Distinguishing between different types of multi-layered PET-based backsheets of PV modules with near-infrared spectroscopy

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Abstract
Degradation of backsheets (BSs) of commercial silicon PV modules is currently recognized as a source of reduced module performance and module failure. Monitoring of the BS state in the field is possible by using non-destructive and highly informative near-infrared absorption (NIRA) spectroscopy. Application of NIRA for the analysis of multi-layer polyethylene terephthalate (PET) based BSs, which dominate the PV module market, is challenging due to a large variety of possible BS configurations that show only small differences in NIRA spectra. In the present work, a spectroscopic tool for the structural identification of PET-based BSs is introduced. The method is based on a principal component analysis of a database of 250 representative NIRA spectra of BSs of different types. It allows a BS with an unknown structure to be assigned to one of 12 different types based solely on its NIRA spectrum. The identification was successfully validated on a test collection of 45 selected BSs and shown to be feasible for the field deployment. Further automation of NIRA measurements and spectral analysis are expected to elevate the proposed tool to the level of a non-intrusive high-throughput field analysis of the BS composition and state in operating PV module grids.

KEYWORDS
multispectral Raman imaging, polyethylene terephthalate, principal component analysis, PV module backsheets, spectral characterization

1 | INTRODUCTION
Degradation of polymer components of commercial silicon PV modules is currently recognized as one of the major factors limiting module performance and lifetime, and causing security and financial risks for the stakeholders of PV installations.1–3 Typically, UV irradiation has the largest impact on polymer encapsulants of Si wafers while climatic stress (high/low temperatures, humidity) affects mostly the polymeric backsheets (BSs) designed to provide a mechanical support to solar cells as well as to insulate and protect the cells from the environmental factors.1–6 The degradation of both encapsulant and BS can influence and accelerate each other, for example via partial BS decomposition by the products of encapsulant hydrolysis and, vice versa, via encapsulant deterioration by moisture and oxygen penetrating through a partially decomposed BS.1,2,5–9 As a result, the long-term behavior and degradation stability of PV module's BSs are critical for the lifetime of PV systems.
modules depend on composition and structure of both encapsulant and BS.\textsuperscript{1,3–5,8,9}

Due to this dependence, as well as the fact that the composition of polymer components is not typically disclosed by the PV module manufacturers, there is a need for fast, non-intrusive, and reliable analytical tools for the identification of encapsulant and BS composition, as well as for the evaluation of their composition-dependent degradation status.

Spectroscopic methods, such as Fourier-transform infrared (FTIR), Raman and fluorescence spectroscopy, were found to be most suitable to address this challenge due to their high chemical specificity and non-destructive character.\textsuperscript{1,7,10–14} However, these techniques are capable of probing only the BS surface layer and cannot provide information on the inner structure of multi-layer BSs that are typically several hundred μm thick. By this reason, the investigations into structure and degradation state of multi-layer BSs using Raman, FTIR and fluorescence spectroscopy typically have an invasive character and need to be performed on BS cross-sections.\textsuperscript{7,13–17} In-depth non-invasive probing by confocal Raman spectroscopy is feasible for new PV modules but typically hindered for field-aged samples due to a strong fluorescence from partially degraded encapsulant and BS materials.\textsuperscript{14}

Recently, near-infrared absorption (NIRA) spectroscopy has been recognized as a viable alternative to other spectroscopic approaches\textsuperscript{14,18} that can be upgraded from lab tests to large-scale field measurements and implemented as a non-destructive and non-invasive high-throughput characterization tool for large PV systems. NIRA can provide a combination of penetration depth (more than a thousand μm), versatility of analytic information, and field applicability unrivaled by other spectroscopic approaches proposed for the characterization of PV modules so far.

