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Laser Sintering of Silver Ink for Generation of Embedded Electronic Circuits in Stereolithography Parts

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Abstract

The requirements for mechatronic devices in terms of functionality, integration density and costs have risen according to the different application areas whereby a high demand for complex mechatronic modules exists. Furthermore, fast implementation of mechatronic modules in series production requires functional prototypes in the early stages of the development process. However, the manufacturing technology offers several methods which are suitable for prototype and small series production. In this context, the stereolithography (SLA) is a suitable technology, which can be used for production of functional prototypes. The layer-wise building process by means of laser polymerization of resin offers the integration of e.g. sensor functions without thermal damaging and opens up new possibilities for the realization of multi-functional components with high integration density. In addition, embedding of electronic circuits provides protection against environmental influences. The following paper presents a hybrid manufacturing technology that combines stereolithography and dispensing system technologies to fabricate mechatronic devices with embedded electronic circuits. This so-called embedding stereolithography (eSLA) requires a flexible and modular system technology which allows continuing the layer-wise process after integration of the electronic circuit. In order to fulfill this requirement, the laser sintering of silver filled conductive adhesive is an appropriate method to create conductive circuits directly after dispensing on the current surface of parts. Additionally, the placement of the electronic components could be realized by preformed cavities of SLA parts and the contacting of them could be done in situ by laser radiation. Thereby, the conductive adhesive is used like solder for fixing and contacting the components. In this paper, the laser sintering of conductive adhesive on SLA parts using UV-laser radiation ($\lambda = 355 \text{ nm}$) is investigated regarding the transition resistance

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of contacted components by four point measurement and the characterization of laser contacted components by cross sections. The investigations are intended to evaluate the beam-matter-interaction of the silver filled conductive adhesive and the UV-laser radiation by an optical analysis of the material, the curing behavior and the long-term stability of the contacting under environmental stresses.

Keywords: Embedding Stereolithography, additive manufacturing, embedded electronic circuit, silver filled conductive adhesive, laser sintering

1. Introduction

In the development and production of mechatronic modules companies are exposed increasing demands in terms of miniaturization, integration of functions and reliability. The use of innovative technology is a key factor to meet these requirements [1]. The currently most common used technology for prototype and series production of 3-D MID (Molded Interconnect Devices) is the LDS process (Laser Direct Structuring). The injection-molded substrate is doped with a laser additive and the surface is subsequently irradiated by a laser beam. Here a local activation of the surface takes place. Subsequently, the activated substrates are putted in a chemical metallization bath whereby a deposition of copper particles occurs at the activated structures of the substrate. A subsequent galvanic finishing process of the copper structures is resulting in an increasing of conductive circuit layer thickness. However, a disadvantage of this technology is that the integration of conductive circuits or electronic components can take place only at the surface. Thus, the component assembly of MIDs is limited by their available surface area. In contrast, Rapid prototyping methods such as solid freeform fabrication (SFF) and layered manufacturing (LM) allow the production of complex 3D components, a flexible design of the part shape and a high accessibility to the part during the building process. Moreover there is the possibility starting and stopping the additive building process. This process feature enables the integration of electronic components and conductive circuits by pick and place systems and direct writing (DW) for example in the matrix of the part [2]. Due to its high build resolution stereolithography is one of the most widely used RP technologies to manufacture highly complex and accurate 3D prototypes [3]. The possibilities for the integration of conductive circuits and electronic components in the 3D matrix are very flexible and at the same time, components can be embedded in different heights of the components instead of only next to each other. This leads to a reduction in size of the mechatronic device and the overall circuit. The adhesive of the conductive circuits can be increased and components can be protected from environmental influences compared with common Printed Circuit Boards design (PCB). In recent years the materials development for SLA and other RP technologies were focused on improving material strength, durability and thermal property. This has generated interest in many areas of research such as rapid manufacturing of fully functional embedded mechatronic devices [3]. The following investigations show that the embedded stereolithography could provide a solution for a direct integration of functional components and the generation of functional mechatronic modules. Because of the automatic, layered design of the parts it is possible to produce 3D components with a large number of variants combined with a maximum flexibility in quantity. Moreover the SLA-process enables creation of parts with a high surface quality and using high temperature resistant resin materials.

