"Copper nano Ink synthesis, Silk screen printing on flexible PCB and optimization of LASER sintering parameters"

By

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A thesis submitted in partial fulfillment of the requirement for the degree of Masters of Science

In

Biomedical Sciences and Engineering

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DECLARATION

It is hereby declared that this research study has been done for partial fulfillment of requirements for the degree of Masters of Sciences in Biomedical Sciences. This work has not been taken from any publication. I hereby also declare that no portion of the work referred to in this thesis has been submitted in support of an application for another degree or qualification in this university or other institute of learning.

Tanzeela Noreen Alvi

DEDICATION

Dedicated to My loving Brother AmadAlvi and my mother whose prayers, inspiring guidance and constant encouragement brightened mycareer.

ACKNOWLEDGEMNT

"In the name of Allah the most Merciful and Beneficent"

All praises are to almighty Allah, The lord of the entire world. It is undeniable that all manifestation of nature bears eloquent testimony to the fact that Allah is the creator, maintainer and regulator of the world. He makes laws foe the evaluation of things and sets them on the path of perfection.

Almighty Allah bestows and blesses knowledge, technology and scientific ingenuity to man through experimental research and remarkable deduction to ponder over the force of nature. the first place therefore, I express my utmost thanks to Almighty Allah, the Omni Parents, omnipotent and creator of the worlds, who has endowed me brain and instable instinct construction of knowledge and body to accomplish my work in the form of thesis(final project report).

No doubt, appreciation is prior to knowledgement, quality of the latter is superior to the essence of the former.

I offer our gratitude to last prophet Muhammad (PBUH) who has given the lesson of love, humanity, parity and justice. He also broke the cage of servitude for golden sayings to see knowledge his obligator for every Muslim.

I am thankful to faculty of my department for their guidance. Every failure stimulates me for performing better in future. Whenever I fall and loss hope for future my family encourages me ,not to give up .Especially my brother Amad Hussain Alvi and my Mother encouragement counts a lot getting the place where I' mstanding. I have belief that every coming moment in my life will bring success and I will found new and better opportunities than before. During my research work I felt our decisions at every stage forecasts our future success. Research work is a team work no single person efforts make everything successful. Every student has his own potential and capabilities; this is the supervisor whose attention, encouragement and positive guidance make him successful. The grooming of student starts from his first institute. In Professional life where you stand and from what quality education you have from your institutions. Well I'm so hopeful for my future studies and career.

In the end I want to express my heartiest gratitude to my best friend Muneba Qureshi and Muneeza Atta Khan for their support in my hard time.

CONTENTS

LIST OF SYMBOLS AND ABBREVIATIONS

3D	Three Dimensional
ACA	Anisotropically Conductive Adhesive
Ag	Silver
CTE	Coefficient of Thermal Expansion
Cu	Copper
DOD	Drop on Demand
DPI	Drops Per Inch
ECA	Electrically Conductive Adhesive
EMR	Electromagnetic Radiation
FEA	Finite Element Analysis
FEM	Finite Element Method
IC	Integrated Circuit
ICA	Isotopically Conductive Adhesive
IPL	Intense Pulsed Light
LASER	Light Amplification by Stimulated Emission of Radiation
PC	Polycarbonate
PCB	Printed Circuit Board
PEN	Polyethylene naphthalate
PET	Polyethylene terephthalate
PI	Polyimide
RF	Radio Frequency
RFID	Radio Frequency identification
SEM	Scanning Electron Microscope

INTRODUCTION

In current years, research on electronics is primarily designed for two issues; In a Semiconductor field, and other packaging technology. Since the development of the transistor in 1940, the number of transistors and function-by-area ratio continuously increasing in a silicon chip (Moore's Law), so that more and faster processing speeds and smaller chip dimensions are developed. Similarly, allowing progress in methods of packaging, Package dense and compact electronics. Major developments electronic packaging steps are SMD components and multichip modules on package and system solutions for wafer level packaging.

Although semiconductor technology and packaging has modernized, relatively little consideration has been given to the technology of a circuit board in recent years. But now, the electronics industry is also revising the circuit board technologies for modern improvements and promises for new types of equipment and applications. Production of flexible and extensible circuit substrates allows devices with high compliance to the different forms and contours. For example, new production technologies enabled electronic devices such as expandable temperature sensors that conform to the human skin and energy harvesters operating in the area of human organ surfaces.

Printed electronics is a new electronics manufacturing to be studied and developed. Printed electronics grow in a important business covers a wide range of different manufacturing techniques with various benefits and drawbacks. Different techniques to for printing include silk screen, gravure and inkjet printing .Printed electronics enables processing of a wide variety of materials and easy processing on flexible substrates, and it is for the production of flexible displays, batteries, radio frequency identification tags (RFID), basic circuit used antennas and components of circuits.

The inkjet printing is one of the interesting electronics manufacturing techniques; it unmasked different high production flexibility and adaptability of digital control and manufacturing. Digital Process Control enables rapid prototyping and high settings from product to product. The inkjet printing is a contactless method of manufacture and hence permits production of a variety of materials and surfaces including 3D topography that would be a challenge for most other manufacturing techniques.

As part of the thesis internal connections related to interconnections between different internal components such as printed antennas and energy storage, as well as the sintering process of metal nanoparticles. Nano metal sintering colors obviously essential to the use of the ink jet in the manufacture of electronics and internal connections between printed components is also important when it moves to a higher level of integration and manufacturing functional systems in place of individual Components.

Connections between external links relate to ink jet printed circuit boards (PCB) and external components, such as conventional surface mount devices (SMD) or silicon chips and external connections to the outside industry for reasons of power and connectivity between various PCB.

The main reason for the use of external connections is an urgent need for external components to improve the increasing functional complexity. Printed semiconductor components such as diodes and transistors have already been made, but the size and performance is far from what is needed for consumer electronics today. Mobility Semiconductor and the channel width (? 10 cm 2 / (V * s) and? 10? M, respectively) two quantities of several the achievable in traditional silicon circuitry (? 1400 cm 2 / (V * S) and? 10 nm). [26] Here, conventional silicon-based components are used in the drawings and so-called hybrid models, based on high performance and reliability of metal semiconductor technology additional oxide (CMOS) and flexibility in the production of new printing techniques.

Research of printed Electronics is a possible alternative to traditional manufacturing-based photolithography in the manufacture of electronic products. The term "printed electronics" covers a wide range of different manufacturing techniques, such as etching, aerosol jet printing and screen exographic. These different printing techniques have substituting function is that all these methods are additive manufacturing techniques, as compared to traditional manufacturing methods are mainly subtractive. Additive technology means a manufacturing process where the material is deposited only in areas where it is needed, while in the manufacturing methods of subtraction, as conventional photolithography, the entire substrate is coated with the material and undesirable later removed. Moving additives subtractive manufacturing methods reduce the amount of energy required and lost during the manufacturing process equipment. For example, in traditional lithography process the majority of the source material in the etching steps is eliminated and therefore no waste of additive manufacturing moves is a significant improvement. The strong harmful solvents and chemicals are also used in etching processes. As environmental awareness of consumers increases, the pressure to move to manufacturing processes to the environment.

Jet printing ink is one of the most promising techniques for printing and has been extensively studied in recent years. [29] {32 advantages thereof, with which it shares spray, compared with traditional manufacturing techniques and other printing techniques ink jet printing include fully digital control process and contact with the free manufacturing. Several benefits Hardware- spray and printing fee as both technologies are in their basic functions. The difference is the ink jet printing using functional materials in liquid form, by spraying using printing materials in the form of vaporized gas.

In recent years there has been a rising interest in the metal nanoparticle (NP) functional inks for printing on flexible substrates. In many ways, it can replace the lithographic process, which is comparatively complex in several stages, and it involve the direct metallization of printed electronic applications, particularly for applications in which they are fragile in use and flexible substrates involved. It has also proved useful for low cost printing organic functional devices, RFIDs, flat panel displays and solar cells.[1]

In recent decade, the metal nanoparticle synthesis has been focused due to their considerable interest in microelectronic applications. Silver and copper nanoparticles fabrication is highest interest due to their potential applications in electronics. Silver nano particles are expensive and electro migration is another limitation for their use in electronics which reduce the reliability of conductive line. Silver is comparatively stable to oxidation. In this research copper nanoparticles are fabricated due to their in expensive nature and high conductivity which make copper an ideal material for use in large scale printing electronics.[2] Copper nanoparticles are prone to oxidation in open environment which limit their wider use. Their fabrication requires ambient conditions. This research study is dedicated to copper nanoparticle fabrication in aqueous media in open environment. Oxidized nano copper ink is then converted to pure copper conductive lines by LASER sintering method.[3] Copper nano ink is best alternative to silver nano ink for their easy production and inexpensive feature. There are various features for copper nanoparticle fabrication, but in this research chemical reduction in aqueous media is adopted. PVP is used as dispersant agent for nanoparticle stabilization and avoiding aggregation. PVP act as surfactant which lowers the surface tension of particles and aid then to disperse.[4] The copper nano powder is dissolved my ball milling into various solvents for optimized conductive ink formulation. The conductive ink parameters, such as its viscosity and surface tension of ink droplet, are optimized for silk screen printing of circuit on flexible substrate. [5]

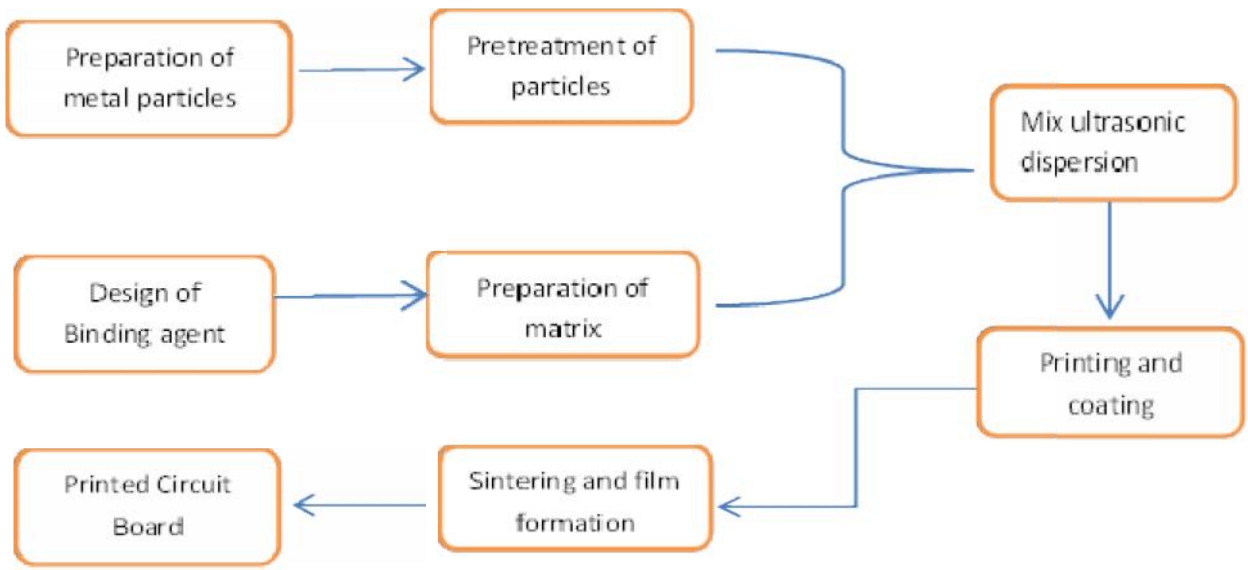
Ink jet printing is advanced and more efficient technique in printable electronics but it has limitations like low viscosity of inks approximately < 100 cps and few picoliters of droplet volume is required for stabilized jetting.[6] When copper conductive nano ink have to be used these features are harder to achieve due to copper ink higher viscous nature and copper nanoparticle higher dispersion instability. These drawbacks hinder their use in ink jet application. Silk screen printing is easy to handle and comparatively not complex like ink jet printing and provide better printing resolution.[2]

The final step after printing of conductive track is sintering .Sintering is desirable because it converts prints tracks into conductive form. There are various sintering methods high temperature oven heating, plasma sintering, micro wave, intense light and UV sintering. High temperature sintering is not applicable when flexible substrates have to be used because high temperature can damage this under lining substrate. Different approaches for low temperature sintering of copper are used now a day. Electrical sintering, plasma, microwave and flash lamp sintering (high intensity and UV) methods are included for low temperature sintering.[7][8]

Flash lamp sintering is more efficient, fast method which converts tracks into high conductive lines within few milliseconds. It minimizes the damage to fragile substrate and it can be used for large scale application. The high energy requirement and its wide spectral emission which reduce flash intensity will affect resultant sintering quality when large scale production is concerned.[9]

This research study is dedicated to LASER sintering methodology .LASER curing is being chosen due to its faster and localized curing by protecting underlining and nearby heat sensitive substrate. [3]The LASER is faster enough that the oxidation is avoided which make it feasible for sintering of copper in ambient conditions. [10]

In this research study, LASER sintering parameters are optimized for best quality of copper sintering. The electrical features are measured on different LASER conditions like power, speed and distance of track from Z- axis of LASER beam. The sintered and unsintered copper tracks are characterized by techniques such as optical microscopy, SEM and XRD.



