

Selective Metallization of Polymers: Surface Activation of Polybutylene Terephthalate (PBT) Assisted by Picosecond Laser Pulses

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The selective metallization of nonconductive polymer materials has broad applications in the fields of integrated circuit technology and metallized patterns. This work discusses a methodology to pattern metal tracks on polybutylene terephthalate substrates. The process consists of three steps: 1) surface patterning with picosecond laser pulses (1030 nm) in air, 2) Pd seeding via treatment in PdCl_2 solution, and 3) selective metallization via electroless copper deposition. Picosecond laser irradiation promotes not only surface roughening but also chemical modification to enable Pd seeding as the polymer surface acquires the ability to reduce Pd(II) -chloride species to metallic Pd. The laser parameters, as well as the PdCl_2 concentration and seeding temperature, have an influence on the polymer surface morphology, the concentration and distribution of metallic Pd, and the copper layer properties. Homogeneous copper layers with well-defined geometries, good coating-substrate adhesion, and high electrical conductivity can be obtained. This is ascribed to the synergistic effect of the chemical surface activation and roughness development (from 0.13 to $\approx 1.6 \mu\text{m}$). As the patterning and surface activation are performed in air, directly on the as-received polymer substrate, this methodology shows great potential for metallization of electronic devices with 3D complex geometries.

photolithographic processes, as well as physical or chemical vapor deposition.^[1] The evaporation techniques usually require the use of high-cost vacuum chambers, photoresist materials, and photomasks. Therefore, many efforts have been devoted to finding alternative methodologies to avoid complex production processes and minimize costs. The laser direct writing technique is a promising alternative for selective patterning and metallization of nonconductive substrates. Despite the capital investment and required operational costs, the use of laser irradiation for metallization purposes can be a viable alternative because of its simplicity, easy control, cleanliness, and possibility to work at industrial scale.^[2]

Laser beams are applied as localized sources of energy to selectively assist the surface activation of dielectric materials for a subsequent metallization process. Polymeric materials usually exhibit high absorption coefficients for ultraviolet (UV) and infrared (IR) radiation.

1. Introduction

The production of metallic tracks on the surface of nonconductive or semiconductive substrates attracts strong scientific interest due to its useful applications in integrated circuit technology and its miniaturization. Conventional methods for selective metallization are usually based on chemical etching,

Whereas UV radiation generally induces breaking of molecular bonds (formation of free radicals) with limited heating effects, IR radiation excites polymer functional groups to higher vibrational and rotational energetic states generating heat.^[3] The accumulation of heat can, in turn, lead to thermal activated reactions that can be conveniently used for surface activation and metallization purposes.^[4] By choosing suitable laser parameters, the surface

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activation and patterning of polymers exhibit little or minimal surface damage.

In the last years, a variety of pathways for laser-assisted direct metallization of nonconductive materials have been proposed. These methodologies are based on processes such as laser-based thermally induced deposition, laser-assisted surface modification for subsequent electroless deposition, and laser-assisted photocatalysis-mediated deposition, among others.^[1,5] Some examples include the patterning of micron-sized platinum features using a continuous-wave (cw) argon ion laser ($\lambda = 514$ nm) to induce the thermal decomposition of platinum metal-organic films coated onto quartz substrates for subsequent electroless plating.^[6] In contrast, the selective activation of diamond substrates with a Cu vapor laser ($\lambda = 510$ nm) and KrF excimer laser ($\lambda = 248$ nm) was also reported.^[7] In this example, laser-induced decomposition of palladium acetyl acetonate ($\text{Pd}(\text{acac})_2$) solid films and $\text{Pd}(\text{acac})_2$ dissolved in dimethylformamide were used to produce catalytic Pd particles for subsequent electroless plating.

Schrott et al.^[8,9] selectively seeded Pd on silica (SiO_2) and polyimide (PI) surfaces to activate them for electroless plating. Excimer laser pulses ($\lambda = 248$ and 308 nm) were used to irradiate SiO_2 substrates immersed in PdSO_4 and $\text{Pd}(\text{CH}_3\text{CO}_2)_2$ solutions. Other approaches reported the laser-assisted silver seeding using Ag^+ -doped PI films irradiated by cw-He-Cd laser ($\lambda = 325$ nm) as well as pulsed Nd:YAG laser ($\lambda = 266$ nm).^[1,10] A similar work reported the preparation of AgNO_3 thin films on glass substrates using the irradiation with femtosecond laser pulses ($\lambda = 800$ nm) and leading to a subsequent formation of Ag seeds and selective metallization via electroless plating process.^[11]

Kordás et al.^[12–15] investigated the preparation of Pd and Cu thin films on different polymers using the laser-induced chemical liquid-phase deposition method. Pd was deposited on PI and mylar (polyethylene terephthalate [PET]) from a $[\text{Pd}(\text{NH}_3)_4]^{2+}/\text{HCOH}$ liquid precursor system by applying XeCl ($\lambda = 308$ nm) and KrF ($\lambda = 248$ nm) excimer lasers.^[15] Another pathway involves a photothermal reaction using a cw-Ar⁺ laser ($\lambda = 488$ nm) and tartrate complex solution of Cu^{2+} ions for the preparation of conductive Cu/CuO patterns on PI surfaces.^[13] In contrast, the use of $\text{Cu}(\text{acac})_2$ (acac = acetylacetonate) and Cu/CuO as polymer additives for the selective metallization of PET and polyamide was also reported by Rytlewski et al.^[16–19] For these purposes, an ArF excimer ($\lambda = 193$ nm) and IR Nd:YAG laser irradiation were used. Furthermore, other approaches such as using polypropylene (PP) doped with multi-walled carbon nanotubes^[20] or PdCl_2 -loaded polyvinylpyrrolidone coatings^[21] as precursors for laser-induced selective metallization were also reported. In addition, organometallic complexes based on palladium (Pd^{2+}), copper (Cu^{2+}),^[22] as well as metal oxides (ZnO)^[23] and composites of copper–chromium oxide ($\text{CuO}\cdot\text{Cr}_2\text{O}_3$) or antimony-doped tin oxide (ATO)^[24,25] have been used as catalyst sources. The active material is finely dispersed in the polymeric matrix. In the so-called laser direct structuring process, the active material can be chemically modified by laser ablation to play a role as a catalyst in a subsequent electroless deposition process.

Zhang et al. used Nd:YAG laser ($\lambda = 1064$ nm) to pattern on polymer surfaces while the substrates were submerged in water.

After subsequent activation with PdCl_2 and SnCl_2 mixtures, followed by electroless plating, selective copper deposition could be achieved.^[26] In contrast, the use of optical energy in the form of very short laser pulses (e.g., picosecond or femtosecond pulses) has been reported to be very advantageous as the heat diffusion into the polymer can be negligible.^[27] Therefore, tunable laser parameters in wavelength and time domains can be used for various applications that require high precision surface patterning without thermal damage to the surrounding areas.^[28–30] Ratautas et al. investigated the selective metallization of different engineering polymers via the selective surface activation induced by laser.^[31–33] Picosecond and nanosecond lasers in the IR and VIS wavelength were used to modify the polymers, and AgNO_3 solutions were used as catalyst precursors for electroless copper deposition. Successful selective metallization was achieved by applying picosecond laser pulses and was ascribed to the change of the surface chemistry of the polymer, which in turn is able to reduce silver ions. On the other hand, the selective metallization of ceramic surfaces assisted by laser has been reported.^[34] Fiber pulse laser ($\lambda = 1064$ nm) was used to selectively pretreat Al_2O_3 for electroless copper plating. The surface activation was attributed to the formation of oxygen defects which, in turn, promoted copper reduction in a formaldehyde-based bath.

This paper presents a novel and simple approach toward the successful patterning of copper metal tracks onto polybutylene terephthalate (PBT) substrates. The selective metallization process consists of the surface modification of the polymer substrates with picosecond laser pulses in atmospheric conditions (air and room temperature), Pd seeding by dipping the substrates in PdCl_2 solutions, and subsequential electroless copper deposition. The influence of the laser parameters and seeding conditions on the surface activation of the polymer will be studied and correlated with the morphological, structural, and electrical properties of the copper layers.

2. Experimental Section

2.1. Substrate Material

Commercial PBT (Arnite T06 200 SNF GN 6021 green) was selected as substrate material. This thermoplastic polymer consisted of a non-reinforced grade, flame-retardant polyester with good chemical resistance in diluted nonoxidizing acidic media. The melting temperature was about 225 °C according to the supplier. The substrate geometry consisted of square-shaped plates ($60 \times 60 \times 2$ mm³) produced by injection molding (by 3D Schilling GmbH).