NIRA probes vibration overtones and combinations of them which are orders of magnitude weaker than the fundamental vibrations in organic polymers typically registered by FTIR.\textsuperscript{19–23} By this reason, NIRA can be applied to almost any kind of sample without additional preparations,\textsuperscript{19–23} it is not sensitive to moderate soiling of PV modules or to inorganic components (cover glass, Si wafers, pigments in BS)\textsuperscript{18} allowing the polymer components of PV modules to be probed both from the front side (encapsulant) and the air side (BS) directly on operating modules in reflectance mode.

For most polymers used in PV modules, such as polyethylene terephthalate (PET), polyamide or ethylene vinyl acetate (EVA) copolymer encapsulant, NIRA spectra reveal characteristic features,\textsuperscript{19,21–23} allowing their accurate and fast identification, and discrimination from other BS components, such as pristine and fluorinated polyolefins. Due to relatively large penetration depth of the NIR light (1 mm and more),\textsuperscript{19} the entire multi-layer BSs can be probed in a single measurement. Finally, NIRA spectroscopy is fast and can be realized using portable miniature equipment, opening possibilities for human-directed or automated field measurements.

At the same time, the unique capability of NIRA to probe the whole BS cross-section poses a challenge for the identification of BS structure using this method. The challenge stems from the fact that different BS structures can produce similar NIRA spectra because spectral contributions of fluorinated polyolefins overlap with the characteristic bands from PET. As a result, spectral patterns differ only on relative contributions from =C–H bands from PET and ~C–H bands from other BS components.

To address this challenge, we propose a method for spectrally identifying PET-based multi-layer BSs by using a combination of NIRA spectroscopy with multivariate principal component analysis. The method is supported by a library of BS cross-sections created by the multi-spectral Raman imaging of different BS types. The approach includes (i) assembling a library of representative BSs from a variety of module types and manufacturers, (ii) identification/mapping of the BS composition and cross-sectional structure by multi-spectral Raman imaging, (iii) performing a multivariate analysis of variance among the NIRA spectra of representative Raman-mapped BSs.

The latter analysis allows reducing each NIRA spectrum to a single point on a principal component (PC) plot assigning all BSs of the same structure to a separate cluster. In this way, a library of clusters was generated using BSs with the known structures and known NIRA spectra. This library can then be used as a basis for independent lab and field identification of BSs in unknown PV modules using solely non-invasive and portable NIRA setup.

2 | METHODS

Raman spectra and spectral maps were detected on a WITec alpha700 confocal Raman microscope equipped with an UHTS 300 spectrometer in a spectral range of 130–3700 cm\textsuperscript{-1} and a resolution of 3 cm\textsuperscript{-1}. The samples were excited by a 532-nm laser with the maximal power of 7 mW. Spectral maps were constructed by scanning square (1000 × 1000 or 500 × 500 μm) sections of the sample with a resolution of 100 × 100 spectral points (100 × 100 pixels with spectral information on each pixel). Raman spectroscopic measurements were performed on BS cross-section samples produced by detaching a piece of BS from a PV module and cutting the cross-section edge along the length of the BS.

FTIR transmission spectra were recorded from the BS air sides in the attenuated total reflectance (ATR) mode using a Vertex 70 spectrometer (Bruker) equipped with a Platinum ATR diamond accessory in the range of 400–4000 cm\textsuperscript{-1} and a spectral resolution of 0.4 cm\textsuperscript{-1}.

NIR reflectance was measured with an optical fiber-coupled portraitive FT-NIR Rocket 2.6 spectrometer (Arcoptix) in a spectral range of 900–2600 nm (3800–11,000 cm\textsuperscript{-1}) with a resolution of 8 cm\textsuperscript{-1}. The samples were excited by a stabilized optical fiber-coupled NIR source SLS201/M (Thorlabs). The NIR lamp and spectrometer were coupled via optical fibers (M35L, 400–2200 nm, fiber core diameter of 1000 μm, Thorlabs) to an RPH-SMA probe block (Thorlabs). The angle between incident and reflected light beam was 90°. The probe was placed on the sample surface and held manually during measurements. Typically, 20 reflectance spectra were collected consecutively and averaged for noise reduction.
3  |  RESULTS AND DISCUSSION

