Layering of Copper-ink using 3D Printing & Characterization

ARIVARASI A and ANAND KUMAR
Department of Electrical & Electronics Engineering
Bits Pilani Dubai Campus
International Academic City, Dubai
UNITED ARAB EMIRATES
P20140002@dubai.bits-pilani.ac.in, akumar@dubai.bits-pilani.ac.in

Abstract: - The use of nano materials, particularly copper is of interest, in areas like printed electronics and chemical engineering. Copper is highly conductive in nature and thin films on a substrate makes the structure more significant. Printing copper requires melting of macro size particles conventionally, whereas the viscous mixture of nano ink composition, utilizing spray mechanism in 3D printing for precision. The copper particles of around 100 nm sizes is used for experimentation and a coating is made with a thickness ranging 6.41 µm to 8.41 µm without usage of laser mechanisms, which is shown through SEM images. The grain size distribution is uniform and porosity is 0.56% measured through optical microscope. Resistivity measured is 7µ ohm cm / $7e^{-8}$ ohm m. The structure will be further utilized for an electrochemical sensing mechanism based on water quality measurement procedure. The advantages are lower processing temperature and usage of vacuum and controlled environment is avoided. This is cost-effective to avoid bigger 3D printing machineries.

Key-Words: - layering, copper, 3D-Printing, sintering, electro less printing, conductive

1 Introduction

Printing of metal particles is of key interest in this micro-nano era. The field of metallic and ceramic Additive Manufacturing (AM) is developing at a rapid pace [1]. Thereby, outline of the additive manufacturing chain comprises of phase 1 process flowing from specification, CAD design, and fault analysis to optimized mode. Phase 2 manufacturing includes generating g-code, and slicing to provide .STL file thereby printing layer by layer. Subsequently, Phase 3 tests for printed object and further post processing and quality checks are performed [1]. There are security challenges mentioned on 3D-Printing technology products right from design until finished product defects. Researches underway addresses few aspects on quality checking procedures as well. Hereby, AM processes can be considered for quality, cost benefits apart from design innovations and realizations. Prototyping is a key mechanism through which innovation can be taken for proof.

In this paper, the metal nanoparticle out of copper is spray printed on Silicon substrate, further characterized and measured. The printed droplet size is of consideration and hence the printing resolution. Spraying fine droplets on silicon substrate provides a fine layer which can be applied for various chemical transduction products.

2 Need of a new 3D printing process

The conventional or existing methods utilize metal powder, wherein costly machines and post-processing setups are in-evitable. 3D printing recommendations for chemical printing processes are hereby stated in terms of temperature, composition, flow rate before actual printing and the surface structure, layer height, drop size post printing. Temperature conditions either through resistive heating or sintering is done, after printing micro/nano metal particles. Chemically, method of electro less plating involves layer by layer procedures involving micro/nano thicknesses, for increased conductivity.

Rapid prototyping in copper substrates has been demonstrated with respect to microfluidics [2]. The problem requires step by step procedure of deposition or spraying through a differing geometry in terms of sensor design. Meanwhile, the resolution of printing has to be finer and finer. While 3D printing allows for innovation in sensor designs, each layer can be assigned with required material / material characteristics and post processing using usual chemical procedures automated by 3D- printing as well. The requirement of printing for a chemical sensing procedure has been explained in [3]. Reasonably, there exists an inevitable need for a new process exhibiting simpler mechanism, cost and be able to process multi-material printing with a finer resolution.

2.1 Printing on to a substrate

There are various 3D printing technologies like Stereo lithography (SLA), micro SLA, Digital Light Processing (DLP), Selective Laser Sintering (SLS), Selective Laser Melting (SLM), Electronic Beam Melting (EBM) etc., Even though these processes print precise layers using lasers or e-beam, the printing on substrate would not be feasible. The tracing of layer uses high power beam such that the substrate would get molten by the time metal is deposited on top. For eg., Poly Methyl Methacrylate (PMMA) [4] melts at 130^0C, which cannot be used for metal deposition, for metals having melting or sintering temperature above 130 degrees. A suitable substrate, which can withstand the higher processing temperatures is required. Selection of substrate which could withstand the very high temperatures is rare and there are high chances of getting melted from the processes those are using laser or ebeam. While processes those utilize UV Nd:YAG can print on polymer substrates, it can ablate the polymer, which is highly design and application dependent [5]. Mostly they follow subtractive manufacturing involving etching [6] [7]. Henceforth, the 3D printing processes which are using laser and ebeam technologies are unable to print on a substrate, which processes metal powders at a higher temperatures. A few aerosol technologies are rare exceptions, yet involving constraints of huge cost and accessibility. Screen printing and ink jet printing produces layers with thicknesses in the range of 0.015-100 µm and 0.05-20 µm respectively.