2.2. Metallization Methodology

The selective metallization process consisted of three main steps: 1) surface patterning with picosecond laser pulses in atmospheric conditions (air and room temperature), 2) treatment in a PdCl_2 -based seeding solution, and 3) selective metallization of the substrate via electroless copper deposition (**Figure 1**). The optimization of the methodology involved the study of different combinations of laser parameters and the treatment conditions

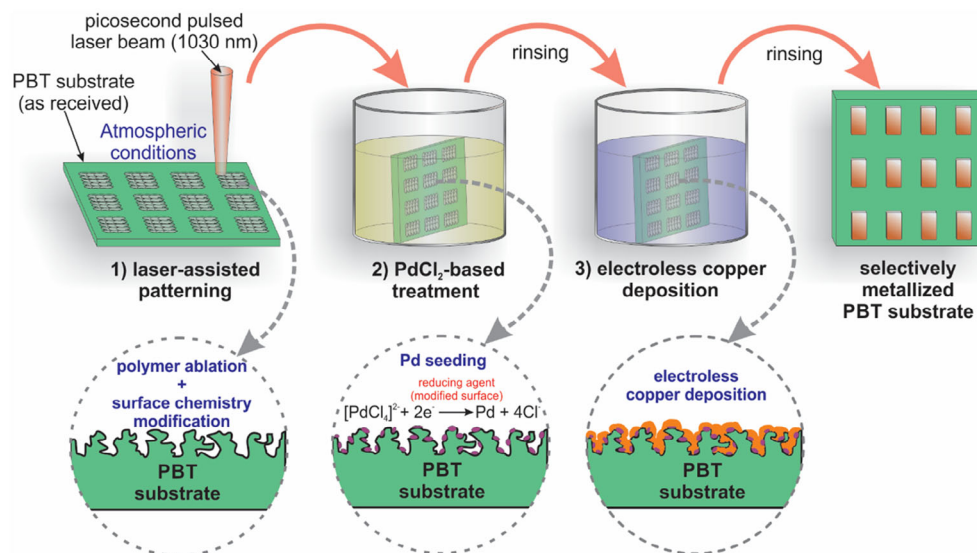


Figure 1. Schematic representation of the process steps for the selective metallization of PBT using laser-assisted patterning.

(PdCl_2 concentration and temperature of the seeding solution) in correlation with the surface morphology and the capability of the patterned areas to enable selective metallization via electroless deposition.

2.2.1. Patterning with Picosecond Laser Pulses

The experiments were carried out using a commercial laser system (TruMicro 5050, company TRUMPF) based on disk laser technology. The active medium consisted of Yb:YAG that emits pulses with a duration (τ) shorter than 10 ps in the IR range ($\lambda = 1030 \text{ nm}$) via a mode-locked oscillator.^[35] In combination with a regenerative amplifier, output powers up to 50 W can be provided and a maximum average pulse energy (E_p) of 250 μJ can be achieved. The pulse duration was measured before laser processing of the samples with a pulseCheck autocorrelator instrument from APE GmbH, Berlin.

A schematic representation of the laser workstation is shown in **Figure 2**. With a computer-controlled laser scanner, the laser beam can be deflected over the sample that allows scan rates (v_s) up to 2.0 m s^{-1} . An F-theta objective (100 mm focal length) was used to focus the laser beam on the surface of the sample. A Gaussian profile with a laser beam quality of $M^2 < 1.3$ was used. The laser beam was scanned over the sample area to be metallized (rectangular features of $0.5 \times 0.8 \text{ cm}^2$) following a unidirectional scanning path as shown in Figure 2 (top view). The beam was focused perpendicular (90°) to the sample surface and resulted in a measured focus diameter (d_f) of 30 μm . The pulse repetition rate (f_R) was set to 25 kHz. Only one pass (scan) was applied to each patterned area.

The laser parameters used for the experiments are summarized in **Table 1**. The distance between two pulses, pulse distance (d_p), resulted from the combination of v_s values and a constant f_R value while the line to line distance is referred to as hatching space (d_L).

2.2.2. Treatment in Acidic PdCl_2 Seeding Solution

A PdCl_2 stock solution was prepared by dissolving 2 g of PdCl_2 (99.9%, Carbolution Chemicals) in $15 \times \text{g L}^{-1}$ HCl. The activation solutions were prepared by diluting the stock solution to reach the concentrations of 0.1 g L^{-1} ($\approx 0.56 \text{ mM}$) and 0.5 g L^{-1} ($\approx 2.8 \text{ mM}$) PdCl_2 . The pH value of the activation solutions was 2.2. Milli-Q (deionized) water was used for the preparation of all solutions. After laser patterning, the PBT samples were directly immersed in the activation solutions for 5 min. Three activation temperatures were investigated: room temperature, 50°C , and 70°C . Afterward, the samples were rinsed twice with distilled water.

2.2.3. Electroless Copper Deposition

After the activation, the samples were immersed in a commercial formaldehyde-based electroless copper bath (ENPLATE CU 872, Enthone GmbH) for 30 min at $(43 \pm 1)^\circ\text{C}$. The working temperature of the bath was controlled with a thermostat. Finally, the samples were rinsed twice with distilled water and dried in the air. A fresh electroless copper bath was prepared on a daily basis.

2.3. Characterization of the Polymer Substrate After Laser-Assisted Patterning and Activation in Acidic PdCl_2 Solution

Scanning electron microscopy (SEM) using an Hitachi S4800 system coupled with an energy dispersive X-ray spectroscopy (EDX) detector was used to investigate the surface morphology, chemical composition, and elemental Pd distribution at the polymer surface after the activation. A carbon layer with a few nanometers of thickness was sputtered on each sample to get a suitable conductivity for SEM investigations. The acceleration voltage used for these purposes was of 30 keV.

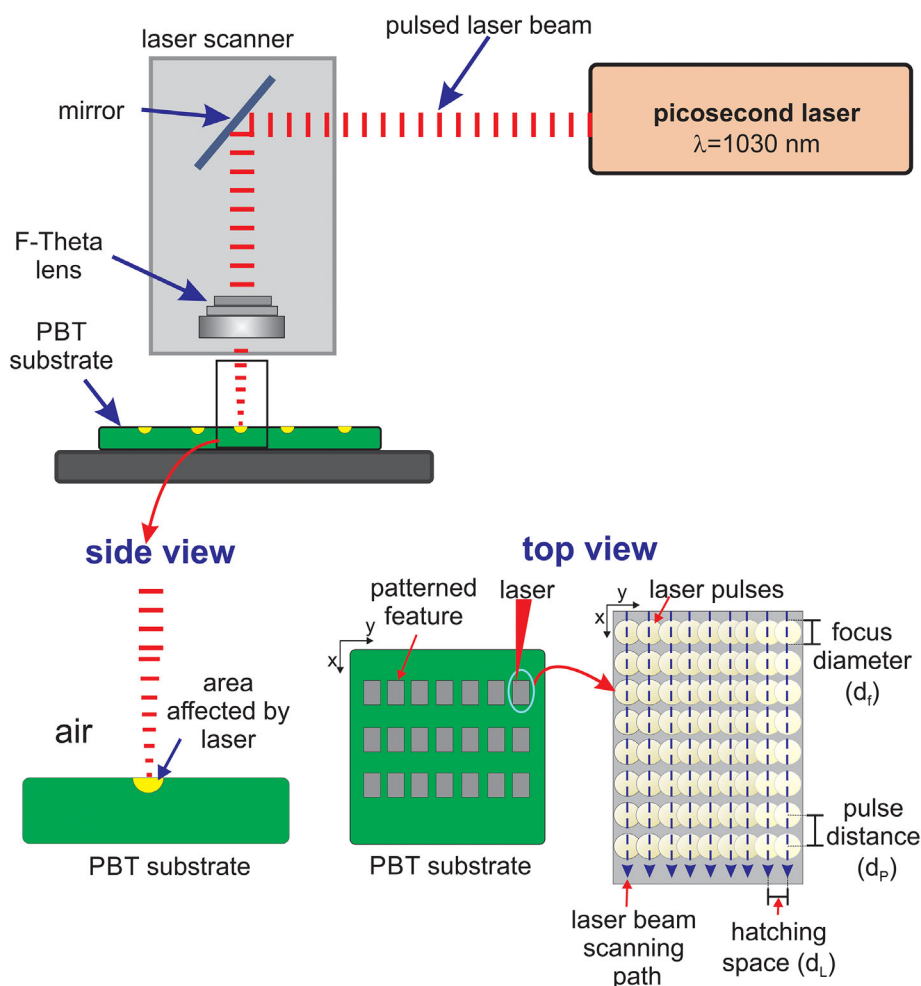


Figure 2. Schematic representation of the setup for the patterning and surface modification of PBT substrates with picosecond laser pulses.

Table 1. Laser parameters for the selective metallization of PBT.

Parameter	Value
Wavelength, λ	1030 nm
Pulse duration, τ	<10 ps
Focus diameter, d_f	30 μm
Average pulse energy, E_p	25, 50, 75, 100, 125, 150, and 175 μJ
Repetition rate, f_R	25 kHz
Hatching space, d_L	10 μm
Pulse distance, d_p	40, 60, and 80 μm
Scan rate, v_s	1.0, 1.5, and 2.0 m s^{-1}

Roughness measurements were carried out with a tactile profilometer (Taylor Hobson-Form TalySurf Series 2) equipped with TalyMap Silver software. Five scans per sample area were performed to calculate the arithmetic average roughness, R_a .

X-ray diffraction (XRD) investigations were performed to study the microstructural changes of the polymeric substrate

after laser treatment and to investigate the presence of Pd seeds after treatment in PdCl_2 solutions. An X-ray diffractometer, Bruker AXS D5000, operating with $\text{Cu K}\alpha$ radiation and Bragg–Brentano geometry was used. The diffraction patterns were recorded with a step size of 0.02° for 2θ ranging from 20° to 80° and a measuring time of 1.4 s per step. For XRD measurements, the sample geometry consisted of fully scanned square-shaped features ($2 \times 2 \text{ cm}^2$).