3.1  |  General description of tested samples

Recently we have reported on the potential of NIRA spectroscopy for the characterization of composition and degradation state of polymer components of commercial silicon PV modules, in particular BSs and encapsulants.\(^1\) We have found that despite the immense diversity of types and power classes of PV modules, as well as a broad spectrum of manufacturers, the BSs are composed of a limited number of polymer materials. These include EVA as encapsulant, PET and polyamide (PA) as core BS insulation layers as well as a series of fluorinated polymers and polyolefins filled with inorganic pigments as protective components of BS shielding PET from adverse climate factors, water ingress, and incoming UV irradiation. The most commonly used fluorinated polymer components include polyvinyl fluoride (PVF), polyvinylidene fluoride (PVDF) or a fluorinated copolymeric coating (FC), while major polyolefin components are polyethylene (PE) and polypropylene (PP).

Our survey investigation encompassed 1180 samples of PV-modules, both new and exploited for different periods on PV power plants in Germany. We identified three major BS types, including non-fluorinated (NF type) BSs, BSs having a single protective fluorinated polymer layer (single fluoropolymer, SF type), and BSs with two identical fluorinated polymer layers (double fluoropolymer, DF type).

The NF group is dominated by polyamide, which was found in roughly 25% of modules tested in the present work. In some old modules, PET-based non-fluorinated BSs were also found, while some of the modern modules showed PP-based BSs. The major part (about 75%) of tested modules were constructed with BSs composed of a PET core layer protected by one or two fluorinated polymer layers. Totally, the multi-layer PET-based SF and DF BSs together with polyamide NF BSs accounted for about 95% of all tested modules.

As shown in our previous report,\(^1\) polyamide BSs can be distinguished from PET-based ones by using characteristic NIRA bands without the need for a sophisticated spectral analysis. The PP-based BSs show neither PA not PET features in NIRA spectra and can also be easily identified. In contrast, multi-layer PET-based SF- and DF BSs show similar NIRA spectra that differ only by the number, order and thickness of the constituent layers. As a result, spectral NIRA discrimination among various multi-layer PET-based BSs becomes a challenging task. In the present work, we limit our discussion to PET-based BSs and exclude PA and polyolefine BSs from the analysis.

To gain insights into the composition and structure of PET-based BSs, we collected BS cross-sections from 84 PV modules differing by type, manufacturer, age, and history (new, shelf-stored, and field-aged modules). The BS samples were characterized by Raman spectroscopy and multi-spectral confocal Raman microscopy, allowing major polymer components and polymer fillers to be identified.

3.2  |  Building multi-spectral Raman maps of BS cross-sections

Confocal Raman microscopy allows probing cross-sections of BSs or BS/EVA assemblies with a spatial resolution of around 1 μm, resulting in 2D maps with a chemical contrast achieved by analyzing characteristic spectral ranges of different BS components.\(^17,18,24\) By using this approach and the above-discussed Raman/FTIR identification of the BS components, we constructed a multispectral Raman map for each particular BS type, visualizing simultaneously composition, order, and thickness of BS layers.

The structure and characteristic features of Raman spectra of the most important polymer BS components and EVA encapsulant as well as details of the multi-spectral Raman mapping were discussed in detail in our previous report.\(^18\) An extended description of the Raman/FTIR spectra of all components of the entire collection of the tested NF, SF, and BF BSs with corresponding cross-sectional BS maps can be found in the Supporting Information. Here, we describe the Raman mapping on a single example of a symmetrical DF-2 BS (Figure 1).

With the composition of each particular BS layer identified by Raman spectroscopy on the first step, a distribution map was then constructed for each component by using characteristic frequencies (frequency ranges) from the Raman spectra (Figure 1, upper panel). For this, a selected area of BS cross-section (typically 500 × 500 μm\(^2\)) was scanned pointwise.

