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ADHESION PHENOMENON OF ELECTRICALLY CONDUCTIVE PATHS PRINTED BY NANOINKS TO TYPICAL SUBSTRATES

The introduction of printing technique to create the electrical circuits with the use of ink contained silver nanoparticles, has given new possibilities for electronic market by reducing application material costs, increasing production yield, adding new functionality to existing products, and enabling new applications. One of such applications, flexible electronics, can be used in flat panel displays, phones, computers, sensors, car industry, smart cards and other low cost electronic devices. A major concern for the manufactures of printed circuitry will be to ensure adhesion to a chosen substrates and the structure ability to withstand bending loadings without cracking. It is particularly important in the case of the elastic substrates exposed to various strain and stresses.

We expect the adhesion of surfaces can depend on the substrate preparation by plasma modifications and/or the addition a small amount of various modifiers e.g. polymer to ink formula [1]. This polymer will prevent the agglomeration of silver particles and we believe that also can improve the adhesion of Ag to the substrate. Printed paths obtained with the use of such silver-based inks and their adhesion to glass and polymer substrates were then briefly studied.

1. INTRODUCTION

Nanotechnology - the newest scientific trend - allows producing the smallest sized of many different materials. The metallic nanoparticles are extensively investigated due to their unusual chemical and physical properties, which big differ from their bulk properties [2-4]. Several promising applications in electrochemistry, microelectroncs, optical, electronic, and magnetic devices, new types of active and selective catalysts and so on can be found just due to these unique and novel properties. For example, the melting point for materials with large-scale fragmentation, less than 10 nm, decreases

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with decreasing of particle size (over 500 °C for 5 nm particles of gold compared to the melting point of the bulk material [5]). Taking advantage of the low melting point of metallic nanoparticles, it is possible to fabricate microinterconnects by ink-jet printing metallic nanoparticle suspensions on substrates, and then sintering at low temperatures. Silver nanoparticles are good materials for such an application [6].

Preparation of stable, concentrated inks of silver nanoparticles with low resistivity is described in this article. Two methods have been used to prepare silver nanoparticles, including chemical reduction of silver compounds and thermal decomposition of silver fatty acids under inert atmosphere. In this research, we use two types of silver with different size to prepare suspensions of silver nanoparticles with different parameters for ink-jet printing. These inks have to meet strict physicochemical properties: viscosity, surface tension, adhesion to a substrate, etc. The main attention in this study is focused to test the adhesion of printed structures to typical substrates.

2. INK-JET PRINTING TECHNOLOGY

2.1. THE METHOD OF INK APPLICATIONS

The ink-jet is a noncontact technique, which is suitable for direct write of patterns and which can deliver precise quantities of materials. This method can mainly be classified based on printhead types into continuous-mode (CIJ) and drop-on-demand (DoD) [7].

This method by which the formation of ink droplets in a continuous is called the CIJ technology [8,9]. While in the DoD system the drop of ink is jetted only when the head is located above the substrate, on which the conductive structure is performed. Now DoD method has wide application in the production of electronic circuits due to low ink consumption and mechanical head positioning system. This translates directly into reduced costs of production as well as increased the resolution of patterns (drops in a range of picolitres). This printing method has been used also in this paper for printing structures by obtained inks on the tested substrates.

2.2. INKS FOR INK-JET PRINTING

Ink-jet technology is based on the shooting drops of ink through the nozzles of small diameter (30-100 microns), which requires the use of inks with adequate properties. Low-viscosity inks containing silver with nanosize particles dispersed in a solvent are commonly used to print conductive structures. To protect the nanosilver against agglomeration and sedimentation the individual particles must be separated from each other. It is only possible by coating them with protective stabilizing substances in the production process. The stabilizer is adsorbed or bound to the surface of silver and forms a protective layer, thus preventing agglomeration with other particles. Only unprotected particles tend to aggregate and form compact micro scale structures. The protective layer is commonly called as surfactant. For removing them it is necessary to apply additional (mostly thermal) treatment process. After this process structures can be obtained conductive structure with perfect electrical properties. However, Kan-Sen Chou et al. [10] have demonstrated that even 5 wt.% of protective coating after sintering of the structure allows to obtain very good electrical conductivity parameters of printed pathways. The rest of protective coating can plays a role an adhesion promoter. Type of protection layers also determines kind of used substrates to print. For flexible electronic the most promising type of protective layer on Ag nanoparticles will be the layer which should be removed in temperature not higher than 150 °C. However for printing on glass the coating can be removed at higher temperature e.g. 230 °C. The final product should posses the physical parameters of good stability over a long period of time, which is related to the safe use of ink jet printing technology. An important parameter is the homogeneous structure, understood as an uniformity distribution of nanoparticles in the total volume of ink. This allows to obtain high and stable values of electrical conductivity, as close as possible to the parameters of pure silver. The basic parameters of ink depend on the size of Ag, which is related to the technology of silver preparation.