Atomic force microscopy (AFM)-based conductivity measurements were performed using a Dimension ICON AFM device from Bruker, Billerica, MA, USA, which was placed in an Ar-filled glovebox (M. Braun Inertgas-Systeme GmbH, Garching, Germany) with H_2O and O_2 concentrations below 10 ppm. PeakForce TUNA mode equipped with a PF TUNA probe (made of silicon nitride with Pt/Ir conductive coating) from Bruker was used for all AFM measurements and allowed the simultaneous investigation of the surface conductivity (due to the presence of metallic Pd) and topography. To make the samples suitable for AFM-based conductivity investigations, a thin carbon layer ($\approx 5 \text{ nm}$) was sputtered onto the sample surface to incorporate the Pd seeds into a conductive network and to obtain an electrical feedback loop between the sample and the

PF TUNA probe. Electrical contact was established by taping an adhesive copper foil to the sample surface and the stage of the AFM device. The images were obtained with a PeakForce set point of 0.25 V, scan size of $10 \times 10 \mu\text{m}$, scan rate of 0.3 Hz, and current amplifier sensitivity of 10 nA V^{-1} . A potential bias of 2 V DC was used to perform the conductivity measurements. To remove tilt and curvature, the height measurement images were processed by a third-order polynomial flattening procedure using Nanoscope Analysis software from Bruker.

2.4. Thickness Distribution and Morphology of Copper Layers

The thickness of the copper layers on PBT was measured via X-ray fluorescence (XRF) using a FISCHERSCOPE X-ray XDV-SDD instrument. The thickness distribution was analyzed by measuring 15 points (array of 3×5 points) over a measuring area with dimensions of $0.8 \times 0.5 \text{ cm}^2$ (copper feature size). Optical and SEM micrographs of the metal deposits were obtained using a Carl Zeiss microscope and a Philips XL30 scanning electron microscope, respectively.

2.5. Adherence of Copper Layers

Tape tests were conducted in accordance with the IPC-TM-650 2.4.1 norm^[36] to evaluate the adherence of copper layers. A strip of adhesive tape 3M was carefully pressed across the surface of copper features with dimensions of $2 \times 50 \text{ mm}^2$ to remove all air entrapment. Afterward, the tape was pulled off by application of a rapid force approximately perpendicular to the test area. The time between application and removal of tape was less than 1 min.

2.6. Resistivity Measurements

The sheet resistance of the copper layers deposited on PBT was measured using four-point probe measurements based on the Van der Pauw method.^[37] The samples were mounted on a measuring platform, and the probes were placed on each of the four edges of the copper structure surface. The resistivity was calculated from the sheet resistance measurements.

3. Results and Discussion

3.1. Morphology of PBT After Patterning with Picosecond Laser Pulses

To investigate different sets of laser parameters, a two-dimensional array with rectangular-shaped features with dimensions of $0.8 \times 0.5 \text{ cm}^2$ was produced. This enables the study of the combination of seven mean pulse energies (E_p values between 25 and 175 μJ) and three scan rates ($v_s = 1.0, 1.5$, and 2.0 m s^{-1}) which results in 21 parameter fields.

Figure 3a shows a computerized vector image of a laser-patterned PBT substrate and Figure 3b shows the photographic image of the PBT substrate after patterning with picosecond laser pulses. A change of color from green to dark gray in all features can be observed. This phenomenon can be attributed to increased surface roughness as well as carbonization (amorphous carbon present on the polymer surface) after laser

ablation. This was also reported for high-density polyethylene containing ATO nanoparticles (HDPE-ATO) and PI samples after exposure to near-infrared (NIR) and UV excimer laser irradiation, respectively.^[38,39] NIR pulsed laser can penetrate polymers from micro- to millimeter scale depending on the laser output power as well as the presence of additives in the polymer (e.g., fillers, pigments, stabilizers, etc.). Consequently, engineering polymers such as PBT, PET, polystyrene (PS), polycarbonate (PC), and polyvinyl chloride (PVC) generally exhibit a higher susceptibility to develop dark laser marking as polyethylene (PE) or PP.^[38,40,41]

Figure 3c–f shows the influence of the average pulse energy, E_p , on the surface morphology of PBT at a constant scan rate ($v_s = 1.0 \text{ m s}^{-1}$). The use of E_p values such as 25 μJ (Figure 3c) and 50 μJ (Figure 3d) resulted in a surface morphology that consisted of non-ablated areas (hills) and ablated zones (valleys). The latter one is also called ablation line width. As E_p increases to values equal to or higher than 75 μJ , the ablation line width expands and overlapping occurs to produce a homogeneous roughening of the whole surface morphology. This is shown in Figure 3e,f, for E_p values of 75 and 175 μJ , respectively. Both micrographs reveal an overall highly porous morphology with very well distributed micro-cavities.

Figure 3c,g shows the surface morphology of PBT patterned areas obtained with a fixed average pulse energy value ($E_p = 25 \mu\text{J}$) and v_s values of 1.0 and 1.5 m s^{-1} , respectively. An increase in the scan rate resulted in the enlargement of the non-ablated area (hills) by 80%. This effect can be ascribed to the increment in the pulse spacing value. Figure 3h shows a narrowing of the non-ablated area caused by the increment of the E_p value from 25 to 75 μJ .

Roughness measurements were performed to evaluate the overall influence of the laser parameters on the surface morphology of the 21 patterns (parameter fields). Figure 4 shows the dependence of R_a with the parameters E_p and v_s . The inset depicts a schematic representation of a single patterned feature and shows the scanning direction used to perform the roughness measurement which is orthogonal to the laser beam scanning path. In general, the slowest scan rate ($v_s = 1.0 \text{ m s}^{-1}$) promoted strong surface ablation of PBT. R_a values up to $1.6 \mu\text{m}$ could be obtained in combination with high E_p values. Higher scan rates ($v_s > 1.0 \text{ m s}^{-1}$) promoted R_a values mostly between 0.4 and $0.6 \mu\text{m}$. This agrees with the SEM observations which exhibited enlarged non-ablated areas for v_s values higher than 1.0 m s^{-1} (Figure 3g,h).

3.2. Study of the Presence and Oxidation State of Palladium After Treatment of Patterned Features in Acidic PdCl_2 Solution

3.2.1. Study of the Presence and Distribution of Elemental Pd by SEM and EDS Investigations

Figure 5a shows an SEM micrograph with an EDS mapping overlay (left) of a sample after laser patterning ($E_p = 25 \mu\text{J}$ and $v_s = 2.0 \text{ m s}^{-1}$) and subsequent treatment in $0.1 \text{ g L}^{-1} \text{ PdCl}_2$ at 50°C . The presence of Pd (indicated by red dots) is more recurrent in the ablated areas, and this is better visualized in the corresponding EDS mapping (right). The presence of Pd

