Adhesion and Electrical Properties of Low Temperature Processed Ag-PMMA-Films in Inkjet Printing

Andreas Rathjen, Jan Zimmermann, Vico Haverkamp, Klaus Krüger; Helmut Schmidt University / University of the Federal Armed Forces Hamburg; Hamburg, Germany

Abstract

A new simple to use approach for the measurement of adhesion strength of inkjet-printed films on their substrate is presented. The need for this new approach utilizing an ultrasonic bath is introduced by a brief explanation of existing methods. The ultrasonic bath method is evaluated by investigating different silver inks on different substrates (ceramic and glass-fibre reinforced plastic). Using the new ultrasonic bath method the temperature range for optimum adhesion on the substrate for different combinations of ink and substrate is evaluated. This temperature is shown not to be the maximum applicable temperature but rather a temperature in the middle section. At the optimum temperature, strong bonds between silver particles are formed without the sintering shrinkage breaking the bond to the substrate.

The influence of using poly(methyl methacrylate) in silver inks on adhesion and resistivity is also investigated and discussed. The organic material shows little impact on the resistivity of printed tracks for sintering temperatures above 150 °C while changing the film adhesion temperature profile.

Introduction

The application of inkjet printing spreads more and more. Not only printed products become more sophisticated each year. Processes used in, after and before printing are manifold as well. The use of new technologies and opening to numerous new fields demand the development of new analysis methods. Data has to be gained on topics that did not need to be taken into consideration so far.

One of these topics is the adhesion of printed structures. Considering low temperature processes, sintering/drying temperatures far below 200 °C are used for silver tracks, while still achieving a resistivity as low as only 1.3 to 3 times the resistivity of bulk silver [1, 2, 3, 4]. The use of modern techniques like laser sintering can reduce temperature stress even more [5]. Curing can be induced at room temperature by exposure to UV light and/or additional treatment with electrolyte solutions [6, 7]. The impact of reduced sintering temperatures and further different post printing treatment processes on film adhesion has to be evaluated.

Adhesion, in this paper, does not stand for mechanical stability against stress by deformation of flexible substrates [6]. Here, adhesion refers to the bond between printed functional material and substrate. This is particularly important when the printed device is operated under harsh conditions, e. g. vibrations in automobiles.

While post-treatment at higher temperatures can ensure stronger bonds, it might be harmful to polymeric substrates or previously mounted CMOS and MEMS devices [8]. Thus, the possibility of lowering the processing temperature expands the flexibility of inkjet printing processes. One approach to improve adhesion for such printed films is the addition of adhesive materials. Here, poly(methyl methacrylate) (PMMA) is discussed as a possible adhesive

Analysis of Adhesion

As of today, there are some well-known methods for the analysis of adhesion, e. g. tape test, bend test [9] and others [10]. They are described below very briefly.

Direct Pull-Off Method

When using the direct pull-off method, a traction mechanism is attached to the film with glue or solder. Then the force needed for vertical pull-off is measured.

Even small variations of the attachment of the traction mechanism and the mount of the specimen strongly influence the results because of an overlap of tractive and shear forces. Under some conditions, the glue can attach to the film itself and, thus, the glue's adhesive strength is measured. Additionally, the glue can generate tension in the film that further distorts the measurement.

Moment Method

The moment method utilizes a glued-on rod like the direct pull-off method. Here, the rod is tilted horizontally while the film is still removed vertically. Though shear forces have a lower impact, the above-mentioned limitations concerning the glue still apply.

Shear Method

The shear method is similar to the tilting method, particularly concerning the disadvantages of gluing. The only difference is that the applied force is a shearing force.

Ultracentrifugal Method

An ultracentrifuge is used to rotate the film. The centrifugal force needed for the separation of the film is used for the characterization of the adhesion.

No glue is needed here. The excessive heat generation due to the high revolution speed can exert a strong influence on the results, particularly when using temperature-sensitive materials.

Ultrasonic Method

The film on its substrate is mounted on a rod. The rod is then oscillated at ultrasonic frequencies. The generated force depends on the used frequency and amplitude. Again, no glue is needed.

Peel Test

The film is reeled off the substrate. Usually, an angle of 90° is used to pull off the film at an already detached part. The result is delivered as work per area.

This method is not applicable for brittle or elastic films. As printed films tend to be brittle, this method is not applicable for our printed films.

Scratch Method

A needle is pulled across the film with increasing pressure. The pressure needed to reveal the substrate is used to measure the adhesion.

