

# RAMAN INVESTIGATION OF SOL-GEL ANTICORROSION COATINGS ON ELECTRONIC BOARDS

## RAMANSKE RAZISKAVE SOL-GEL PROTİKOROZIJSKIH PREVLEK NA ELEKTRONSKIH VEZJIH

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Due to its non-destructive character and high spatial resolution, confocal Raman spectroscopy was found to be a good technique for detecting spray-deposited sol-gel coatings on electronic boards (EBs). EBs are demanding substrates to cover because of their non-flat surfaces, containing various metals, alloys, pins and other elements. Nanocomposite coatings were made on the basis of bis end-capped organic-inorganic hybrid precursors, *bis*-(3-(3-(3-triethoxysilyl)propyl)thioureido)propyl terminated polydimethylsiloxane (PDMSTU) and *bis*-[3-(triethoxysilyl)propyl]tetrasulphide (BTESPT), imparting a hydrophobic character to the produced anticorrosion coatings. Reactions of hydrolysis and condensation were initiated with an addition of the 0.1 M HCl catalyst. Nanoparticles were introduced in the sols as trisilanol-heptaioctyl-polyhedral oligomeric silsesquioxanes (up to 5 nm). The obtained sols were spray deposited on the test substrate, i.e., the aluminium alloy AA 2024, and also on EB. The coatings on AA 2024 were used for potentiodynamic electrochemical and surface (SEM, AFM) characterisation of the prepared coatings. Extensive Raman spectroscopy measurements of the uncovered and covered EBs revealed that the sol-gel coatings on various elements and pins of EBs are clearly visible in the Raman spectra and that this is an appropriate technique for detecting the coatings on such demanding substrates.

**Keywords:** Raman spectroscopy, sol-gel, electronic boards, anticorrosion coatings, nanoparticles

Glede na nedestruktivni značaj in veliko prostorsko ločljivost ramanske spektroskopije smo to tehniko študirali s stališča možnosti detekcije napršenih sol-gel prevlek na elektronska vezja. Elektronska vezja so zahtevne podlage, kar zadeva njihovo prekrivanje, saj njihova površina ni ravna, na njej se nahajajo različne kovine, zlitine, konice in drugi elementi. Nanokompozitne prevleke smo pripravili na osnovi dvostransko funkcionaliziranih organsko-anorganskih prekurzorjev *bis*-(3-(3-(3-trietoksisilil)propil)tioureido)propil zaključenega poli(dimetilsiloksana) (PDMSTU) in *bis*-[3-(trietoksisilil)propil]tetrasulfida (BTESPT), ki v pripravljene protikorozijske prevleke vneseta hidrofoben značaj. Reakcije hidrolize in kondenzacije smo začeli z dodatkom katalizatorja 0,1 M HCl. Nanodelce smo v sole vključili kot trisilanol-heptaizooktil-poliedrične oligomerne silseskvioksane (do 5 nm). Tako pripravljene sole smo nanесли na preizkusne podlage, in sicer na aluminijevo zlitino AA 2024 in tudi elektronska vezja. Prevleke na AA 2024 smo uporabili za potenciodinamične elektrokemijske meritve in površinsko (SEM, AFM) karakterizacijo. Obširne ramanske meritve nezaščitenih in zaščitenih elektronskih vezij pa so pokazale, da lahko sol-gel prevleke na različnih elementih in konicah elektronskih vezij jasno ugotovimo v ramanskih spektrih in da je zato ta tehnika primerna za detekcijo prevlek na zahtevnih podlagah.

**Ključne besede:** ramanska spektroskopija, sol-gel, elektronska vezja, protikorozijske prevleke, nanodelci

## 1 INTRODUCTION

Raman spectroscopy has been recognised as a very useful tool for the investigation of organic and inorganic materials in various fields, for example in art and archaeology<sup>1</sup>, for the investigation of electrode materials for lithium electrodes<sup>2</sup> as well as the materials produced from organic-inorganic hybrids<sup>3,4</sup>. Raman spectra show the energy shift of the excitation light (laser) as a product of an inelastic scattering of the molecules in a sample, resulting in obtaining the information about their chemical structure, i.e., Raman spectra represent the fingerprints of the molecules. Moreover, this vibrational technique can be useful for proving the correctness of technological processes<sup>3</sup>, for instance, the efficiency of a deposition process for the coatings on various substrates, since it does not require background measurements and

is a non-destructive technique. Such complex substrates include, for example, electronic boards (EBs) composed of various materials (metals, alloys, soldering alloys, plastic materials, etc.). Raman spectroscopy can clearly detect sprayed protective coatings on various individual elements of EBs.