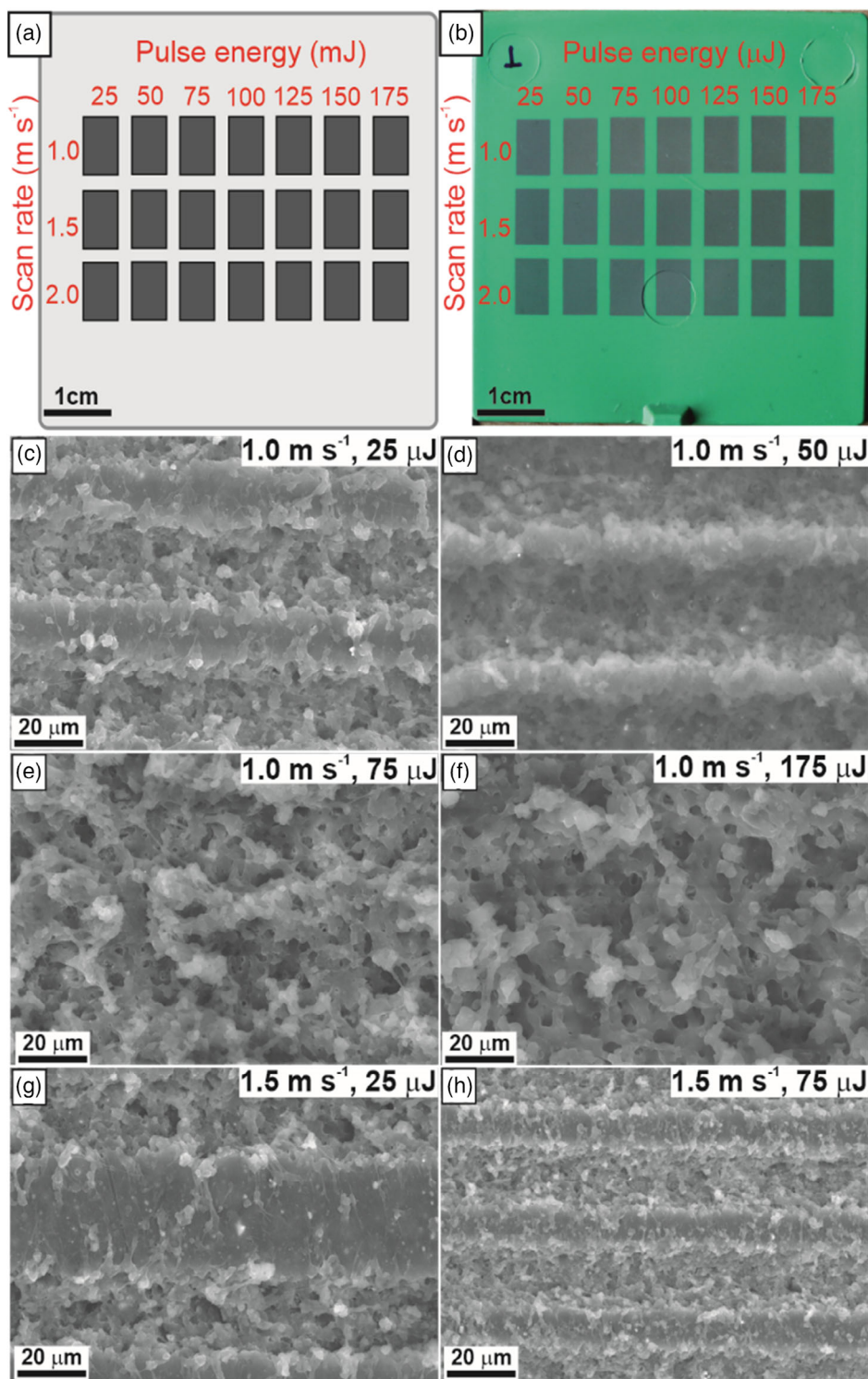


Figure 3. Surface morphology of PBT after laser patterning with different average pulse energy (E_p) and scan rate (v_s) values: a) computerized vector image of the 21 features and b) photographic image of the PBT substrate after laser patterning. Surface morphologies of PBT obtained at $v_s = 1.0 \text{ m s}^{-1}$ and E_p values of c) 25 μJ , d) 50 μJ , e) 75 μJ , and f) 175 μJ as well as $v_s = 1.5 \text{ m s}^{-1}$ and E_p values of g) 25 μJ and h) 75 μJ .

in non-ablated areas can be ascribed to the presence of debris material/fumes that splashed out from ablated areas during the irradiation process.

Laser irradiation can promote photo- and thermochemical reactions such as degradation and/or cross-linking of molecular chains as well as surface amorphization.^[42] These complex

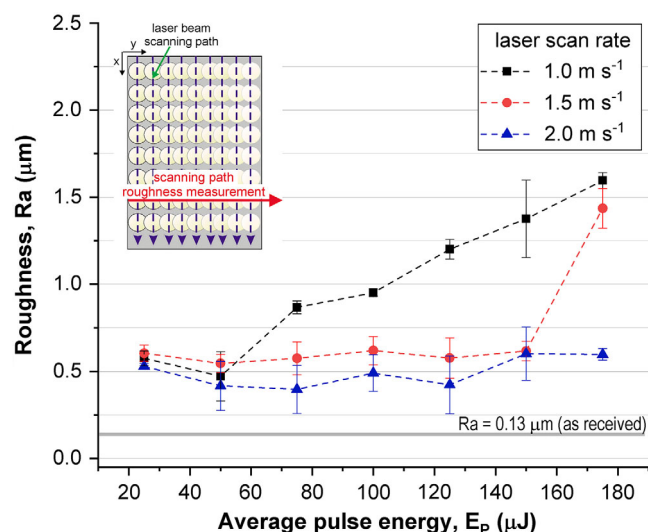


Figure 4. Development of average roughness, R_a , on PBT depending on the average pulse energy (E_p) and the laser scan rate (v_s). Inset: schematic representation of a patterned feature showing the laser beam scanning path as well as the scanning direction used to perform the roughness measurement.

reactions, in turn, might modify the polymer surface by incorporating new functional groups yielding an activated surface that promotes the reduction of Pd(II) species to Pd. Although the surface ablation is not homogeneous for this particular set of laser parameters, the presence of Pd could be detected and, therefore, ascribed to occur via direct ablation or indirect modification (presence of activated debris).

Figure 5b–d shows SEM micrographs and corresponding EDS maps of three features patterned on PBT. The features were produced using a fixed combination of laser parameters ($E_p = 75 \mu\text{J}$ and $v_s = 1.0 \text{ m s}^{-1}$) to produce homogeneous surface micro-roughening (see Section 3.1). The samples were subsequently immersed for 5 min in 0.1 and 0.5 g L^{-1} acidic PdCl_2 solutions at 50 and 70 °C. The EDS mappings reveal the presence of palladium in patterned areas of PBT surfaces treated in 0.1 g L^{-1} PdCl_2 at both temperatures (Figure 5b,c). A uniform Pd distribution can be observed over the whole analyzed area in both cases. As expected, the use of 0.5 g L^{-1} PdCl_2 solution also resulted in a homogeneous Pd distribution (Figure 5d).

Elemental quantification of Pd corresponding to the integral area studied by EDS mapping (Figure 5b–d) is shown in Table 2. Similar surface conditions (sample area and roughness) can be assumed for the three samples as the laser parameters were kept constant during sample processing. Therefore, the quantification of Pd can be compared among these samples. The Pd quantification for the sample seeded at 50 °C with PdCl_2 0.1 g L^{-1} solution was not possible as the obtained value was close to the limit of detection (LOD) reported for SEM–EDS.^[43,44] By increasing the temperature of the activation solution from 50 to 70 °C, an increase of Pd concentration to $0.3 \pm 0.1 \text{ wt\%}$ is observed. Similarly, by increasing the concentration of PdCl_2 from 0.1 to 0.5 g L^{-1} , the Pd content increases from 0.3 ± 0.1 to $0.5 \pm 0.1 \text{ wt\%}$. In addition to carbon and oxygen, Br and Sb were

detected as they are typical components of flame retardant substances in commercial polymers.

3.2.2. Study of the Oxidation State of Palladium by X-Ray Diffraction and AFM-Based Conductivity Investigations

XRD investigations were carried out to confirm the presence of Pd in its reduced state (metallic Pd) as well as to study the changes on the microstructure of the polymer after exposure to laser irradiation. Figure 6 shows the diffractograms of pristine PBT samples (as received) as well as samples after laser patterning ($E_p = 75 \mu\text{J}$ and $v_s = 1.0 \text{ m s}^{-1}$) and treatment in PdCl_2 solutions.

It is known that PBT has two triclinic crystal modifications: α and β forms.^[45,46] Curve (i) of Figure 6 shows the diffractogram of the as-received PBT substrate (reference) which consists of a group of diffraction peaks of a mixture of α and β crystal modifications (PDF 35-1876 and PDF 35-1877, respectively^[47]). It has been reported that the β form occurs under mechanical stress.^[46,48] This latter condition is expected as the substrates were produced by injection molding methodology. The elevated background between 15° and 25° 2θ values indicates also the presence of an amorphous phase of PBT.

The irradiation with picosecond laser pulses of the samples and subsequent treatment for 5 min at 70 °C in 0.1 g L^{-1} (see curve (ii)) as well as 0.5 g L^{-1} PdCl_2 solutions (see curve (iii)) produced microstructural changes in the polymeric material. To simplify the analysis, only selected reflections of the α form [planes (003), (0–22), and (021)] and β form [planes (0–12), (012), and (0–24)] of PBT are indicated with drop lines. In both cases, the signal intensities of the planes (0–12) and (0–24) decreased after laser irradiation while the (012) showed an increment. Furthermore, the intensities of several planes corresponding to the α form of PBT (e.g., (003), (0–22), and (021)) diminished after laser irradiation. This can be ascribed to the structural (and morphological) changes resulting from the laser ablation of the polymer material. In contrast, an additional diffraction peak at a 2θ position of 40.06° can be observed for the samples that were treated in 0.1 and 0.5 g L^{-1} PdCl_2 solutions (curves (ii) and (iii), respectively). The new reflection matches with the (111) plane of Pd which is located at a 2θ position of 40.1° (PDF 46-1043).^[49]

3.2.3. AFM-Based Conductivity Measurements

AFM-based conductivity measurements were carried out to investigate the electrical properties of a PBT sample after laser-assisted activation and treatment in acidic PdCl_2 solution. In this way, the electrical properties as well as the topography can be studied simultaneously. A PBT substrate was subjected to picosecond laser pulses ($E_p = 75 \mu\text{J}$ and $v_s = 1.0 \text{ m s}^{-1}$) as well as a subsequent treatment in 0.5 g L^{-1} PdCl_2 solution for 5 min at 70 °C. The sample was positioned on a copper plate (holder) and the electrical contact was established at the edges of the PBT substrate with silver paint and copper tape (Figure 7a). A schematic representation (transverse view) of an arbitrary area of analysis (indicated in a red square, Figure 7a) as well as the AFM probe–sample surface interaction is shown in Figure 7b.