The Raman spectrum was registered in each particular point with a step of 5 μm and an array of 10,000 spectra was collected. Then, a map of the scanned area was built by integrating Raman intensity for each point in a specified frequency range. In particular, R-PVF layers can be visualized by integrating Raman scattering intensity in the range of rutile vibrations, 150–750 cm\(^{-1}\), while PET layers can be mapped by using the frequency range of 1550–1800 cm\(^{-1}\) where characteristic C–C and C–O vibrations can be found. Additionally, the C–H vibration range is typically scanned at 2700–3000 cm\(^{-1}\) providing a general component map because such vibrations can be found in each of the BS components (Figure 1, medium panel). In the final step, all maps were combined and an appropriate color coding of components was applied, resulting in a multi-spectral map (Figure 1, lower panel) showing at the same time the composition and structure (layer number, order and thickness) of the BS.

The Raman mapping of BS cross-sections adopted in the present study does not allow any adhesive layers between air-side, core, and inner BS layers to be reliably distinguished and chemically identified. However, as the reported thickness of adhesive layers are relatively small (on the order of 1 μm) and the chemical composition of such adhesives is close to that of BS layers we do not expect any critical influence of these layers on the accuracy of the spectroscopic NIRA identification of different BS types.

Totally, we collected 84 multi-spectral maps of BS cross-sections from the NF, SF, and DF types and recognized twelve distinctly different BS configurations, summarized in Table 1.
The NF group of BSs revealed three BS configurations. In particular, some old PV modules (more than 20 years of commission) showed NF BSs composed of a single layer of PET filled with inorganic pigments (NF-1 and NF-2 types in Table 1). The NIRA spectra of such BSs are identical to those of pure PET. Additionally, we recognized a third type of multi-layer PET-based NF BSs which can be found in modern PV modules (type NF-3 in Table 1).

The SF group includes BSs with a single rutile-filled fluoropolymer layer, mostly found on the BS air side, a PET core and additional inner layers of rutile-filled polyolefins (PE, PP). This group features a broad variability of possible BS configurations, differing in materials used and thickness of air and inner layers.

The DF group combined BSs with a symmetric structure composed of a core PET layer sandwiched between two identical rutile-filled fluoropolymer layers. Also in this group, a variety of BS configurations can be found differing in the thickness of fluoropolymer and PET layers and rutile content.

3.3 | NIRA spectroscopic analysis of PET-based BSs

One of the advantages of NIRA as compared to other spectroscopic techniques of the BS characterization is a large penetration depth of near-IR light of up to 1.0–1.5 mm. The BS thickness of commercial silicon solar modules is typically smaller, about 300–500 μm, so near-IR light can penetrate the entire cross-section of the BS and even the encapsulant behind it. By this reason, we expect that NIRA spectra contain spectral signatures of all components of multi-layered BSs.

NIRA spectra were collected both in the lab from modules aged between 2000 and 2020 and in the field from several PV power stations in Germany with PV modules of different type, commissioned between 2010 and 2012. For each particular batch of samples, at least one representative module was characterized by multi-spectral Raman mapping and then NIRA spectra collected from this tested module, as
well as from other similar modules from the batch. We assumed that modules with identical NIRA spectra and selected from the same batch as the one subjected to Raman mapping have all the same BS structure. This assumption was checked for several cross-sections from batches of NF-1, SF-2, and DF-3 type modules, which revealed the same cross-section structure and identical NIRA spectra. In this way, we collected 840 NIRA spectra of PV modules with PET-based BSs with the BS structure known from the representative Raman mapping as discussed above.

