1,8-Octanedithiol as an Effective Intermediate Layer for Deposition of Cu Electrodes via Inkjet Printing and Laser Sintering on III–V Triple-Junction Solar Cells

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This research study combines surface modification techniques with back-end-of-line (BEOL) methods for cost-effective, scalable front contact electrode deposition on III–V solar cells. Copper nanoparticle grids are deposited by inkjet printing on surface-modified III–V solar cells. The deposition of a self-assembled monolayer (such as 1,8-octanedithiol) as an intermediate layer is a proven method for surface modification to improve the wettability of the substrate surface and the adhesion of the printed copper nanoparticle structures on the substrate to perform inkjet printing of coherent and narrow electrode structures. Then, the printed copper ink is converted to a conductive copper grid by a picosecond pulsed laser with optimized settings and an additional galvanic plating step is required for the thickening of inkjet-printed and laser-sintered seeding layer for solar cell applications. As a result, an ohmic copper contact on III–V layer with low contact resistivity (5 mΩ cm²) is realized successfully. The processed solar cell shows a functioning behavior with 20% conversion efficiency.

1. Introduction

Power conversion efficiencies (PCE) of solar cells based on III–V semiconductors, like gallium arsenide (GaAs), are the highest among commercially available solar cells.[1,2] For example, one of the highest efficiencies reported for III–V/Si tandem cells had a conversion efficiency of 35.9% measured at AM 1.5G.[2] However, III–V devices are produced using comparatively costly processes, including the costs for layer deposition tools, deposition conditions, batch size, deposition precursors, process time, and back and front contact metallization.[3] Thus, reducing their high manufacturing costs is essential to make these devices winning competitors to other commercial photovoltaics.[3]

As mentioned earlier, one of the cost drivers in III–V solar cell fabrication is their front contact electrodes and their deposition methods.[4] Therefore, the application of low-cost front contact processes and materials has attracted many research interests.[4,5] Among different low-cost materials, copper (Cu) nanoparticle (NP) inks are possible candidates as low-cost electrodes for III–V semiconductor-based solar cells.[6] Recently, they have been applied considerably as electrode materials for various electronics (e.g., solar cells) due to their low production cost compared with silver or other noble metals.[6–12]

Two III–V-based substrate types were used in this research work. The first one consists of a III–V triple-junction solar cell architecture with a layer sequence of GaAs(cap layer)/AlInP(window layer)/GaInP(top cell)/GaInAs(middle cell)/Ge(bottom cell) and the other one is III–V GaAs wafer with a layer sequence of GaAs(cap layer)/AlInP(window layer)/GaAs substrate. These substrates both have a similar cap and window layer as the top-most layers. As the interaction between the front contact grid and GaAs cap layer governs the contact’s electrical behavior, the process development tests were first done on III–V GaAs wafer. Then, the optimized front contact deposition process was applied to III–V triple-junction solar cell to evaluate the solar conversion efficiency. The GaAs thin film used as a cap layer is grown in the epitaxy process and is required for providing a reliable electrical interconnection between the window layer and the metallic electrodes. The window layer is used to form a p–n junction with the absorber layer (cell).

A fundamental factor in contact formation is the adhesion of Cu NP ink electrodes on the substrate.[13] For this purpose, modification methods for enhancing the adhesion of metal ink on a substrate include mixing additives such as polymers, surfactants, and silanes to the ink and modifying the chemical properties of the substrate.[13–17] As these approaches might increase the contact resistivity of metal on the substrate, it is important to optimize them to achieve well-defined deposited structures with strong adhesion and low contact resistivity.[13]

Besides poor adhesion, the diffusion tendency of Cu atoms or ions into the semiconductor such as GaAs has also become a critical problem for applying Cu as an electrode on III–V solar cells featuring GaAs as a cap layer, similar to samples in our...
study. Therefore, adhesion improvers acting as diffusion barriers for Cu contacts on GaAs cap layer are required. Diffusion barriers are mostly inorganic layers such as Ni, Ti, TiN, and TaN. However, organic layers with head and terminal groups of thiol, amine, halide, alkyl, and silanes have also attracted research interest in recent years for their application as diffusion barriers and adhesion improvers.

For deposition of inorganic intermediate layers, standard methods are evaporation methods under high vacuum, considered high-cost processes. For surface modification with organic layers, besides the costly evaporation methods, a conventional cost-effective method is the solution-based deposition of a self-assembled monolayer (SAM) with controlled thickness to avoid increased contact resistivity and surface damage.

