drop (rate of cooling), the probe detects positive peaks while negative peaks were detected in the temperature rise (rate of heating) conditions. Therefore, as the temperature rises uncompensated charges are dominating due to the screening charges (q_{sc}) implying the negative voltage peaks. While the temperature drops, the uncompensated charges are dominating due to the polarization of crystal (P_s) resulting in positive voltage peaks.

Fan shape microheater at 100µm (tip to surface distance) was considered as the basis for the PEE experiment with an applied voltage of about 12 V, since higher occurrence of peaks were observed, yielding a better clarity of the PEE behavior.

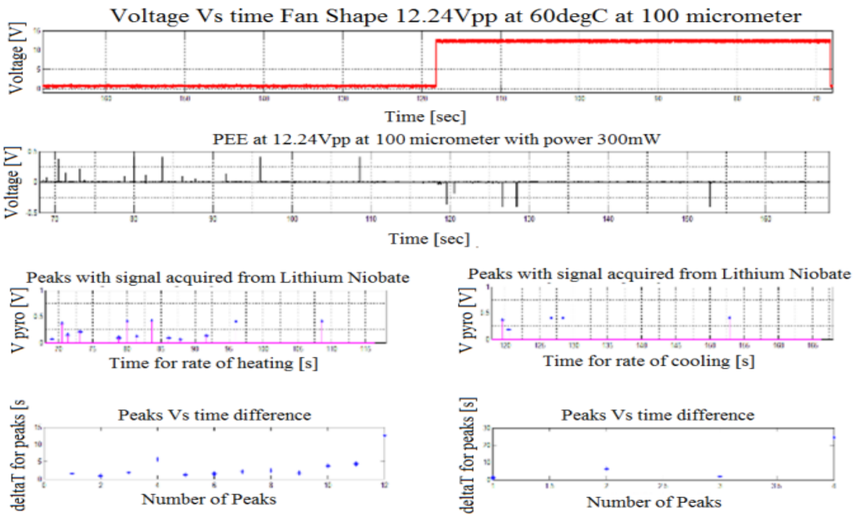


Fig 6: Fan Shape Microheater: a) 12.25V Step Voltage signal applied, b) Output pyro data from oscilloscope, c) (left) pyro data with peaks for time up to down, d) (right) pyro data with peaks for time down to up, e) (left) distance between the peaks vs. the distance between the time for voltage signal up to down, f) (right) distance between the peaks vs. the distance between the time for voltage signal down to up.

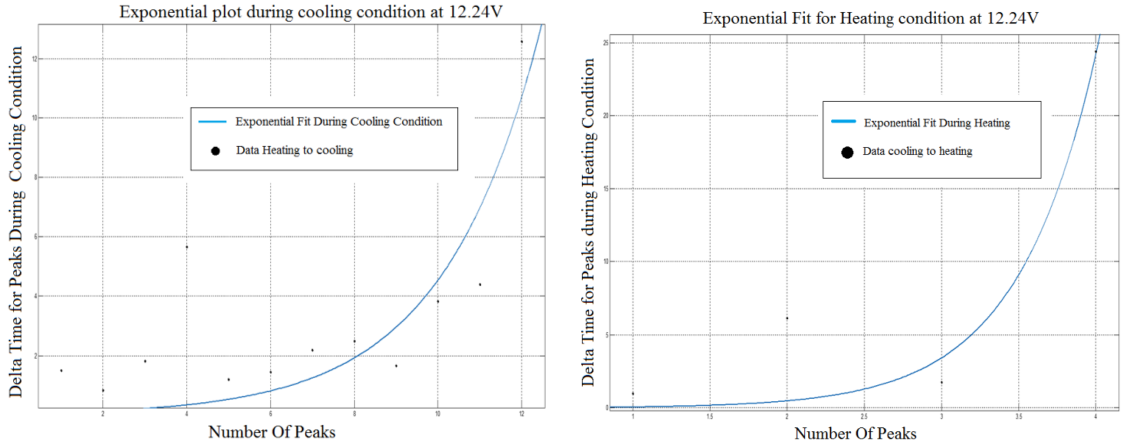


Fig 7: Exponential fit for the cooling condition of the fan microheater(Above); Exponential fit for the heating condition of the fan microheater (below).

The fitted curve shown in figure 7 for the fan shape microheater at 10mHz shows an exponential behavior for distance between the peaks with time. The exponential increment in the distance between the peaks, attributed to the rate of heating and cooling of the crystal (due to the microheater).