2.1.1 Challenges in current 3D printing methodologies

Sensor printing costs, precise surface finish, faster response, multiple function incorporations, space constraints, functional mechanisms, temperature handling and material collaborations are of importance in current 3D printing methodologies. Inkjet printing of nano particle is prominent for 2D designs [8], whereas novel sensor design requires geometry customizations and printing friendly processes. Comparing to inkjet printing technology, 3D printing allows varied sensor designs and allows printing complexities in geometry, considering the AM advantages. SLS sintering is followed by inkjet printing in most of its applications [9][19]. In case of Polyol process, it involves vacuum usage, which can be avoided using novel printing methods [10].

The usage could be either vacuum or helium surrounded / background environment [11]. On the other hand, LIFT (Laser Induced Forward Transfer) 3D printing process melts the metal through laser which requires high power laser and related setups [12]. Similarly lasers are predominantly used for tracing [13]. Copper precursors needs huge chemical pre-processing steps making the printing process very complex and depends on melting temperatures as well [14]. Few processes which involve electro-less plating of copper, mask projection are combined and laser etching would lead to a cumbersome procedure [15]. Meanwhile, varieties of materials are printed using 3D printing using current processes. The interface used, material supply and temperature handling have key issues. Chemicals and liquid handling needs critical designs. The stepping of motor is reconsidered often for precision. Internal manufacturing defects could cause huge loss from 3D printing misalignments and geometry defects. Hence, product quality is of higher importance. Printing metal on a substrate requires careful analysis and process design. The result will be of significance due to concept of layering on a substrate using varied 3D geometries with nominal temperature processing.

Among the alloys of copper, copper-sulphate is experimented initially for sintering test. Printing metal particles will involve sintering as they have to get infused together for a uniform surface layered on a substrate. The design needs incorporation of sintering in future 3D printing design/machine trends. Sintering plays a key role in metal deposition on substrates. For the selection of copper alloys or copper particles the sintering is experimented.

After depositing copper sulphate on a silicon substrate, sintering is performed using a muffle furnace, $CuSO_4$ is turned to anhydrous state. The general equation is considered for analysis.

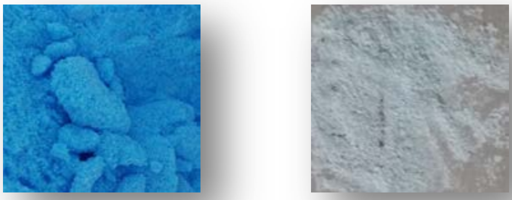
$$CuSO_4.5H_2O \rightarrow CuSO_4 + 5H_2O \qquad - (1)$$

On further sintering using oven, copper oxide is obtained with sulphur trioxide.

$$CuSO_4 \rightarrow CuO + SO_3 \qquad - (2)$$

1 gm of $CuSO_4$ is taken for sintering. . At 110^0C, the copper sulphate starts decomposing and colour changes to light blue. For sintering, oven temperature is set to 200^0C, while it becomes anhydrous white colour powder.

Fig. 1 shows pure copper sulphate taken for sintering. After sintering, the powder is turned white with no water molecules.



(a) $CuSO_4.5H_2O$ (b) $CuSO_4$ Anhydrous

Fig1 : Sintering on copper sulphate

Consequently the sintering continues at four different temperatures 63, 109, 200 and 600 degrees. Copper (II) sulphate pentahydrate *decomposes* before melting. It loses couple of water molecules upon heating at 63^0C, followed by two more at 109^0C. The final water molecule is lost at 200^0C. Complete dehydration occurs when the only unbound water molecule is lost. At 650^0C, Copper (II) sulphate decomposes into copper (II) oxide (CuO) and sulfur trioxide (SO_3). Fig. 2 demonstrates heating $CuSO_4$ at four different temperatures.

a. 63^0 C

b. 109^0 C

c. 200^0C

d. 600^0 C

Fig 2: Sintering test in Muffle furnace at different noted temperatures. The copper salt is decomposed and then water molecules removed without any fusion or melt happening.