In addition, organic SAMs are considered adequate intermediate layers for the deposition of Cu on semiconductors. The SAM molecules are composed of three groups: head, terminal, and spacer (Figure 1). The head and terminal groups must have high affinities to attach to the substrate and conductive metal. In this respect, Cu’s considerable adhesion improvement on GaAs was already shown by applying organic SAMs that modify and control the semiconductor surface properties during Cu structuring processes. Another benefit of the organic intermediate layers is that they can be applied as a monolayer on the surface with a thickness of several angstroms rather than several hundred nanometers typical for inorganic intermediate layers.

To select the proper SAM molecule for intermediate layer formation, its head group’s selectivity, bonding to the metal and substrate, and packing density must be considered. Of the organic candidates for the head and terminal groups, such as carboxylic acids, thiol, amine, chloride, bromide, cyanide, and alkyl, the most popular ones for contacting Cu on semiconductors are thiol- and amine-terminated SAMs due to their high affinity to attach to Cu. Among the thiol-terminated SAM molecules, 1,8-octanedithiol (ODT) is used widely as an intermediate layer for metal/GaAs interface. Due to having thiol groups on both sides, ODT can form a covalent bond to GaAs and Cu, leading to enhanced adhesion of Cu on GaAs. Felmet et al. applied ODT for patterning Cu directly on GaAs, yielding a resistivity of $3.1 \times 10^{-7} \Omega \text{m}$.

Besides the low-cost electrode materials, low-cost BEOL processes, such as inkjet printing for deposition of Cu front electrodes, are beneficial replacements for expensive, standard front contact processes like photolithography and metal evaporation. In this context, we focus on drop-on-demand inkjet printing for the presented work as it provides a more controlled printing process than continuous inkjet printing. However, many factors play vital roles in applying inkjet-printed electrodes as electrical contacts. For instance, the ink has to show good printability, high conductivity, and low contact resistivity to be used as front contacts on solar cells. The main challenges for printing electrodes with adjusted shape and thickness are modifying the adhesion of printed structures and the ink’s wetting behavior on the semiconductor.

As a result, the ink’s wetting behavior is controlled by adjusting the surface hydrophilicity/hydrophobicity via surface treatments. These surface treatments might include dip or spin coating of solvents or chemicals, UV irradiation, plasma treatments, and organic and inorganic layer deposition processes. Also, the modification of substrate surface wettability is performed carefully to avoid printing with low resolution, droplet merge, or line bulge.

Moreover, Cu NPs in the respective inks are coated with polymers or chelated with organic groups to avoid particle agglomeration and oxidation. Therefore, a sintering step after printing is required to eliminate the organic fractions. The sintering step caps the NPs, induces a merging of the NPs, and creates the required conductivity in contact grids. Laser sintering is one of the most efficient and fastest sintering methods for Cu NP inks. In this method, the NPs absorb energy from a continuous or pulsed laser source (in this work NIR Nd:YAG 1064 nm 10 ps), as the nanosize of the particles increases laser sintering affinity and enhances light absorption compared with larger particles. More specifically, laser sintering provides high amounts of concentrated energy in a relatively short time. After transforming the absorbed laser energy into heat, this released heat causes the NPs to be uncapped and melt. Therefore, Cu NPs do not have enough time to oxidize, and they merge with their adjacent particles and eventually form a conductive Cu structure.

This current research work shows the optimization of the inkjet printing of Cu NP ink on ODT-coated III-V GaAs wafers and ODT-coated III-V triple-junction cells. Challenges of printing narrow Cu NP structures featuring a width in the micrometer range and a thickness in the nanometer range on III-V substrates are investigated and overcome. Afterward, this Cu nanoparticle ink layer is thickened with an additional galvanic plating step.

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**Figure 1.** Scheme of Cu ink contact on GaAs using an ODT(1,8-octanedithiol)-based SAM as the intermediate layer.

**Figure 2.** Scheme of inkjet printing of Cu NP ink on GaAs cap layer.
This research also investigates the electrical contact between the front metal contact and GaAs cap layer. Since the cap material is not transparent, it needs to be removed selectively. Therefore, after inkjet printing, laser sintering, and electroplating of the Cu ink on the GaAs cap layer, the residual cap needs to be removed selectively by acid etching to evaluate and realize front contact grids in a working III–V triple-junction solar cell.

2. SAM Layer Deposition on GaAs Cap Layer

ODT is deposited as an intermediate layer according to the SAM method performed by Felmet et al.\textsuperscript{[29]} An ODT SAM is formed spontaneously on GaAs cap layer’s surface by adsorption and is organized into relatively large ordered domains (Figure 1). However, since multilayer ODT might act as an insulating layer, it is crucial to have a monolayer ODT on GaAs cap layers’ surface. Thus, different solution concentrations, treatment time, and post-treatment time were investigated to obtain a packed monolayer of ODT on the GaAs cap layer. A packed monolayer ODT on the substrate’s surface has a similar amount of free SH groups and SH groups bonded to the semiconductor.