One of used method for production of nanomaterials for ink-jet application is synthesis by thermal decomposition. This method is based on decomposition of silver fatty acid at high temperature in neutral atmosphere. In this way the end product has been obtained as a dark violet waxy substance composed of individual particles in the range of 3-8 nm and very narrow size distribution (Fig. 1a, 2a). This fully controlled production process allows to prepare nanosilver with carboxylate type of protective coating - Ag1, which should be removed in temperature higher than 200 °C [7].

a) b)

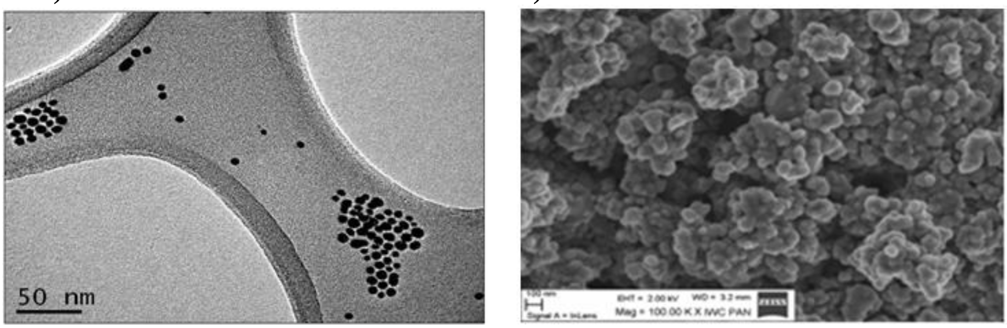

Fig. 1. TEM picture of Ag1 (a) and SEM picture of Ag2 (b)

a) b)

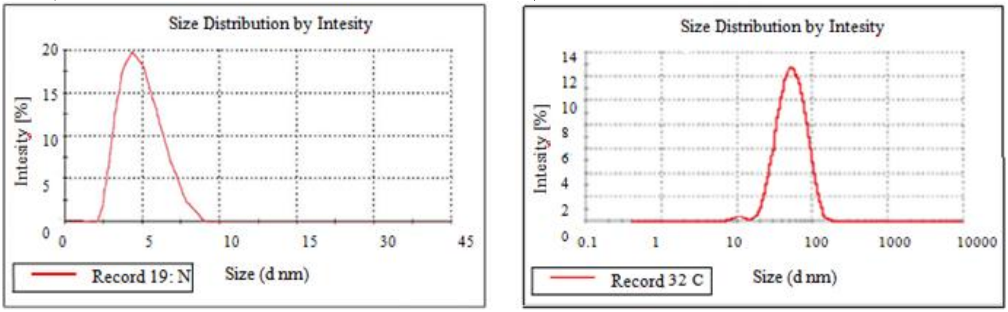

Fig. 2. Distribution of nanosilver particles Ag1 (a) and Ag2 (b)

Another way to get nanosilver with very high repeatability properties is chemical reaction. The nanosized silver was obtained by a simple reduction of silver salt using reducing agent and stabilizing polymeric agent also known as protective coating. The nanosilver with polymer coating - Ag2 - have larger particles about 50-70 nm (Fig. 1b, 2b). The ink with this filler will need relatively low 150 °C sintering temperature. This allows printing on low-cost flexible polymer substrates such as PE, PET, etc.

For ink preparation both types of obtained nanopowders were dissolved in selected solvents. Nano-Ag1 with smaller particles was dispersed in organic non-polar solvent, and the dark brown liquid with metal concentration inside formulation of about 45 wt.% was obtained. The second conductive ink based on obtained Ag2 nanoparticles with size in range about 60 nm was composed mainly of polar solution. Two prepared compositions: ink1 and ink2 (obtained with Ag1 and Ag2, respectively) is expected to be environmentally friendly. The base properties of produced inks are presented in Table 1.