When analyzing brittle films, e. g. printed structures, chipping can cause premature revealing of the substrate. The needle method therefore delivers a measurement of printed film hardness rather than film adhesion.

Tape Test

When using the tape test (EN ISO 2409), a tape with defined adhesion is pressed on the film. The tape is then pulled off in a well-defined angle and speed. Using tapes with different adhesions, quantitative information can be gained.

To conduct the tape test as intended, a grid structure (size depending on the substrates hardness and layer thickness) has to be scratched into the film. The fraction of removed film allows for a rating of the adhesion. Brittle films, however, are partly removed just by scratching the grid structure into the film.

The presented methods for the analysis of adhesion come with some disadvantages for the analysis of printed films. Many of them require a more or less extensive preparation that, in some cases, causes problems for the execution of the experiment or the interpretation of the results.

A solution to overcome these problems should omit mechanical traction mechanisms to apply force to the printed structure. Here, a method is proposed that utilizes an ultrasonic bath to apply force to the film. Results are quantified by measuring the weight of the specimen before and after ultrasonic bath treatment. This method is described further in the next section.

Materials & Methods

Ink Preparation

Different silver inks are used for the research in this paper. For inks containing 300 nm silver particles the Silver Powder #11000-10 (Ferro GmbH, Germany) is used with butyl diglycol as dispersant and ethyl cellulose for ink stabilization. These ingredients are manually mixed, followed by three roll-milling cycles. Further dilution with butyl diglycol provides an ink with the desired solid substance content (SSC) and viscosity.

Using similar inks, many different electrical components have been printed. Among these are multilayer capacitors on ceramic substrates [11] and through silicon vias in silicon wafers [8].

In order to print Ag-PMMA-inks, the poly(methyl methacrylate) is dissolved in 2-butanone (20 vol.-%). This solution is then added to the silver ink to achieve the desired ratio of silver to PMMA.

For inks containing PMMA (density of 1.18 g/cm³), the SSC by weight is much higher than for inks containing only silver particles (density of 10.49 g/cm³), when aiming for a viscosity of 10 to 25 mPas. While printable pure silver inks reach a SSC of 30 wt.-%, Ag-PMMA-inks reach a SSC of up to 50 wt.-%.

Another silver ink used (Silverjet DGP-40LT-15C) is provided by Sigma Aldrich Co. LLC., US. Curing temperatures for this ink are stated to be as low as 120 to 150 °C. This is achieved by the use of particles smaller than 50 nm. The ink is delivered ready to use with a SSC of 30-35 wt. % in triethylene glycol monomethyl ether.

Substrates

The first investigated substrate is ceramic (Rubalit 708S, CeramTec GmbH, Germany). It can easily withstand temperatures above 1000 °C.

Additionally, glass-fibre reinforced plastic (GRP) substrates are used for the experiments (PCL370HR). They are provided by Isola GmbH, Germany. The glass transition temperature is about 170 °C. However, the substrates can withstand temperatures of 260 °C for about 60 minutes. Higher temperatures and longer heating times lead to delamination of the GRP substrates.

Printing

For electrical measurements, lines are printed (width 1 pixel, 5 layers) with small contact pads at their ends (5 × 5 pixel). Drop spacing is adjusted to 140 µm. With this value best results are obtained

The measurements of film adhesion are based on weight measurements. Thus, larger areas of printed silver ink are needed for reliable results. Accordingly, areas of 42 × 42 mm² are printed on each substrate for adhesion measurements.

Sintering temperatures are applied for 30 minutes for each film and each track.

Measuring Electrical Properties

Electrical characterization in this paper is focused on the resistance of the printed silver tracks. To obtain comparable results, the resistivity is used, relating the measurement to the tracks' cross-sectional area and length (Ωmm²/m). A Keyence VHX-1000 digital microscope is used for the measurement of silver track height and width.

A LCR-Meter (ST 2826, Sourcetronic GmbH, Germany) is used for the electrical measurements.

Measuring Film Adhesion

For the measurements of film adhesion, each substrate is weighed before and after printing to obtain the exact amount of printed silver. A flask is then filled with isopropanol. After curing the substrate is placed in the liquid and then treated in the ultrasonic bath for 5 minutes at 40 °C. Detached silver particles and flakes are rinsed off the substrate. Another weighing delivers the fraction of removed silver.