To determine the treatment conditions resulting in an optimized ODT SAM on GaAs cap layer, four samples were treated with different deposition conditions and studied by X-ray photoelectron spectroscopy (XPS).\textsuperscript{[29,33]} In Figure 3, normalized sulfur S2p-doublet XPS binding peaks of these various surface treatments are compared. Sample “a” is a GaAs cap layer surface treated for 24 h in 10 mM ODT/ethanol solution followed by ultrasonication of 10 min in ethanol. The ultrasonication step helps to remove the residual unattached ODT molecules from the surface.\textsuperscript{[44]} Sample “b” has similar conditions to sample “a”, but with only 12 h of deposition duration instead of 24 h. Sample “c” is a GaAs cap layer treated with 5 mM ODT solution for 24 h deposition duration and 10 min of ultrasonication. Sample d has similar conditions to sample “a”, but with 15 min of ultrasonication time instead of 10 min. In Figure 3, the peaks at 162 and 164 eV represent the ODT groups attached with one head to the GaAs surface and have the other head accessible, respectively.\textsuperscript{[44]} Sample “a” shows a slight shift in the S2p doublet peak toward the higher binding energy, which can be attributed to the fact that free SH groups have more intense signals than SH-GaAs because of their positioning on the surface, whereas the path of the S2p photoelectrons
attenuates the SH-GaAs signal through the molecular layer. Figure 3b,c XPS results indicate that a shorter deposition duration (sample “b”) and a lower solution concentration (sample “c”) lead to physisorbed ODT, showing a more significant amount of S–H bonds. Figure 3d illustrates that a longer ultrasonication time of 15 min (sample “d”) leads to detachment or destroying the ODT molecules. Therefore, it shows a higher amount of S–H bonds. The deposition parameters of the sample “a” were chosen for further work. The peak observed around 160 eV is attributed to the Ga3s peak. The peak at 157 eV is attributed to As3p surface plasmon loss peak.

### 3. Printing Process Development for Cu NP Ink on ODT-Coated GaAs Cap Layer

The interaction of Cu and Ga/As at the interface defines the wetting behavior of Cu ink on the GaAs cap layer. This interaction depends on the substrate’s surface free energy, the free energy at the interface between the ink and the substrate, and the ink’s surface tension. Generally, good wetting is achieved with low surface tension and high surface energy. If the wetting behavior does not meet the application’s requirements, modifications to the ink and/or pretreatment of the substrate might be carried out. Preliminary characterization of the printed structure is done using optical microscopy and contact profilometry to determine layer thickness, homogeneity of the thickness height, line definition, and line width. Considering that the relevance of these parameters is application dependent, the optimization thereof is achieved by developing a unique print strategy.

The final aim of developing the inkjet process is to deposit a Cu ink structure on ODT-coated III–V triple-junction solar cells. To optimize the printing parameters, print tests were first carried out on ODT-coated III–V GaAs wafers and then on ODT-coated III–V triple-junction solar cells. Therefore, III–V GaAs wafer and III–V triple-junction solar cell (AZUR SPACE) with a doping level of \( n = 1 \times 10^{19} \text{ cm}^{-3} \) for the topmost layer were cleaved in 2 × 2 cm pieces and cleaned via standard wafer cleaning methods with different polar and nonpolar solvents. Afterward, ODT surface treatments were performed by putting the wafers for 24 h in 10 mM ODT/ethanol solution followed by an ultrasonication of 10 min in ethanol. The following requirements were given for printing: layer thickness of more than 250 nm and less than 400 nm with a layer thickness homogeneity of \(<\approx 50 \text{ nm}\). Although the lateral resistance would be improved by higher layer thickness, the diffusion of laser beam energy, which induces heat required for uncappping NPs and producing conductive metal structures, is limited and insufficient for thick layers. The laser sintering reduces the thickness of the inkjet-printed layer up to 50 nm depending on the distribution of organic contents. Due to the profilometer stylus’s low force (2.941995E-5 N), no thickness changes were observed after the profilometer measurements.