2. Embedding stereolithography

Stereolithography enables the fabrication of a part from a designed CAD model. The digital data of this model has to be placed in the virtual building space of the stereolithography machine. Further support is

generated automatically by data preprocessing software. As the building operation is performed layer wise, the geometrical data of the part and the support construction has to be sliced in adequate digital layers with a height of typically 0.1 mm. Each of these layers is fabricated by spreading a liquid photo-resin over the building platform with a coating system. Afterwards an UV-laser beam ($\lambda = 355 \text{ nm}$) is used to cure the material on the resin surface according to the given layer information. Finally the building platform is lowered. By repeating this procedure the complete component is created layer by layer.

On basis of conventional SLA a new hybrid production technology is investigated, which enables the integration and joining of electronic components during the SLA-process by means of stereolithography and laser sintering of silver ink. At first a housing shell with cavities is created by conventional SLA. In these cavities functional electronic components can be placed after removing the fluid resin of the cavities by laser ablation. In the next step, the functional components can be connected with fluid silver ink using a micro dispensing system. The fluid silver ink is exposed by laser radiation ($\lambda = 355 \text{ nm}$) and sinters subsequently. After sintering process, the upper housing of the components is fabricated by continuing the building process, see Fig. 1. It is important to note that the embedded structures as well as the components must not overtop the current top layer of the part. Otherwise there is a collision between coating system and integrated components respectively conductive circuits. By using vias or plated through-holes it is possible to create conductive joints to conductive circuits in upper layers of the SLA-part. Vias can be also created by laser ablation during the building process.

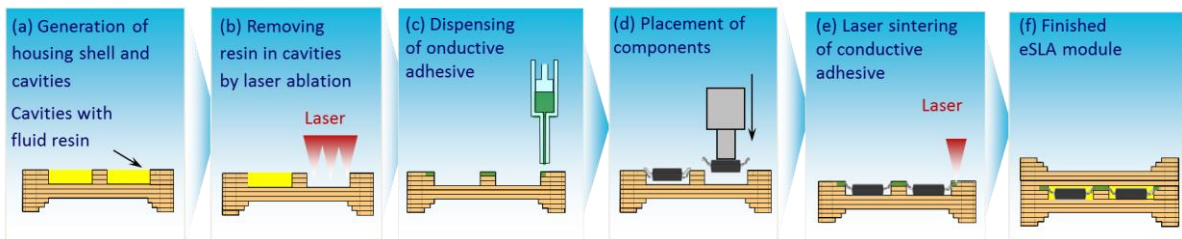


Fig. 1. (a) Generation of housing shell; (b) Removing of resin residues by laser ablation; (c) Dispensing of silver ink; (d) Placement of components; (e) Laser sintering; (f) Continuing of the process and finishing

3. Materials and systems

3.1. Resin

The utilized material is an epoxy-based SLA-resin which approximately achieves the mechanical and thermal properties of technical plastics in electronic production. The used SLA-resin in this work is Somos NanoTool (DSM) which enables the production of parts with a high stiffness and a high temperature resistance (up to 263 °C).

3.2. Silver ink

A single component (1 K) silver ink (Elecolit 3043, Co. Panacol) is used in experiments. The amount of the silver particles in the silver ink is approximately 80 wt.-% and the viscosity is 4.0 to 5.0 Pa·s. The small size of the silver particles with $< 10 \mu\text{m}$ and the low viscosity allows dosing by means of a micro dispensing system. The common sintering process of the silver ink is realized by oven sintering at 110 to 150 °C for 10 to 30 minutes.

3.3. Laser system

The laser beam source used for laser sintering is a pulsed solid state laser (Nd:YVO4) with wavelength of 355 nm. The maximum nominal power is 3 W at a frequency of 40 kHz. The sintering process of the silver ink is carried out with focused ($d_f = 50 \mu\text{m}$), defocused ($d_f = 75 \mu\text{m}$) and highly defocused ($d_f = 100 \mu\text{m}$) diameters.

4. Experimental results and discussion

4.1. Optical analysis

For the direct production of electrically conductive structures the curing of the silver ink is performed by a downstream laser irradiation after application by means of micro dispensing system. Achieving a fast curing of the silver ink, the irradiation by means of laser radiation is performed at 355 nm, because there is very high absorption in the ultraviolet spectral range, see Fig. 2. For this reason, a very high heating and a rapid sintering of the silver ink is expected by laser exposure using a wavelength of 355 nm. The Figure 2 shows the measurement of the absorption of the used silver ink with a layer thickness of approximately 26 μm and of the substrate material Somos NanoTool.