Table 1. Ink specifications

Name	Ink1	Ink2
Number of components	One	One
Consistency	Very low viscous ink	Very low viscous ink
Color	Dark violet	Dark green to gray
Percentage of silver filler [wt.%]	45	20
Viscosity [mPas]	Up to 35	5-6.5
Thixotropy index (1/10)	~1.0	~1.0
Surface tension value [mN/m]	28.5-35	~35
Recommended curing & sintering conditions in convection oven	230 °C-60 min	150 °C-60 min.

The tested inks were long-term stable, despite a high concentration of nanofillers. This was possible due to the using a such small silver particles size. Only this type of fluids with low viscosity and very homogenous structure similar to ,,true fluid" is working very stable during extremely long time. However, the high concentration of metallic nanoparticles and their uniform distribution in the total volume, can cause unwanted stress of structure during the sintering process. While this can in turn cause significant weakening of the forces of adhesion metallic layer to the substrate. Therefore, the parameters of the ink should be selected on the basis of a compromise between the level of electrical conductivity, and the tightening of the limit values in the layer and the forces that connect it to the substrate.

2.3. SUBSTRATES FOR INK-JET PRINTING

Flexible or printed electronics needs many kinds of substrates for printing in the ink-jet technology e.g. Mylar, PET (polyester), PI (polyimide), PEN (polyethylen-napthtalate), PVC (polyvinyl chloride), PC (polycarbonate), Aramid paper, FR4, Glass, Low Temperature Co-fired Ceramic (LTCC) etc. The used substrates are manufactured from various materials, dissimilar in terms of thermal and chemical resistance and strength. The strength of the material on high temperature is one of the key requirements especially in flexible electronics. During the process, the substrate is exposed to elevated temperatures, which can cause damages. For this same reason, it is expected that the sintering temperature of the ink was as low as possible, what gives the possibility of using the low-cost flexible substrates.

In the current paper due to differences in the sintering temperature of tested inks, we have chosen PET foil and glass as substrates. One type of tested ink (ink2) was printed on flexible substrate because have relatively low - 150 °C sintering temperature. The sintering temperature of the another studied ink (ink1) was 230 °C and it limits the using of such type of substrates. In this case the high temperature ink was printed on glass. The choice of material also depends on the relevant requirements in the production process, as well as later in process of exploitation. An important criterion of selection, which we considered was the kind of used ink, and thus its temperature sintering.

Glass has a variety of both chemical and physical properties. One of the most important properties of the glass is its excellent chemical resistance to aggressive substances. It is not only resistant to the action of fluorine and phosphoric acid. This makes the glass, one of the most durable construction materials, so that is used in all areas of life including electronics. However, more and more this traditional materials are replaced by plastic, especially in flexible electronics. The most widely used polymer, which has good electrical and mechanical properties and low price is polyester. PET has very good dielectric, mechanical and strength properties, thus it is used in many industries. This foil is insoluble in common solvents. Dissolution of the material is only possible in perchlorethylene at higher temperature conditions. PET is also characterized by a high ratio of the geometric stability and high mechanical strength. Polyester has low moisture absorption coefficient. The material is thermally resistant stability at 115-170 °C [11]. But this is too little strength to use the high temperature ink.

3. ADHESION

3.1. EXPLANATION OF ADHESION PHENOMENA

The ability to produce a connection between two different materials is affected by two phenomena known as adhesion and cohesion. The two terms are mutually independent and should not be equated. The easiest way to forces of adhesion is defined as the forces acting between molecules of different materials, while the cohesive forces occur between the molecules of the same material [15].

Adhesion is possible due to physical adsorption, which means the existence of intermolecular interactions in contact with the substance and determines attractive forces called van der Waals forces. These forces are the result of electrostatic interactions such as dipole, dispersion and magnetic interactions. Dipole interactions occur in particles with permanent electric dipoles, and also induced dipoles, where can be observed formation induced dipole moment by neighboring polar molecule. For molecules that do not have permanent dipoles the dispersion forces are present consisting of the producing the instantaneous dipole moments caused by the movements of electrons in the particle. Magnetic interactions are caused by the movement of electrical charges of atoms of a particular structure.

The combination of the two materials can also based on the phenomenon of chemisorption. This occurs when chemical bonds are formed between atoms and molecules on the surface of materials. This process focuses on the issue when combining the adhesion surface using adhesives. Adhesion forces associated with the phenomenon of chemisorption are usually larger than those associated with physical adsorption, however depend on the chemical reactivity of cross-joined materials.