For process development purposes, the printed structures were split into two parts, rectangles and lines. The first experiments focused on rectangular structures and the second ones on printing lines. The final design, that is, the contacting grid for III–V triple-junction solar cells, consists of lines and a rectangle (as fingers and contact area). The printing strategy is adapted to the ink wetting behavior to achieve the desired contact geometry. The ink droplets in a line printed with a single-pixel setting only interact with each other in one dimension. Each drop in one row of drops forming a line can only interact with the two adjacent neighbors and therefore only in one dimension. For printing the structures featuring more than a single line (rectangles), adding one or more pixels to the width of the line adds a dimension in which pixels can interact with each other and thus influences layer thickness homogeneity and structure width relative to pixel width.

#### 3.1. Printing Rectangular Structures

Initial printing tests of rectangular structures show various results regarding the shape and thickness of printed structures. In the current study, the printing ink formulation and components are constant, while surface properties and printing parameters are modified to adjust printing results. As the main focus here was to adjust the layer thickness between 300 and 500 nm, only parameters and printing methods resulting in a thickness in this range are presented. Three different printing methods were investigated to print the layer with adjusted thickness and roughness. These three methods are standard, chess board structure, and saber angle methods. For a standard printing method, structures printed at a printing resolution of 300 dpi lead to the average layer thickness of around 250–300 nm (Figure 4a). Perpendicular to the print direction, a deviation of 100 nm in layer thickness was observed. With respect to the thickness homogeneity, the results achieved with this printing setup were not satisfactory. Therefore, a new approach was tested by decreasing step acceleration and printing a chess board structure. For the chess board structure printing, every second pixel in X and Y direction was printed, followed by printing in the “free” spaces in the next step, which results in a jagged profile at resolutions below 400 dpi (Figure 4b), using this method at 450 dpi results in an average layer thickness of 300 nm (Figure 4c). However, a nearly linear decrease from 350 to 200 nm of the thickness was observed in the print step direction.

Since the required structures were narrow (3 mm × 6 mm), a ‘saber angle’ method was thus tested. In this method, the print angle is adjusted so that the distance between the nozzles, perpendicular to the swath direction, is equivalent to the desired resolution. In the printing concept, steps are needed to achieve a resolution higher than the native resolution of a printhead and/or structure wider than the printhead and are defined as the number of passes (swaths) that the printhead makes over the substrate to complete a print job. Based on the above results, it was noticed that the thickness homogeneity correlates to the steps and not the step acceleration. The structure is printed in a single swath by saber angle method, thereby removing the need for steps. A typical profilometry result of the ‘saber angle’ method is shown in Figure 4d. 304.14 dpi is the resolution for printing done in Figure 4d.

Comparing the ‘chess board’ and ‘saber angle’ methods shows the steps’ effect on the printed layer homogeneity. In Figure 4c, there is a clear downward trend in layer thickness due to the interactions of printed pixels/droplets. In Figure 4d, the layer thickness is inhomogeneous, similar to Figure 4b; however, this...
can be attributed to the coffee stain effect, as the thinnest point is at the structure’s center. The ‘valley’ near the center in Figure 4d appears due to single-nozzle malfunctioning and blockage.
Figure 4e shows that ODT on GaAs cap layer influences the wettabillity of GaAs surface, and a homogenous layer with 400 nm thickness of Cu printed with standard method and 300 dpi is obtained, which was impossible to achieve on plain GaAs cap layer with similar printing setups at 300 dpi (Figure 4a). The structures have different widths within the boundaries of this experiment and therefore, the length (X-axis) differs between graphs. However, layer thickness homogeneity is not influenced by the absolute width of the printed structure.

3.2. Printing Lines

Printed lines (with widths in the range of 100–300 μm) are inherently more sensitive to variation of ink and substrate properties than the broader printed structures (like rectangles). Therefore, the single-pixel lines are printed using a single nozzle. In this context, the print process development focuses more on ink-substrate interaction, that is, surface and/or ink modification, than on the deposition process itself, that is, the order in which drops are deposited.

The substrates for printing, 2 × 2 cm pieces of III–V GaAs wafers and III–V triple junction solar cells (AZUR SPACE) with a GaAs cap layer with a doping level of n = 1E19 cm⁻³ for the topmost layer, were cleaned by the standard wafer cleaning methods with different polar and nonpolar solvents.[48] ODT surface treatments were performed by soaking the wafers for 24 h in 10 mM ODT/ethanol solution followed by ultrasonication of 10 min in ethanol. Further surface modifications were performed using three rinsing procedures: dipping (30 s) in 1,3-propanediol or 1,3-propanediol: ethanol [1:1] or ethanol.