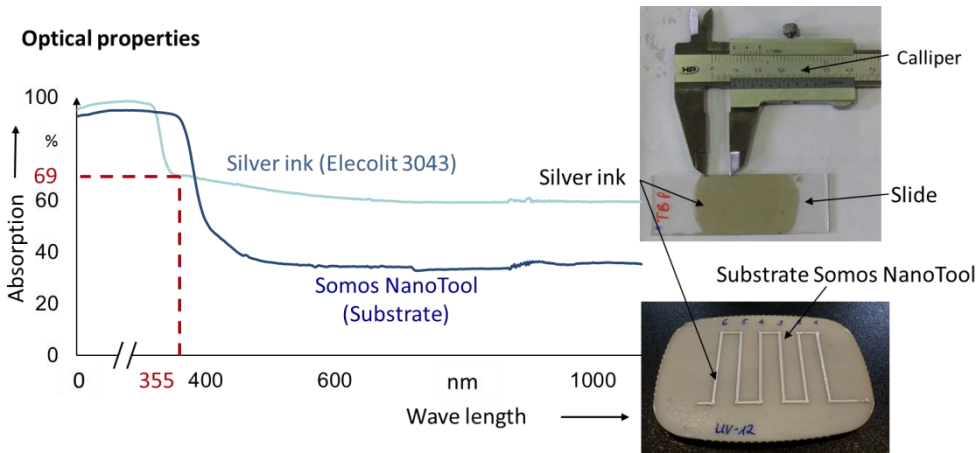


Fig. 2. Optical analysis of silver ink Elecolit 3043 and Somos NanoTool

The silver ink was applied in the liquid state for measuring on a glass slide. The falsification of the result of the absorption coefficient of silver ink in the range 200-322 nm is due to the high absorption of the glass slide in this wavelength range, see Fig.2.

4.2. Beam-matter-interaction

The downstream sintering process of the silver ink by means of laser exposure should take place as quickly as possible. In addition, it is desirable using small number of laser scans for sintering the silver ink to have a stable and reproducible process. The absorption of an incoming laser beam on the silver ink is affected by a combination of 3 mechanisms / methods [4]. First, the absorption takes place by the epoxy based resin surrounding the silver particles. Then, the absorption by the silver particles themselves takes place, and thirdly, the absorption of the radiation occurring by effects of reflection at silver particles and resin takes influence on the sintering process. Because of this combination of different laser beam matter interactions, the absorption of laser radiation takes place in the uppermost microns of the applied structure, see Fig. 3 [4]. Any further heating below this layer is resulted by heat convection and not by laser beam absorption [5]. Due to the heat accumulation in the deep regions of the applied layer evaporation of volatile organic compounds is achieved. For curing of silver ink, a substrate has to have low thermal conductivity in order to achieve a sufficiently long heating of the silver ink in the lower regions near the substrate material [6, 7]. Using substrates having a high thermal conductivity would lead to rapid dissipation of heat and thus results in incomplete curing of the silver ink and a bad connection to the substrate [4]. The thermal conductivity of Somos NanoTool is 0.47 W/m·K. This is very low compared to metal particle filled plastics with 15 – 20 W/m·K for example [8]. Materials having a relatively high thermal conductivity such as metal particle filled plastics are characterized by higher heat dissipation when locally exposed by laser irradiation compared to non-filled plastics. This results in an increased temperature drop at the substrate-ink interface making it more difficult to cure the ink in this area [4]. The result is a structure, which is cured in the upper area by laser irradiation. However, in the lower part the silver ink near to the substrate is still liquid. In contrast, the use of a thermally insulating substrate effects sufficient heat accumulation in the interface silver ink/substrate during irradiation. Thereby curing of silver ink in deeper regions of the layer can be achieved, because the accumulated heat supports the sintering process. At the same time low laser intensities may be used for curing.