### 3.4 | NIRA analysis of group NF

The NF-1 type BSs are composed of rutile-filled PET and their NIRA spectra (Figure S10a, curve 1) are very close to the NIRA spectrum of pure PET. The most prominent spectral band at 1660 nm, as well as a triplet at 2130/2155/2180 nm, are characteristic for PET and originate from $\text{C} = \text{H}$ vibrations in benzene rings of PET chains.\(^{20,22}\)

Oxygen-containing functionalities of PET can be observed at 1955 nm (C–O vibration) and 2085 nm (C–O–C vibration).\(^{20,22}\) Adsorbed water reveals a characteristic band at 1910 nm.\(^{22}\) Other peaks, including a distinctly resolved complex band at 1730 nm, correspond to various overtones and combinations of C–H vibrations.\(^{19,20,22,25}\)

The NIRA spectrum of NF-2 BS (Figure S10a, curve 2) is expectedly similar to that of NF-1 and shows a more distinct water-related 1910 nm band due to a deeper degradation state of such BSs, most probably because the BaSO₄ pigment is not efficient in absorbing UV irradiation and more prone to water uptake as compared to rutile titania.

The NIRA spectrum of NF-3 BS (Figure S10a, curve 3) shows the same features; however, the $\text{C} = \text{H}$ band at 1730 nm is much more intense as compared to NF-1 and NF-2. We assigned this feature to the presence of an inner PE layer revealed by cross-sectional Raman studies.

### 3.5 | NIRA analysis of group SF

Figure 2 shows a representative gallery of air side (panel 1) and cross-sectional (panel 2) microphotographs, multi-spectral Raman maps (panel 3) and corresponding air side NIRA spectra (panel 4) for each of SF BS types distinguished by the Raman mapping. The NIRA spectrum of NF-1 sample is added as a reference.

The SF-1 type BSs were found only in old modules, so this BS type was considered to be of low relevance to modern PV systems. On the contrary, BSs with SF-2 to SF-4 structure were frequently found in tested PV modules of various power classes and stemming from different manufacturers.

The NIRA spectrum of SF-2 BS shows prominent features both in the $\text{C} = \text{H}$ and $-\text{C} = \text{H}$ vibration ranges (Figure 3b, curve 1). A multi-spectral Raman map of SF-2 (Figure 2) shows a very thin air side rutile-filled fluoropolymer coating layer which allows most of the NIR light to penetrate deeper to PET core layer. As PET is not filled with light-scattering pigments, the light penetrates further into the inner rutile-filled PE layer and the resulting signal shows the presence of both PET and saturated polymers (FC, PE). By comparing intensity ratios of aromatic $-\text{C} = \text{H}$ and aliphatic $-\text{C} = \text{H}$ bands, \(I_{1660\text{nm}}/I_{1730\text{nm}}\) for different BS types we can evaluate the relative contribution of core PET layer and air (inner) layers of aliphatic polymers (PVF, PE, etc.) to the NIRA spectrum collected from the BS air side.

The complex character of the air side NIRA spectra can be exemplified by delaminating a SF-2 BS sample and separating the R-FC/PET layer from the inner PE/EVA layer. The NIRA spectrum of the R-FC/PET part (Figure S10b, curve 2) shows a decreased contribution from the $-\text{C} = \text{H}$ band due to the elimination of the inner PE and EVA

### Table 1 | Summary of the BS cross sections studied in the present work

| Group | Type | Structure | Air side (μm) | Core layer (μm) | Inner layer (μm) | L_{BS} (μm) | N_{CS} | N_{NIRA} |
|-------|------|-----------|---------------|----------------|----------------|-------------|--------|----------|
| NF    | NF-1 | R-PET     | 100–110       | -              | -              | 100–110     | 5      | 43       |
| NF-2  | B-PET| -         | 110–120       | -              | -              | 110–120     | 6      | 9        |
| NF-3  | R-PET/PET/R-PE | R-PET (60) | PET (150) | R-PE (60) | 270 | 3 | 18 |
| SF    | SF-1 | R-PET/EVA/R-PVF | R-PET (120) | EVA (480) | R-PVF (35–40) | 635–640 | 3 | 9 |
| SF-2  | R-PVDF/PET/R-PE | R-PVDF (10) | PET (180–185) | R-PVF (10) | 200–205 | 4 | 30 |
| SF-3  | R-PVDF/PET/R-PE | R-PVDF (30) | PET (330) | R-PVF (80) | 440 | 7 | 56 |
| SF-4  | R-PVDF/PET/R-PE | R-PVDF (40) | PET (280–295) | R-PVF (25–30) | 390–400 | 15 | 55 |

*Note: R, rutile; B, BaSO₄; L_{BS}, total BS thickness; N_{CS}, number of cross sections studied by Raman spectroscopy; N_{NIRA}, number of modules tested by NIRA spectroscopy.*
layers. The NIRA spectrum of the delaminated PP/EVA layer shows only –C–H-related features along with a low-intensity C–O–C vibration of EVA at 2140 nm (Figure S10b, curve 3).