Dipping in 1,3-propanediol or 1,3-propanediol: ethanol [1:1] was identified to result in the desired substrate surface wettability under specific scenarios. The thickness of a printed layer on III–V GaAs wafer dipped in 1,3-propanediol was about 300 nm while printing with 300 dpi and keeping thickness homogeneity inside the desired window (See Figure 5a,b). Likewise, printing on ODT-coated III–V GaAs wafer dipped in 1,3-propanediol: ethanol [1:1] resulted in a printed line with a layer thickness of about 300 nm while printing with 300 dpi and keeping a thickness homogeneity inside the desired window at the center of the line (see Figure 5c,d). Similarly, printing on a III–V triple-junction solar cell, dipped in 1,3-propanediol, showed comparable results as III–V GaAs wafer treated with the same method (see Figure 5e,b). Thus, the defining factor for ink wetting behavior on the substrate is the wettability of the topmost layer of the substrate surface (GaAs cap layer). In other words, materials below the substrate surface/cap layer have little or no effect on surface wettability. Based on this observation, it can be assumed that an ODT-coated III–V triple-junction solar cell, treated with the same method as an ODT-coated III-V GaAs wafer, exhibits the same wetting behavior as the topmost surface layer is similar in both samples. As coffee stain affects the edges of the printed line, it is necessary to print at least 20–50 μm of the homogenous thickness in the middle of the line for laser sintering. After laser sintering, the non-sintered area is washed off via 2 min ultrasonication of the sample in ethanol. The width after sintering was 25–30 μm, which increased to 60–70 μm after electroplating.

4. Laser Sintering: Cu Thickness and Contact resistivity of Cu on GaAs Cap Layer

After printing, a sintering step is required to remove the organic fractions and merge NPs, as Cu NPs in this particular ink are coated with polymers or chelated with organic groups to avoid particle agglomeration and oxidation. Laser sintering is one of the efficient and fast sintering methods for Cu NP inks which uncaps the NPs, induces a merging of the NPs, and creates the required conductivity in contact grids.[50–53] In this regard, some studies were focused on inkjet printing and sintering of Cu NPs. For instance, Jun et al.[54] showed inkjet printing a synthetic NP ink uncapped via thermal annealing with a resistivity of 1.2 x 10⁻⁸ Ω m. Low sheet resistance of 1 x 10⁻³ Ω m⁻¹ with a resistivity of 1.2 x 10⁻⁸ Ω m was realized by adding some Cu complexes to that ink.[54] In another study, Kim et al. investigated that adding a reducing agent to the NP ink improves the quality of the printed Cu layer after sintering.[55] In comparison with the resistivity of Cu NP, bulk Cu shows a resistivity of 1.7 x 10⁻⁸ Ω m.[56]

Moreover, in comparison with the studies mentioned earlier, our previous study revealed that printed and laser-sintered structures of Cu NP ink on GaAs cap layer show a contact resistivity of 8 mΩ cm² and resistivity of 1.1 x 10⁻⁷ Ω m for a laser-sintered Cu layer with a thickness of around 400 nm.[6] It should be mentioned that the GaAs cap layer is n-type with a charge carrier concentration n = 10E19 cm⁻³.

In general, the thickness of deposited conductive thin films considerably influences their electrical contact behavior.[6,56] However, deposited films with a thickness in the nm range may have higher resistivity than bulk Cu due to the porosity, the dependence of carrier mobility on crystallinity, and materials’ nanostructure.[57–59]

Furthermore, the deposition of the organic SAM as an intermediate layer influences Cu electrical behavior, if a reaction occurs between Cu and intermediate layer. For example, Maestre Caro et al. showed SAM silane layers with different head groups from halogens to thiol and amine groups lead to the sheet resistance of Cu layer of 0.3–0.5 Ω fl⁻¹.[6] Compared with the work of Maestre Caro et al., in our study, the minimum Cu layer sheet resistance achieved with the adjustment of laser parameters was 0.23 Ω fl⁻¹. However, the intermediate ODT layer used here is not silane based. Moreover, Felmnet et al. applied ODT as an intermediate layer for Cu on GaAs. They used nanotransfer printing for the deposition of Cu on ODT-coated GaAs substrate. They reported a resistivity of 3.1 x 10⁻⁷ Ω m for Cu NP layer, compared with 0.8–1.1 x 10⁻⁷ Ω m in our study.[6]

Besides low contact resistivity, high reproducibility is one of the essential factors in all fabrication processes. For a laser-sintered and inkjet-printed electrode, layer thickness, amount and distribution of the uncapped NPs determine the electrodes’ electrical behavior. Thus, Cu ink was deposited with a layer thickness of 250 and 400 nm on ODT-coated GaAs cap layer to investigate the influence of the layer thickness on laser sintering results and the electrical behavior of electrodes.