Numerous enterprises have realised that the enormous amounts of electronic waste can be reduced with the application of anticorrosion coatings on various electronic components. However, the anticorrosion coatings for EBs must respond to a unique set of corrosion-related problems, since different elements (materials) are positioned in close proximity. This gives rise to a great possibility of galvanic corrosion, the corrosion of contact surfaces and joints or a growth of dendritic silver. In addition, the surfaces of EBs are not flat, so it is difficult to cover them homogeneously with a coating. Nowadays,

conformal paint coatings (polyurethane, acrylic, epoxy, etc.) are mostly used for the protection of EBs, but such coatings are expensive and do not usually offer satisfactory adhesion and protection (<10 years)<sup>5</sup>. Many conformal coatings, in particular the widely used acrylic coatings, often delaminate from the corners of the leads and EBs, and develop cracks, in which water may be entrapped, dissolving contaminants. This can result in dendritic growth between the components of the leads, leading to shorts, excessive power consumption and, therefore, EB malfunctions<sup>5</sup>.

Nanocomposite barrier coatings prepared from organic-inorganic hybrid precursors, consisting of nanoparticles (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, ...) or polyhedral oligomeric silsesquioxanes (POSS) are believed to be promising materials for successfully replacing conformal coatings. The preparation of good sol-gel nanocomposite coatings starts with an appropriate selection of precursors, nanoparticles, inhibitors and additives<sup>6</sup>. By introducing the appropriate groups to the composition we can achieve, in addition to the resistance to corrosion, that the sol-gel coatings also provide high oxidation, abrasion and water-resistant properties. In this work, bis end-capped ethoxysilyl-functionalised precursor *bis*-(3-(3-(3-triethoxysilyl)propyl)thioureido)propyl terminated poly(dimethylsiloxane) (PDMSTU in **Figure 1**) was synthesised as the organic-inorganic precursor for sol-gel nanocomposite coatings<sup>7</sup>. This organic-inorganic hybrid precursor also comprises a poly(dimethylsiloxane) chain, which imparts its hydrophobic character to the deposited anticorrosion coatings. The nanoparticles were included as polyhedral oligomeric silsesquioxane trisilanol-hepta-isooctyl-POSS (TS-IOc<sub>7</sub>-POSS in **Figure 1**), which, due to the open-cage structure, can bind in the sol-gel matrix via a formation of siloxane bonds. Another bis end-capped precursor, i.e., bis-[3-(triethoxysilyl)propyl]tetrasulphide (BTESPT in **Figure 1**), was included in the composition of the sol to increase the siloxane bonding in the coatings. The efficiency of the BTESPT

coatings for the preparation of anticorrosion coatings for various alloys (AA 2024-T3<sup>8</sup>, AZ31 Mg<sup>9</sup>) has already been demonstrated. In the present paper, we would first like to show that the PDMSTU-based nanocomposite coatings can be applied on EBs with the spray-deposition technique. In addition, the suitability of Raman spectroscopy for detecting deposited coatings on all the different elements of an EB substrate is shown.

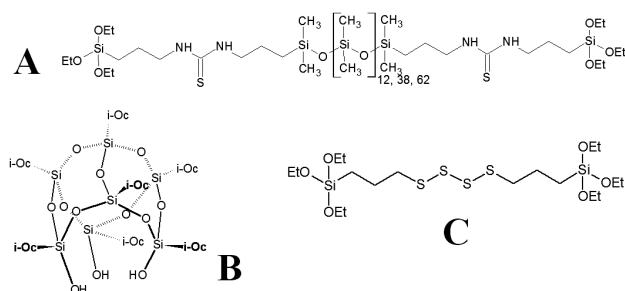
## 2 EXPERIMENTAL WORK

The organic-inorganic hybrid precursor *bis*-(3-(3-(3-triethoxysilyl)propyl)thioureido)propyl terminated polydimethylsiloxane (PDMSTU) was synthesised from aminopropyl terminated poly(dimethylsiloxane) 1000 (PDMS 1000)<sup>7</sup>. 23 g of PDMS 1000 was dissolved in 40 ml of tetrahydrofuran and 12.5 g of (3-isothiocyanatopropyl)triethoxysilane was then added dropwise. The solution was refluxed for 2 days and the progress of the reaction was followed using FT-IR spectroscopy. After the conclusion of the reaction, tetrahydrofuran was removed *in vacuo* and a highly viscous yellow PDMSTU product was obtained.