As such a powder, the fusing nature is absent during sintering, whereas when the particle sizes reduces considerably, the sintering will result in fusing of particles together. Atomic diffusion of powdered materials gets accelerated at high temperatures. Sintering nano particles fuses together the particles and creates a single geometry, wherein atoms in the powder particles diffuse across the boundaries of the particles. Sintering temperature is far less than the actual metal melting temperature. Nano particles exhibit far greater benefits of working in the case of pure metal processing.

Moreover, conductive inks are widely used in printed electronics and thin film applications. They possess higher conductivity and thermal stability. Compared to silver ink, copper ink is cost effective and environment friendly [12][17]. Copper is suitable for large scale production. It is feasible for 3D printing and other printing methodologies. Surface conductivities can be modified using chemical processes.

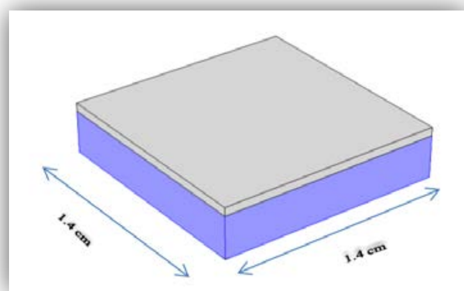
In this experimentation, the 3D printing of nano-copper ink is performed by controlled geometry deposition and subsequent sintering results in micro resolution layering of copper surface. The characterization results are provided therein.

3 Problem Solution

The controlled deposition on a substrate requires definite modeling geometry with slicing procedure followed by gcode printing, layer by layer.

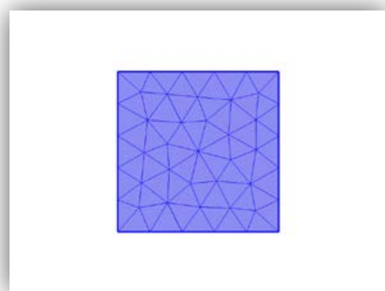
3.1 Geometry Structure

The geometry is modeled using Comsol Multiphysics 5.0 using 3D design structure. The substrate Si is chosen with the first layer being copper of thickness 1 micron. During printing the hardware takes the minimum resolution based on component physical constraints and built in stepping mode.

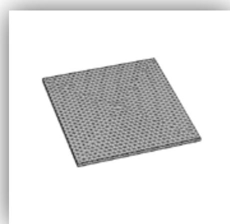


a. STL file and model of Cu on Si

The .mph file from comsol is converted to .STL format using the export option in geometry. Thereby STL file is saved and further taken for slicing using slice3r. Print run monitors the status of printing in production.



b. Top surface of Cu model



c. Meshed 3D file for Cu printing

d. circular model

Fig 3: Geometry files for prototype printing of Cu on Si. b, c, d are tetrahedral meshed figures of different shapes.

The square shaped design is taken for layering copper on Si substrate for prototyping. The geometry could be designed for any kind of shape layering through CAD model. The extruder design for various metals and chemical processings can be modeled as in Fig. 4, which uses each nozzle for depositing corresponding nano inks in suitable viscosity, surface tension through piezo transducing model. The sequence of drop is controlled by microcontroller. The linear view of spray nozzle design is provided in Fig. 4. This is design representation and prototype utilizes existing spray nozzle usage.

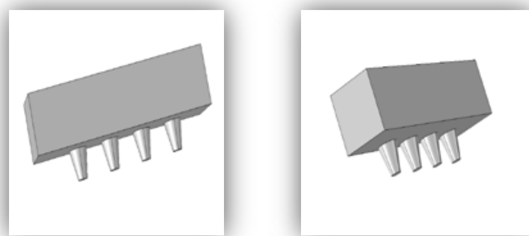


Fig 4: Extruder spray design for four nozzle structure (Quadruple nozzle for multi material printing)

3.3 3D printing of copper

Once the design is sliced and gcode been created, the ink is provided to a syringe spray nozzle connected to FDM 3D printer in Fig. 6 and the particles are nicely sprayed on the substrate according to geometry. Copper ink constituents include copper particles along with potassium hydroxide with toluene mixture to maintain viscous solution of 1 to 2 cPs. Without toluene, the solution viscosity is 4 cPs. Toluene has been widely used as solvent in printing [16]. The copper particles containing ink of is provided through a thin tube to feed into the nozzle which utilizes a spray mechanism.