Morphological investigations were performed by scanning electron microscopy (SEM) (Figure 6) and showed an inhomogeneous distribution of NPs in the Cu layer with a thickness of...
250 nm after laser sintering (Figure 6a). Areas with different topographies for a layer of 250 nm Cu NPs were observed by atomic force microscopy (AFM) (Figure 7b). In contrast, a Cu NP layer with a thickness of around 400 nm on ODT-coated GaAs cap layer provides significantly more homogenous distribution of NPs on the GaAs surface (Figure 6b).

Laser fluence is the most influential parameter for laser sintering of NPs. It is defined as energy applied to the unit area. To achieve low contact resistivity at the metal–semiconductor interface and to realize a conductive metal layer, an optimal level of the applied fluence is needed. Application of this optimized fluence level means exposing the sample to a laser power, which leads to a high amount of uncapped NPs and simultaneously avoids ablation of the printed structure. This amount of uncapped NPs enables the required conductivity of the contact grids and reduces the contact resistivity. However, fluence values higher than this optimized value lead to ablation of the ink resulting in a nonohmic electrical contact.\[6\]

Figure 5. a) Printed lines on III–V GaAs wafer, dipped in 1,3-propanediol microscopic image, b) profilometer line scan of (a), c) printed lines on ODT-coated III–V GaAs wafer, dipped in 1,3-propanediol: ethanol [1:1 microscope image, d) profilometer line scan of (c), e) printed line of III–V triple-junction solar cell dipped in 1,3-propanediol microscopic image, and f) profilometer line scan of (e). Line counting starts from the bottom in (a), (c), and (e).
To assess the electrical behavior of the printed Cu NP layer on ODT-coated GaAs cap layer, current–voltage (I–V) characteristics were derived from transmission line measurement (TLM). For this purpose, laser-sintered Cu NP squares (500 μm × 500 μm) were deposited on ODT-coated III–V GaAs wafer with different distances (82, 144, 205, 271, 329 μm). The I–V characteristics of these squares were measured for samples featuring 250 and 400 nm laser-sintered Cu layers. Figure 7a shows the Schottky behavior of 250 nm Cu layer on ODT-coated III–V GaAs wafer, demonstrating the poor electrical behavior of this layer on GaAs cap layer. Moreover, further optimization to adjust the laser parameters for sintering of the 250 nm layer did not show reproducible results. We assume that an inhomogeneity in the distribution of solid content through the entire layer causes the poor connection between the sintered Cu NPs. As a consequence, the results are nonreproducible. In contrast, Cu NP structures with a thickness of 400 nm reproducibly show an ohmic contact behavior on ODT-coated GaAs cap layer (Figure 8a). The laser parameters were investigated for the optimum laser fluence value to result in good adhesion of laser-sintered Cu and an ohmic behavior between metal and semiconductor. The optimized fluence was found in the range of 6.5–8.5 mJ cm⁻². I–V characteristics of samples sintered at 8.5 mJ cm⁻² display a contact resistivity between 2 and 5 mΩ cm² (Figure 8b). As mentioned, in our previous study, a printed and laser-sintered structures of Cu NP ink on GaAs cap layer without any ODT layer show a contact resistivity of 8 mΩ cm².

5. Photovoltaic Performance of III–V Triple-Junction Solar Cells with Cu Ink Front Contact

To enhance the electrical conductivity of the copper contact fingers and decrease their sheet resistance and to evaluate the electrical characteristics of the contact between inkjet-printed and laser-sintered Cu NP on ODT-coated III–V triple-junction solar cells, the laser-sintered Cu layer was electroplated and thickened via a conventional electroplating method.

Samples were plated in an electrolyte solution of Cu²⁺(SO₄)²⁻. Primary results of electroplating revealed a deposition rate of 0.02 μm min⁻¹ for an applied current of 0.4 mA for 8 mm² area of copper layer. To speed the process, several samples were electroplated simultaneously. To achieve selectivity in Cu deposition of the inkjet-printed seeding layer, reduced illumination while electroplating and low current density were applied. Due to the overspraying, some ink particles could be deposited on the surface near the edges of the structure. Those particles can
unwantedly be electroplated on the surface resulting in an undesired plating of the solar cell's surface.

After the growth of 10 μm of Cu, the samples were etched in a solution mixture 50:50 of citric acid (50 wt%) and hydrogen peroxide (10 wt%) to open the window layer (InAlP:Si), and then the frontside antireflective coating and backside metal contacts were deposited. The backside was coated sequentially by Au/Ag/Au (50 nm/2 μm/50 nm), covering the whole backside of the samples except an edge of 1 mm.\(^{[62]}\)

After processing, the solar cells were evaluated in a 3 Zone Solar Simulator (Auratec), which features a spectrum close to the AM0 standard for space application with an irradiance of 0.136 W cm\(^{-2}\). III–V triple-junction solar cells prepared via AZUR SPACE standard processes were used as a reference. These reference samples feature front contact Ag/Au metallization applied by electron-beam physical vapor deposition.