In this paper, the adhesion force was treated as joining two surfaces, which is determined by the limit value of mechanical stress required for the separation of layers.

3.2. METHOD FOR MEASURING THE ADHESION – PULL-OF TEST

Adhesion to the base substrate is one of the main problems which solution is essential to obtain high-quality electronic circuits. It is obvious that in order to solve this problem one must perform tests of measure this force. There are various methods of measurement, different both in terms of how to perform experiments and the type of measured material. The technique of wasted forms, measure the force per unit area (N/m^2) [12].

One of the most popular ways of measuring the adhesion strength is the pull-off test. To examine those forces on tested surface the specific handle must be perpendicularly glued. After curing the tensile device is installed that provide a gradual increase in force, directed perpendicular to the surface. The device works on sample holder for force facing up and causes it to drift. After separation of the tested layer from the substrate or to time of achievement of the desired value the measurement is finished. The measured value is in MPa (N/mm^2). The essence of the test method shows the Fig. 3.

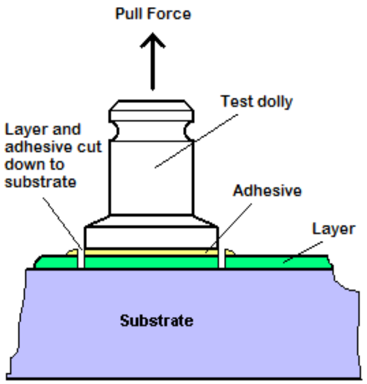

Fig. 3. Graphical representation of the measurement of adhesion forces by pull-off test

Pull-off strength measurements depend on both material and instrumental parameters. Results obtained by each test method may give different results. Results should only be assessed for each test method and not be compared with other instruments.

In this work for pull-off test the LLOYD LRX Instrument equipped with 500N force cell was used and the results were read by a computer containing software "MT NEXYGEN Material Test and Data Analyses Software". The dolly was glued by using a two-component epoxy adhesive LOCTITE 907. The measurement were made automatically and the result was presented on a computer.

4. THE RESULTS OF ADHESION MEASUREMENTS

The printouts ware performed by Fujifilm Dimatix Printer DMP-2811. Printer head has 16 nozzles of 22.5 microns diameter located linearly with 254 microns space between each hole. The volume of the generated droplet is 10 pikoliters. Fujifilm device allows to make prints at a resolution of 100 to 5080 dpi (dots per inch), which corresponds to the spacing between the drops from 254 to 5 microns. Printout of conductive structures was made at a resolution of 1270 dpi (20 microns) and 846.67 dpi (30 microns). As a source of silver nanoparticle the inks, which exact data are included in Table 1, ware used.

4.1. TEST ADHESION OF HIGH TEMERATURE INK TO GLASS

Electrically conductive films have been printed by ink1 on the microscope slide glass with a thickness of 1 mm. The samples, containing printed square structure with sides of 6 mm were annealed for one hour in a convection oven at 230 °C to evaporate the solvent and to remove the protective coatings on silver particles. The sample have been shown in Fig. 4:

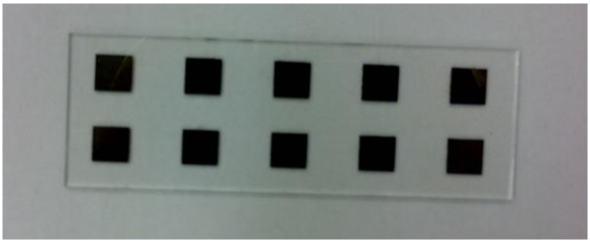

Fig. 4. Glass substrate with printed structure by ink1

After cooling, samples were ready to pull-off test, which were done with the use of LLOYD LRX Instrument. Table 2 shows the obtained results from 10 measurements in each four measurement series.

Table 2. Results of adhesion measurements

Number of measurement series	Average force of detachment [MPa]	The standard deviation
1	0.452	0.047
2	0.439	0.043
3	0.411	0.047
4	0.421	0.024

The statistical average value of the results was 0.431 MPa and the standard deviation - 0.04.

The measurements show a moderate adhesive properties of glass and its parameters are sufficient to meet the conditions of the manufacturing process. Visible deviation in the results due to the adhesive, which flows outside of the contacts. The adhesive located on the glass during pull-off process increases the adhesive strength. However, the large number of measurements makes that the experience was successful and the conductive structures were completely detached from the glass (Fig. 5).