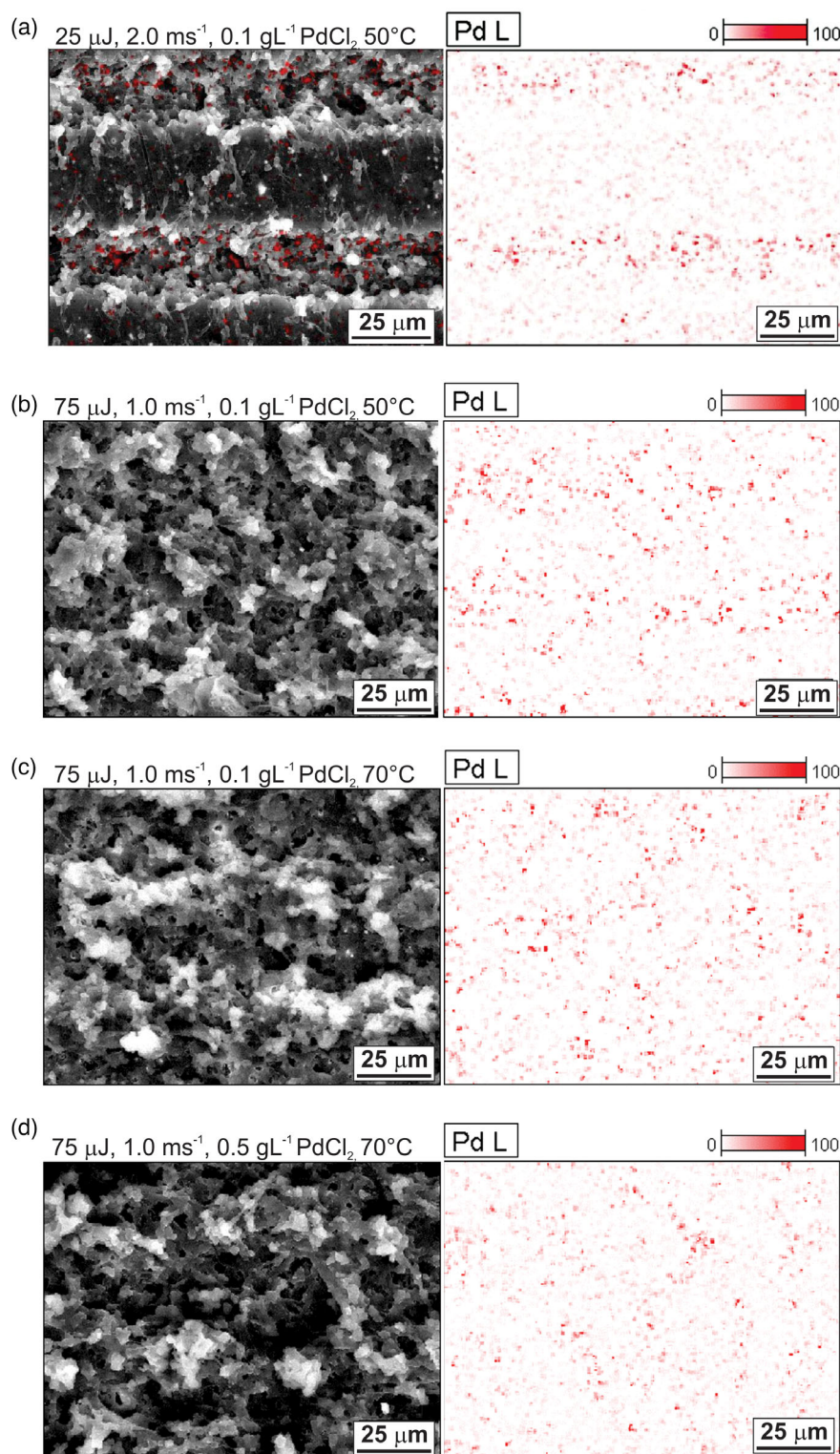


Figure 5. SEM micrographs (1000×) and EDS mappings of PBT surfaces after patterning with picosecond laser pulses and subsequent activation for 5 min in a) 0.1 g L⁻¹ PdCl₂ and 50 °C ($E_p = 25 \mu\text{J}$ and $v_s = 2.0 \text{ m s}^{-1}$), b) 0.1 g L⁻¹ PdCl₂ and 50 °C ($E_p = 75 \mu\text{J}$ and $v_s = 1.0 \text{ m s}^{-1}$), c) 0.1 g L⁻¹ PdCl₂ and 70 °C ($E_p = 75 \mu\text{J}$ and $v_s = 1.0 \text{ m s}^{-1}$), and d) 0.5 g L⁻¹ PdCl₂ and 70 °C ($E_p = 75 \mu\text{J}$ and $v_s = 1.0 \text{ m s}^{-1}$). SEM micrograph combined with EDS mapping is shown in a) to highlight the palladium distribution depending on the surface patterning.

Table 2. Chemical composition of PBT features after patterning with picosecond laser pulses and activation in acidic PdCl_2 solutions by EDX analysis. Laser parameters: $E_p = 75 \mu\text{J}$ and $\nu_s = 1.0 \text{ m s}^{-1}$.

Sample	Concentration [wt%]				
	C	O	Br	Pd	Sb
PBT: $0.1 \text{ g L}^{-1} \text{ PdCl}_2$, 50°C	52.2 ± 0.5	33.7 ± 0.5	11.0 ± 0.3	Value close to the LOD ^{a)}	3.1 ± 0.1
PBT: $0.1 \times \text{g L}^{-1} \text{ PdCl}_2$, 70°C	51.5 ± 0.7	32.7 ± 0.5	12.3 ± 0.4	0.3 ± 0.1	3.3 ± 0.1
PBT: $0.5 \text{ g L}^{-1} \text{ PdCl}_2$, 70°C	52.2 ± 0.6	32.6 ± 0.4	11.3 ± 0.3	0.5 ± 0.1	3.4 ± 0.1

^{a)}The LOD with SEM-EDS technique for non-light element analysis is typically about 0.1 wt%.^[43,44]

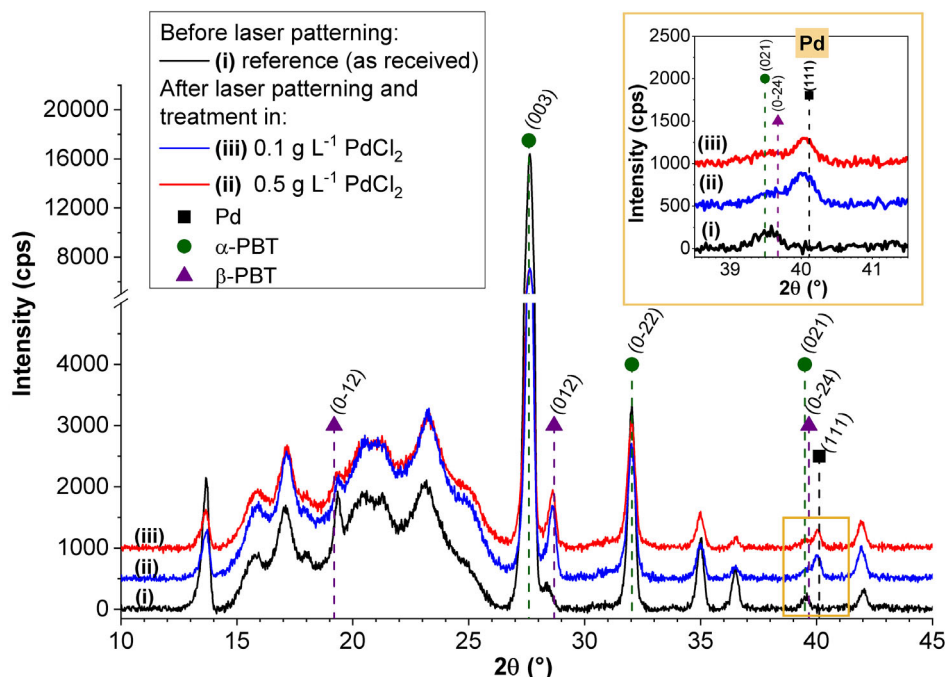


Figure 6. XRD diffractograms of PBT samples: i) reference (as received) as well as after laser treatment with picosecond laser pulses and subsequent treatment at 70°C for 5 min in ii) $0.1 \text{ g L}^{-1} \text{ PdCl}_2$ solution and iii) $0.5 \text{ g L}^{-1} \text{ PdCl}_2$ solution. The inset shows the appearance of the (111) reflection of Pd after the treatment of the sample in activation solutions. An offset is added to the diffractograms for better visibility. Laser parameters: $E_p = 75 \mu\text{J}$ and $\nu_s = 1.0 \text{ m s}^{-1}$.

The surface topography consisting of bumps with sizes in the microscale and a maximum height of about $2 \mu\text{m}$ (Figure 7c,e) results mainly from the laser ablation processes and agrees with the SEM observations (Figure 3e). On the other hand, Figure 7d shows the current distribution in the same area of study. The current map clearly shows zones with higher conductivity (bright areas) compared to a much less-conductive background (dark areas). Because of the significant difference of conductivity values between Pd and carbon (sputtered thin layer), the bright areas can be ascribed to the presence of metallic Pd at the polymer surface. A 3D-AFM image, as well as its overlay with the current map image, is given in Figure 7e,f, respectively. Both images indicate that the polymer surface is partially covered by clusters and/or noncontinuous thin layer of Pd. These results agree well with the SEM and EDS observations.

3.3. Influence of Activation Parameters on the Metallization of Copper Features

3.3.1. Effect of the Concentration and Temperature of the PdCl_2 Solution on Copper Electroless Deposition

To evaluate the deposition onset as well as the deposition rate, the samples were activated for 5 min in PdCl_2 solutions at different conditions, whereas the copper deposition time was fixed to 30 min for all cases.