The sol for the spray deposition on the EB substrate was prepared in ethanol by mixing PDMSTU : BTESPT : TS-IOc<sub>7</sub>-POSS in a molar ratio of 1 : 2 : 0.5. As a catalyst of the sol-gel reactions, 0.1 M hydrochloric acid was applied in a molar ratio of PDMSTU : 0.1 M HCl = 1 : 18, based on the number of ethoxy groups in the PDMSTU and BTESPT precursor molecules. The sol was stirred for 4 days before spraying on the EB substrate. The time of the application was determined by following the hydrolysis and condensation reactions using FT-IR measurements (not shown). The sol gelled in ten days. For a comparison between morphological properties (SEM, AFM) and electrochemical measurements, the PDMSTU-based coating was deposited on the aluminium alloy AA 2024, also using the spray-deposition technique. Prior to spraying the sol on AA 2024, the substrate was polished and cleaned in hexane, acetone, methanol and distilled water. The deposited coating was thermally treated at 150 °C for half an hour prior to the treatment.

SEM micrographs were recorded on a FE-SEM Supra 35 VP electron scanning microscope.

An electrochemical potentiodynamic measurement of the PDMSTU-based coating deposited on the AA 2024 substrate was recorded on a PGSTAT 302N potentiostat-galvanostat. The coating was mounted as the working electrode in a K0235 flat cell (Princeton Applied Research) filled with 0.5 M NaCl. The reference electrode was a saturated Ag/AgCl electrode and the counter electrode was the Pt grid. The samples were held at an open circuit potential for 1800 s prior to scanning the potential with a scan rate of 0.5 mV/s from -0.9 V to -0.2 V.



**Figure 1:** Structures of the precursors for the preparation of sol-gel nanocomposite anticorrosion coatings for EBs: A) *bis*-(3-(3-(3-triethoxysilyl)propyl)thioureido)propyl terminated poly(dimethylsiloxane) (PDMSTU), B) trisilanol-hepta-isooctyl-POSS (TS-IOc<sub>7</sub>-POSS) and C) *bis*-(3-(3-(3-triethoxysilyl)propyl)tetrasulphide) (BTESPT)

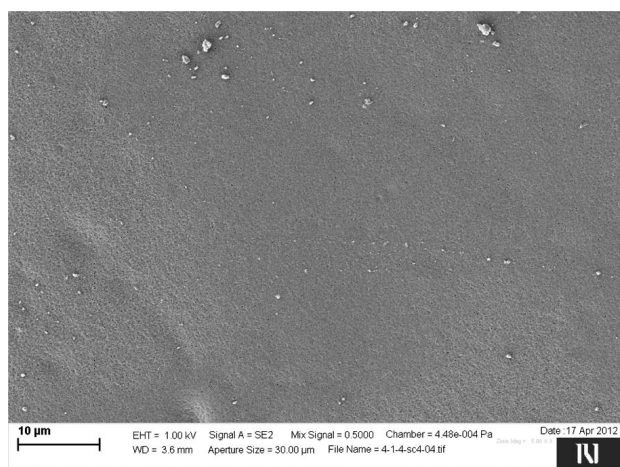
**Slika 1:** Strukture prekurzorjev za pripravo sol-gel nanokompozitnih protikorozijskih prevlek za elektronska vezja: A) *bis*-(3-(3-(3-trietoksisilil)propil)tioureido)propil zaključen poli(dimetilsiloksan) (PDMSTU), B) trisilanol-heptaizooktil-POSS (TS-IOc<sub>7</sub>-POSS) in C) *bis*-(3-(trietoksisilil)propil)tetrasulfid (BTESPT)

Raman spectra of the uncovered and covered EB were collected using a confocal Raman spectrometer WITec alpha 300, combined with the AFM and SNOM (Scanning Near-Field Optical Microscopy) techniques. The excitation line used was 532 nm.