4. Pyroelectric effect based applications

4.1 Pyro-jetting of liquid droplet

Pyro-jetting is the behavior of a liquid to eructate a small volume of liquid (especially in Micro and Nano liters) from a liquid droplet using the pyroelectric field of crystal. The pyro-jetting behavior of liquid droplets was performed using different microheater designs: oil (density 900 Kg/m^3), OIR 906 (density 970-1040 Kg/m^3), PDMS (density 965 Kg/m^3) and water (density 1000 Kg/m^3).

In the following setup, a glass substrate was placed with a liquid droplet which acts as a liquid reservoir, then at a distance of ~ 1mm from the receiver end of thin glass slide using a spacer. The microheater (thickness~300nm), fabricated on $LiNbO_3$, crystal using the photolithography process was placed over the thin glass slide (~ 500um). A drop of each liquids (Oil, PDMS, OIR & water) was place on the glass substrate using a pipette. The voltage was applied to the respective microheater and the jetting of droplet due to the pyroelectric behavior of the lithium Niobate crystal was observed.

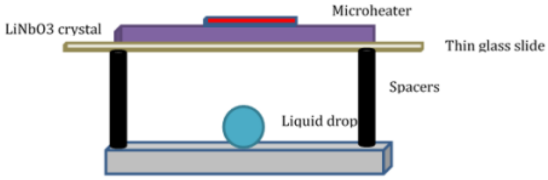


Fig8: Set up for the pyro-jetting of droplets

When the voltage is apply to the microheater the variation in temperature in the crystal results in a surface charge density on the crystal creating an electric field between the liquid reservoir on the glass substrate and receiver glass plate. The electrostatic force assists a small volume of liquid droplet towards the thin glass surface, which is label as the jetting of liquid droplet. Generally, the jetting of liquid droplet was observed when an electric power of 300mW was applied to the microheater while keeping the substrate with the liquid droplet and receiver glass slide at a distance of ~1 mm.

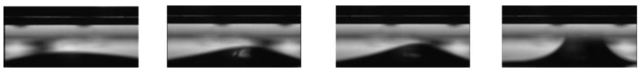
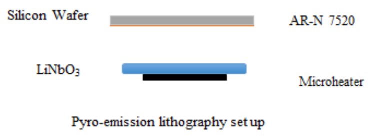


Fig 9: Sequence image of pyro-jetting of PDMS using fan shape microheater(from left to right).

4.2 Pyro-emission lithography using microheater

Investigation has been performed using pyroelectric materials as an electron source for lithography applications and electron projected patterns [6]. Here, we demonstrate that using S shape microheater (3.5mm*3.5mm*300nm), imprinting of a localized circular spot of ~500um diameter can be achieved on the desired substrate. The imprinting patterns can be varied by varying the microheater designs. In the following setup, the S-shape microheater was fabricated on the +Z surface of the $LiNbO_3$ crystal.

A silicon wafer was coated with AR-N 7520 series negative e-beam resist using a spin coater. The film thickness of 1.4µm was obtained at 4000rpm. The silicon wafer was placed >1.5mm on the top of the –Z surface of $LiNbO_3$ using spacers. The setup was placed under vacuum (6e-5 mtorr). The rectangular pulse voltage was applied to the microheater for 30 min with a 50% duty cycle. The cooling was considered in the vacuum condition only. A localized spot size of ~500µm was observed on developing the AR-N 7520 negative e-beam resist silicon wafer using AR300-47 developer.



(a)

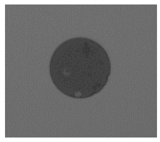

(b)

Fig10: a) setup of the complete system, b) spot observed after the development of the silicon wafer.