Chapter # 2

LITERATURE REVIEW

In the last few years, printed electronics gain remarkable attention. Printed electronics concerned with conductive materials in printable form, their printing techniques, and applications. These electronics has immense importance in field of flexible electronic device fabrication. As compared to old electronic devices, flexible printed electronic devices are greatly being developed and used. These newer devices can be produced efficiently in less cost and are preferred for their flexible nature. The printed circuits are of special importance for use in solar cells, electrodes, sensors, RFIDs (Radio frequency identification tags), flexible displays and transistors. Various printing techniques like ink-jet, roll-to-roll, screen or micro contact printing are used for developing printed circuits. Conductive polymers, semi-conductors, carbon materials and Nano-particles are the commonly used printing materials for printing electronic circuits using the fore mentioned printing techniques [11].

Conductive ink solutions are utilized through various printing techniques to make better electronic circuits at micro and macro scales. Ideally the conductive ink materials should exhibit high conductivity, solution formation, low temperature processability and environmental stability. Thus organo-metallic substances, conductive polymers and metallic nano-particles are used for making conductive inks. In this regard the organo-metallic substances have high content of organic residues while conductive polymers have high resistance [12]. Metal nano-particle patterns thus provide an excellent alternative with better performance and low cost benefits. When compared to conventional metal oxides, better performance has been reported with silver and copper nano-particles for making conductive inks[13]. Conductive inks are applied to flexible plastic substrates for fabricating printed electronic devices like organic photovoltaic cells and light emitting diodes. The conductive inks are generally made from metal nano-particles, the conductivity of which is improved through heat or other sintering treatments [14].

In this review, we will discuss on different metal nanoparticle ink dispersions. Metal nanoparticle size affected by their method of production which can alter their conductive capability. Moreover, Metal nanoparticle size is important for printing and sintering treatments. Hence it is concluded that smaller the nanoparticle size, better will be conductivity of flexible printed tract. One class of MNPs inks are silver Nano inks which is most commonly used for their excellent conductive features. Copper and composite metal inks are also elaborated in this review with their fabrication methods. Due to copper Nano ink instability, there is a challenge for making their patterns conductive and stable. Different sintering techniques are acquired for this purpose. Copper nanoparticles tend to oxidize , which effect their conductivity. Sintering techniques can stabilize oxidized metal nano particles by reducing them and their fusion into continuous conductive pattern.

For flexible electronics, low temperature sintering is concerned due to under lining flexible substrate protection which can be damaged from high temperature sintering method. There are a number of low temperatures sintering methods for example Microwave, UV light sintering, intense pulse light sintering, plasma sintering, and laser sintering methods. In this review all sintering techniques are with their advantages and disadvantages with reference to their applications.

METAL NANO INKS: THEIR FABRICATION REQUIREMENTS AND CHALLANGES

Copper, gold and silver are the commonly used metals for making conductive inks. In comparison copper has low resistivity and less cost of synthesis but the presence of surface oxide layer which is often created during synthesis of copper nano-particles reduces their electrical conduction significantly. For reducing the surface oxide layer procedures like annealing in a hydrogen atmosphere or reduction of oxide layer by laser treatment are adopted but none of these approaches result in complete removal of surface oxide layer. The good performance of electronic devices is ensured by the low resistance of conductive layer; for copper based solutions formic acid vapors are used for annealing to decrease the resistance of copper by removing the surface oxide layer but high reactivity of formic acid at elevated temperatures can damage the electronic devices [12].In this review, silver and copper metal nano ink fabrication their printing and sintering techniques are elaborated. There are various protocols reported for silver and copper nano ink fabrication which are discussed.

SILVER CONDUCTIVE INKS

D. Kim et al. 2006 synthesized a conductive nano-silver ink along a suitable procedure for synthesis of conductive pattern by making use of ink-jet printing. Silver particles with diameter of 21nm were incorporated for metal printing. Results showed that the pattern becomes more conductive and exhibited metal like appearance at a lower heat temperature of 200ºC. Several parameters printing including substrate temperature, amplitude of pulse, moving velocity of xy-stage and head frequency were optimized to attained conductive track with higher resolution and a smooth track. Thus these results proposed that by making use of ink-jet printing any desired conductive pattern can be adapted to flexible devices that are organic thin film transistor (OTFT) and organic light emitting devices (OLED). Thus this nano-sized silver conductive ink can be fabricated on flexible substrate for various desired application to flexible electronics.[15]

Kosmala et al. 2011 proposed a simple and cheap method of preparation of silver nano-particles with diameter of 50 nm by silver ion reduction in the presence of AOR by reagent hydrazine. The method proposed the fabrication of silver ink by combination of silver nano-particles in water with addition of PEO-PPO-PEO and then subjected it to high intensity focus ultrasound. The sizes of silver agglomerates were reduced from ∼200 nm to ∼50 nm. Conductive inks were produced by using high intensity focused ultrasound (HIFU) and triblock copolymer. Several parameters that determined the stability of ink were thoroughly studied that includes content of co-polymer and the period of HIFU treatment. Results showed that viscosity of conductive ink was much reduced once subjected to sonication. Surface tension and viscosity of ink consisting of 5% silver was found to be 30 mN m^{-1} and 2 mPa s at 25ºC respectively. The prepared ink was printed on Al_2O_3 ceramics and low-temperature co-fired ceramics (LTCC) and the results showed that the ink showed low resistivity.[16]

Walker and Lewis 2012 proposed a reactive silver ink by modifying Tollen's method to meet the requirements of an optimal ink. Designing of ink needs certain requirements to be fulfilled. Foremost among them includes that the procedure of synthesis of ink should be simple, easy and its yield should be high enough. Secondly the viscosity of ink should be lower enough to make it suitable with domain of patterning procedures that are airbrush spray, inkjet printing and direct ink writing. Thirdly the patterns featured show conductivity at room temperature moreover should be able to attain bulk conductivity upon annealing at mild temperatures (<100°C). The other most important requirement is that ink should not undergo particle precipitation and should be stable at room temperatures. Tollen's method was modified to synthesize silver ink. Silver acetate was first dissolved in aqueous ammonium hydroxide followed by titration of formic acid into the solution. During initial mixing the synthesized silver particles were removed by a process of sedimentation thus leads to production of stable and clear supernatant consisting of reactive silver ink.[17]

Faddoul, Reverdy-Bruas, and Blayo 2012 proposed a procedure of formulating water based silver flakes that were able to print on the LTCC substrate. Formulated ink showed the electrical resistivity and viscosity of 1.6 to 3.3×10−8m and 320 Pa s. Low viscosity ink tends to show improved line formation and best line formation was attained with conductive paste carrying 70–72% silver. Yield stress of the formulated pastes was also studied using Hershel-Bulkley model. Results showed that as content of silver increased more increment in yield stress was observed. Yield stress was observed to increase to 501 Pa for ink carrying 75% silver content. Further results showed that elastic paste, moduli of paste and their behaviour during printing is vital to formation of uniform lines. The increased in silver content tends to decrease the width of line. Results explained that due to sintering linewidth and its thickness decreased. The formulated lines showed conductivity even before the process of sintering but after sintering lower electrical resistivity and sheer resistance was measured. Thus the results attained from printed lines showed water based silver flakes tend to have vast application in electronics.[18]

Nie, Wang, and Zou 2012 proposed the synthesis of silver conductive film through inkjet printing silver citrate on the flexile PET substrate. The prepared conducive ink consists of silver citrate, 1,2-diaminopropane , methanol along isopropanol to adjust ink's viscosity. Due to synthesis of silver amine complex the prepared ink could be cured at lower temperature as the formed complex lessens the temperature of decomposition from 180ºC to 135ºC and thus prepared ink possessed suitable adhesion feature along high reflection. Results showed that the prepared ink had good stability and a shelf life of 60 days .The prepared ink was subjected to various characterization techniques that are four-point probe method, energy dispersive X-ray spectroscopy (EDS) and scanning electron microscope (SEM) and various parameters including electrical conductivity, surface morphology and composition were studied.

Furthermore, RFID antenna was patterned using inkjet printing technology and thus it leads to vast application in the field of electronics.[19]

Zhai et al. 2013proposed a method of making environment friendly conductive ultraviolet (UV) inkjet ink. Using oxidation reduction method silver nano colloids were prepared followed by the process of polymer coating. Coating of polymer was done in a solution of silver nitrate, glucose, triethylamine (Et3N) and poly (vinyl pyrrolidone). The concentration of glucose and AgNO3 strongly affects morphology of particles. Smaller sized colloids were prepared using small concentration of glucose. Reducing the input amount of Et3N generated smaller sized particles. Temperature also impacts on the morphology of particles within range of 25-100ºC. Moreover, composite containing the water based UV resin and silver nano-colloids enhanced the adherence feature in contrast to silver nano colloids that is prompt by the its operation in flexible electronics. The conductive patterns over PI substrate were achieved by evaporating water from solution followed by UV curing and sintering. A range of experiments were administered testing various contents of silver, width of track and lastly temperature of sintering. So water based UV inkjet ink has noticeable edge in flexible electronics.[20]

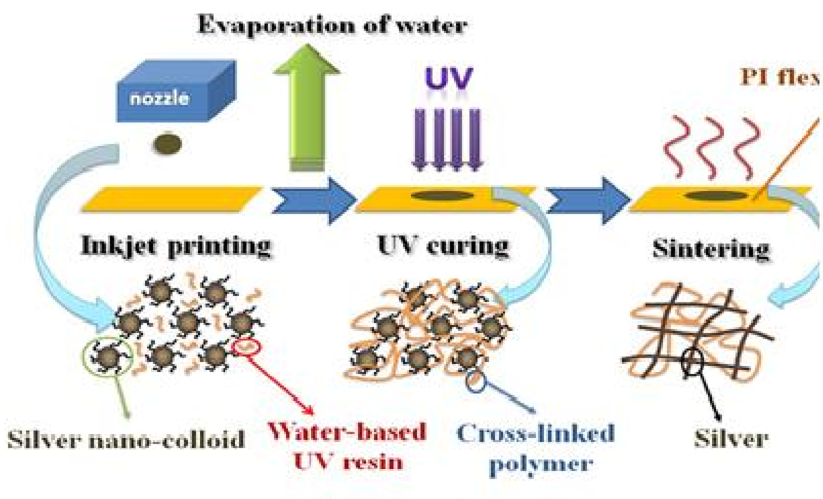


Fig 1.Formation process of conductive patterns.(Zhai et al. 2013)