### 3 RESULTS AND DISCUSSION

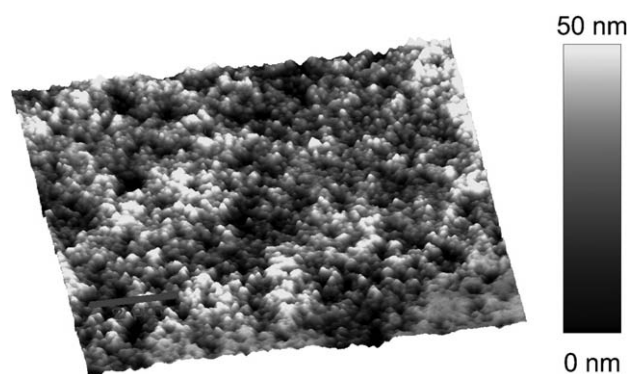
The SEM micrograph revealed a homogeneous surface of the PDMSTU-based coating, but some defects on the surface can also be observed (**Figure 2**). AFM, on the other hand, confirmed the nanocomposite character of the coating, with a roughness factor of 110 nm (**Figure 3**).

A potentiodynamic measurement of the spray-deposited PDMSTU-based coating on AA 2024 revealed a cathodic current density that is lower, by about two decades of magnitude, than that of the pure AA 2024 substrate (**Figure 4**). Moreover, the anodic current density was lower by about one to two orders of magnitude (**Figure 4**). These values are comparable to those of the anticorrosion coatings prepared by dip-coating on the AA 2024 substrates from 1 % sols of bis-(3-(3-(3-triethoxysilyl)propyl)ureido)propyl terminated polydimethylsiloxane (PDMSU)<sup>10</sup>, i.e., a similar precursor with the urea instead of thiourea groups between the poly(dimethylsiloxane) and ethoxysilylpropyl parts of the molecule (**Figure 1**). The PDMSU coatings, on the other hand, showed a better performance when prepared from more concentrated, 4 %, sols, i.e., the sols with an increasing thickness confirming their physical barrier character. Moreover, our PDMSTU-based coatings revealed superior properties compared to the pure BTESPT coatings made from water/ethanol solutions<sup>8</sup>. Specifically, the hydrophobic BTESPT coatings revealed a decrease of about one order of magnitude in the cathodic current density and of about 1–2 orders of



**Figure 2:** SEM micrograph of the spray-deposited PDMSTU-based coating on AA 2024

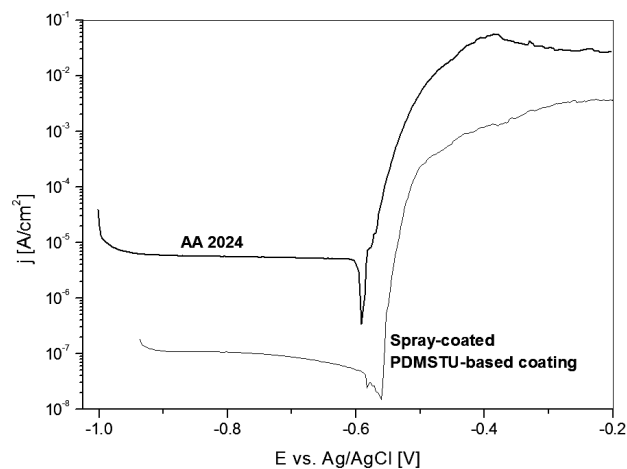
**Slika 2:** SEM-posnetek prevleke, pripravljene na osnovi PDMSTU in napršene na podlago AA 2024



**Figure 3:** AFM image of the spray-deposited PDMSTU-based coating on AA 2024

**Slika 3:** AFM-posnetek prevleke, pripravljene na osnovi PDMSTU in napršene na podlago AA 2024

magnitude in the anodic current density. A decrease in the cathodic current density of one order of magnitude in relation to the response of the pure AA 2024 substrate was also observed for the ethoxysilyl-functionalised POSS compounds, enabling a formation of compact tri-dimensional networks of regular POSS cubes via sol-gel reactions<sup>11</sup>. However, the addition of perfluoropropyl groups to the structure of these POSS compounds increased the reduction in the cathodic current density, even to above two orders of magnitude<sup>12</sup>, which is superior to that of our PDMSTU-based coatings. The contact-angle measurements showed that poly(dimethylsiloxane) chains introduced some of the hydrophobic character to the PDMSTU-based coatings; the contact angle for water was 97° for the coatings on AA 2024 in the initial state and the surface-energy value was 32.1 mJ/m<sup>2</sup>. The value was higher than the surface-energy values for the coatings prepared from PDMSU (29.7 mJ/m<sup>2</sup>)<sup>10</sup>, ethoxysilyl-functionalised POSS (28.7 mJ/m<sup>2</sup>)<sup>11</sup> and perfluoropropyl ethoxysilyl-func-