5. Conclusion

Thermal analysis of four different microheater designs namely meander, fan, spiral and S shape on $LiNbO_3$ was performed both theoretically and experimentally using COMSOL Multiphysics and FLIR SC7000 series thermo camera. Steady state and transient state study were investigated to better understand the thermal behavior of different heater designs. The PEE was further investigated from the -Z face of the $LiNbO_3$ surface using two-point probe method at ambient conditions. The electric field generated due to the thermal variation on +Z surface using microheater, resulting in the dielectric breakdown of air (3 x 10^6 V/m) between the probe metallic tip and –Z surface of $LiNbO_3$ surface. The dielectric breakdown of air makes it partially conducting and enabling the metallic tip to detect the emitted electron from the -Z surface of $LiNbO_3$. The occurrence of dynamic peaks were evaluated analyzing the temporal distance trending between the electrical peaks that shows the dependency of the rate of heating and cooling condition on the PEE in a transient condition. We also demonstrated the pyroelectric effect for the pyro-jetting of liquid droplets of various density as sensor application. The results obtained provide a novel method for generating, manipulating, detecting and controlling the PEE from $LiNbO_3$ crystal using microheaters. We also demonstrated few pyroelectric effect based applications such as pyro-jetting of liquid droplets and pyro-emission lithography.

References:-

[1] G. Velmati, N. Ramshanker and S. Mohan, "2D simulations and electro- Thermal Analysis of micro-Heater Designs Using COMSOL for Gas Sensor Applications", *Proceedings of the COMSOL Conference 2010*, India.

[2] El Mostafa Bourim, Chang-Wook Moon, Seung-Woon Lee, Vadim Sidorkin, In Kyeong Yoo, "Pyroelectric electron emission from −Z face polar surface of lithium niobate monodomain single crystal", *Journal of Electroceramics*, Volume 17, Issue 2-4, pp 479-485, Dec. 2006, doi: 10.1007/s10832-006-0387-y.

[3] Darhuber, Anton A., Valentino, Joseph P., Troian, Sandra M., Wagner, S., "Thermocapillary actuation of droplets on chemically patterned surfaces by programmable microheater arrays", *Journal of Microelectromechanical Systems*, vol.12, no.6, pp.873,879, Dec. 2003, doi: 10.1109/JMEMS.2003.820267.

[4] Ferraro P., Coppola S., Grilli S., Paturzo M. and Vespini V., "Dispensing nano–pico droplets and liquid patterning by pyroelectrodynamic shooting", *Nature Nanotechnology*, 5, 429–435, (2010), doi: 10.1038/nnano.2010.82.

[5] V. Vespini, S. Coppola, S. Grilli, M. Paturzo and P Ferraro, "Milking liquid nano-droplets by an IR laser: a new modality for the visualization of electric field", *Meas. Sci. Technol.*, 24 045203, (2013), doi: 10.1088/0957-0233/24/4/045203.

[6] D.W.Kim, C.W.Moon and In.K.Yoo, "Pyroeletric emission lithorgraphy", *J Korean physical society*, Vol.42, April 2003, pp. S1196_S1198.

[7] O. Gennari, S. Grilli, S. Coppola, V. Pagliarulo, V. Vespini, G. Coppola, S. Bhowmick, M. A. Gioffre, G. Gentile, V. Ambrogi, P. Cerruti, C. Carafagna and P. Ferraro, "Spontaneous Assembly of Carbon-Based chains in polymer matrixes through surface charge templates," *Langmuir*, vol. 29, pp. 15503-15510, 2013.

[8] S. Grilli, S. Coppola, V. Vespini, F. Merola, A. Finizio and P. Ferraro, "3D lithography by rapid curing of the liquid instabilities at nanoscale," *PNAS,* vol. 108, no. 37, pp. 15106-1511, 2011.
[9] C. O'Mahony, M. Hill, P. J. Hughes and W. A. Lane, "Titanium as a micromechanical material," *J.Micromeceh.Microeng.,* vol. 12, no. 4, pp. 438-443, 2002.
[10] W. m. Chang, W. . l. Seung, s. Vadim and k. y. in, "Pyroelectric electron emmision from -Z face polar surface of lithium niobate monodomain single crystal," *J electroceram,* vol. 17, pp. 479-485, 25 july 2006.

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Publications:

Article: Spiral formation at microscale by μ-pyro-electrospinning

journal name: Soft matter "Under review"

Conference paper: Fotonica AEIT Italian Conference on Photonics Technologies, 2015, At turin

DOI: 10.1049/cp.2015.0129

Tutorship:

AFM/ EFM for Maters students

1) Capri project: 4 hours (2 hrs theory+2 hrs practical) 08/09/2015
2) STEPFAR project : 4 hours (2 hrs theory+2 hrs practical) 21/09/2015
3) CERVIA project: 4 hours (2 hrs theory+2 hrs practical) 20/10/2015
4) STEPFAR project : 4 hours (2 hrs theory+2 hrs practical) 26/10/2015