L. Liu et al. 2015 proposed the synthesis of monodisperse silver nanoparticles (NPs) by method of oxidation reduction in water. Slightly soluble silver compounds were synthesized which acted as a precursor of Ag-NPs. For the synthesis of precursor, tri-ethylamine was introduced to the aqueous solution of AgNO3, polyvinyl pyrrolidone and glucose. Furthermore, various anion species that are –SO42−, –PO43−, –CO32− and –Br− were added to aqueous solution. Various parameters including ratio of nitrate-glucose along temperature of reaction was studied. Moreover the electrical conductivity of synthesis Ag NPs were investigated and results revealed that the –CO32− mediated Ag NPs were having lowest resistivity. Silver NPs in combination with ethanol can be used as ink which can be printed on flexible substrate like PET followed by sintering at lower temperature. An electrical resistivity of 5.72 μΩ cm was observed. So the results suggested the synthesis of silver NPs as cost effective material and its vast application in flexible electronics.[21]

COPPER CONDUCTIVE INKS

Wei.Yu et al (2009) proposed a method based on chemical reduction to prepare monodispersed pure-phase Copper colloids using water and ethylene glycol (E.G). Time required for the completion of reaction was 8h to achieve copper colloid of pure phase. On comparison, it was analyzed that the reaction rate in E.G was higher than in water as E.G. The quantity of the reducing agent can be decreased to large extent. Ascorbic acid acts as a reducing agent and antioxidant of colloid copper as it attacks free radical along reactive species. Results of thermogravimetry analysis (TGA) showed that the prepared carbon NPs oxidized at above 210ºC as a result CuO is produced and they tend to have good stability. Polyvinyl pyrrolidone (PVP) concentration determines the size of copper particles. As PVP concentration increases smaller size copper particles were obtained. Along PVP feature of controlling size it also acts as polymeric capping agents. As a fact PVP prevent nuclei to aggregate through the polar groups.[22]

Jeong et al. 2011 proposed a method to synthesize aqueous based Copper ink. Cu ink was formulated by incorporating air stable along water dissolvable Cu NPs with thin layers of oxide. Various solvent compositions of Cu ink were checked for attaining the stable jetting, high conductivity, uniform surface morphology and narrow line width. Thus as a result extremely conductive Cu properties with low resistivity, uniform and controlled surface shape and line of width as thin as 45 μm were printed on flexible substrate. Moreover, results of the study proposed that Cu-NPs were resistant towards oxidation in the presence of aqueous based ink.[23]

Q. M. Liu et al. 2012 proposed the preparation of Cu-NPs by using aqueous solution reduction method; upon reduction of Cu2+ with ascorbic acid Cu-NPs were prepared. Several determining factors affecting the preparation of Cu-NPs that are solution pH and the average size were studied. With a selective range of pH, Cu particles were prepared. The Cu particles with the smallest size were prepared at pH 7. At pH 9 and 11 Cu particles couldn't be prepared. Sizes of Cu particles were determined by average size of Cu2O. Similarly larger Cu particles were otained when larger Cu2O particles were used. By measuring the XRD the reaction process was studied and results showed that Cu(OH)2 acts as a precursor which further leads to formation of Cu2O which further upon reduction produced Cu particles.[1]

Chatterjee et al. 2012 proposed a technique for the formulation of copper nano-particles (Cu-NPs) by reduction of CuCl2 in presence of gelatin. The prepared NPs were subjected to various characterization techniques including x-ray photoelectron spectroscopy, spectrophotometry, transmission electron microscopy x-ray diffraction, atomic force microscopy and dynamic light scattering. The NPs obtained were highly stable and were about size of 50-60nm. Furthermore, by using various techniques that are flow cytometry, agar plating and phase contrast microscopy the antibacterial activity of prepared Cu-NPs was measured. Results showed that the formulated lower concentration Cu-NPs are efficient against E.coli. The size of population of filamentous cells was dependent on the concentration of Cu-NPs, higher the concentration of Cu-NPs more filamentous cells were formed and the filament size was also observed to increase from 2:5 m to 7:20 m. The study suggested that the killings of cells by Cu-NPs in E. coli strain are tolerant to antibiotics. In addition, the antibacterial characteristic of Cu-NPs was detected in Gram-positive Bacillus subtilis and Staphylococcus aureus.[24]

Deng et al. 2013 proposed another simple, cost effective and high throughput technique in order to synthesize Cu-NPs at room temperature. Copper nano-inks are considered as cost effective in contrast to silver and golden nano-inks. Copper acetate, hydrazine and short chain carboxylic acids were used in preparation of Cu ink. Carboxylic acid concentration plays a vital role in synthesis of Cu-NPs. Using higher concentration of lactic acid, citric acid and alanine much stable Cu-NPs with diameter less than 10nm were synthesized. Results of thermogravimetric analysis (TGA) suggested that lactic acid and glycolic acid adsorbed on Cu-NPs can be eliminated from surface at temperature of 125°C. Conductive copper films were synthesized by drop coating nanoparticles onto slide followed by sintering at lower temperature. The resistivity measured of synthesized copper films using glycolic acid was 25.5 ±8.0 and 34.8±9.0μΩ•cm after annealing treatment at 150ºC and 200ºC whereas in contrast to lactic acid the resistivity measured was 21.0±7.0 and 9.1±2.0μΩ•cm after annealing treatment at 150ºC and 200ºC respectively.[25]

H.Guo et al (2013) described a catalytic method for synthesis of improved Copper nanowires (CuNWs) using nickel ions. Metal nanowires are commonly used for making of transparent conductor to substitute the tin-doped indium oxide. CuNWs provided extended space for electron transport and light transmission. By making use of Cu NWs ink transparent electrodes were fabricated. Results showed that the fabricated electrodes were having a low sheet resistance along improved and better transparency. Furthermore, CuNWs were subjected to test flexibility and stability and no change in resistance was observed.[13]

Zhang et al. 2013 proposed a simple, cheap and novel technique for preparation of Cu-NPs by Polyol method. Polyol are considered to have to distinct properties of anti-oxidation, dispersion and monodispersing. Cu conductive ink with distinct features of viscosity and liquidity was prepared in mixed solvents. Over polyimide substrate Cu conductive ink was silkscreen printed. Furthermore, heat treatment under inert environment at 250ºC for 30 min results in conductive films as copper nanoparticles undergone complete sintering. By polyol method conductive films with improved resistivity as high as 18.9 μΩ•cm approximately 10 times higher than copper's resistivity were prepared.[2]

Jeong et al. 2013 suggested a procedure for the preparation of Cu-NPs by using oleic acid as capping molecule. XPS and TEM analysis showed that Oleic acid is adsorbed to Cu surface such that it protects the Cu surface from oxidation because of a fact that meanwhile during reaction it forms a mono-dentate bond without leaving any unreacted oleic acid. On removal of protective oxide layer the surface oxide free Cu showed the resistivity low as 4mUcm and thus Cu electrode layer was prepared. Using electro-hydrodynamic inkjet method and graphene transistors the Cu patterns were printed achieving 5mm width of a line. Thus it leads to possible application and uses in printed electronics.[12]

Wang et al. 2015 proposed fabrication of conductive ink composed of poly-dopamine (PDA) and silver ammonia solution. Through inkjet printing and utilizing the prepared ink, the desired pattern was fabricated. Catalytic ink ensured suitable linkage among copper pattern and the used substrate. Ag nanoparticles of ink have tendency to acts as a catalytic seed of electro-less copper to easily fabricate copper pattern. The main advantage while incorporating this method is it doesn’t need any sintering so a vast range of flexible substrate can be used due to adherent feature of PDA. Different kinds of material can be generated by combining various catalysts and PDA and thus this leads to emerging application in the field of energy, medical and the synthesis of catalysts.[27]

H. Lee and Yang 2015 optimized solvents to enhanced the quality of patterns and to improve the dependency of material more than conditions of a process. Results showed that heat flow, less absorbing cross-section and IPA have improved features of pattern shape and pattern conductivity. Further by using different molar ratio of various solvents and polyvinyl pyrrolidine (PVP) were processed by technique of laser sintering and as a result a reliable process window was obtained. Results suggested that ink composing of significant quantity of PVP and higher molar ratio leads to improved conductivity along broader process window. Furthermore, results suggested that the copper electrode prepared using process of laser sintering and incorporating IPA as a solvent was having a lowest resistance of 13lXcm at 100 nJ of laser pulse energy and 0.6 mm/s of scan speed.[4]

Wiley 2015 proposed a method to turn on or off the growth of Copper nanowires (CuNWs) by making use of Cu2O octahedra as a photocatalyst. Cu2O octahedra have the ability to absorb light of wavelength less than 619nm which then reduce Cu (OH)2 to form a CuNW. During the process as electron source gets diminished so hydrazine was used as source of electrons and acts as a hole scavenger. This technique was then used in patterning the growth of CuNWs onto particular areas of substrate by use of photomask. An alternative to photomask can be a focused laser and thus different patterns of nanowire can then be done onto substrate.[28]

COMPOSITE INKS

Eom et al. 2011 proposed the concept behind the electrical conductive mechanism of an isotropic hybrid Cu paste through experimentally characterization using various analysis techniques like Energy dispersive X-ray spectroscopy, Scanning electron microscopy (SEM) and Scanning Calorimeter,. The hybrid Cu paste was prepared by mixing Cu powder, fluxing resin and solder powder. In a meanwhile of curing process the oxide layer is eliminated with rise in temperature and in this manner electrical connection between Cu and metal solder is produced. The electrical conductivity of Cu paste was experimentally measured and correlated with already available silver paste. This study suggested the similarity between hybrid Cu paste and Ag paste with respect to electrical and thermal characteristics with exception of optical function. In addition, hybrid Cu paste is suggested to be used as an alternative to Ag paste due to its low cost. [29]

Wu et al. 2014 proposed a synthesis technique of carbon–core/Ag–shell nanoparticles via reduction of silver ammonia. As a result, the produced C@Ag nanoparticles consist of shell thickness from 10-40nm and core diameter of 360 nm. Results were further confirmed by several analysis techniques that include SEM along TEM which suggested that carbon cores were coated by Ag. This study showed that C@Ag nanoparticles based conductive ink can be synthesize in abundant amount along it have improved electrical properties and thus can be used in synthesis of easy, flexible and cost effective electronic devices. Results showed that C@Ag nanoparticles conductive ink can replace the silver paste by a convenient screen printing process. [30]

Farraj, Grouchko, and Magdassi 2015 proposed a method to obtain highly conductive pattern through inkjet printing technology and using a metal complex based ink. Copper based ink due to its conductivity of 16% of bulk copper and resistivity of 10.5 mΩ•cm was fabricated for printing conductive patterns on plastics. Along the fabrication of conductive ink the decomposition mechanism was also studied. Several advantages of metallo-organic decomposition inks (MOD) are suggested including that they are stable chemically, have a low decomposition temperature along they undergo self-reduction in contrast to copper salt MOD ink are supposed to be easily prepared and they are much more easier to processed through inkjet printing technology. Moreover, the printed patterns were fabricated on substrates that are exceptionally flexible like polyethylene naphthalateand polyethylene terephthalate.[31]

Chang et al. 2015proposed the fabrication of nano organic silver composite conductive ink to the flexible electronics. The ink printed on flexible substrate after sintering at 250ºC turned into highly conductive silver metal. The ink consist of appropriate features for inkjet printing with viscosity of 2•3 cps and surface tension of 26–29 dyne cm^{-1}. The resistivity and adhesion of ink was also measured to be 11•7μΩ cm and 5B respectively. The ink was subjected to different analysis to various characterization techniques to measure the morphology before and after the heat in order to observed the mechanism happening during synthesis and sintering process. [27]

PRINTING OF METAL CONDUCTIVE INKS

Screen printing, gravure, inkjet printing and flexography are the commonly used electronic printing methods for producing cost effective electronics. For electronic circuits particles of organic polymers or metals are used for printing, into which certain additives are added to improve the printing properties. Silver nano-particles are reported for their use in the conductive ink along with different additives. The printing characteristics are determined by the carrier fluid, carrying the metal nano-particles. In order to keep the nano-particles well segregated and separated, dispersing agents are also added into the electronic ink. The fluid like consistency is achieved for the ink by the additives used; they also provide the necessary adhesion for the ink on the substrate and help to maintain the shape of the pattern after being printed. The wet ink, after printing is sintered to achieve the desired function[33].