**Figure 4:** Potentiodynamic measurement of the spray-deposited PDMSTU-based coating on AA 2024

**Slika 4:** Potenciodinamične meritve prevleke, pripravljene na osnovi PDMSTU in napršene na podlago AA 2024

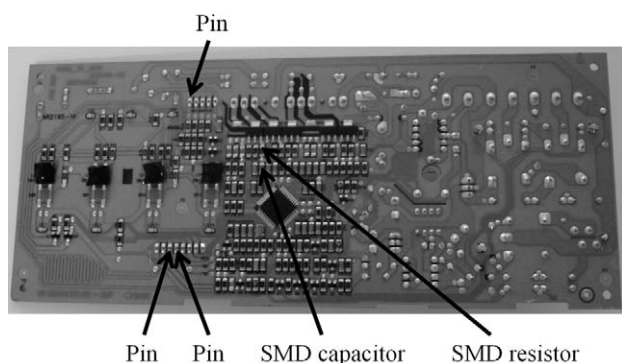


**Figure 5:** Measurement of the Raman spectra on the uncoated and coated EB substrate

**Slika 5:** Merjenje ramanskih spektrov nezaščitenega in zaščitenega elektronskega vezja

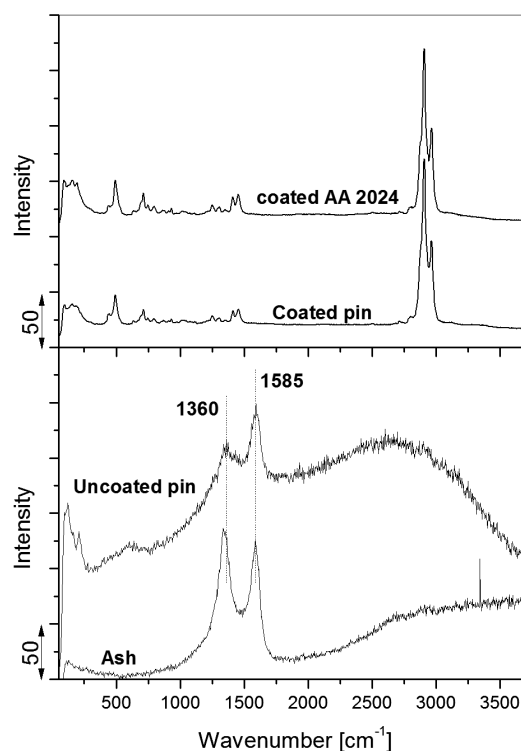
tionalised POSS ( $12.4 \text{ mJ/m}^2$ )<sup>12</sup>. Since a good corrosion inhibition can be partly ascribed to the low surface value of the anticorrosion coatings, the coatings with the perfluoropropyl groups have been found to be the best in this respect. For comparison, the contact angle for water of the AA 2024 substrate was  $86^\circ$  and the surface-energy value was  $37.1 \text{ mJ/m}^2$ , respectively.

The most critical issue in the preparation of the anticorrosion coatings for EBs, apart from the development of the coatings' composition, is the coverage of all the elements (except the specific connectors that are masked during the spray deposition of a coating) on the non-flat EB surfaces. The coverage of pins often remains questionable, since the coating solutions may tend to flow down the slopes. When the sols exhibit proper rheological properties, this effect of sagging is prevented and all the elements are efficiently covered by the coating. Such defects in coverage can certainly be recognised during various end industrial application tests, but these are time consuming and costly. The proposed Raman spectroscopy is a more straightforward



**Figure 6:** Positions of the pins and other elements that were measured on the uncoated and coated EB using Raman spectroscopy

**Slika 6:** Pozicije konic in drugih elementov, na katerih smo izmerili ramanske spektre na nezaščitenem in zaščitenem elektronskem vezju