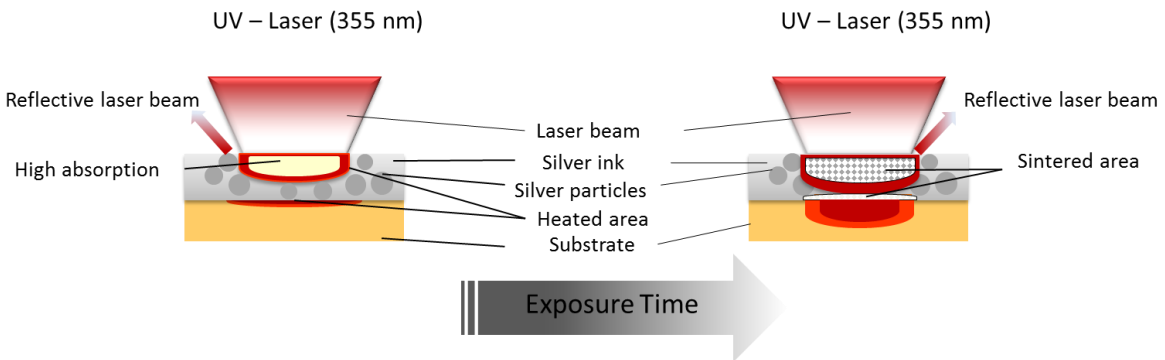


Fig. 3. Beam matter interaction of silver ink exposed by UV-355 nm laser radiation

The generated conductive circuits in the test have a width of about 800 μm and a height of about 200 μm , as shown in Fig. 4. The substrate material is cleaned and dried before dispensing the silver ink on it. The surface of the substrate must be free of particles to avoid unwanted absorption effects during laser irradiation. Preliminary investigations have shown that the heat generated in the interface silver ink/substrate is sufficiently high only by focused laser irradiation and at the same time by small laser scan velocities, see Fig. 4. The number of scans is constant at $n = 2$ to achieve a complete sintering of the silver

ink. A higher number of scans lead in the experiments to thermal damage in the upper regions of the silver ink. The necessary line energy E_s for curing the dispensed silver ink is up to 1.4 J/mm. This leads to very high thermal heating, which results in blistering in the material. Responsible for this effect is the rapid evaporation of volatile organic compounds (volatile solvent), which takes place in localized arrangement through bubble or pore formation [4]. The consequence is a porous and bloated structure due to the formation of pores. In addition, there is small ablation in the top material region, as shown in Fig. 4. The laser emits centered on the applied silver ink and is moved through a scanner system along the applied structure. By the use of laser intensities lower than 0.7 J/mm and a change of the irradiation strategy from linearly toward meander shape a sufficient curing of the silver ink cannot be achieved. The criterion "no cured" describes the appearance of grease at the interconnection or moving the conductor on the substrate at low pressure. In addition, the use of higher laser intensities than 2.2 J/mm results in stronger ablation and in thermal damage to the entire interconnection. The bubble or pore formation is increased and the porosity increases additionally.

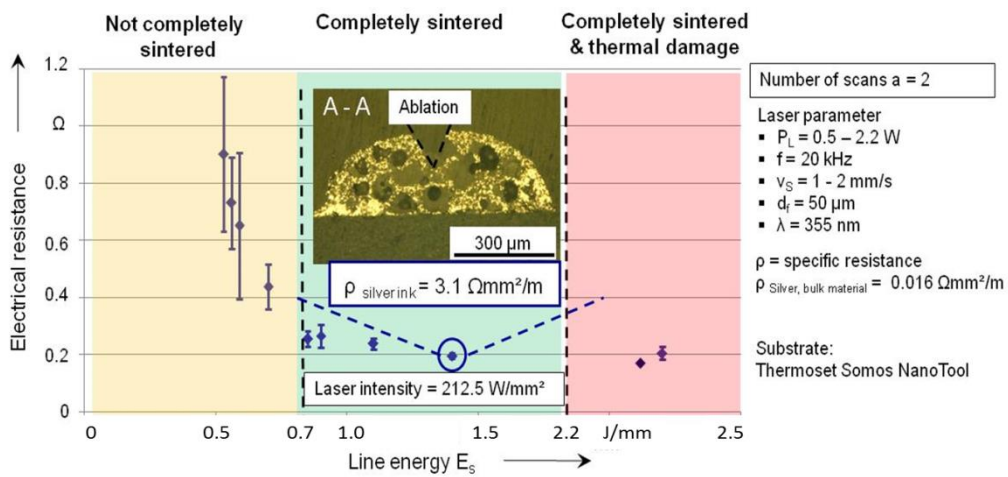


Fig. 4. Influence of line energy E_s on electrical resistance

The influence of the absorption coefficient of the substrate material is negligible due to the very high surface absorption of silver ink at a wavelength of 355 nm. However, the low thermal conductivity of the substrate material is decisive for giving a sintering of the silver particles at the interface silver ink/substrate.

4.3. Contacting of electrical components

The contacting of electronic components by means of silver inks is mostly carried out by diode laser [9]. The laser irradiation in the infrared range enables uniform heating of the silver ink and the electronic component due to the absorption behavior. This leads to a low thermal stress for the materials. However, the contacting of electronic components by means of UV laser radiation leads to a high thermal stress for the materials, because the UV radiation is absorbed near the surface [9]. Therefore, a uniform heating of component and silver ink is difficult to achieve.