The drop on demand technique was used for inkjet printing, where by a pressure pulse is applied to the ink chamber with small opening, in this way a droplet is formed and is placed mechanically by placing the print head over the desired position. The ink must have appropriate viscosity and adequate rheological and physical properties to allow flow of the ink through the print head. High viscosity requires large pulse pressure while low viscosity generates satellites along with the ink droplets[34].

“Coffee staining” is often observed while printing with organo-metallic inks. In this phenomenon the solute gets concentrated at the edges thus decreasing the material in the centre. Using concentrated solutions can minimize the effects of coffee staining. Increasing the mass deposition rate per unit length can increase the width of the line and thickness of the membrane at slow substrate speed and high frequency[35][36].

To deposit inks on different substrates, inkjet printing is a widely used technique. The drop on demand (DOD) technique of inkjet printing is widely being used in printed electronics. Its use has been established for printing conductive tracks, organic light emitting diodes, rectifying diodes and passive electronic components. But for the widely used fiber reinforced printed circuit board, the results of inkjet printing have not been established[37].

SINTERING TECHNIQUES SUITABLE FOR FLEXIBLE ELECTRONCS

SINTERING BY BAKING AT LOW TEMPERATURE

Smith et al. 2006 proposed inkjet printing and low temperature conversion of conductive silver. Utilizing a range of various substrates, silver containing organo-metallic ink was printed onto them using drop-on-demand inkjet printer. The printed tracks were given thermal treatment at 150ºC. Thus using lower temperature opens gateway to use a vast range of substrate. Substrate used consists of soda lime glass, polyimide film, Kapton, PET and carbon and glass fiber reinforced epoxy composites. Simultaneous this process carries several shortcomings that are its time consuming process, non-area specific; many substrates will undergo shrinkage upon thermal sintering temperatures and gas emission from the substrates. Results suggested the resistivity to be 1.3 -2 times that of bulk silver. Results suggested that the dependency of track width on certain variables like contact angles, drop size and the nearby droplet spaces. The contact angle observed to be dependent on energy and roughness of surface. Furthermore a firm relation between increasing width of track and decreasing contact angle was observed. Results proposed that track width, thickness and mass deposition rates can be monitored by modulating size and velocity of droplet. [34]

Van Osch et al. 2008 proposed the procedure for the synthesis of thin conductive patterns using flexible polymer substrate. Polyarylate substrate used consists of lower surface energy such to prevent the wetting of nanoparticle suspension but simultaneously sufficient enough to limit bulging. As a result of inkjet printing, tracks with diameter of 40µm were achieved. Furthermore, the silver tracks were sintered for one hour and at temperature of 200 °C; in contrast to bulk silver resultantly conductivity of 13% to 23% was attained when dot spacing of 5lm and 25lm was used respectively. Using a 4-point method resistance was calculated whereas the resistivity of about 1.59 × 10-8 Ω.m was determined employing resistance, the length and the cross sectional area of track and afterwards the resultant resistivity was then related to that of bulk silver. The fabricated silver tracks are suggested to be used in numerous applications like radio frequency identification tags or in electrodes of thin-film transistor circuits.[38]

B. Lee et al. 2009 synthesized copper conductive ink as an alternative to costly silver ink. Conductive ink was synthesized by combination of copper hydroxide powder and copper (II) neodecanoate .The mixture was milled by three ball milling in terpineol for five times. Copper (II) neodecanoate was prepared by mixing neodecanoic acid and copper nitrate hydrate. Copper nitrate hydrate acts as a precursor to copper hydroxide. In order to increase the metallic amount of the ink and to achieve a suitable viscosity copper hydroxide was incorporated. The conductivity feature of prepared ink was studied with respect to copper hydroxide in terms of temperature, annealing time and size of particle. Copper film was prepared by printing conductive ink onto glass substrate and was cured in 3% H2 atmosphere for duration of 30 min. Results showed that inverse relation exists between resistivity and time period of heat treatment. It was observed that resistivity at 250ºC was 5.4µΩ and gradually decreased to 4.4µΩ at 320ºC Viscosity measured of prepared ink was in the range of 104 –105 mPa s and it was observed by increasing the amount of Cu (OH)2 the viscosity increased significantly. Results suggested that the sintered conductive ink was prepared at low temperature of 250ºC.[39]

MICROWAVE SINTERING

Perelaer, De Gans, and Schubert 2006 proposed a cost effective, rapid, simple and easy method of using microwave radiations for sintering purpose. In contrast to laser method of sintering that sinters the conductive patterns selectively but on the other hand it's much expensive and complicated. Silver conductive patterns were sintered on polymer substrate by making use of microwave radiations. Microwave radiations sintered the printed tracks by careful selective heating. Polymer substrate is basically transparent to the radiations used so a very slight energy is absorbed by the polymer while the conducting NPs absorbed the radiations completely because of its dielectric loss factor. Moreover the resistivity and cross sectional area of track is measured and latter was found to be 3.0 × 10-7Ωm that is 5% of bulk silver. Results suggested the proposed method to be more time effective in contrast to laser by factor of 20. [40]

Perelaer et al. 2009 proposed that the flash micro-wave sintering of inkjet printed dispersions depends on antenna area, procuring time and the geometry of track. The conductive antenna's existence evidently boosts up the sintering of nanoparticles. The influence of antenna is highly noticeable when the ink line already shows some extent of conductivity. By the use of metal antenna, duration of 1s is requires to attained the effective level of sintering via microwave heating. The extent of sintering for such smaller exposure time highly relies upon the resistance of pre-cured tracks. Moreover, the width of track increase the level of initial conductance because of enhanced absorption of energy as the surface area increased. With the microwave flash sintering tracks showed approximately 10 to 34% higher conductivity values in contrast to theoretical value of bulk silver when sintered by conventional sintering methods. The method of printing followed by sintering via microwave flash can be used in printed electronics that is in generation of conductive properties with less usage of polymer substrate. Furthermore, its major advantage refers to its improved processing speed with low temperature, which resultantly cuts down the expenditure of processing as polymer like PEN can be used.[37]

ELECTRICAL SINTERING

Allen et al. 2008proposed a new method for sintering metallic nanoparticles by applying voltage. Metallic nanoparticles are usually consists of golden or silver nanoparticles which are mostly covered by protective covering. Electrical sintering is achieved by inkjet printing silver nanoparticles onto temperature sensitive photo-paper. As a result the conductivity boost to more than five times during process of sintering as current is flowed through the entire structure. The proposed method is relatively fast such that major transition occurred only within 2µs because of the reason that strong positive feedback is generated by the voltage boundary conditions. Moreover, the proposed method is more advantageous in contrast to thermal oven sintering as it's feasible for patterning, reduces substrate heating, it have systemic control of final conductivity along it allows in-situ process monitoring. The proposed technique allows electrical functionalization of nanoparticles. Furthermore, the method is valid to various conductive materials and possibly also to semi-conductive materials. One of the conductive materials is indium tin oxide (ITO) that is used in display purposes. So electrical sintering allows functionalization of nanoparticles structures. Nonetheless, thermal oven sintering possesses several disadvantages that are its substrate limited as low cost substrate will get affected on exposure to sintering temperatures, gas is emitted from the substrate and this process is not area specific.[41]

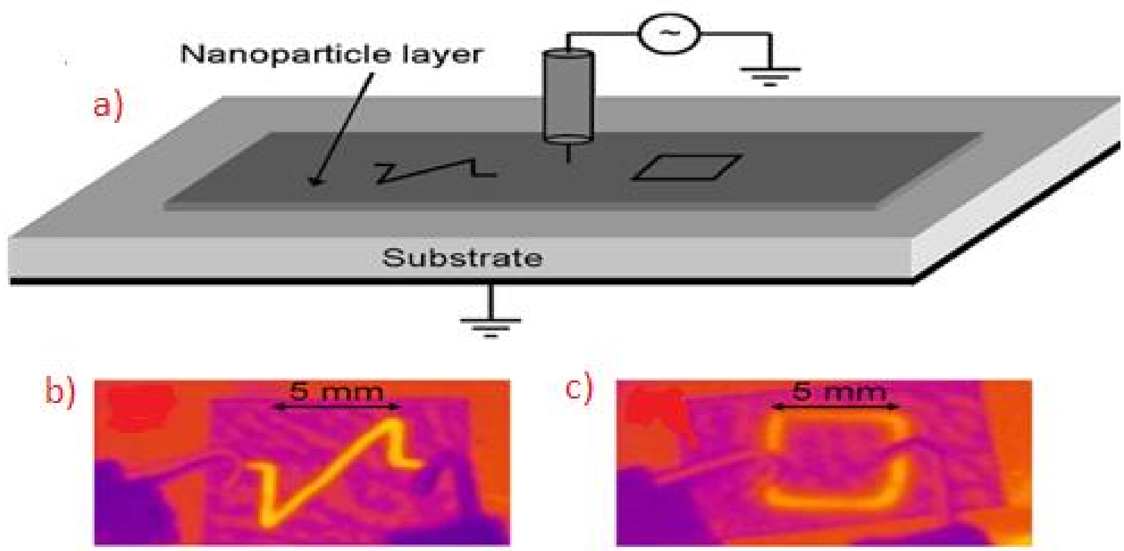


Fig2. (a) Representation of AC sintering between a probe above nanoparticle layer and ground plate. (b) pulse shaped conductor track (c) square shaped conductor tracks(closed-loop) (Allen et al. 2008).

CHEMICAL SINTERING

Magdassi et al. 2010 described the procedure of coalescence of nanoparticles without the use of heat. The silver nanoparticles when interacts with oppositely charged polyelectrolytes they experienced coalescence. The procedure of coalescence is activated by alteration of surface characteristics of the nanoparticles, by neutralization of charge and lastly by desorption of the stabilizer. As the nanoparticles can be sintered at room temperature so conductive tracks can be patterned on plastic substrate and even on paper. Thus the findings of study suggested that the sintering can be attained by placing a metal nanoparticles on substrates pre-coated with the poly-cation and thus through it various conductive tracks on numerous temperature-sensitive substrates can then be achieved. Furthermore, conductive patterns were attained on the substrates including plastic electroluminescent device by the combo of sintering and inkjet printing. Results suggested the process application in flexible and plastic electronics. In addition, it's also suggested that it can be conducted with coagulants, different metals and numerous types of nanoparticles including quantum dots.[42]

Grouchko et al. 2011 proposed a novel conductive ink consisting of silver nanoparticles which carries in-built sintering mechanism that is provoked amid of drying of printed patterns. Until now, no metallic ink has been reported that facilitates the development of conductive patterns by one stage of printing. Printed conductive patterns must be pursued by sintering at higher temperatures thus resulting in substrate limitation in printed electronics. The silver nanoparticles which are sustained by polymer undergo process of self-sintering immediately because of presence of destabilizing agent. The destabilizing agent carried Cl- ions which led to separation of substrate's anchoring groups from the surface of nanoparticles and thus resulted in sintering of Cu nanoparticles. Results suggested that the developed silver nano particles ink leads to immense conductivity values. Highest known conductivity value of pattern achieved from nanoparticles at room temperature that is upto 41% was attained by a sole conductivity step.[43]