Results & Discussion

Electrical Properties

For a reasonable evaluation of the achieved resistivity, a comparison with bulk silver has to be made. Bulk silver has a resistivity of 0.016 Ωmm²/m. **Figure 1** shows the resistivity of silver tracks of different solid substance compositions with 300 nm silver particles, cured at different temperatures. For an ink with 50 % silver and 50 % PMMA in its SSC by volume, resistivity ranges from 8.7 Ωmm²/m at 100 °C curing to 0.18 Ωmm²/m at 250 °C curing. Without PMMA, a resistivity of 0.06 Ωmm²/m is achieved. Thus, with PMMA minimum resistivity is about 11 times higher than the bulk resistivity, without PMMA it is about four times higher, which is slightly higher than the values reported in the introduction.

It is obvious that the trend in resistivity is similar for the pure silver solid substance and the very large polymeric fraction of 50 vol.-%. However, a conductive track is achieved at 100 °C for the ink with PMMA, whereas this is not the case for the pure silver ink. This can be attributed to the fact that the printed tracks with silver and PMMA show a more homogeneous printing appearance and, thus, a slightly better connection in the printed material overall.

Even a large fraction (50 %) of PMMA in a printed track does not impair the resistivity severely. In fact, PMMA shows to be a possible tool for achieving improved printing results. Thus, PMMA might be a suitable material for the improvement of film adhesion.

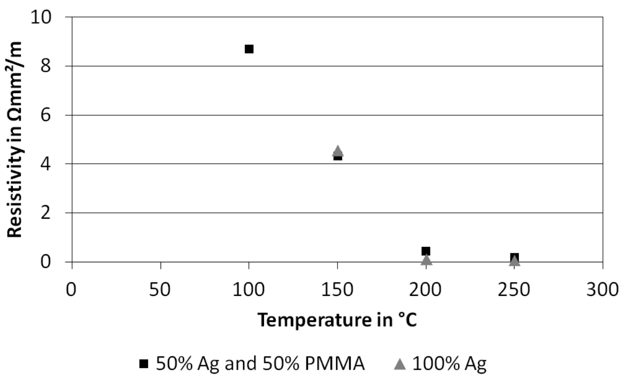

Figure 1. Resistivity of conductive tracks vs. curing temperature for 300 nm silver particles. The legend shows the composition of the solid substance content by volume.

As expected, for smaller particles lower temperatures suffice for reaching a low resistivity (**figure 2**). Here, resistivity ranges from 3.0 Ωmm²/m at 100 °C curing to 0.59 Ωmm²/m at only 200 °C curing. This means, while adding PMMA does not impair resistivity too much at low temperatures, the use of larger particles does.

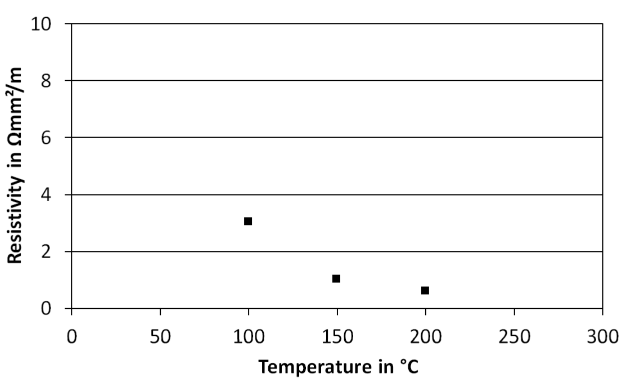

Figure 2. Resistivity of conductive tracks vs. curing temperature for 50 nm silver particles.

Film Adhesion

Film adhesion is investigated for printed structures treated at temperatures from 100 °C to 300 °C for 60 minutes. The results for an ink with 300 nm silver particles, cured at different temperatures, are shown in **figure 3**. All of the printed film is removed when temperatures of 100 °C are used. Raising the treatment temperature lowers the ratio of removed mass until a value of 200 °C is reached. At this point, almost no printed silver is removed. However, raising the treatment temperature even more leads to an increased removal of the printed film.

This results from two processes. In the lower temperature range, each step towards a higher temperature leads to stronger bonds between the particles. Temperatures above 200 °C cause even stronger sintering of the silver particles. The ratio of removed mass rises nonetheless, because the sinter shrinkage of the silver particles weakens the bond to the substrate itself. This statement is backed up by the fact that for films treated with lower temperatures, only small particles are removed from the substrate as is evident by the turbidity of the isopropanol in the ultrasonic bath. When using higher temperatures, no turbidity occurs. Instead, large flakes of silver are removed from the substrate.