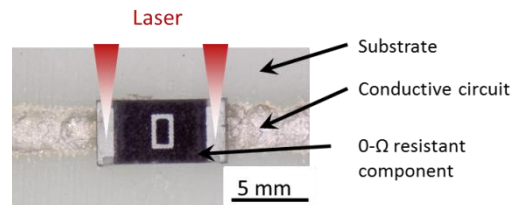
The process chain for contacting the components in the investigations is similar to the process in the 3-D MID serial production. First, dispensing of the connection medium (silver ink) is carried out. Then placing of components and finally joining of both partners by laser irradiation. The laser irradiation is carried out using

single-point method in the following tests. Joinings are made at the two contacts of a 0-Ω resistor component. Here, the connections are created one at a time. The used UV-355 nm is the same as for sintering experiments. The absorption of the laser radiation is on the metal tab, as shown in Fig. 5. For this reason the largest heat generation is on the surface of the metal tab, which is visible by development of annealing colours. By heat diffusion, the heat energy is transferred to the silver ink. Thus, the silver ink is heated and sintered indirectly.

In the experiments carried out with the 0-Ω resistor components, the frequency parameter is held constant at $f = 20$ kHz. The parameters laser power P_L , exposure time t_e and focus diameter d_f are varied, see Table 1. The aim of the parameter study is the creation of a thermally undamaged and adherent contact with low transition resistance. To evaluate the quality of the joinings an optical analysis is performed by cross-sections in addition to the measurement of the transition resistance. Furthermore, a shear test is used to determine the adhesive strength of the contacts, see Fig. 5. In carrying out the test, a shear blade shears orthogonal to the surface of the contacted component. The occurring shear forces are detected in N (Newton). The fracture pattern are analyzed and evaluated as a function of the used contacting parameters.

Table 1. Test plan for contacting 0-Ω resistant component by means of UV-355 nm laser

Substrate	SomosNanoTool
Electrical component	0-Ω resistant component, type CR1206
Interconnection medium	Silver ink - Elecolit 3043
Process parameters	$P_L = 2.7 / 3.25 / 3.42 / 3.87$ W $t_e = 400 / 600 / 800$ ms $f = 20$ kHz focused ($d_f = 50$ μm) defocused ($d_f = 75$ μm) highly defocused ($d_f = 100$ μm)



In addition, the measurement of the transition resistance and the adhesion of contacted 0-Ω resistor components is carried out in response to a damp heat test (85 °C @ relative humidity of 85 %) and a thermal shock test (-40/+125 °C). These tests are intended to realize an accelerated aging of the contacts. Thus, a statement about the long-term reliability can be made.

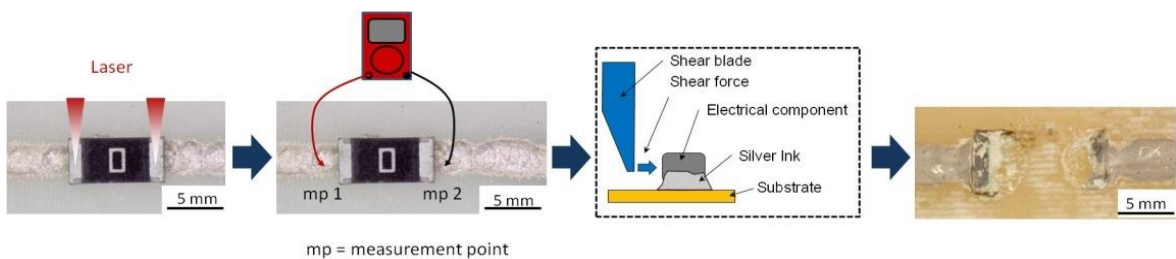


Fig. 5. Proceeding of creating contacts by UV-355 nm laser exposure and their electrical and mechanical characterization

Figure 6 shows the electrical transition resistance of contacts in dependence of the focus position and the laser power P_L . It has been shown in the experiments, that an exposure time of $t_e = 600$ ms in combination with different laser powers P_L is sufficient to create adhering and electric conductive contacts by using the following focus diameters $d_f = 50$ μm (focused), $d_f = 75$ μm (defocused) and $d_f = 100$ μm (defocused), see