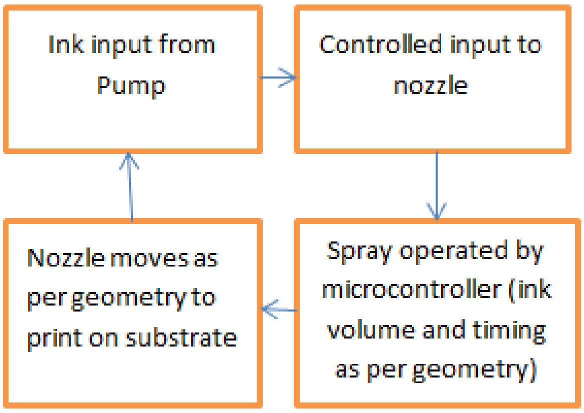


Fig 5: Printing Flow

The print flow is depicted in Fig. 5. With a flow rate of 5 μl/min with a pressure spray mechanism, a minute layer of copper is layered for required height. Here, in this case single layer is required.

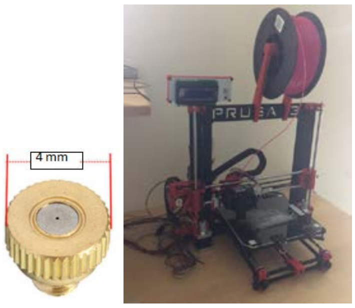


Fig 6: FDM printer used for spraying on Si using a spray nozzle.

3.3 Sintering of copper particles

The copper ink is spray printed on Si substrate for 30 seconds, which is then sintered for drying and fusing. Sintering is understood as a kind of metallurgical process in which the powdered material is compressed and heated to form a desired solid shape. Fig. 7 showcases sintered surface.

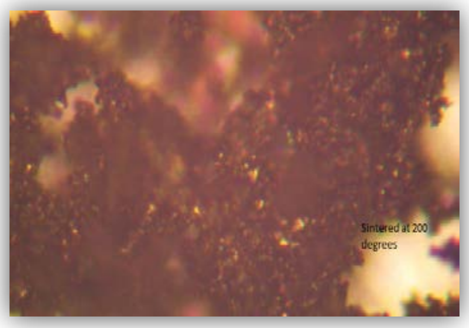


Fig 7: Sintering using muffle furnace at 200 degrees

Sintering at 200 degrees using oven has dried the particles and fusion has taken place. A few pores or seen after sintering as a result of excess drying and the temperature is to be reduced further. The particles are seen sticky to the surface and to neighboring particles. For greater adhesion to Si, Ti adhesive can be 3D printed in nanometer thickness for further prototype models. The printed structure looks like in Figure 8. A uniform coating is seen which can be further applied with plating solution for sensor application.

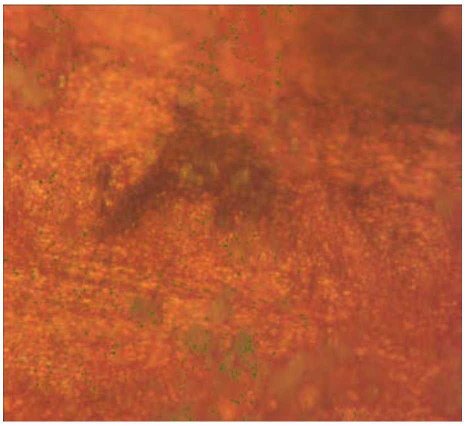


Fig 8: Surface of printed copper

3.4 Results & Characterization

The optical microscope used for characterization is an optical type having trinocular inverted category with plane optics and incident light illumination. Magnification range is 100X to 1000X and the measurements are performed in 1000X. Resistance measured using four point probe. The following table 1 illustrates the measured results.