The NIRA spectrum of SF-3 BS shows strongly reduced PET-related band at 1660 nm as compared to the –C–H features at 1730 nm (panel 4 of Figure 2). As this BS type shows a much thicker
air side rutile-filled fluoropolymer layer as compared to SF-2 (Table 1) we assume that the NIR light is strongly scattered in the air side layer and only partially penetrates into the core PET layer. This assumption is supported by the normal-hemispheric solar reflectance values reported for such type of BSs in a previous study as well as by spectral observations made for SF-4 BSs, where the PET-related feature at 1660 nm is suppressed even more (panel 4 of Figure 2). As the air side layers of SF-3 and SF-4 are of the same material and thickness the strongly suppressed character of PET band can be assigned to a rough topography of the SF-4 air side, while SF-3 demonstrates a smooth and uniform air side (panel 1 of Figure 4). The uneven morphology of the SF-4 air side is expected to contribute to strong scattering of NIR light resulting in generally low resolution of all spectral features.

The NIRA spectra of SF-5 BSs were found to be strongly distorted by interference pattern which is specific for this particular BS type. The interference pattern blends with NIRA spectrum changing irregularly for different modules and probing points and making impractical a spectral analysis of such BSs in the NIR reflectance mode.

3.6 | NIRA analysis of group DF

A gallery presented in Figure 3 shows that the cross-sections of such BSs are similar differing in the thickness of PVF and PET layers (panels 2 and 3). Accordingly, NIRA spectra of DF-type BSs reveal the same structure only varying in the \( I_{1660\text{nm}} / I_{1730\text{nm}} \) ratio. Similar to SF-type BSs, delamination of DF BSs shows the complexity of their NIRA spectra. The NIRA spectrum of a DF BS without the air side R-PVF layer (Figure S10c, curve 2) reveals a much higher \( I_{1660\text{nm}} / I_{1730\text{nm}} \) ratio, while the delaminated R-PVF (curve 3) shows only C-H-related spectral features. Therefore, the \( I_{1660\text{nm}} / I_{1730\text{nm}} \) ratio is expected to reflect variations in the thicknesses of both PVF and core PET layers of DF-type BSs.

In line with expectations, we observe a reduction in the \( I_{1660\text{nm}} / I_{1730\text{nm}} \) ratio from DF-1 BSs with the thinnest air side layer (10 μm) over DF-3 and DF-4 with an intermediate thickness of R-PVF layer (25–30 μm) to DF-4 which has the thickest R-PVF layers (45–50 μm). The latter samples have expectedly the least pronounced spectral PET features among all DF type BSs studied in the present work (Figure 3, panels 2 and 3). The DF-2 BSs deviate somewhat from this tendency, most probably due to a thicker core PET layer as compared to DF-3 and DF-4 BSs.

Summarizing, we found that NIRA spectra of all tested multi-layer PET-based BSs have similar structure differing mainly in relative intensities of PET- and aliphatic polymer-related features. In principle, the type of BS can be evaluated directly from the NIRA spectra using the \( I_{1660\text{nm}} / I_{1730\text{nm}} \) ratio. However, the variation of this ratio is relatively small and, considering different signal-to-noise ratio and signal intensity observed for BS of different types, the reliability of such evaluation is not expected to be satisfactory.
3.7 | Multivariate analysis of the NIRA spectra

3.7.1 | Methodology of multivariate analysis of NIRA spectra

To increase the accuracy of the BS type determination from NIRA spectra, we processed the original spectra using a multivariate analysis. Such analysis allows detecting small variances in a large number of similar spectra and categorizing the spectra into separate groups according to their similarity. In this approach, an array of samples is collected and analyzed and a set of principal components (PC) is determined responsible for variance between the samples in the tested array. In the present case, we analyze an array of NIRA spectra for BSs of different type, taking each wavelength as an independent variable and obtain a set of PCs arranged according to their contribution to variance among the spectra.