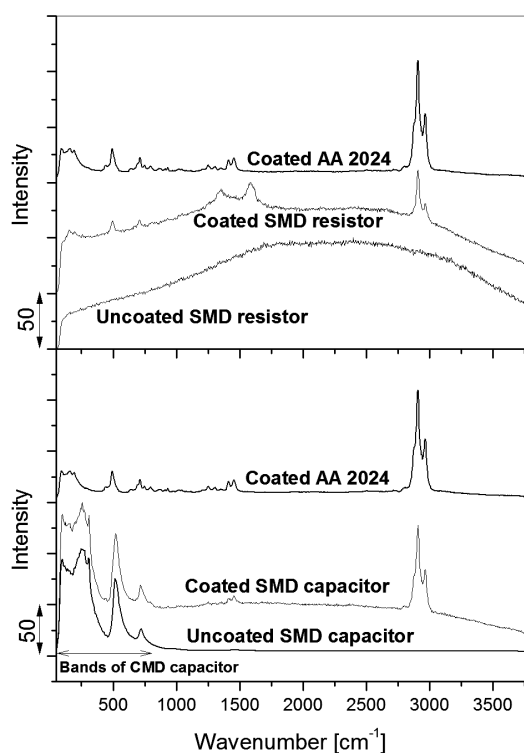


**Figure 7:** Raman spectra of the uncoated and coated pins on the EB substrate. The PDMSTU-based coating on the AA 2024 substrate is given for comparison, as well the characteristic Raman spectrum of an independent ash sample.

**Slika 7:** Ramanski spektri nezaščitenih in zaščitenih konic na elektronskem vezju. Za primerjavo podajamo ramanski spekter prevleke na osnovi PDMSTU, ki je napršena na podlago AA 2024. Podajamo tudi značilen ramanski spekter vzorca saj.

and quicker way of determining a possible non-coverage in the coatings. The PDMSTU-based coating sprayed on EB was therefore placed under the laser beam of the Raman spectrometer (**Figure 5**) and investigated at different points and elements (**Figure 6**). In **Figure 6**, only the elements that are described in this text (pins, SMD resistor and SMD capacitor) are shown, but other positions on EB were also studied.

**Figure 7** shows the Raman spectra recorded on the pins of the uncoated and coated EBs. The spectra of the uncoated pins revealed two peaks, at  $1.385 \text{ cm}^{-1}$  and  $1.360 \text{ cm}^{-1}$ , which can be assigned to the presence of carbon. Namely, the spectrum of the ash sample revealed similar bands that are marked in the literature as G- and D-lines<sup>2</sup>. The so-called G-band corresponds to the strong C-C stretching  $E_{2g_2}$  mode of the hexagonal graphite structure. The D-line ( $A_{1g}$ ) that appeared from  $1.350 \text{ cm}^{-1}$  to  $1.360 \text{ cm}^{-1}$ , on the other hand, is the consequence of a turbostratic disorder, i.e., a disorder along the  $c$  axis due to a weak interlayer bonding<sup>2</sup>. When the EB substrate was covered with the PDMSTU-based coating, the characteristic bands of the coating appeared in the Raman spectrum (**Figure 7**). For comparison, the same bands also appeared in the Raman spectrum of the spray-deposited PDMSTU-based coating on the AA



**Figure 8:** Raman spectra of the uncoated and coated SMD-resistor and SMD-capacitor elements on the EB substrate. The PDMSTU-based coating on the AA 2024 substrate is given for comparison.

**Slika 8:** Ramanski spektri nezaščitenega in zaščitenega SMD-upora in SMD-kondenzatorja na elektronskem vezju. Za primerjavo podajamo ramanski spekter prevleke na osnovi PDMSTU, ki je napršena na podlago AA 2024.

2024 substrate. Similarly, in the case of the SMD resistor and SMD capacitor, it was also found that the bands of the PDMSTU-based coating appeared in the Raman spectrum (**Figure 8**). In addition to the modes of the coating, carbon bands were also observed on the SMD resistor. On the other hand, the uncoated SMD capacitor revealed some bands by itself and they remained in the Raman spectrum of the covered SMD capacitor, in addition to the modes of the PDMSTU-based coating (**Figure 8**). The depicted spectra measured on the covered EB clearly revealed that the coating was successfully deposited covering all the different elements and parts of the investigated substrate. Other elements and pins were also investigated, but the results have not been shown due to a lack of space.