Figure 8 shows the effect of two different PdCl_2 concentrations (0.1 and 0.5 g L^{-1}) at two different temperatures (50 and 70°C) on the ability of the polymer surface to promote metallization. At 50°C , the use of $0.5 \text{ g L}^{-1} \text{ PdCl}_2$ solution enabled the metallization of all features (Figure 8b), whereas the use of $0.1 \text{ g L}^{-1} \text{ PdCl}_2$ solution resulted only in a partial metallization

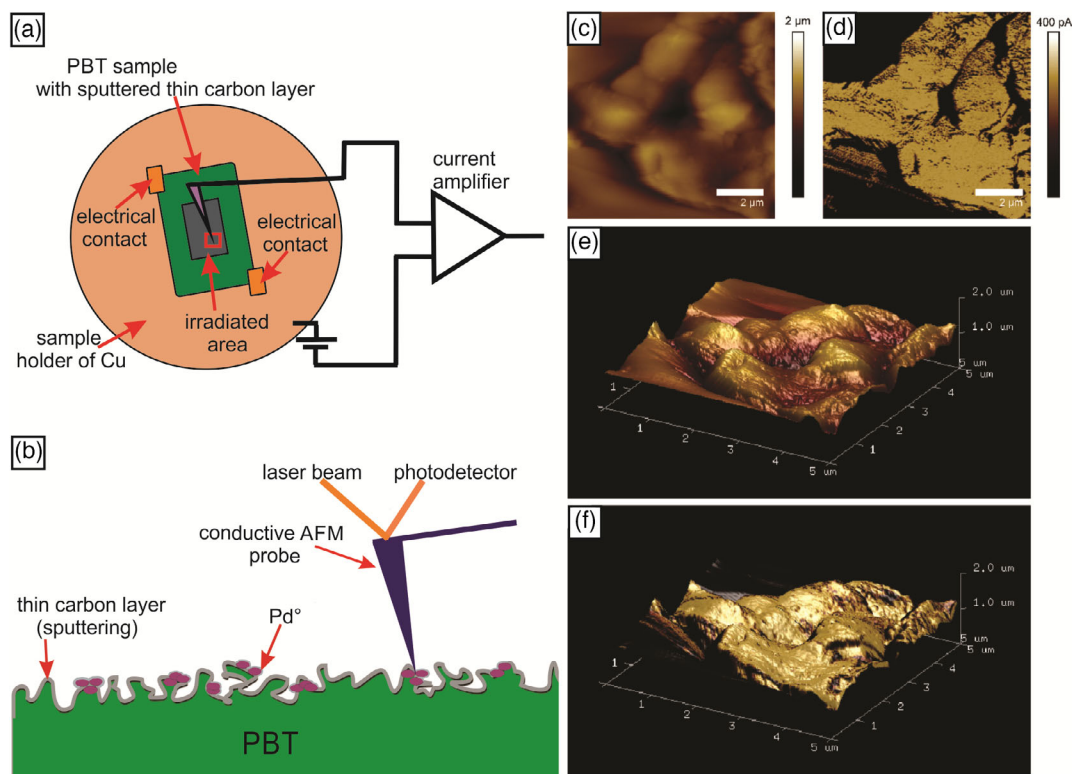


Figure 7. a) Schematic representation of the AFM-based conductivity sample assembling and b) schema of the sample surface interaction with the conductive AFM probe. AFM images of a PBT substrate area subjected to picosecond laser pulses ($E_p = 75 \mu\text{J}$) and $v_s = 1.0 \text{ m s}^{-1}$ as well as a subsequent treatment in $0.5 \text{ g L}^{-1} \text{ PdCl}_2$ solution for 5 min at 70°C : c) topography (height), d) AFM-based current map, e) 3D topography (height), and f) 3D topography overlay with AFM-based current map.

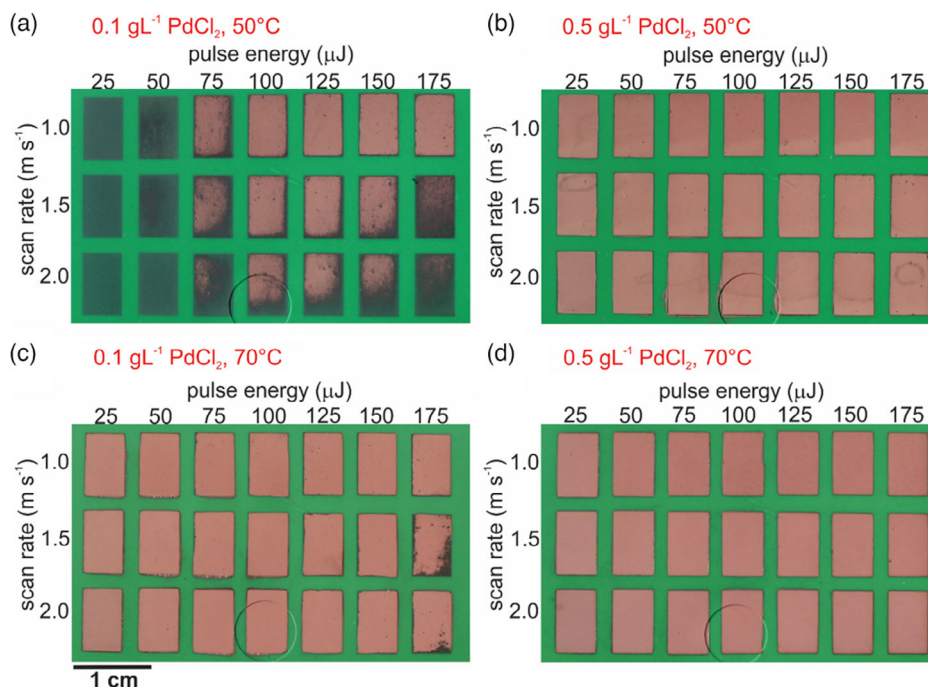


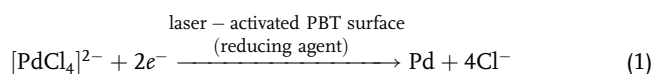
Figure 8. Macroscopic view of copper structures on PBT after 30 min of electroless deposition. Substrates were activated with picosecond laser pulses and subjected to treatment for 5 min in a) $0.1 \text{ g L}^{-1} \text{ PdCl}_2$ solution at 50°C , b) $0.5 \text{ g L}^{-1} \text{ PdCl}_2$ solution at 50°C , c) $0.1 \text{ g L}^{-1} \text{ PdCl}_2$ solution at 70°C , and d) $0.5 \text{ g L}^{-1} \text{ PdCl}_2$ solution at 70°C .

(Figure 8a). These results agree well with the EDS analysis of elemental Pd. For instance, the results shown in Table 2 confirm that the Pd concentration present at the PBT surface after treatment in PdCl_2 0.5 g L^{-1} solution was higher than with PdCl_2 0.1 g L^{-1} seeding solution. The amount and uniform distribution of Pd seeds are crucial parameters for the successful formation of a closed copper layer during electroless plating.

The temperature of the seeding solution has a significant influence on the metallization of PBT. Irradiated PBT features subjected to treatment for 5 min in PdCl_2 solutions at room temperature showed no copper deposition for any feature (image not shown). Seeding at 70°C can lead to the metallization of all features (Figure 8c,d), whereas at 50°C only some features could be metallized (Figure 8a). Figure 8 d shows a metallized sample previously subjected to seeding at 70°C with 0.5 g L^{-1} PdCl_2 solution. These conditions were found to be optimal as all copper features could be metallized without any macroscopic defects such as pores, voids, or non-metallized zones.

The results have shown that the reduction of Pd (II) into Pd (0) occurred by immersing freshly prepared laser-irradiated PBT samples in acidic PdCl_2 solution at temperatures above 50°C . Under those conditions, the predominant Pd(II) species in solution is the complex PdCl_4^{2-} .^[50] In all cases, the time between laser irradiation and immersion of the sample in the seeding solution (intermediate time) was less than 2 min. Under those conditions, the onset of copper deposition occurs just some seconds after immersion of the Pd seeded sample in the electroless bath. Experiments were also carried out with longer intermediate times (not shown). It was observed that the longer the intermediate time, the lesser the ability of the laser-activated polymer surface to reduce Pd(II) and, consequently, to enable metallization. This suggests an activation mechanism mainly via chemical modification of the polymer surface.

In this study, the interaction between picosecond NIR laser pulses and commercial PBT surface resulted in phenomena such as laser ablation and chemical surface modification. After laser irradiation, the PBT surface turns into a metastable state in which new functional groups/chemical compounds might be formed. Although the characterization of the surface chemistry is challenging due to its lability in environmental conditions, the reducing nature of the laser-treated surface was demonstrated with the detection of metallic Pd after immersion in acidic PdCl_2 -based solutions (Equation (1))



Studies on the selective metallization of polyamide 6 with AgNO_3 as catalyst precursor suggested that aldehydes reducing groups might be formed after irradiation with picosecond NIR laser pulses.^[31] Furthermore, it has been reported that the thermal decomposition of PET via IR laser ablative degradation can yield acetaldehyde among other volatile products as well as nonvolatile oligomers having C=O functional groups.^[51,52] In contrast, the formation of an electrically conductive glassy carbon thin layer due to laser-induced surface carbonization is another possible effect that might contribute to mediate the reduction of Pd(II) to Pd.^[39] To get more insights regarding the surface chemistry of the polymer after laser irradiation as

well as its lability, in situ characterization techniques must be the focus of further work.