Fig. 6. For this reason, the results in Figure 6 are shown using an exposure time of $t_e = 600$ ms. The variation of the focus diameter has great influence on the thermal damage to the contacted component. Upon irradiation of components in the focus ablation and carbonization of the metal tab can be clearly seen in all experiments. By using a laser power of $P_L = 3.42$ W and an irradiation in focus leads to a functional damage to the component, as shown in Fig. 6. This effect shows that the used laser intensity is too high. However, irradiation with strongly defocused adjustment results in clearly reduced thermal damage to the components. The contact resistance of the contacted components increases yet. The reason is that the heat generation achieved by irradiation with strong defocused laser beam diameter is too low and therefore the silver ink will not fully sintered. The remaining residues of volatile organic compounds in the silver ink result in lower electrical conductivity and poor adhesion behavior. A variation of the irradiation time t_e or the laser power P_L has been no improvement of these negative effects within the investigation.

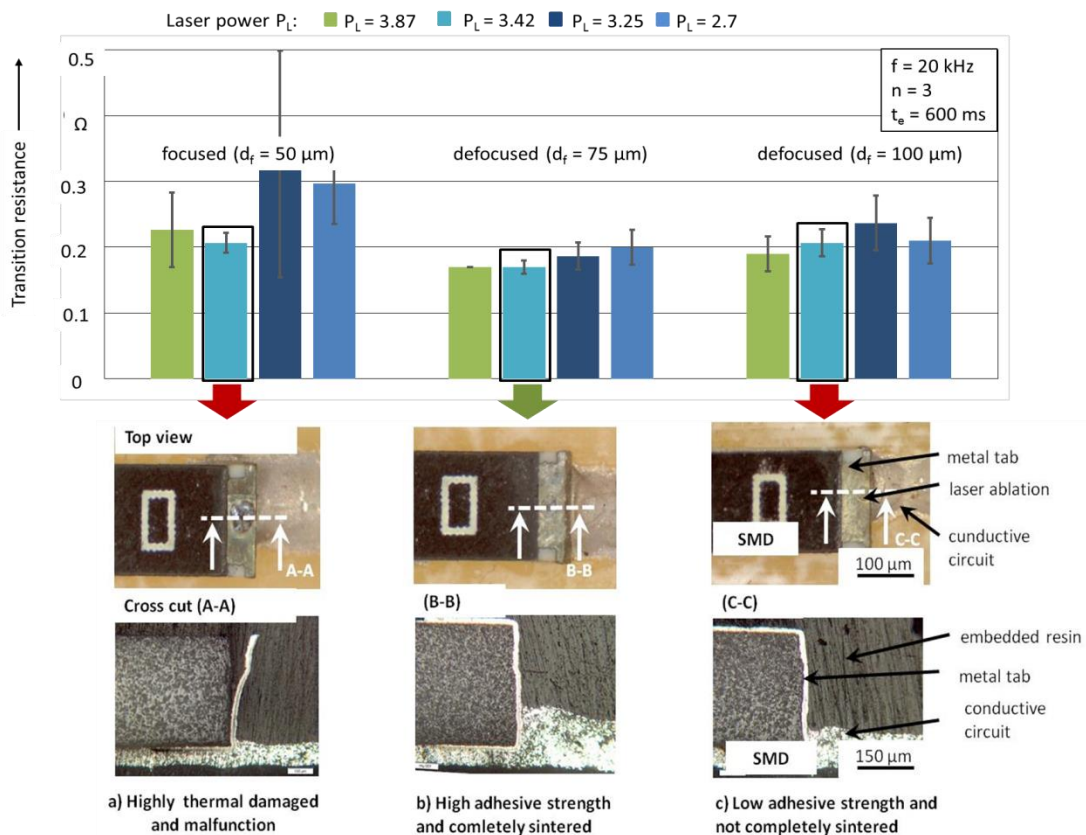


Fig. 6. Influence of laser power P_L on transition resistance

However, the contacting of the components with defocused laser diameter ($d_f = 75 \mu\text{m}$) shows sufficiently well test results for use in electronic applications. Depending on the laser power P_L the transition resistance of the contacts is between 0.17 and 0.20 Ω. At the same time low standard deviations are detected within the test series. This suggests a stable process. Additionally Figure 6 shows an ablation and a

sign of annealing colors on the surface of the metal plate. However, this effect could not be completely prevented within the complete test series, despite varying the exposure time t_e and the laser power P_L .