Chen et al. 2012 developed silver ink with self-reduction feature to prepare films onto substrate poly(ethylene terephthalate). Diethanolamine (DEA) was mixed in a solution of silver ammonia in order to form a clear and stable solution. DEA disintegrates and generates formaldehyde which resultantly synthesizes silver nano-particles upon its reaction with silver ammonium ions. The post-treatment temperature was adjusted between 50 and 100ºC as thermogravimetric analysis (TGA) suggested the evaporation of solvents observed to be occurred at temperature higher than 100ºC. Silver printed tracks were observed to have best conductivity with thermal post analysis at 75°C for duration of 20 min. Resistivity of silver printed tracks was measured to be 4 times as higher as that of pure silver. SEM results suggested silver films consists of fused silver nanoparticles of diameter of around 80−100 nm. Results of XRD analysis suggested that silver films consist of face centered cube nano-crystalline phases. Furthermore, it's suggested to use ink to develop silver patterns using pen-writing method on PET substrate and for printing tracks in embedded PCBs, RFID tags and lastly in micro-electromechanical systems.[44]

CAMERA FLASH SINTERING

Yung et al. 2010 proposed the requirement of new sintering techniques of metal tracks that is inkjet printing through camera flashes and studied onto various substrates in contrast to already available sintering methods. Already available sintering techniques include microwave sintering, thermal sintering and electrical resistance sintering but all are associated with some drawbacks. Thermal sintering cannot be used for heat sensitive material like PET. Similarly, microwave sintering is also substrate limited as the temp of vessels rise to 200ºC. Likewise, the electrical sintering is used for only simpler track and its voltage limited as voltage used must be selected for initial resistivity and dimension of tracks. Through dispersion of non-radiative energy and exothermic photochemical reactions the light absorbed by material can produce heat. The produced heat localized to nano-structures where heat flow to nearby nano-structures is passive resultantly accelerated increase in temperature is observed. This phenomenon is known as Enhanced Photothermal Effect of Nanostructures. It's likely to use camera flash light for the purpose of sintering as ink-jet printed tracks contains metal nanoparticles. Silver nano-particles (Ag-NPs) were prepared using chemical reduction method. Using silver nitrate, polyvinyl pyrrolidone and formaldehyde, Ag-NPs were prepared. Synthesized Ag-NPs were inkjet printed on multiple substrates that are Polyimide, Polyethylene Terephthalate and photographic paper. After sintering by camera flash, photo thermal effects in Ag-NPs are generated which make it conductive. Changes in electrical resistivity of conductive track in each three of the substrates with respect to number of camera flashes was investigated and recorded. Results suggested through camera flash all non-conductive tracks changes to conductive tracks. Furthermore the photographic paper showed lowest thermal conductivity of 0.04 W/K m whereas PI in contrast showed the highest 0.52 W/K m. This is because the photographic paper showed lowest thermal conductivity so upon sintering it inhibits the heat spread to substrate and thus maintain a suitable temperature required for curing and fusing Ag-NPs. The printed tracks on various substrates were subjected to special characterization analysis that is SEM to study substrate effect on microstructures.[35]

UV LIGHT SINTERING

Polzinger et al. 2011 described the UV curing as approach for the sintering of inkjet printed tracks using polyimide and thermoplastics as substrates. Resistivity attained using PI substrate was four times higher in contrast to that of bulk silver. Results suggested UV radiations to be a quick procedure for curing purpose of printed silver structures and roll-to-roll process is quickly achieved. UV curing is also suggested to be used for high performance thermoplastics and thermoplastics with low glass transition temperature. Results suggested although the mechanism of sintering is yet not fully inferred because of the large diversity of properties among various substrate materials, further research and inspection of UV curing is in process.[7]

INFRARED SINTERING

Denneulin et al. 2011 proposed the sintering of silver nano ink using Infrared method (IR). The duration of sintering treatment was optimized by using infrared (IR) drying method. IR treatment was done on glass and surprisingly comparable resistance was attained using old heating method (200ºC, 5 min) and IR sintering within 3min. Low resistance was achieved when paper substrate was subjected to IR treatment for just 2min. In contrast to results available in literature a corresponding level of conductivity is achieved by lowering the temperature of sintering and the duration of treatment. The results of this study proposed that sintering that performance of sintering is directly dependent on the substrate nature and its features. The trials accomplished with corona pre-treatment indicated that sintering of silver nanoparticles can be initiated by an electrical pre-treatment after printing and before drying. Using corona electrodes the current flow is produced which leads to heating by spreading of conductive pattern. The study proposed that the problems associated with the sintering of metallic nano particles ink can be overcome by reducing the time of sintering and working with paper substrate. Moreover it suggested that paper can be used as substrate for inks. Most important gain of this proposed method is low consumption of energy. However, disadvantages like monitoring through expensive gas and working under controlled atmosphere are also linked with this new technique. [45]

Tobjörk et al. 2012proposed cost effective and rapid sintering by using incandescent lamps to achieve conductive patterns of metal nanoparticles ink; ink-jet printed using paper as a substrate. Two types of metal nano particle sink consist of commercially available silver nanoparticle ink and alkanethiol protected gold nanoparticles. The roll-to-roll compatible IR sintering is specifically appropriate for paper substrate due to certain features of paper that includes high diffuse reflectance, higher thermal stability and low thermal conductivity. Moreover, better light absorbance of printed NPs was suggested by the use of paper as a substrate due to multiscattering on the paper. Resistivity values as lowered as 25μΩcm and 10μΩcm of the ink -jetted Au-NPs and ink-jetted Ag-NPs, respectively were reported which is ten times less than bulk resistivity of Au and Ag, respectively. Results suggested the darkening of the paper fibers when exposure time and intensity was elevated. Furthermore, with the use of paper as a substrate both occurrence of crack and coffee ring effect was significantly reduced in comparison to glass and plastics because of paper porosity feature and its improved adhesion.[46]

INTENSE PULSE LIGHT SINTERING

H. S. Kim et al. 2009 proposed a new method of using intense pulse light to sintered copper nanoink patterned on low-temperature substrate. IPL use with intensity of 50 J/cm2 and distance of 14mm is considered to be advantageous as it have the ability sinter Cu-nanoink in a very less time (2 min) without causing any damage to polymer substrate. Furthermore, the micro-structure of Cu-nano ink was characterized using several characterization techniques that includes atomic force microscopy (AFM), scanning electron microscopy (SEM), X-ray micro tomography, X-ray powder diffraction (XRD) and optical microscopy. Results suggested that sintered film consists of grains with neck-like junctions. Sintered film exhibited resistivity of around 5 µcm that is 3 times higher as that of resistivity of bulk copper. The proposed method can be used in electronics using low temperature polymer substrate.[47]

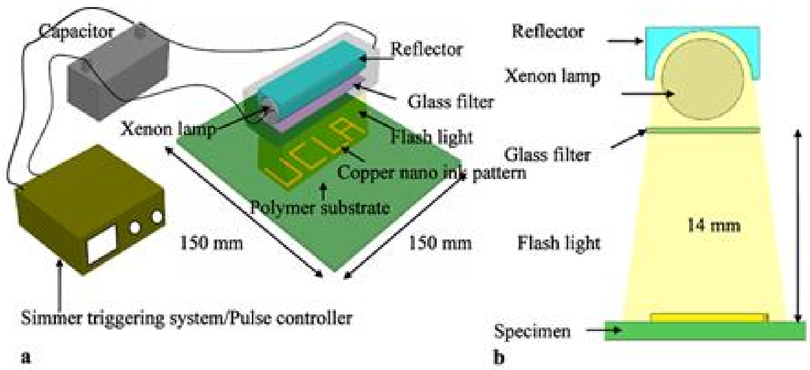


Fig 3. (a) Schematic representation of pulsed light sintering system (b) Setup showing Xenon flash lamp (H. S. Kim et al. 2009)

D. J. Lee et al. 2011 proposed the sintering of the nanosilver films by making use of intense pulsed light (IPL). Contrast studies were simultaneously conducted by thermally sintering the same inkjet-printed films. Swelling and the microstructures inside the nano films were synthesized by light pulses from xenon lamps. Certain parameters including film thickness and intensity of incident light played a vital role in determining the morphology and microstructure of IPL- sintered Ag films. Most importantly, the organic additives played critical part in the development of the hollow microstructure within the sintered nanosilver film. The resistance and intensity of light was observed to be inversely related to each other. Furthermore, the results suggested that IPL-sintered Ag films showed higher resistance in contrast to thermally sintered Ag films. The particular study also suggested that the IPL sintering process is quicker and simultaneously it didn't cause any thermal damage or shrinkage to substrate. Thus IPL sintering can be used for the rapid and accurate synthesis of printed electronics using flexible substrate.[48]

Tai and Yang 2011 designed conductive pen by incorporating nano-silver colloid as ink and by using gel-ink pen for the writing purpose. The designed pen was used to layout the conductive patterns using paper as a substrate. The use of silver nano ink results in lower sintering temperature and immense conductivity values whereas the use of conductive ink ensures manageable line width. The flexibility and foldability of the substrate was achieved by using paper as a substrate. Besides the fact that paper based circuits carries various disadvantages comprising of mechanical fatigue, non-resistance to water and fire, and weak strength but results suggested its application in development of conductive tracks and in making of flexible circuits. The designed pen implements a promising way to develop conductive patterns and to prepare the cost-effective, disposable and configurable circuit boards.[49]

Abbel et al. 2012proposed the rapid, suitable and functional method in order to developed conductive silver lines by the combination of inkjet printing and sintering using photonic-flash. The concept behind the method was localized ink heating followed by focusing the light to attain higher intensity and lastly implementation of the short pulsed energy to inhibit excessive heating of the heat-sensitive polymer. To optimize sintering circumstances for various ink-foil combinations a number of specifications that are intensity of light, frequency of flashing and the frequency of pulses can be regulated. As a result, conductivity as higher as 16% of bulk silver was achieved. Moreover, a system was described for controlling the development of temperature amid of flash sintering and thus explained that the substrate glass transition point surpassed for brief duration and thus inhibits deformity.[14]

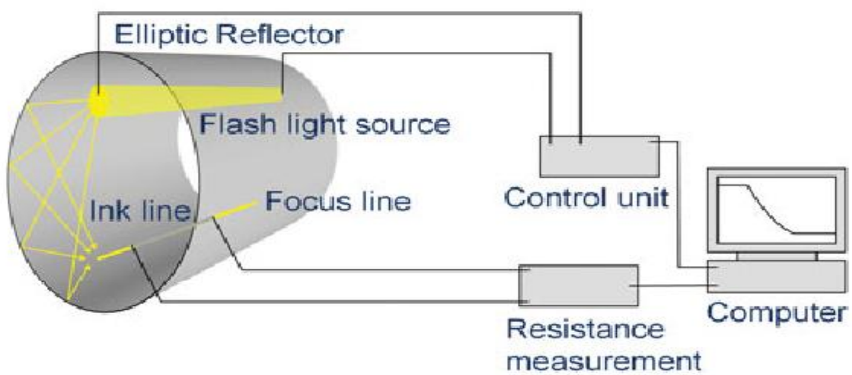


Fig4. Schematic representation of expermintal setup (Abbel et al. 2012).