The results for 300 nm particles on ceramic substrates show that for optimum adhesion to the substrate, a fairly low treatment temperature of 200 °C has to be chosen. A comparison with figure 1 shows that this temperature is very close to the temperature of minimum resistivity. This means, when aiming for the highest film adhesion, resistivity is not a limiting factor for this ink.

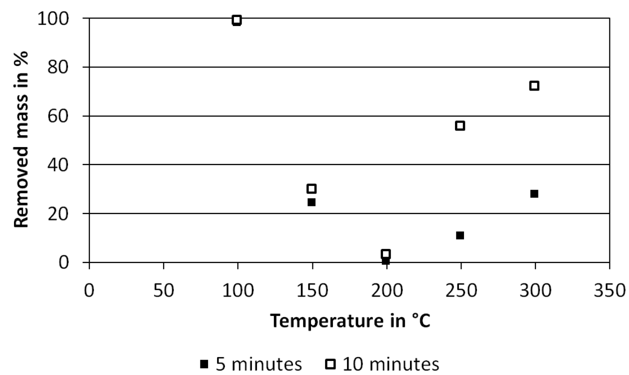

Figure 3. Removed mass fraction of 300 nm silver particle films on ceramic substrates after ultrasonic bath treatment for 5 and 10 minutes treating time vs. curing temperature.

Over the whole temperature range, the removed mass fraction is lower for 50 nm silver particles on ceramic substrates than for 300 nm silver particles (**figure 4**). Even for a treatment temperature of 50 °C, the removed mass fraction is clearly lower and the minimum for the removed mass is reached at 150 °C already. This is due to the fact that the energy used for the creation of the larger surface area of the silver powder does not have to be applied thermally after printing.

Additionally, only a very slight raise in the removed mass fraction is observed for higher temperatures. This, as well, can be explained by the smaller particles used. Here, the film removal at lower temperatures occurs in large flakes instead of small particles. This means, the temperature range in which sinter shrinkage loosens the bond to the substrate lies below the temperature of minimum removed mass. For temperatures above 150 °C, it can be assumed that a strong bond between the silver particles themselves has formed as well as to the substrate.

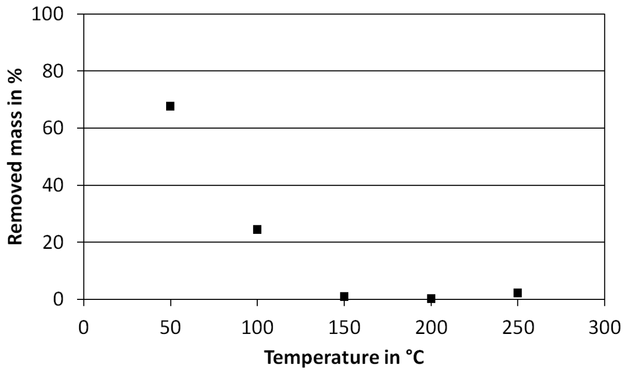

Figure 4. Removed mass fraction of 50 nm silver particle films on ceramic substrates after ultrasonic bath treatment for 5 minutes treating time vs. curing temperature.

Before reviewing the results of 300 nm silver particles on GRP, it has to be taken into consideration that GRP substrates outgas while heated (**figure 5**). The outgassing causes the GRP substrate (about 16 g) to lose a significant amount of mass (more than 40 mg at 250 °C) compared to the printed silver films (about 29 mg). To compensate for the lost mass due to outgassing, every measurement using these substrates is corrected based on the substrate mass.

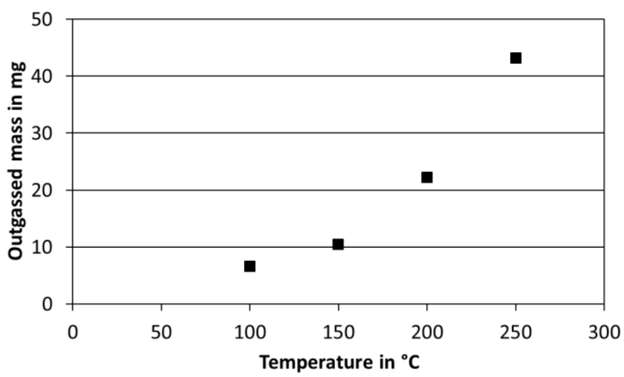

Figure 5. Lost mass due to outgassing for GRP substrates at different temperatures (30 minutes).