4.4. Environmental stress tests

To examine the reliability of the contacts a standardized damp-heat test at 85 °C and relative humidity at 85 % for 250 hours and a thermal shock test at -40/+125 °C for 750 cycles is performed. All generated contacts, which were made with the parameters in Table 1, are examined in these tests for artificial aging. The tested contacts in Figure 7 were irradiated with a laser power of $P_L = 3.42$ W and an exposure duration of $t_e = 600$ ms. In addition, for ease of illustration only the contacts which were exposed by defocused ($d_f = 75$ μm) laser beam are presented in Fig.7. These showed in comparison to the contacts, which were exposed in focus ($d_f = 50$ μm) and defocused ($d_f = 100$ μm), the best results after the tests of artificial aging.

Laser parameters: Laser power $P_L = 3,42$ W, defocused ($d_f = 75$ μm)

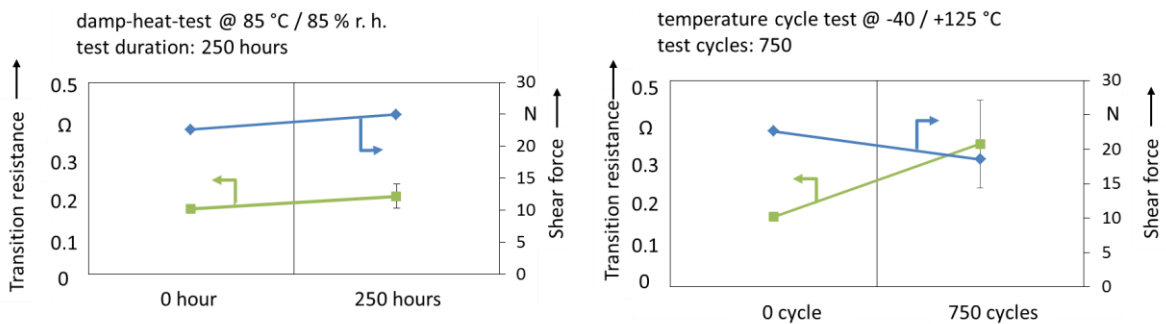


Fig. 7. Influence of environmental stress tests on transition resistance

To make any statement about the durability of the contacts, measurement of contact resistance and adhesion strength is carried out after environmental stress tests. The contacts after the damp heat test show a slight increase of the contact resistance after 250 hours of exposure. One reason for this is the storage of moisture in the sintered conductor structure. This effect causes a poorer transmission of currents between the individual silver particles and thereby an increase in the electrical resistance. Furthermore, an increase in the adhesive strength of the contacts after the damp heat test is noted. Outsourcing of 250 hours at a constant high temperature of 85 °C can lead to a further sintering of the silver ink and thereby a better adhesion to substrate and component. A corrosion of the conducting circuits by high humidity during the test cannot be found. The measurement of transition resistance of contacts after thermal shock test shows a strong increase by more than 100 percent after 750 cycles. Furthermore, a slight decrease in adhesive strength can be seen. The fracture pattern after shearing of the components of the substrate surface shows, that large parts of the interconnect structure are sheared together with the component. This fracture pattern results in the different coefficients of thermal expansion (CTE) of the substrate and silver ink, which leads to high shear forces at the interface silver ink / substrate during the change of temperature from -40 to 125 °C. This results in the formation of micro cracks in the sintered conductive structure. These micro cracks lead to a degradation of the adhesive strength of the component on the substrate. In addition, they contribute to an increase in electrical resistance.

5. Conclusion

A new approach for flexible manufacturing of mechatronic modules by combining stereolithography and UV-laser sintering of silver ink is presented. The investigations show the feasibility of in situ generation of conductive circuits and contacts of using UV-laser ($\lambda = 355 \text{ nm}$). The irradiation with high laser intensities and the near surface absorption of the UV-laser radiation results in a strong heating of the silver ink. The material is sintered by heat transfer and gets electrically conductive. The high line energies of $E_s = 1.4 \text{ J/mm}$ leads to an immediate evaporation of the volatile organic compounds in the material which results in formation of pores. The consequence is a porous and bloated structure due to the formation of pores inside the silver ink. Joining the components is carried out by irradiating the metal tabs of electronic components (SMD). By heat transfer the silver ink is sintered and generates an adhesive, electrically conductive contact. By this type of contacting, local temperature peaks occur and indications of thermal damage and annealing colors on the electronic component are visible. The best results are achieved with a defocused exposure ($d_f = 75 \text{ }\mu\text{m}$) and an exposure time of $t_e = 600 \text{ ms}$. By using this laser parameter, contacts with a transition resistance of $0.2 \text{ }\Omega$ can be generated. Moreover, a small ablation of the metal tab and slight signs of annealing colors are visible, which have not any negative affect on the joining.