From the \(I-V\) characteristics displayed in Figure 9, it can be seen that the front contact of the processed cell with printed and electroplated contacts is functional, and a working solar cell was achieved using the newly developed front side metallization processes. In addition to standard spectra, the solar cell is exposed to blue or red light. Thus, it is boosted, and \(+BB/+RB\) in Figure 9 means blue/red boost. During \(+BB\) measurement, the top cell is saturated by blue light, and the \(I-V\) curve of the middle cell is visible. The middle cell determines the maximum current. During \(+RB\) measurement, the middle cell is saturated by infrared light, and the \(I-V\) curve of the top cell is visible. The top cell determines the maximum current.

As shown in Table 1, the sample with inkjet-printed front contact grid showed an open-circuit voltage \((V_{oc})\) of 2.64 V and a short-circuit current density \((J_{sc})\) of 14.9 mA cm\(^{-2}\). The maximum power point (MPP) was determined at a voltage of 2.20 V with a current density of 12.4 mA cm\(^{-2}\), resulting in a fill factor (FF) of 69%. The solar cell efficiency thus could be calculated to be 20%. The reference cell showed a \(V_{oc}\) of 2.72 V and a \(J_{sc}\) of 17.65 mA cm\(^{-2}\). The MPP was determined at a voltage of 2.32 V and a current density of 15.45 mA cm\(^{-2}\).
Table 1. Current–voltage data of cells prepared with AZUR SPACE standard metallization and inkjet-based metallization.

|                  | \( J_{sc} \) | \( V_{oc} \) | \( J_{mp} \) | \( V_{mp} \) | FF | \( \eta \) |
|------------------|--------------|--------------|--------------|--------------|----|----------|
| Reference cell prepared with AZUR SPACE standard metallization method | 17.65 | 2.72 | 17.2 | 2.43 | 87 | 30.37 |
| Test cell prepared with inkjet-based metallization method | 14.9 | 2.64 | 12.4 | 2.20 | 69 | 20 |

2.43 V with a current density of 17.2 mA cm\(^{-2}\), resulting in an FF of 87%. The solar cell efficiency thus could be calculated to be 30.37%.

The current generated in the processed cell with a printed and plated grid was lower than a reference triple-junction cell fabricated by AZUR SPACE standard processes. This can be assigned to the differences in the shadowing percentage of grids and defects in the antireflective coating, such as thickness variation or composition errors. The processed cell with a printed and plated grid showed a higher reflectivity than the reference sample in the range of 370–850 nm (Figure S1, Supporting Information). The shadowing percentage of the electrode on the reference cell was 2% of cell area, and for the inkjet-printed and plated one was 7–8%.

The cell's \( V_{oc} \) was 80 mV lower than the reference. The loss in \( V_{oc} \) is attributed to the damaged top cell passivation or the damaged Ge cell. These damages are considered to occur to the window and active layer during electroplating or etching. Moreover, a reduced \( J_{sc} \) might cause a loss in \( V_{oc} \).

In addition, the printed and laser-sintered grid on the ODT-coated III–V GaAs wafer showed good adhesion on the GaAs cap layer while electroplating. In contrast, the samples without ODT showed poor electrode adhesion on III–V triple-junction solar cells, and a solar measurement could not be performed. However, the contact resistivity for Cu NPs ink printed on coated and uncoated GaAs cap layer did not show significant differences.

6. Conclusion

In conclusion, Cu NP ink as a low-cost front contact electrode was deposited on ODT-coated III–V GaAs wafers and ODT-coated III–V triple-junction solar cells. Inkjet printing of a Cu NP ink combined with an ultrafast uncapping laser-sintering step was applied and optimized successfully as a cost-effective front contact deposition method applicable to GaAs-based devices.

The printing challenges, such as uncontrolled wetting and poor adhesion of the printed structure on the substrate surface, were addressed and overcome via surface modification by deposition of an ODT SAM on the GaAs cap layer. Therefore, coherent and narrow Cu NP ink structures were printed on ODT-coated GaAs cap layer. ODT was shown to improve ink printing results on the surface of GaAs considerably, and a homogenous Cu layer was obtained with a thickness of 400 nm printed with a printing resolution of 300 dpi. The printed Cu NP ink structures were uncapped and sintered using a picosecond pulsed laser. The controlled thickness of the Cu layer leads to effective laser sintering and yields a homogenous distribution of NPs on the GaAs surface without cracks in the layer structure, resulting in increased layer conductivity and reduced contact resistivity.