Joo, Hwang, and Kim 2014 studied comparison analysis of flash light sintering effects of copper nano-ink, copper micro-ink and the combination of copper nano-ink and copper micro-ink. In order to attain improved conductivity levels of Cu films, several parameters including the proportion of nano-particlesto micro-particles, energy density, pulse number, on-time, and off-time were adjusted. Flash light irradiations were conducted to check the temperature fluctuation of copper films, in situ detection of resistance and lastly the flash light sintering procedure. Furthermore, various characterization analysis techniques were subjected to characterize the sintered films.The results suggested that lower specific surface area and a higher melting point of Cu micro-particles resulted in relatively higher resistivity of Copper micro-ink in contrast to Copper nano-ink. The sheet resistance renascent method was detected in Cu micro-ink film due to delamination by PVP evaporation. The mixed Cu nano-/micro-inks with various amounts of Cu nano/micro particles were prepared and followed by flashlight sintering. Results suggested that Copper nano-/micro-ink with proportion of 50:50 wt% were observed to showed lower resistivity (80μΩcm) with a smooth surface. In addition no substrate damage and phenomena of delamination was observed. The proposed method suggested that copper nano-/micro-ink have numerous applications including flexible electronics.[51]

Jha et al. 2015 proposed the novel technique to limit copper penetration into silicon by encapsulating copper surface by nickel layer. As one of the convenient and cost effective way to develop conductive tracks is using the sintered copper nanoparticles which are further reduced by using intense pulsed light (IPL). The property of copper to oxidize and diffusion makes it difficult to use as workable solution for fabricating patterns. Nickel has the ability to limit diffusion of copper and to prevent oxidation of copper. In this method Cu2O@NiO were prepared at room temperature through solution phase synthesis technique and the IPL sintering. Through this process synthesis of alloys at the copper–nickel interface were prevented. The Cu2O@NiO dispersions were placed onto substrate by making use of ultrasonic spray and were subjected to reducing treatment by IPL. IPL sinters the particles and thus lower resistivity is achieved. Furthermore, the thickness of the layer was managed by optimizing the processes so that a uniform layer deposited on the Copper oxide particles. Lastly the thermo-electrical characteristics of silicon before and after heating with Cu and Cu@Ni were investigated. Results suggested that nickel layer prevents the penetration of copper into silicon. [8]

Joo et al. 2015proposed that copper nanoparticles (NPs) and copper nanowires (NWs) can be used to improve the accuracy of electrode pattern subjected to mechanical fatigue. The prepared inks with various concentrations of Cu NWs were printed on a flexible substrate that is polyimide and were further sintered using the xenon lamp. Furthermore, the inner and outer bending fatigue tests were carried out. Results suggested that Cu NW/NP ink film consisting of 5 wt % Cu NWs exhibited relatively lower resistivity (22.77 μΩ•cm) in contrast to that of Cu NPs and Cu NWs ink that is 94.01 μΩ•cm and 104.15 μΩ•cm, respectively. The change in resistance of 5 wt % Cu NWs and Cu NW/NP film increased to 4.19 in contrast to 92.75 of only Cu NPs film after performing fatigue test. Moreover, several characterization analysis including scanning electron microscopy (SEM) and X-ray diffraction (XRD) of Cu NW/NP ink film were conducted. The results suggested that proposed study can be used to improve the performance of flexible electronics subjected to mechanical fatigue. [9]

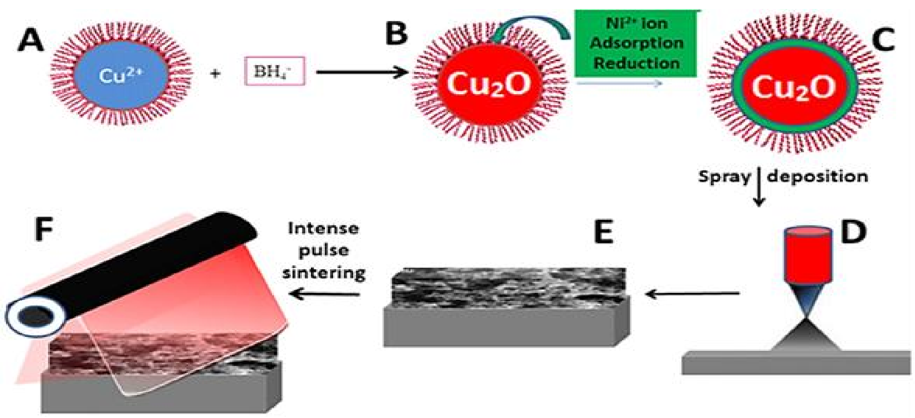


Fig 6. Synthesis and thermal processing used to mitigate the diffusion of copper into silicon. (A) A Cu-ammonia complex capped with a surfactant is formed at the start of the synthesis. (B) Cu2O NPs are formed upon oxidation of complex and further Ni2+ ions are added which are absorbed by the Cu_2O (C) NiO layer formation occurs upon addition of reducing agent. (D–E) The prepared inks are sprayed on the substrate surface. (F) Lastly the intense pulsed light sintering reduces the Cu2O@NiO (Joo et al. 2015)

LASER SINTERING

Kumpulainen et al. 2011 proposed the new method of sintering in contrast to oven sintering to be used in printable electronics for production of cost effective and extensive electronics. Two laser types that are pulsed and continuous laser for the purpose of sintering are proposed through this quick and selective sintering can be achieved. In printable electronics inks are supposed to be printed on substrate surface consisting dispersing agents and carrier fluid. These additives were supposed to contribute to printing features by altering viscosity and thus separating NPs of ink. During sintering method the additives evaporated form the ink. Moreover, further heating incites the particles to agglomerate. There is need to use lower sintering temperature for small sized particle. Convection oven is used for the process of sintering but this process is time consuming and thermal loads on nearby materials become too high as patterns from layers of various types of inks are formed. So laser sintering is preferred over oven sintering. Through laser a wide range of fragile substrate can be used as a material can be laser treated locally, inside or any intricate pattern. Both laser types were used to sintered silver nano particles and both carry advantages and disadvantages. Pulse laser generates pulses thus they leads to improved and better penetration. Selective sintering and short pulses only treat metal areas and thus less amount of heat is generated in nearby materials in comparison to continuous laser that is smoother but it leads to large amount of heat production in substrate. But the diode laser resulted in improved sintering speed and electrical characteristics. This is because of the reason that diode laser beam consists of larger beam diameter and it resulted in continuous energy production during process whereas in contrast to pulse laser the performance compromised due to its repetition rate, spot size, large pulse overlaps and pulse peak power. In order to attained reliable and improved quality sintering, smooth sintering is a necessity and this is achieved by continuous laser sintering. Laser sintering is suitable for sintering sheets consisting of components that are sensitive to high heat it's a quick approach to be used in comparison to convection oven sintering. Time required for laser sintering is determined by the length and the dimension of traces.[33]

Hong et al. 2013 described the novel fabrication of a metallic grid based transparent conductor. This was achieved via laser sintering silver nanoparticles ink without using vacuum or photolithography. Using laser beam as a heat source, nanoparticles ink was transformed into conductive tracks. In addition, by using computer-aided design program various metal grids (triangle, square, and hexagonal) were prepared. Results suggested the transmittance and sheet resistance to be 85% and <30Ω/sq respectively at a grid size of >300μm. An extraordinary stability with regard to adhesion and bending was observed on the conductor lines patterned on glass and flexible substrate. Moreover, it's suggested to extend the proposed method to flexible substrates as the proposed method lacks the requirement of any vacuum or high temperature and simultaneously the conductor also exhibits the remarkable mechanical properties. A touch screen panel is prepared and it demonstrated a steady functioning under constant mechanical stress.[53]

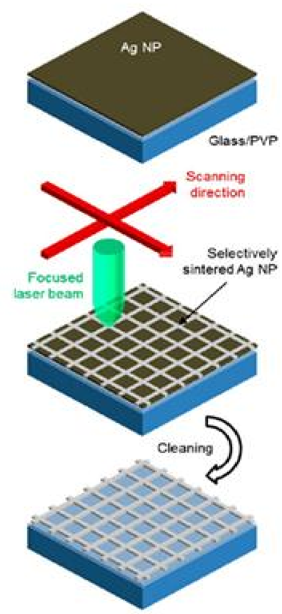


Fig 5.Schematic representation of sintering of Ag Silver nanoparticles for the fabrication of transparent conductor. (Hong et al. 2013)

Zhai et al. 2013 proposed the development of conductive inkjet ink by combination of water-based UV resin and silver nano-colloids. The prepared ink was inkjet printed to fabricate conductive track on flexible substrate. Various ratios of nano-colloids and resin were used to prepared different weight ratios of conductive ink. While inkjet printing the nano-colloids get detached from one and another and the water evaporates from the ink via heating. The ink is further exposed to UV light thus the photo-initiator disintegrates and initiates the polymerization of C C double bonds. Lastly the films are subjected to sintering in muffle furnace at various temperature settings for duration of 3 h. Another suitable alternative for muffle furnace sintering is xenon lamp. In a meanwhile of sintering process the silver nano-colloids connect with each other and thus the sintered ink turns into double continuous phase leading to formation of conductive tracks on flexible substrate. Silver nano-colloids appears as disorder fashion before sintering but as the temperature is increased to that of melting point of nano silver , particles move in various direction and thus three dimensional network is formed. [20]

Lopes et al. 2014 prepared the hybrid composed of stereolithography (SL) and direct print (DP) system. The study was conducted to study the possibility of utilizing SL laser for purpose of curing conductive ink traces. The hybrid carries the ability to fabricate three-dimensional (3D) structural electronic devices. This result in improved design and thus production flexibility contributes towards decline in weight, volume along the potential of fabricating system in numerous complicated shapes to be used in various applications. Laser curing procedure was studied with different wavelengths, inks and several factors like energy, laser wavelength and scanning location were also examined. This was done to define the circumstances most suitable for in-situ laser curing of direct-print dispensed conductive ink. Furthermore, the results suggested that adequate curing was achieved using higher laser power and slow scan speed but simultaneously it produced the charring effect of ink. In contrast to using lower laser power results in reduced charring effect but ineffective curing. The results also suggested the use of stereolithography laser to cure effectively a flake-based silver ink pattern on ink scanning in contrast to off axis laser curing which subsequently caused delamination. The results suggested the use of thermal post curing improves the conductivity of an embedded trace simultaneously excluding the requirement of laser curing before embedding the pattern and thus shortened the time required. In addition, statistical study proposed that improve volumetric ink curing was achieved by curing at wavelength of 325nm in contrast to curring achieved at wavelength of 355 nm owing to lower silver reflectance. Though the DPSS laser (355nm) have greater life span and is cost effective in contrast to omnichrome laser (325nm). So the finest substitute for purpose of curing conductive ink is to utilize 355 nm DPSS laser.[10]

APPLICATIONS

Now a day, flexible printed circuits are used in flexible touch screens, LEDs, RFIDS, thin film transistors and for fabricating electrodes for biomedical devices.

There is a device for storage and remote data transmission called RFIDs (Radio Frequency Identification Tags). There are two components of RFIDs (silicon microchip and an antenna) which are responsible for power supply and communicating with reading equipment. Currently, metal Nano inks make possible direct printing of RFIDs on flexible substrates such as PI, PET, paper and Plastic sheet. These RFIDs are comparatively low cost and efficient in conduction because conductivity is important for their function. Silver and copper are excellent source for printing such antennas. These antennas are widely used in medical devices.[54][55]

The metal nano inks are also used for fabricating thin film transistors. It is reported that silver nano inks are printed as electrodes on flexible substrates and sintered for producing TFTs having resistivity around 2.5×10-7 - 3.10×10-7Ω.cm [56]. It is also demonstrated that Ag-Cu composite nano ink is used for electrode production in silicon wafer based TFTs [57].

Light emitting devices are produced by sandwiching semiconductor layers between metal electrodes. Recently the silver and copper conductive inks are used for LED electrode fabrications which are fascinating due to their high conductive and flexible circuit nature. Silver electrodes are fabricated for generating four layers LED. When electronic current is applied across electrodes, the semiconductor layer emits intense light. Electrodes produced by metal conductive ink printing for ECG are also reported. Another application is EIT (electrical impedance tomography). Silver nano ink are suitable for EIT due to its good electrical, adhesive features .Moreover these electrodes induce negligible pressure on skin. Its promising use is in pulmonary EIT for new born and breast cancer detection. Metal conductive inks are reported for use in bio electrical mapping. The most interesting feature of these electrodes is their printing suitability in any skin contour and area. These electrodes are used other than EIT in EEG, EMG, ECG and first aid defibrillation. Body temperature mapping is promising research area in future in which metal nano conductive inks thermocouples can be used[58]. Metal nano inks can be printed for signal transmission for physiological data. It can be demonstrated for body heat detection system. This can be applied for non-invasive tumor diagnosis and cure. These electrodes can also be referred for their role in antibacterial and chemical tumor treatment[59][60].

These liquid metal nano inks represent wide area of applications in biomedical field and other electronic industry. It is expected to provide promising influence on biomedical and other electronic industry as well as in research area.