3.3.2. Morphology and Thickness Distribution of Copper Structures

After laser patterning with different parameter fields, all samples were subjected to treatment in 0.5 g L^{-1} PdCl_2 solution at 70°C for 5 min followed by electroless copper deposition for 30 min. **Figure 9a** shows the optical micrograph of the copper layer grown on an irradiated surface with $E_p = 25 \mu\text{J}$ and $v_s = 1.0 \text{ m s}^{-1}$. Despite the high coverage achieved, the copper layer still replicates the surface morphology of the PBT after laser irradiation (Figure 5a). The corresponding SEM micrograph (Figure 9b) shows that the copper layer has grown continuously through the surface micro-cavities (no voids, cracks, or other defects could be detected) and possesses cauliflower-like morphology. A similar morphology, with a more homogeneous surface coverage, was obtained for the copper layer grown on an irradiated surface with $E_p = 75 \mu\text{J}$ and $v_s = 1.0 \text{ m s}^{-1}$ (Figure 9c,d). In contrast, the resulting copper layer deposited on an irradiated surface with a higher scan rate ($v_s = 1.5 \text{ m s}^{-1}$) shows more compactness (Figure 9e,f).

Figure 9 demonstrates that the deposition of continuous copper layers was possible in all cases. The morphology and degree of compactness of the layers are influenced by the surface properties of PBT, which in turn depend on the laser parameters used for surface patterning. Furthermore, the concentration and distribution of the catalyst (Pd) also play an important role in the deposition characteristics of copper, such as nucleation, grow mode, and deposition rate.

The influence of the laser parameters as well as the seeding temperature (conditions: 0.5 g L^{-1} PdCl_2 , 5 min) on the rate of copper deposition was investigated by measuring the thickness of the copper layers after 30 min of electroless deposition. **Figure 10a** shows the thickness distribution of a variety of copper features obtained when the Pd seeding was performed at 70°C . The combination of $v_s = 1.0 \text{ m s}^{-1}$ and E_p values in the range between 75 and $125 \mu\text{J}$ promoted the fastest layer growth. These results have a good correlation with the results described in Section 3.2 as the catalytic activity of the PBT surface for electroless deposition is directly proportional to the amount of uniform distribution of Pd seeds. The maximum thickness value was $3.0 \mu\text{m}$ ($E_p = 100 \mu\text{J}$ and $v_s = 1.0 \text{ m s}^{-1}$), which results in a maximum deposition rate of $0.10 \mu\text{m min}^{-1}$.

Performing the Pd seeding at 50°C led to a decrease in the Cu deposition rate. As shown in Figure 10b, the maximum thickness value was $2.4 \mu\text{m}$ ($E_p = 100 \mu\text{J}$ and $v_s = 1.0 \text{ m s}^{-1}$), which results in a maximum deposition rate of $0.08 \mu\text{m min}^{-1}$. Except for the edge zones, there is a relatively uniform thickness distribution in every rectangular feature as the maximum standard deviation value was $0.16 \mu\text{m}$ (15 measurements per feature were considered for standard deviation calculation).

3.3.3. Electrical Properties of Copper Layers

As previously discussed, the laser parameters used to modify the PBT surface can indirectly influence the properties of the copper layers such as the electrical resistivity. The electrical resistivity

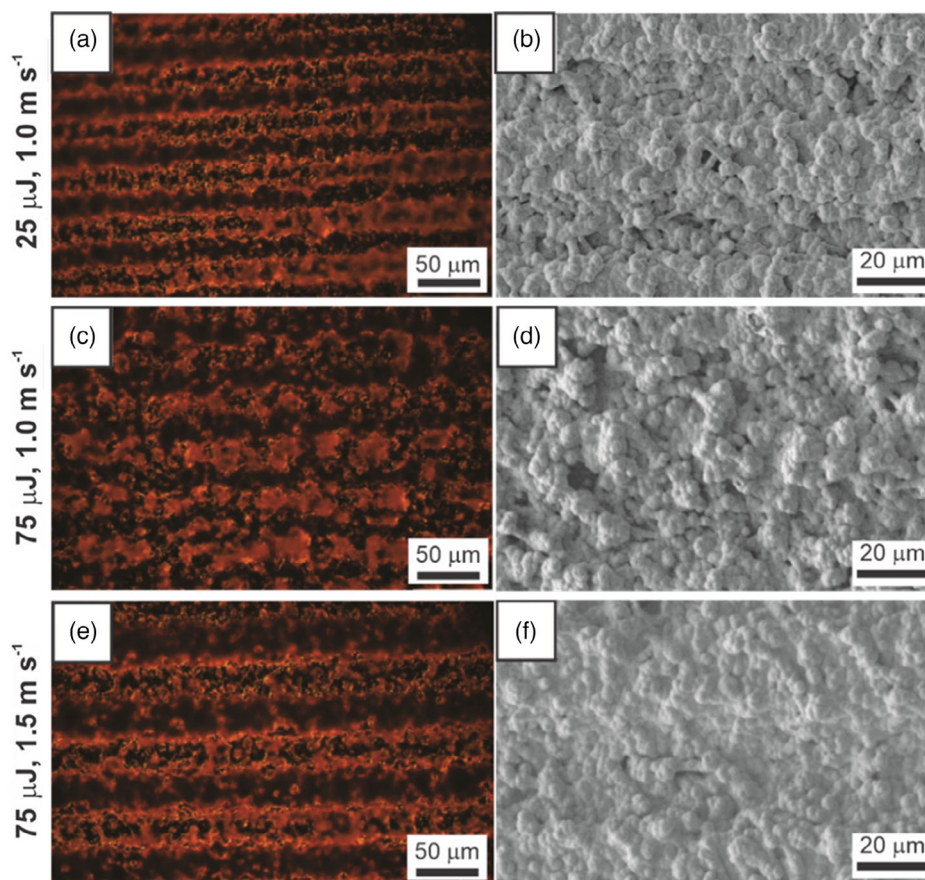


Figure 9. Morphology of copper deposits on PBT surfaces obtained via surface laser patterning with picosecond laser pulses under different conditions, treatment in 0.5 g L^{-1} PdCl_2 solution for 5 min at 70°C and electroless copper deposition for 30 min. Optical micrographs (a,c,e) and their corresponding scanning electron micrographs (b,d,f).

depending on the laser pulse energy and scan rate is shown in Figure 11.

The electrical resistivity values of all copper layers are relatively similar as they vary within a range between 3.8 and $5.7 \mu\Omega \text{ cm}$. These values are in accordance with reported values for electroplated (2.0 – $8.3 \mu\Omega \text{ cm}$)^[53] or electroless (3.3 – $6.2 \mu\Omega \text{ cm}$)^[54] copper films. The electrical resistivity of bulk copper is $1.78 \mu\Omega \text{ cm}$.^[55]

The small differences in electrical resistivity can be ascribed to the properties of the copper layers such as the grain size, degree of texture, roughness, as well as the presence of impurities.^[56] By increasing E_p values from 25 to $100 \mu\text{J}$, the electrical resistivity of copper increases slightly, especially at $v_s = 1.0 \text{ m s}^{-1}$. When a combination of $E_p = 75 \mu\text{J}$ and $v_s = 1.0 \text{ m s}^{-1}$ is employed, the morphology of the layer becomes more heterogeneous (Figure 9d) and the slight increase of the electrical resistivity might be mainly related to the higher degree of roughness achieved at those conditions.^[57] In contrast, the slight decrease of electrical resistivity achieved with E_p values higher than $100 \mu\text{J}$ might be less influenced by morphology changes but by other layer properties described previously. As the variation of the electrical resistivity values fits within the range reported in the literature, it can be concluded that the copper deposits have a very good quality in terms of electrical properties.

3.3.4. Adhesion Tests

Figure 12 shows the results of the adhesion test. Figure 12a shows an image of three copper layers after the tape test. The layers were prepared with different laser parameters: P1 ($E_p = 75 \mu\text{J}$, $v_s = 1.0 \text{ m s}^{-1}$), P2 ($E_p = 75 \mu\text{J}$, $v_s = 2.0 \text{ m s}^{-1}$), and P3 ($E_p = 25 \mu\text{J}$, $v_s = 2.0 \text{ m s}^{-1}$). All layers were prepared with the same seeding parameters (PdCl_2 0.5 g L^{-1} ; 5 min ; 70°C) as well as electroless plating conditions (30 min , 43°C). The good adherence of all layers can be ascribed to the surface roughening of the PBT substrates (as a result of laser treatment) as well as the good distribution of the catalyst. In some cases, some traces of copper were found on the adhesive tape after the tests. However, this material did not come from the laser-patterned area but from zones adjacent to the edges of the copper features (Figure 12b). Some excess copper deposition can be seen in the left part of the edge (yellow drop line) of the patterned area prepared with parameters P1. As the layer at these zones lacks a minimum degree of roughness, the excess copper can be removed easily with the tape. The deposition of copper near the edges of the laser-treated area can be ascribed to the presence of debris material which can be active for metallization. This issue can be improved by optimizing the cleaning procedure after laser irradiation and/or Pd seeding.