Moreover, a well-distributed monolayer ODT is required to provide a conductive contact between Cu and GaAs cap layer. XPS studies were performed to select the optimized deposition conditions. Furthermore, XPS studies of the ODT SAM layer deposited on the GaAs cap layer revealed that the deposition condition of 24 h in 10 mm ODT in ethanol, followed by ultrasonication for 10 min, resulting in a monolayer ODT on GaAs. These deposition parameters provide controlled thickness of the intermediate layer to avoid high contact resistivity and surface damage.

I–V characteristics of sintered Cu on ODT-coated III–V GaAs wafer showed the desired ohmic metal–semiconductor contact, with a low contact resistivity of 5 mΩ cm\(^2\) obtained by an efficient fusion of laser-sintered Cu at the metal/semiconductor interface.

The inkjet-printed and laser-sintered Cu grid on ODT-coated III–V triple-junction solar cells was thickened via an additional electroplating step. Then the window layer was etched, and the solar cell was processed and showed a PCE of 20%. Reducing the shadowing and optimizing the antireflective coating are necessary to obtain higher PCE. As the standard metallization method results in a 30% conversion efficiency, higher power efficiency is also required for inkjet-based metallization.

In conclusion, this work demonstrates the applicability of a surface modification method to apply inkjet printing of Cu NP ink combined with laser sintering to deposit front contact electrodes on III–V substrates. This approach illustrates a straightforward and cost-effective industrial method, showing the potential as a future alternative process for deposition of front contact electrodes on III–V-based devices. Inkjet printing and laser sintering are readily scalable, and improved electrical behavior of the Cu ink on GaAs cap layer is possible via a modification of the ink formulation.

7. Experimental Section

Inkjet Printing: Inkjet printing was done using a PiXDRO LP50 printing platform. In combination with a FUJIFILM Spectra SE 128 print head, Cu ink (Dycotec ink (DM-CUI-5002), 40–45% solid content) was deposited on each substrate. The print head, and printing parameters, are presented in Table 2. The substrates after printing were dried in a vacuum oven at 800 mbar below ambient pressure and 50 °C for two hours. Print direction \( Y \) was the stage moving away and toward the operator, while the print head moved in steps along the X-axis. Quality factor is the number of different nozzles used to print a single line in print direction. Step size is the distance moved by the printhead in x-direction (assuming the print direction is y) before printing the next swath and is measured in pixels. For example, step size 1 prints all lines sequentially, and step size 2 skips one line and prints the next one, before returning to print the line which is skipped.

The print head was precleaned with ethanol, purged with air for 5 min, and then left to dry at room temperature for 30 min. Usually, the meniscus vacuum pump is used to create under pressure in the ink reservoir to prevent the ink from flowing out. Purging creates overpressure, thus pushing inks, cleaning solvents or air out through the print head. The ink was filtered with a 5 μm PTFE filter and allowed to flow freely into the print head and thoroughly wet the nozzle plate. Then, the ink was held in place with the meniscus vacuum and with the nozzle plate still wet, for 30 min, which allowed for any trapped air to escape. The print head was then purged for 1 s, and the nozzle plate wiped. All nozzles were checked for proper
function in the drop watcher, and the unstable nozzles, excluded from the print job.

**Laser Sintering**: Laser sintering was performed using a diode-pumped, picosecond laser (wavelength of 1064 nm). The EdgeWave PX200-P1-CF laser is based on an Nd:YVO4 crystal. Maximum pulse repetition rate was 50 MHz and reached a power of up to 100 W. Laser parameters are shown in Table 3. After laser sintering, the nonsintered area was washed off via 2 min ultrasonication of the sample in ethanol.

**Characterization Methods**: XPS: The XPS results were measured using a ‘Multiprobe’ ultrahigh vacuum surface analysis system (Omicron Nanotechnology with a base pressure of around 5 x 10^{-10} mbar). The excitation source was a DAR400 X-ray tube with Al anode and an XMS000 quartz crystal monochromator (excitation energy of 1486.6 eV [Al K\alpha line] with an energy broadening of around 0.1 eV). The peak analysis was performed using Unifit2017 spectra processing software. The fit procedure was a convolution of Gaussian and Lorentzian peak profile (Voigt profile).

Scanning electron microscopy: SEM images were made with a Nanoscope III atomic force microscope (Digital Instruments, Santa Barbara, CA).

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords**

1, 8-octanediol intermediate layer, copper nanoparticle inks, III–V solar cells, inkjet printing, laser sintering

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