Table 1: Characterization using optical microscope

Particle	**Porosity**	**Coating thickness**	**Grain size distribution**	**Resistivity**
Copper particles 100 nm	0.56%	6.41 µm to 8.41 µm	Uniform with 2 µm	7µ ohm cm / $7e^{-8}$ ohm m

The SEM characterization and measurements are provided. As copper film thickness reduces, the resistivity decreases [14]. Fig. 9 showcases the uniform distribution of copper particles over silicon substrate, which is a result of printed ink and sintered. Fusion between metal particle has taken place. The coating layer thickness or printing resolution varies from 6.41 to 8.31 µm as provided in Fig. 10. The geometry has confined to the perfect deposition boundaries due to 3D printing process. The conductivity can be further increased by applying plating solution to the surface. Thereby, proving the 3D printing of copper particles successfully.

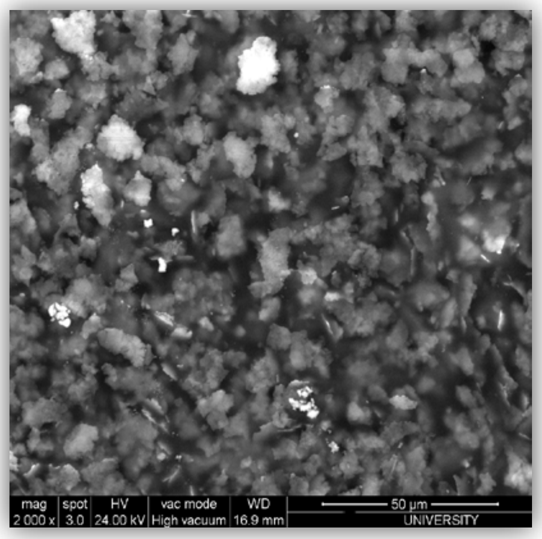


Fig 9: SEM Image of Copper particles

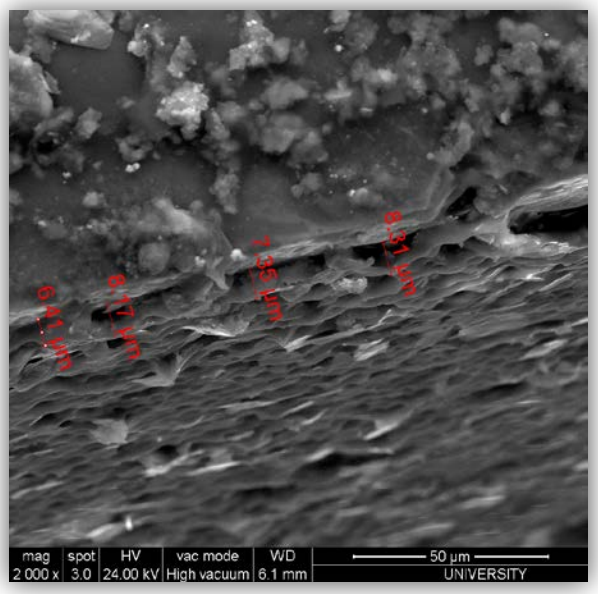


Fig 10: SEM Image of Copper particles on Si substrate

4 Conclusion

The 3D printed copper particles are sintered in oven to 200^0C , which is characterized using optical and SEM microscopes. Printed copper coating ranges from 6.41 to 8.31 µm above 1 cm width Si substrate. The resulting resistivity is valid for a copper surface and hence it is applied for further surface processing. The conductivity can be explained through resistive nature, where nanoparticles increase conductivity due to its small particle nature. Recommendation will be to use xenon sintering [17] compared to oven sintering to improve resolution and efficiency. Thermal curing [18] can provide oxidation to a certain extent, whereas optical curing could be preferred in the case, which is integrable with the 3D printer.

References:

[1] Takiya, T., Fukuda, N., Umezu, I., Sugimura, Zeltmann, S.E., Gupta, N., Tsoutsos, N.G., Maniatakos, M., Rajendran, J. and Karri, R., 2016. Manufacturing and security challenges in 3D printing. Jom, 68(7), pp.1872-1881.

[2] Abdelgawad, M. and Wheeler, A.R., 2007. Rapid prototyping in copper substrates for digital microfluidics. Advanced Materials, 19(1), pp.133-137.

[3] Kavya, Arivarasi A., Anand Kumar R., Jegatha Nambi Krishnan. (2016) Design & Material Characterization for 3D Printing Sensor. International Journal of Circuits and Electronics, 1, 128-133.

[4] Li, J., Chen, D. and Chen, G., 2005. Low-Temperature thermal bonding of PMMA microfluidic chips. Analytical letters, 38(7), pp.1127-1136.