For the lower temperature range, the results for 300 nm silver particles on GRP are similar to those on ceramic substrates with a slightly lower removed mass fraction (**figure 6**). In the higher temperature range, there is no rise in the removed mass fraction as in the case of ceramic substrates. This can be explained by the fact that the GRP substrates are softened by the heat. Thus, the shrinking silver film can slide over the substrate surface without loosening its bond. In fact, the bond to the substrate should be even stronger for higher temperatures due to sintering of the boundary interface between silver film and GRP substrate.

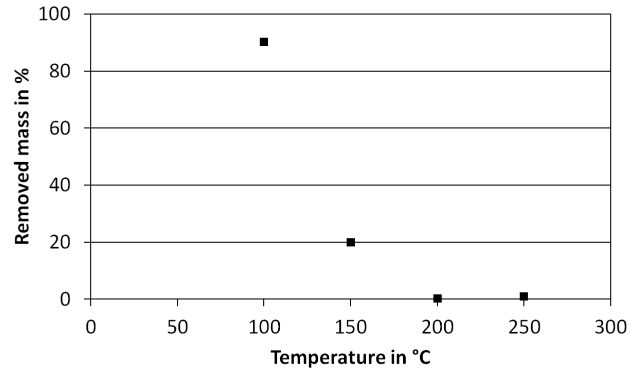

Figure 6. Removed mass fraction of 300 nm silver particle films on GRP substrates after ultrasonic bath treatment for 5 minutes treating time vs. curing temperature.

When adding PMMA to a 300 nm silver particle ink, the adhesion is expected to be stronger for the same sintering temperature. This effect is evident in **figure 7**. The removed mass fraction is reduced by the addition of PMMA as compared to the pure silver ink. The lowest temperature at which almost no part of the film is removed is reduced by almost 40 °C.

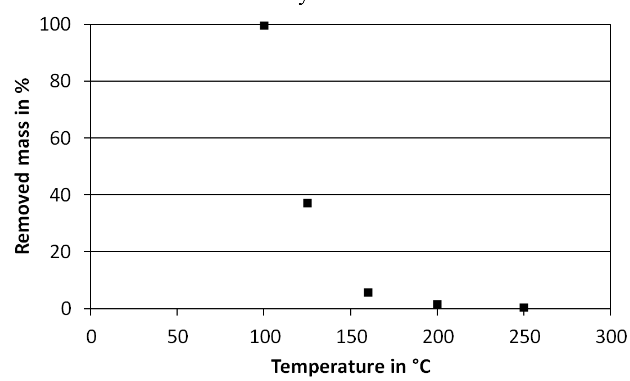

Figure 7. Removed mass fraction of 300 nm-Ag-PMMA-films (1/3 PMMA, 2/3 Ag in SSC) on ceramic substrates after ultrasonic bath treatment for 5 minutes treating time vs. curing temperature.

Conclusions

This paper presents a technique for the investigation of film adhesion suitable for inkjet printed films. Printed films are treated in an ultrasonic bath. The measurement of the removed weight is used as an indicator for film adhesion.

As shown, adhesion as measured by the presented ultrasonic bath method strongly depends on the used ink and substrate. The minimum of removed material is reached for temperatures far below 250 °C for all used inks. Overall, higher temperatures lead to stronger adhesion. However, stress in the film due to sinter shrinkage can lead to large flakes breaking off the substrate for certain combinations of substrate and ink.

Substrates that soften at the applied temperature can help improve adhesion. This is shown by the use of GRP substrates. There, the soft substrate loosens the stress induced in the film due to sinter shrinkage.

Comparing smaller (50 nm) and larger (300 nm) particles concerning their adhesion after low temperature sintering, the expected results emerge. Larger particles need higher temperatures for sintering and, thus, for low resistivity and high adhesion.

The effects of adding PMMA to conductive silver inks are investigated. It is shown that even large amounts of PMMA do not impair the resistivity of conductive tracks severely. In fact, PMMA can improve printing results and, more importantly, PMMA can improve film adhesion. Thus, not only the use of smaller particles should be taken into consideration when it comes to low temperature processes in inkjet printing. The use of small particles in combination with polymeric adhesives might reduce the needed temperature even more. The advantage over other techniques is that no chemical after-treatment or other additional equipment is needed.

Future investigations will consider conductive polymers. Such polymers are expected to deliver even better results concerning resistivity while maintaining the PMMA's advantage of strong adhesion at low temperatures.

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Author Biography

Andreas Rathjen obtained his diploma in physics at the University of Hamburg, Germany, in 2010. He has been a research associate at the Institute of Automation Technology of the Helmut Schmidt University since 2011. His work concentrates on reduced curing temperatures for printed electronics and process development.