MATERIALS AND METHODS

PREPARATION OF COPPER NANOPARTICLES

The basic concept of nanoparticle synthesis was reduction of Cu-acetate with ascorbic acid as reducing agent in aqueous media. The copper acetate solution was dissolved in ascorbic acid solution under magnetic stirring at room temperature for 2 hours. The higher concentration of the reducing agent decreased the reaction rate and higher yield of copper nanoparticles were obtained. After the completion of reaction the precipitated copper nanoparticles were washed with ethanol by centrifugation at 8000 rpm for 15 minutes. The washing procedure was repeated for several times until the unreacted contaminants were removed. The washed nanoparticles were dried under vacuum oven for 24 hours.

COPPER INK FORMULATION & SILK SCREEN PRINTING

The dried nano powder was dissolved in polyol solvent and PVP was also added as dispersing agent. The mixture was ultra-sonicated for 8 hours. After ultra-sonication the mixture is ball milled for 24 hours. The well dispersed ink formulation was obtained .The copper nano powder and polyol solvent was dissolved in different ratios and ideal consistency of ink was achieved with was suitable for silk screen printing.

Teflon flexible paper (approx. 0.5 mm width) was used as flexible substrate. A silk screen printer with RFID circuit pattern was used for printing copper nano ink on flexible substrate. After printing of circuit post processing was done by curing the circuit under room temperature in ambient conditions.

LASER SINTERING

SAMPLE PREPARATION

The thin film of copper nano ink printed of flexible substrate was dried on hot plate at 70 ◦C so that the solvent was evaporated completely.

LASER SETUP

CNC-LS240A LASER system was used. The LASER beam specifications areCO_2 LASER source which have 30-120 Watts energy. The LASER machine is specifically for cutting purpose but under low power, it was used for sintering of coper conductive track.

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SINTERING

The LASER variable commands were LASER power, LASER beam speed of scanning, scan repetitions and Z – axis distance from the printed lines. These parameters were recorded and optimized for best sintering of conductive tracks. The LASER beam speed was reduced for increasing the time for particle LASER interaction as particle grain growth increased .LASER power was optimized at which ideal sintering and annealing of nanoparticles was achieved. The Z-axis of LASER beam is maintain at three different positions .The middle position among the three specified distances was effective for optimized sintering of copper film. After sintering the copper films resistance was measured by multimeter and recorded.

Copper nano ink sintering is of course against oxidation. By minimizing the sintering duration oxidation can be avoided. It can be done by using LASER beam in one direction rapidly; it is likely to shorten the sintering time one controlled way. The laser power and speed of the LASER and substrate as well due to increase in thermal energy of LASER beam. The sintered copper film was observed with change in colour to darker shade after LASER induction. The colour change shows the reduction of oxides of copper into the pure form and copper particles fused in continuous path. Induction on track is two parameters for analyzing the effect of LASER sintering on copper track. The power has to be increased for achieving minimum resistance .At certain increase in LASER power value the resistance of track decreases as the copper particles are annealed and minimum resistance is achieved. After that level the increase in LASER power damages the track.

RESULTS AND DISCUSSION

The copper nanoparticles were analyzed by different techniques .The morphological analysis was carried out by scanning electron microscope (JEPC JSM-6490LA , Analytical Low Vacuum SEM ,Japan) , Optical Microscope (LabMed iVU3100) and X-ray diffraction (XRD theta-theta STOE , Germany) .By these methods the particle size , shape , elemental analysis was analyzed . After formulation of copper ink by dispersion in organic solvents, ink was printed on Teflon flexible substrate of 0.5 mm with silk screen printer. A RFID pattern of 2 mm conductive line width was printed .The ink physiological parameters was optimized like viscosity and metal particle load. Viscosity of ink was measured by rheometer which was 21.5 cps with 50% metal particle load.

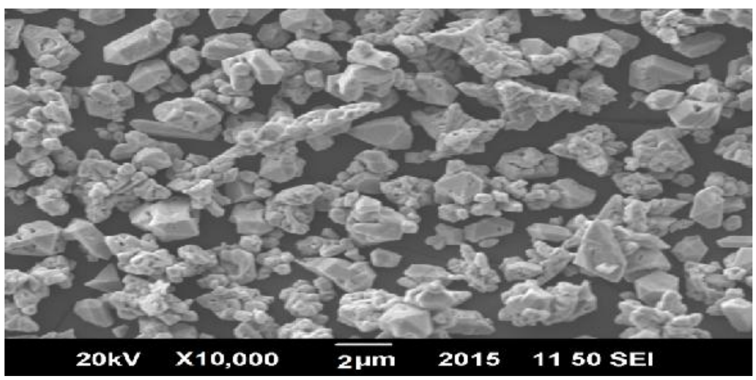


Figure 3 The SEM image of copper nanoparticles after dispersion in PVP and solvent by ball milling

XRD is an important and easy technique for size, article nature and shape determination. Here copper nanoparticles are successfully prepared via aqueous phase chemical reduction of copper acetate. The XRD characterization confirms that copper nano power with size less than 50 nm.

43.50, 50.59, 74.28 are values of peaks of 2 which are corresponding to (111) , (200) and (220) planes. These peak values are notified and analyzed by comparing with JCPDS, copper file number 0.4-0.836 and ASTM 03-1005[61][1]. The crystal unit cell structure of copper is face centered cubic copper phase according to standard powder diffraction card .The XRD studies confirmed the obtained particles are copper nanoparticles without any impurity phases of copper e.g. Cu2O ,CuO , and Cu(OH)2 . [61]

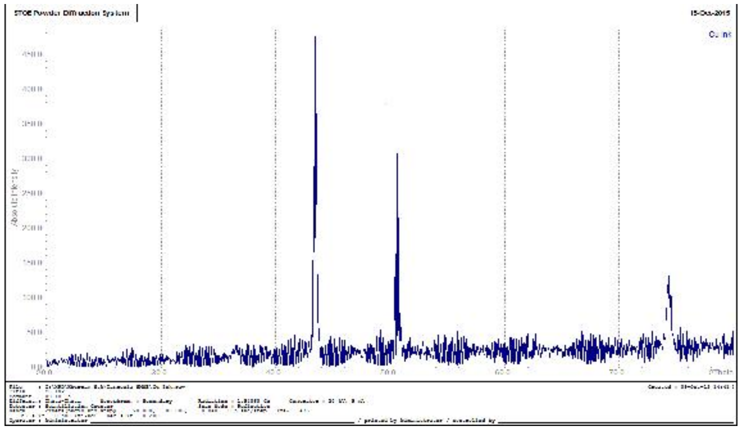


Figure 4 XRD of copper nanoparticles

2Ǿ values are given below which are obtained from XRD DATA.

20.000	1
20.040	10
20.080	1

Skip some lines…..

43.400	396
43.440	186
43.500	477
43.520	160
43.560	365

Skip some lines

50.480	241
50.520	18

50.590 310

50.600 47

Skip some lines

74.240 121

74.280 133

74.320 100

74.360 121

Table 1

Peak position,2θ	**1000xSin2 θ**	**1000xSin2 θ / 45**	**Reflection**	**Remarks**
43.50	137.31	3	111	$1^2 + 1^2 + 1^2 = 3$
50.59	182.56	4	200	$2^2 + 0^2 + 0^2 = 4$
74.28	364.53	8	220	$2^2 + 2^2 + 0^2 = 8$

Table 2

Experimental diffraction angle [2θ ꞊in degrees]	**Standard diffraction angle [2θ ꞊in degrees] JCPDS Copper: 04-0836**
43.48	43.297
50.56	50.433
74.28	74.130

From this study the particle size calculation was calculated by using the formula of Debye-Scherrer which is given below,

$$\mathbf{D} = \frac{0.9\lambda}{\beta \cos\theta}$$

After printing the circuit, pattern was dried at hot plate at 50 degree for 2 hours. The pattern was LASER treated at different power and speed of LASER beam .The Z-axis distance from the pattern was optimized where the pattern was sintered accurately .The distance of Z-axis of LASER beam was fount 3cm from target. The resistivity was measured and documented at various LASER powers .The power of LASER where coper film was sintered ideally was 30 watts. Beyond that value thermal degradation started. The sintering speed was 100 ms-1.[4]The resistivity of sintered patterns were measured and found to be close to reported copper ink circuits, which are given in graphs.The sintering mechanism was carried out in three steps.

1. Solvent evaporation
2. Removal of PVP by thermal degradation
3. Growth of grain boundaries by neck formation

The copper nano particles were annealed (neck formation), PVP thermally degraded and removed and continuous pattern was formed. The sintering mechanism was analyzed morphologically by SEM and EDS analysis. The EDS analysis represents that the oxides of copper reduced into pure copper by LASER treatment .The gradual LASER scanning phases changed the track physiological and chemical nature.

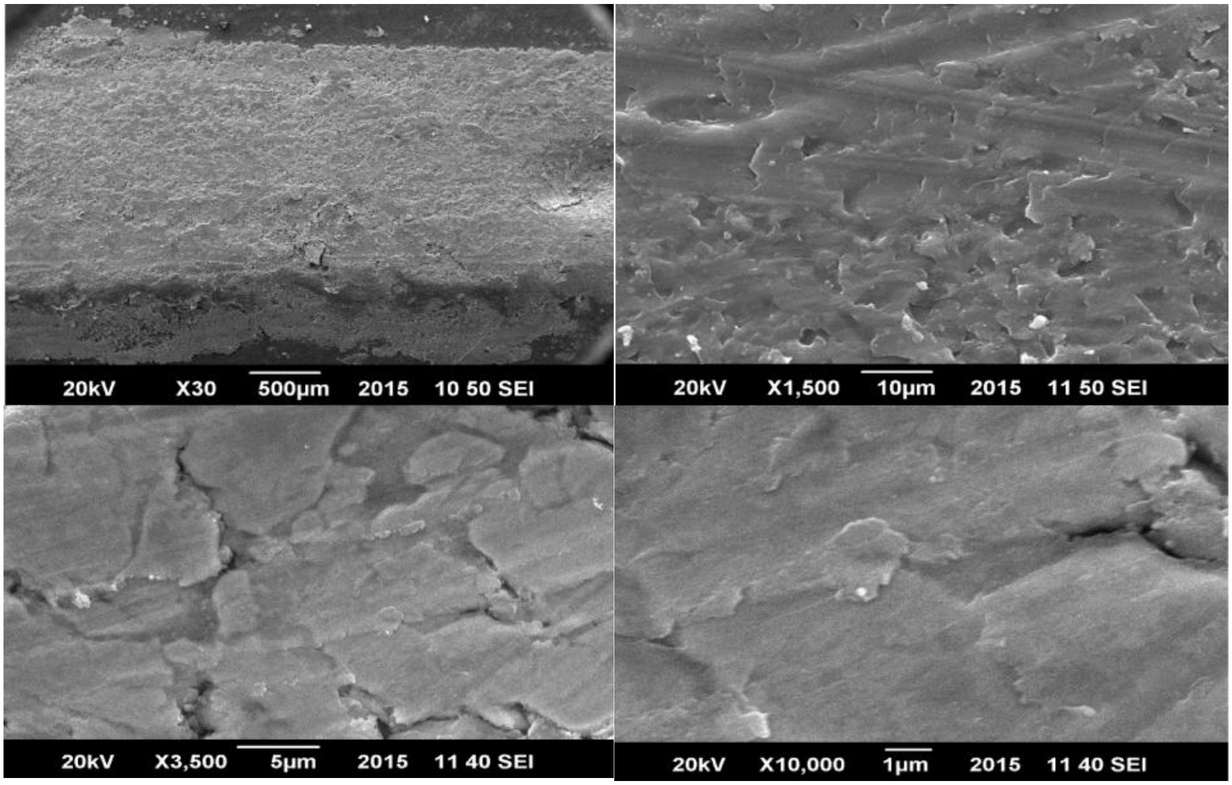


Figure 5 LASER sintered Copper nano ink printed track SEM images are shown .The gradual change in microstructure shows that the copper particles annealed and grain boundaries are formed.