[5] Zakariyah, S.S., Conway, P.P., Hutt, D.A., Selviah, D.R., Wang, K., Rygate, J., Calver, J. and Kandulski, W., 2011. Fabrication of polymer waveguides by laser ablation using a 355 nm wavelength Nd: YAG laser. Journal of Lightwave Technology, 29(23), pp.3566-3576.

[6] Maekawa, K., Mita, M., Yamasaki, K., Niizeki, T., Matsuba, Y., Terada, N. and Saito, H., 2008, May. Packaging of electronic modules through completely dry process. In Electronic Components and Technology

Conference, 2008. ECTC 2008. 58th (pp. 950-955). IEEE.

[7] Hong, C.M. and Wagner, S., 2000. Inkjet printed copper source/drain metallization for amorphous silicon thin-film transistors. IEEE Electron Device Letters, 21(8), pp.384-386.

[8] Soltani, A., Kumpulainen, T. and Mäntysalo, M., 2014, May. Inkjet printed nano-particle Cu process for fabrication of re-distribution layers on silicon wafer. In Electronic Components and Technology Conference (ECTC), 2014 IEEE 64th (pp. 1685-1689). IEEE.

[9] Ko, S.H., Pan, H., Grigoropoulos, C.P., Luscombe, C.K., Fréchet, J.M. and Poulikakos, D., 2007. All-inkjet-printed flexible electronics fabrication on a polymer substrate by low-temperature high-resolution selective laser sintering of metal nanoparticles. Nanotechnology, 18(34), p.345202.

[10] Park, B.K., Kim, D., Jeong, S., Moon, J. and Kim, J.S., 2007. Direct writing of copper conductive patterns by ink-jet printing. Thin Solid Films, 515(19), pp.7706-7711.

[11] Kim, H.S., Dhage, S.R., Shim, D.E. and Hahn, H.T., 2009. Intense pulsed light sintering of copper nanoink for printed electronics. Applied Physics A: Materials Science & Processing, 97(4), pp.791-798.

[12] Takiya, T., Fukuda, N., Umezu, I., Sugimura, A., Ueguri, S., Yoshida, H. and Han, M., 2012. Low temperature bonding of metals by deposition of nanoparticles at the interface. Applied Physics Research, 4(1), p.42.

[13] Visser, C.W., Pohl, R., Sun, C., Römer, G.W., Huis in‘t Veld, B. and Lohse, D., 2015. Toward 3D printing of pure metals by laser-induced forward transfer. Advanced materials, 27(27), pp.4087-4092.

[14] Henley, S.J., Kula, M., Brunton, A.N., Chan, C.W.A., Dixon, R. and Dunne, B., 2015, June. Low-cost copper conductive grids for thin-film solar cells formed by screen printing and laser sintering. In Photovoltaic Specialist Conference (PVSC), 2015 IEEE 42nd (pp. 1-3). IEEE.

[15] Li, Z., Rahtu, A. and Gordon, R.G., 2006. Atomic layer deposition of ultrathin copper metal films from a liquid copper (I) amidinate precursor. Journal of The Electrochemical Society, 153(11), pp.C787-C794.

[16] Rathnayake-Arachchige, D., Hutt, D.A., Conway, P.P., D'Auria, M., Lucyszyn, S., Lee, R.M. and Robertson, I.D., 2013, December. Patterning of electroless copper deposition on low temperature co-fired ceramic. In Electronics Packaging Technology Conference (EPTC 2013), 2013 IEEE 15th (pp. 630-634). IEEE.

[17] Lee, H.H., Chou, K.S. and Huang, K.C., 2005. Inkjet printing of nanosized silver colloids. Nanotechnology, 16(10), p.2436.

[18] Kim, H.S., Dhage, S.R., Shim, D.E. and Hahn, H.T., 2009. Intense pulsed light sintering of copper nanoink for printed electronics. Applied Physics A: Materials Science & Processing, 97(4), pp.791-798.

[19] Wei, Y., Li, Y., Torah, R. and Tudor, J., 2015, April. Laser curing of screen and inkjet printed conductors on flexible substrates. In Design, Test, Integration and Packaging of MEMS/MOEMS (DTIP), 2015 Symposium on (pp. 1-4). IEEE.