The Raman spectra measured on the coated EB substrate (**Figures 7 and 8**) clearly revealed that Raman spectroscopy is extremely well suited to the investigation of complex objects that do not allow a sample preparation. This is also due to the improvements in instrument configurations, for example, the use of confocal micro-Raman spectrometers that allow effective spatial resolution and Raman imaging as well as achieving a better contrast<sup>1,2</sup>. When non-typical samples, such as EBs are in question, Raman spectroscopy is important due to

its non-destructive character, certainly when carefully set excitation conditions are used. In addition, the detection of coatings on the metallic parts of EBs is easy, since almost all the metals show no Raman bands. However, Raman spectroscopy is not a useful quantitative technique and it would be difficult to determine the amount of coating on various elements of EBs, since the sensitivity of the Raman response depends on the polarizability of the molecules and the characteristics of the measured spot. Another important drawback of Raman spectroscopy is the fluorescence caused by certain organic or other materials, i.e., in the case of the EB substrate, it was found on plastic areas. Nevertheless, all the aforementioned facts clearly show that Raman spectroscopy is a suitable technique for detecting the protective sol-gel coatings on EBs, not only after a deposition of the coatings, but also after their exposure to accelerated corrosion tests. The excellent spatial resolution of the confocal Raman spectrometers allows a detection of the corroded parts of the coatings on EBs and thus a determination of the most vulnerable parts of EB substrates.

## 4 CONCLUSIONS

Potentiodynamic electrochemical characterisation of the coatings prepared from organic-inorganic precursors bis-(3-(3-(3-triethoxysilyl)propyl)thioureido)propyl terminated poly(dimethylsiloxane) (PDMSTU) and bis-[3-(triethoxysilyl)propyl]tetrasulphide (BTESPT) revealed that the coatings possess the properties similar to the other coatings made of poly(dimethylsiloxane) or tetrasulphide-based precursors. Specifically, the cathodic current density of spray-deposited coatings was lower, by up to two orders of magnitude, than the cathodic current density of the pure AA 2024 substrate. The prepared coatings were also spray deposited on an electronic board (EB) and Raman spectroscopy was shown to be an appropriate technique for detecting the sol-gel protective coating on this substrate due to its non-destructive character and a high spatial resolution. On the basis of the present results, Raman spectroscopy will be used in future to determine the sites, at which corrosion has started after an exposure of the coated EB substrates to accelerated corrosion tests, including Raman imaging of larger surfaces. In order to assure a complete coverage of the elements, the sols will be studied using a detailed rheological characterisation. The sol with the optimal rheological properties will be chosen for further application.

## Acknowledgement

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## 5 REFERENCES

- <sup>1</sup> P. Vandenabeele, H. G. M. Edwards, L. Moens, *Chem. Rev.*, 107 (2006), 675–686
- <sup>2</sup> R. Baddour-Hadjean, J. Pierre Pereira-Ramos, *Chem. Rev.*, 110 (2010), 1278–1319
- <sup>3</sup> M. Gnyba, M. Keränen, M. Kozanecki, R. Bogdanowicz, B. B. Kosmowski, P. Wroczyński, *Opto-Electronics Rev.*, 10 (2002), 137–143
- <sup>4</sup> I. Jerman, A. Šurca Vuk, M. Koželj, F. Švegl, B. Orel, *Prog. Org. Coat.*, 72 (2011), 334–342
- <sup>5</sup> McCullough, J. L. Wayt, J. N. Butch, US patent 6,127,038, 2000
- <sup>6</sup> D. Wang, G. P. Bierwagen, *Prog. Org. Coat.*, 64 (2009), 327–338
- <sup>7</sup> M. Koželj, Synthesis of substituted trialkoxysilanes and their application for the preparation of materials via sol-gel procedures, Dissertation, University of Ljubljana, Ljubljana
- <sup>8</sup> D. Zhu, W. J. van Ooij, *Electrochim. Acta*, 49 (2004), 1113–1125
- <sup>9</sup> M. F. Montemor, M. G. S. Ferreira, *Electrochim. Acta*, 52 (2007), 7486–7495
- <sup>10</sup> M. Fir, B. Orel, A. Šurca Vuk, A. Vilčnik, R. Ješe, V. Francetič, *Langmuir*, 23 (2007), 5505–5514
- <sup>11</sup> I. Jerman, A. Šurca Vuk, M. Koželj, B. Orel, J. Kovač, *Langmuir*, 24 (2008), 5029–5037
- <sup>12</sup> I. Jerman, B. Orel, A. Šurca Vuk, M. Koželj, J. Kovač, *Thin Solid Films*, 518 (2010), 2710–2721