When the set of most important PCs is determined, the first two PCs are taken for further analysis and a map of tested samples is presented as a 2D plot of PC1 versus PC2. Each single point in this plot corresponds to a spectrum in the tested array. The points corresponding to similar samples tend to form clusters within a BS-specific region. If the tested array contains different samples, several distinct and easily distinguishable clusters are observed in the 2D plots. This procedure is well-reported for various spectroscopic analyses including probes of the BS degradation state with NIRA.

To perform PC analysis, we selected 250 NIRA spectra from the original database of 840 samples. The selected spectra included all identified BS types, except for SF-5, proportionally to their fraction in the original database. A further increase in the number of spectra does not increase accuracy in cluster positions and shape but results in longer computation times. Each spectrum ranged from 900 to 2600 nm with values from 910 points taken as variables. In the same way, we selected 45 NIRA spectra of all BS types (except for NF-3, SF-1, and DF-3) as a test set for evaluation of the accuracy of the PC analysis.

3.7.2 | Results of PC analysis

We found that the first two PCs account for 68% of variance between the tested spectra (see a “Scree plot” in Figure S11a) allowing the PC analysis results to be presented as a 2D plot (Figure 4a). Increasing the number of PCs to 3 or 4 adds only 5% of variance and does not affect the analysis in a major way.

The distribution of PC1 across the wavelengths (PC1 “loading spectrum”) was found to have extrema on the wavelengths characteristic for PET, that is, at 1660 nm and 2130/2155/2180 nm (Figure 4b). This finding indicates that the major part of variance between the tested spectra is observed on the PET-characteristic wavelengths, which aligns with our expectations. The loading spectrum of PC2 shows additional extrema on the wavelengths typical for –C–H vibrations of saturated polymers (Figure 4b). Therefore, a combination of PC1 and PC2 shown in Figure 4a is an integral presentation of spectral differences on wavelengths specific for –C–H vibrations of PET and –C–H vibrations of the rest of BS components.

The PC1-PC2 plot presented in Figure 4a shows a distinct clustering of all tested BS types. In particular, all NF samples can be found in the same quadrant II. The NF-1 and NF-2 BSs expectedly cluster close to pure PET, while NF-3 is shifted due to a contribution from the inner PE layer and resides on the same ordinate as PET/PVF/EVA sample, both having very similar NIRA spectra.

The SF-1 and SF-2 BSs that comprise thin fluoropolymer layers are also situated in quadrant II but far apart from each other on the PC1 axis. The SF-3 and SF-4 can be found in quadrants III and IV, respectively, the separation between these samples stemming from differences in the thickness of core PET and inner PE layers.

DF-type BSs form separate clusters as well, with clusters located along a straight line from quadrant I through the center of coordinates to quadrant III (Figure 4a). Three observations can be made from this sequence:

i. DF BSs with distinctly different thickness of R-PVF layers, such as DF-1, DF-2(3,4), and DF-5, form separate clusters and can be reliably distinguished on the 2D plot.
ii. DF-3 and DF-4 BSs of the same structure collected from modules of different manufacturers form strongly overlapping clusters and, therefore, the origin of the BS samples seems not to affect adversely the results of NIRA/PC analysis.
iii. DF-2 and DF-3(4) BSs though having the same composition and thickness of R-PVF layer, differ in the thickness of core PET layer and form separate clusters in the PC plot, thus allowing to see separately the effects of thickness variation of PET layer and R-PVF layers.