It was observed that there was noticeable decrease in volume of copper film after sintering due to solvent evaporation and dispersant decomposition furthermore the metal particle fused together. The sintering time duration was few milliseconds that minimized the oxidation rate of the copper film. The speed of LASER beam determined the sintering time duration. The speed and power of LASER was two variables that were analyzed for their sintering effect on copper film. The power of LASER was increased as the minimum resistance was achieved with a certain power level. Beyond that value the thermal degradation started of copper film and substrate.

As the sintering mechanism progressed the reflectivity of copper track was increased and surface became more fine and lustrous. For comparison of reflectivity change of unsintered and sintered copper films, Optical Microscopy was carried out. The images are shown in the figure. The change in colour of copper film was also observed. The surface became shiny bronze from dull reddish brown .This due to reduction and fusion of copper nanoparticles along with the decomposition of dispersant and solvent evaporation.

Figure 6Unsintered copper printed film Optical microscope image at 40X

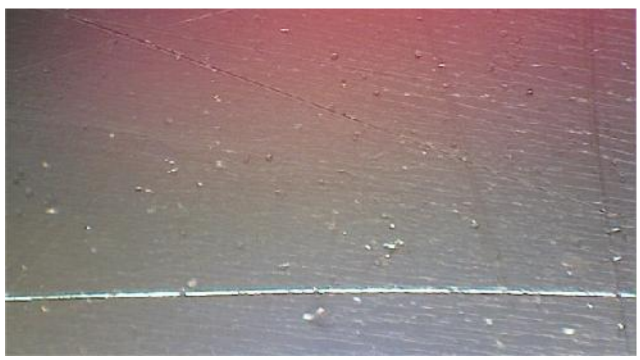
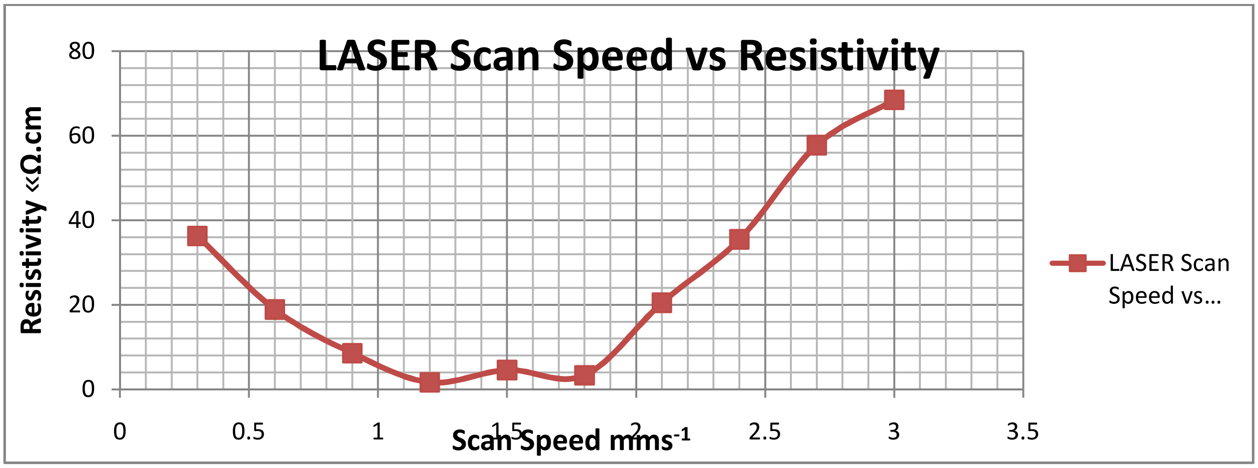
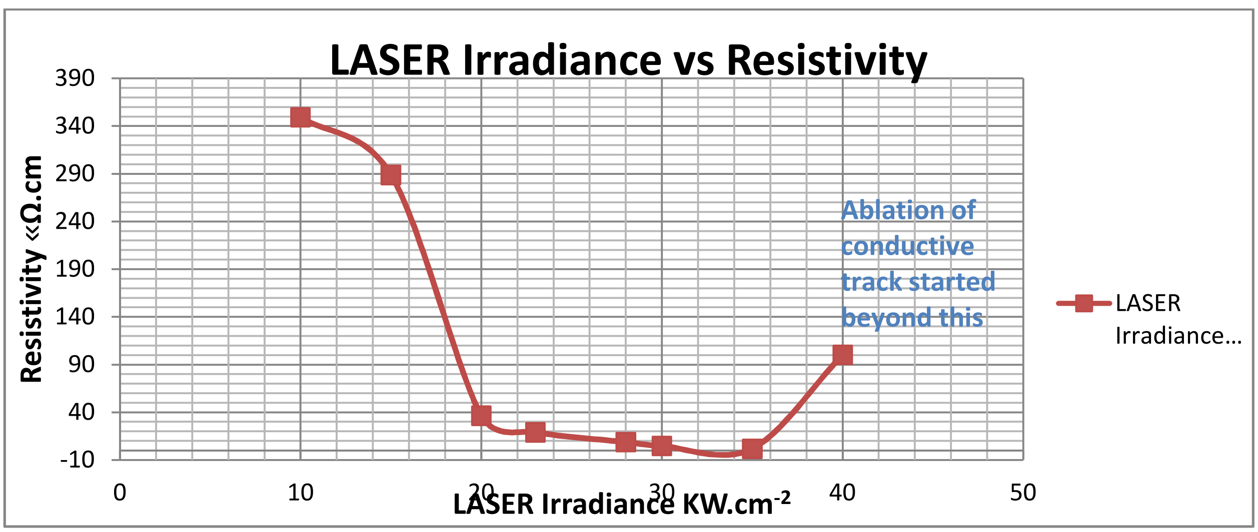


Figure 7 Sintered copper printed film Optical microscope image at 40X

The oxidation process could be possible during sintering process. In this research study the sintering process was carried out in open environment rather than in inert condition which could be important for preventing oxide layer formation over the copper film during sintering process. The LASER speed was increased for rapid annealing and dispersant decomposed instantly and solvent evaporated. The minimum time copper film to sinter was crucial for avoiding oxidation in ambient conditions. All processes were carried out at room temperature. By varying the different speed values of LASER beam, change in resistivity was measured until minimum resistivity was achieved at 1mmS-1 .In fact; the oxidation process affected the conductive behavior of the copper film.





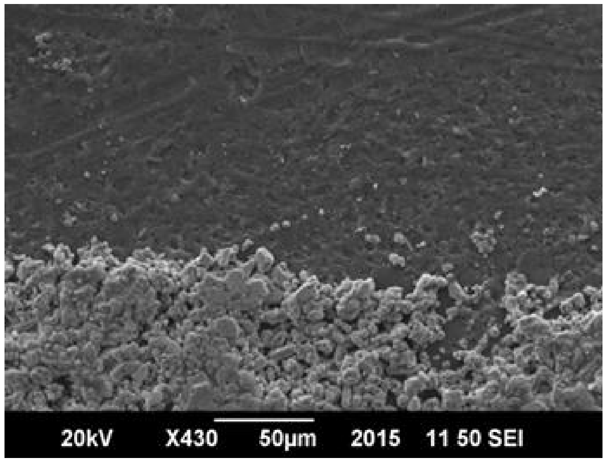


Figure 8 Boundary between sintered and un –sintered portion of the copper track. There is clear difference between these two portions. The sintered portion has fused copper particles and smoother surface morphology with change in colour.

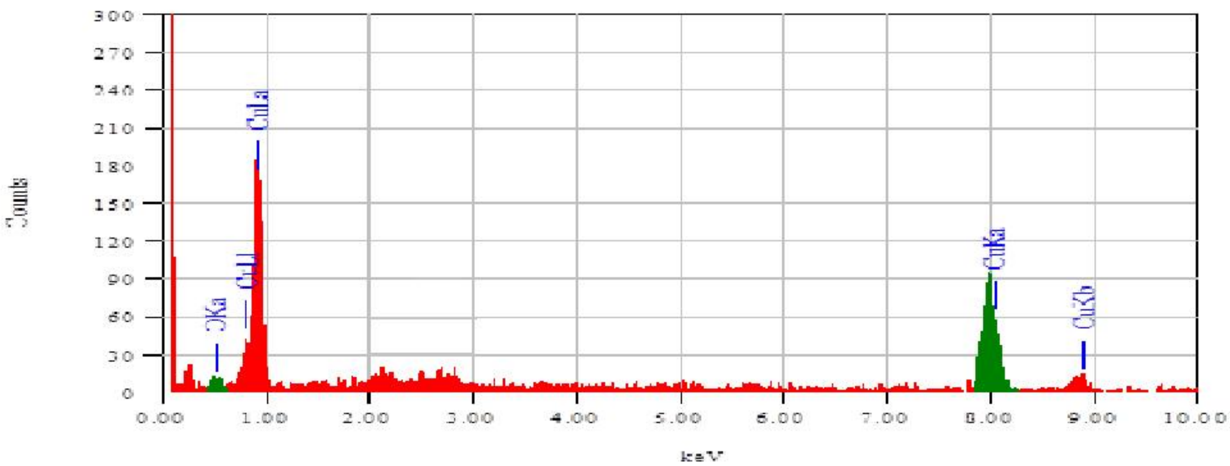


Figure 10 The EDS result graphical representation after sintering depicts the percentage of oxygen becomes negligible

Element	(keV)	Mass%	Error%	Atom%	Compound Mass%	Cation K
O K	0.525	0.39	1.77	1.53	-	0.4116
Cu K	8.040	99.61	7.34	98.47	-	99.5884
Total		100.00	-	100.00	-	-

The EDS analysis represents the content of oxygen was decreased after sintering process.The LASER treatment reduced the oxidized copper nanoparticles during synthesis and storage.Along with the reduction of copper, PVP and solvent evaporation (thermal degradation) occurred ,which was another reason for low oxygen content of sintered copper film.[3]

Finally all results proves that the LASER sintering is potential alternative to conventional sintering methods which are carried out in anti-oxidizing conditions.

CONCLUSION

In this research, copper nanoparticles were synthesized in a simple and environment friendly aqueous method of copper sulfate reduction in ambient conditions. The obtained nano particles were characterized and it was evaluated that the copper nano particles are pure without any high amount of impurities. The conductive ink was formulated with well dispersed and stable nano particles in normal storage conditions by using diethylene glycol as a organic solvent. The solvent provide inert organic phase that prevent copper particles from oxidation during storage. The nano particles were dispersed in solvent by ball milling. PVP act as dispersant for metal particles in solvent it also acted as reductant that prevent nano particles from oxidation in solvent. The well dispersed copper nano particles ink was screen printed on Teflon paper as flexible substrate. Solvent ethyl glycol ratio was optimized with metal particle load for formulating ink composition. Solvent nano particle and PVP amount was optimized for achieving required viscosity in accordance with silk screen printing. The copper conductive ink is best commercial and technical interest in printable microelectronics.

The laser treated conductive track was optimized for best conductive results. The power 30 Watt was ideal laser power where minimum resistivity was calculated. The laser treatment was performed in ambient conditions the laser speed was evaluated which was 1mm/s where sintered track showed minimum resistivity. The reflectivity and surface morphology proved that sintered pattern was reflective and the nano particles fused relative to un sintered pattern. The resistivity and micro structural study of sintering mechanism depicts laser sintering method is reliable and simple without any complex steps. The all experiments were carried out in ambient conditions and the results are similar to the reported sintering results which were carried out in non-oxidizing conditions.

Finally it is clearly concluded that direct laser sintering is better method for generating faster with high resolution conductive copper pattern on flexible substrates in ambient conditions without complex procedures. The laser sintered flexible PCB has wide range of applications in solar system RFIDs and medical electronics where flexibility of circuit is required.

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