Fig. 5. Samples printed by ink1 on glass after pull-off test

4.2. TEST ADHESION OF LOW TEMPERATURE INK TO POLYESTER

Electrically conductive films on polyester (PET) with a thickness of 100 μm have been obtained in the same way like the structures on glass. However, the structure were deposited by ink2 both on the substrate without plasma modification, as well as on foil treated irradiation of a plasma with two working gas compositions. The used plasma was composed of argon and oxygen in ratio 8:2. The time of interaction of the plasma on film was 30 s and included one page of polymer surface. After modification by plasma we have expected better adhesion to the substrate. In such conditions, there are usually two processes: etching of polymers and deposition on the surface of the plasma polymer layers. In either case it comes to changes in the nature of the material surface and introduce her specific functional groups which can significantly increase the adhesion of metal contained in the ink [13]. It has been already shown that it is possible to improve the adhesion properties for polyimide foil from 58 kPa to 113 kPa by plasma modification [14]. Next the printed square shaped structures (Fig. 6) were annealed for one hour in a convection oven at low temperature - 150 °C. In this case already this temperature was enough to remove the polymer coating and obtain good resistance.

Fig. 6. PET substrate with printed structure by ink2

Modification of the substrate lead to the loss of its hydrophilic properties over time. Contact angle of plasma-modified substrates by dielectric barrier discharge was reduced. As it is well known, the strength of adhesion depends on the wetting angle and it is the smaller the binding strength of polymer coating and substrate will be higher.

On the modified in this way PET and the PET without modification the pull-of tests were carried out. The results of average values from 10 measurements in each of 4 series were shown in Table 3:

Table 3. Results of adhesion measurements

Number of measurement series	Average force of detachment [MPa]	Modification by plasma (20% oxygen, 80% argon)
1	The adhesion strength greater than the force of cohesive	Yes
2		No
3		Yes
4		No

Measurement of force connecting the conductive structure to polyester have showed that the cohesive strength of the substrate is smaller than the adhesion strength of the printed layer to this substrate. The same results have been obtained for both plasma-modified and unmodified substrates. Appearance of the sample after the experiment was shown in Fig. 7.

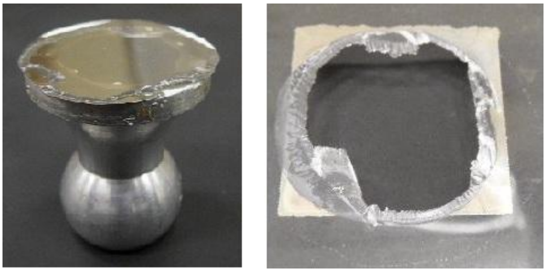

Fig. 7. Samples printed by ink2 on PET after pull-off test

Measurement of adhesion using pull-off test showed that in the case of polyester foil the adhesion strength of printed structures were higher than the forces of cohesion of this plastic substrate. It should be noted that the tensile strength of PET is between 200-300 MPa, so the adhesive strength must be greater than this value. Such a large adhesion can be the result of using the ink with nanosilver rounded by polymer coating. As it is known the improving the mechanical properties and increasing adhesion to the substrate of printed structures can be also made by the addition a small amount of polymer to ink formulation. This polymer can prevents the silver particles from agglomeration and moreover create an additional binding of Ag nanoparticles with the substrate.

5. CONCLUSION

This work describes the issues related to application of conductive structures by ink-jet technology on glass and flexible substrates used in printed electronics. It was also presented the main technological problem which is the adhesion of coatings deposited on these substrates. The main part of the work has focused on the characterization of prepared inks and exploitation the phenomenon of adhesion. All obtained fluids were stable during printing process so that we have obtained the optimal performance and reliability of the printing system and the best printed pattern. The greatest challenge this inks was the adhesion to a substrate, which ensures reliability of electric circuits.

The study was designed to test the adhesion strength of printed structures to used substrates. The experiments show good adhesion properties of structures printed by high temperature ink (ink1) to glass - about 430 kPa, sufficient to meet the conditions of the manufacturing process using ink-jet method. The studies show also that the conductive paths printed by other tested low temperature ink (ink2) have good adhesion both to modified plastic foil - PET and without modification. The adhesion force is larger than strength of this material, which fully complies with expectations. As already mentioned, the polymer coating on the surface of silver nanoparticles in this case could play additional role as an adhesion promoter.

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