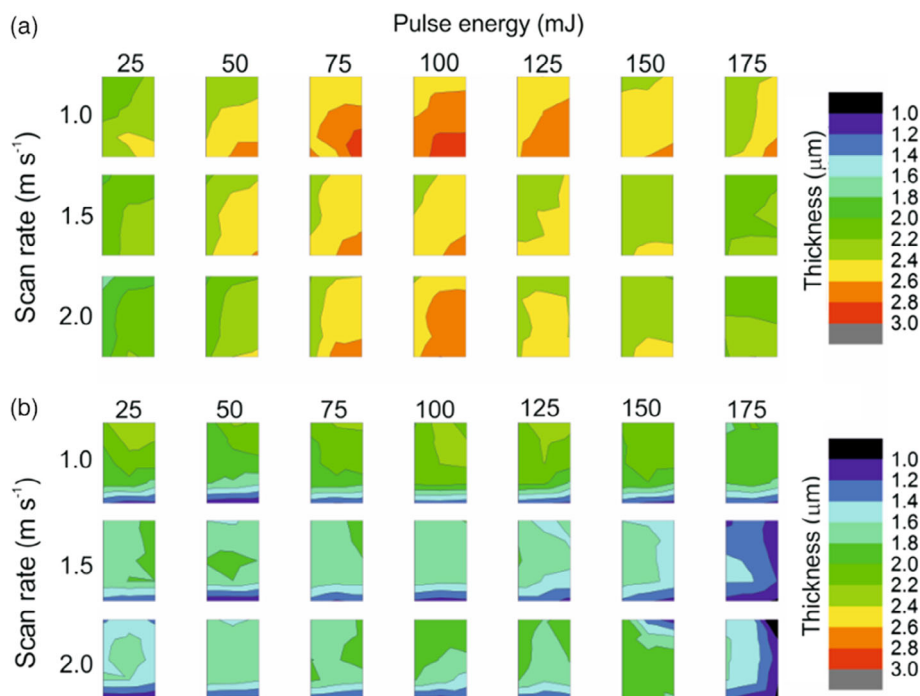


Figure 10. Thickness distribution of copper layers on PBT after 30 min of electroless deposition determined by XRF. PBT substrates were previously subjected to laser patterning and treatment in 0.5 g L^{-1} PdCl_2 solution for 5 min at a) 70°C and b) 50°C .

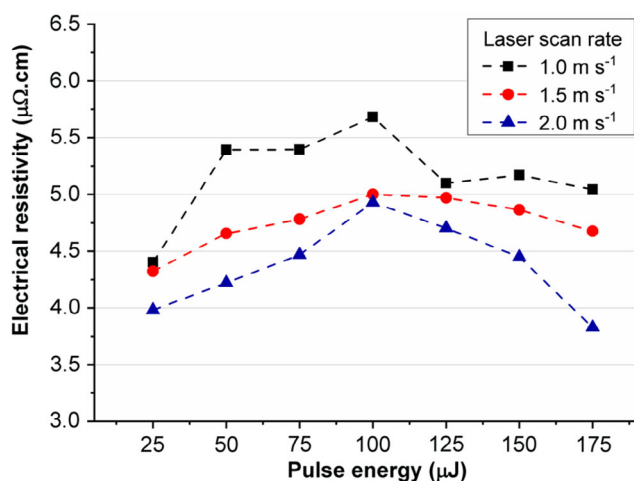


Figure 11. Electrical resistivity of Cu structures on PBT. Laser patterning was conducted using different combinations of pulse energies and scan rates. The patterned substrate was treated for 5 min in 0.5 g L^{-1} PdCl_2 solution at 70°C followed by Cu electroless deposition for 30 min. The error bars are not visible in the plot due to their small values.

A cross-sectional SEM micrograph of the copper layer deposited with P1 parameters ($E_p = 75 \mu\text{J}$, $v_s = 1.0 \text{ m s}^{-1}$) after the tape test can be seen in Figure 12c. It can be observed that the deposit has grown following the rough surface morphology obtained after laser irradiation. The good adherence is ascribed to the mechanical anchoring of the layer to the substrate and the uniform coating thickness is an indicator of a good catalyst

(Pd seeds) distribution. The measured thickness ($2.8\text{--}3.6 \mu\text{m}$) is in good agreement with the XRF-based measurements shown previously in Figure 10.

Figure 12d shows a copper layer grown on a PBT substrate irradiated with lower pulse energy and higher scan rate ($E_p = 25 \mu\text{J}$, $v_s = 2.0 \text{ m s}^{-1}$) in contrast to the sample from Figure 12c. The copper layer also has a homogeneous thickness distribution ($2.4\text{--}2.7 \mu\text{m}$). Despite the lower roughness of the substrate, the copper layer has enough adherence to withstand the tape test.

To illustrate the promising applications of the proposed methodology for selective metallization, the university logos of the participating institutions were metallized as shown in Figure 13. The logos were accurately patterned onto a PBT substrate even though they show a higher degree of complexity.

4. Conclusion

The selective metallization on PBT was successfully achieved with a laser-assisted methodology. The use of picosecond laser pulses can modify the substrate producing highly rough surfaces that can be adjusted by the selection of the laser parameters. The irradiation of picosecond laser pulses also can lead to the chemical modification of the polymeric surface in a way that the surface acquires the ability to reduce Pd(II) ions into metallic Pd clusters/thin layers during a treatment in PdCl_2 solution. The concentration of metallic Pd can be influenced by the temperature and PdCl_2 concentration in the seeding solution. The copper deposition onset occurs just some seconds after the immersion of the samples in the electroless plating bath. With this method,

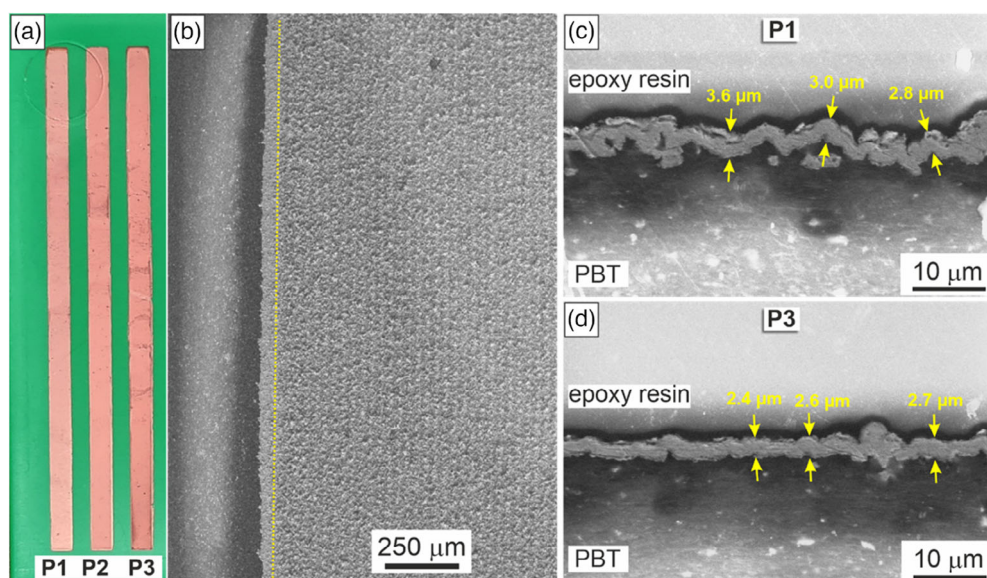


Figure 12. a) Copper features after the tape test according to IPC-TM-650 norm.^[36] Laser parameters: P1 ($E_p = 75 \mu\text{J}$, $\nu_s = 1.0 \text{ m s}^{-1}$), P2 ($E_p = 75 \mu\text{J}$, $\nu_s = 2.0 \text{ m s}^{-1}$), and P3 ($E_p = 25 \mu\text{J}$, $\nu_s = 2.0 \text{ m s}^{-1}$). Seeding parameters: PdCl_2 0.5 g L^{-1} ; 5 min, 70°C . Electroless deposition: 30 min, 43°C . b) SEM micrograph of a copper layer (P1) before the tape test showing the growth of copper on zones adjacent to the edges of the laser-patterned area. SEM micrographs of the copper layers in cross section after the tape test: c) P1 and d) P3.



Figure 13. Digital photo of the university logos on PBT surface after metallization assisted by picosecond laser pulses. Laser parameters: $E_p = 75 \mu\text{J}$, $\nu_s = 1.0 \text{ m s}^{-1}$. Seeding parameters: PdCl_2 0.5 g L^{-1} ; 5 min; 70°C . Electroless deposition: 30 min at 43°C .

copper structures with well-defined geometries, strong adhesion to the substrate, and low electrical resistivity were obtained. An important aspect is that the selective metallization was successful in a broad range of laser parameters, provided its combination with suitable Pd seeding parameters.

The metallized patterns show a great potential for applications in electronic devices. As the substrate activation (laser irradiation) is performed in air, the present method offers flexibility to pattern components with complex geometries. Furthermore, this approach can be conveniently applied at industrial scale as the methodology does not involve the use of expensive additives (catalytic fillers) in the polymer matrix or the application of seeding precursors in solid phase, liquid phase, and so on before or during laser patterning.

Further work shall focus on the elucidation of surface chemistry of PBT (and other polymers) just after laser patterning and its lability. Aspects such as the optimization of the PdCl_2 concentration for seeding as well as the improvement of the cleaning procedure after laser irradiation/seeding can also be proposed for future work.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data available on request from the authors.

Keywords

copper electroless plating, laser-assisted activation, palladium, picosecond laser pulses, polybutylene terephthalate, selective metallization

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