The test of artificial aging should give an estimation of the long-term stability of the generated contacts. After a simulated environmental stress by damp heat test, there was a deposition of moisture in the interconnect structure and thereby a decrease in conductivity. At the same time a further sintering of the silver ink could take place by the influence of constant temperature of $85 \text{ }^\circ\text{C}$ for 250 hours. This leads to an increase of the adhesive strength of the components. In addition a thermal shock test at $-40 / +125 \text{ }^\circ\text{C}$ was carried out for 750 cycles in experiments to study the long-term reliability. The analysis of the results shows an increase of transition resistance and a reduction of adhesive strength of the contacts. This is due to the high thermal shock stress in combination with a high CTE-mismatch between substrate and conducted circuit. This results in high shear forces in the interface substrate/conductive circuit, which cause micro cracks within the sintered silver ink. These micro cracks lead to mechanical degradation of the adhesion strength and an increase in electrical resistance. At the same time, the specific electrical conductivity of the conductive circuits generated by sintering of silver ink conductor tracks by means of laser is also less

The generated conductive structures in this work are primarily intended for the transmission of signal streams. However, a comparison with other technologies concerning the generation of conductive structures for 3-D MID components, such as the LDS technology, is limited. A direct comparison of the two technologies shows that the values measured for adhesion strength of conductive circuits and electronic components are lower in this work, as those which are obtained by means of LDS technology. However, a great advantage of this technology is that the conductive structures can be created directly on the substrate without downstream process steps such as oven sintering or chemical metallization. Thus, it is possible to integrate these electrical structures in components during rapid prototyping process. In this context, these structures can be embedded in the matrix of the component and protected from environmental influences. Therefore, the adhesive strength is not a decisive criterion feature. The electrical conductivity may also be increased by generating higher layer thicknesses.

In further work, the generation of conductive circuits and contacts is examined by exposure with diode laser ($\lambda \approx 1\mu\text{m}$). The lower absorption of the silver particle ink using this wave length should result in reduction of thermal damage. The lower laser intensity, caused by the larger focus diameter ($d_f \approx 600 \text{ }\mu\text{m}$) should also lead to uniform heating of the SMDs during contacting process.

References

- [1] J. Franke, J. Gausemeier, C. Goth and R. Dumitrescu, MID-Studie 2011 - Markt- und Technologieanalyse, Paderborn: Studie im Auftrag der Forschungsvereinigung Räumliche Elektronische Baugruppen 3-D MID e.V., 2011.
- [2] F. Medina, A. Lopes, A. Inamdar, R. Hennessey, B. C. J. Palmer, D. Davis, P. Gallegos and R. Wicker, Hybrid Manufacturing: Integration Direct Writing and Stereolithography, El Paso, Texas, 2005.
- [3] A. Lopes, M. Navarrete, F. Medina, J. Palmer, E. MacDonald and R. Wicker, Expanding Rapid Prototyping for Electronic Systems Integration of Arbitrary Form, El Paso, Texas, 2006.
- [4] E. Fearon, T. Sato, D. Wellburn, K. G. Watkins and G. Dearden, Thermal effects of substrate materials used in the laser curing of particulate silver inks, Proceedings of Lane, 2007.
- [5] R. Jardini, M. A. Maciel, S. R. A. Scarparo and L. Moura, "Improvement of the spatial resolution of properties using infrared laser stereolithography on thermosensitive resin," *Journal of Materials Processing Technology*, Volume 172, pp. 104-109, 20 February 2006.
- [6] J. Chung, K. Seunghwan, C. P. Grigoropoulos, C. Dockendorf and D. Poulikakos, "Damage-free low temperature pulsed laser printing of gold nanoinks on polymers," *Journal of heat Transfer*, Volume 127, pp. 724-732, 7 July 2005.
- [7] J. Chung, K. Seunghawn, N. R. Bieri, P. Costas and D. Poulikakos, "Conductor microstructures by laser curing of printed gold nanoparticles ink," *Applied Physics Letters*; Volume 84, pp. 801-803, 2 February 2004.
- [8] C. Heinle, Simulationsgestützte Entwicklung von Bauteilen aus wärmeleitenden Kunststoffen, Erlangen: Dissertation, 2012.