By using the spectral database presented in Figure 4a, we can identify the BS type of an unknown sample. To do this, we add its NIRA spectrum to the database, perform the PC analysis for the “database + 1” set of spectra and determine the geometrical position of the unknown sample on the 2D PC plot relative to reference samples from the database, for which the BS structure is known.

3.7.3 | Validation of PC analysis results

We applied this method for the test set of 45 BSs of different types and found that each test sample added to the database appeared within the expected cluster (Figure 4c). The non-PET BSs, such as polyamide and polypropylene were both found outside any of the PC clusters of NF, SF, and DF-type BSs showing also the feasibility of identifying unknown BS types using the present BS database.

We can identify an unknown sample only if similar samples were previously characterized by multi-spectral Raman mapping and were included in the database of NIRA spectra. This constitutes a limitation of the proposed method. Unknown samples with a completely unknown architecture may not be identified correctly. To overcome
this limitation, we continue to analyze new samples and multi-layer BSs with Raman/NIRA spectroscopy and add them to the database, gradually increasing the reliability of the proposed spectral analysis. We note that this method allows the structure of multi-layer PET-based BSs to be identified by using only NIRA spectroscopy, which means that such analysis can be performed both in the lab and in the field. Other important BS materials found in modern PV modules, such as polyamide or polypropylene, can be easily identified using NIRA spectroscopy by the presence/absence of characteristic bands with no more sophisticated analysis needed. The proposed NIRA-based approach can cover all practically important BS materials currently used in the commercial silicon PV modules.

We tested the feasibility of using NIRA-based identification for the field measurements on a multi-MW solar power plant in Germany. The tested PV modules showed only NF- and SF-type BSs but these two types of BSs as well as different configurations of the SF-type BSs were successfully identified (more detail in a previous study\(^29\)). As the PC analysis can be easily automatized and a single NIRA measurement is fast, taking less than 1 s per BS (for the acquisition of a single spectrum), we expect high feasibility of automated identification of BS structure performed in a high-throughput regime. The NIRA identification of the BS type for the case field study reported in a previous study\(^29\) allowed certain failure behavior of PV modules to be tentatively associated with specific BS types, including occurrence of mechanical damage, potential-induced degradation, isolation problems, and metal bus corrosion. In view of these data, the automated NIRA analysis can become a potent addition to conventional techniques such as thermography, IV measurements, EL imaging, and so forth. Additionally, NIRA can become indispensable for the discrimination between fluorinated and non-fluorinated BS materials necessary for the selection of proper recycling technologies for discarded PV modules.\(^30\)

Our test field deployment of the method showed several limiting factors that currently pose challenges on the way to the high-throughput NIRA characterization. The manual character of the acquisition of NIRA spectra and hindered access to the PV modules in the test field campaign allowed only about 20–25 spectra per hour per operator to be registered and processed. The manual procedure should be performed during daytime and also requires a direct contact of the NIRA probe with the module air side. These and other limitations may be overcome by combining distant NIRA probing from a mobile robotized setup with a synchronous automatized spectra processing and BS identification based on the present BS database.

4 | CONCLUSIONS

We propose a spectroscopic tool for the identification of structure and composition of multi-layer PET-based BSs of commercial silicon PV modules that can be used both for the lab and field applications. The tool is based on a multivariate principal component analysis of a database of 250 NIRA spectra of BSs of different types. It allows the NIRA spectrum of an unknown BS sample to be assigned to one of twelve different BS types from a library of BS structures, and is even capable to identify new types within limits. The library currently contains cross-sectional data for more than 80 PET-based BSs from PV modules of different type and manufacturers. Raman maps are built on the basis of preliminary spectroscopic Raman/FTIR identification of particular BS components and show the structure (number, order, thickness) and the composition of each BS layer. Each map is associated with a specific NIRA spectrum registered from the module air side and containing spectral information on all components of the multi-layer BS.

The NIRA spectra of each of BS types identified by Raman imaging show differences in relative intensities of aromatic and aliphatic C–H vibrations and form distinct clusters on PC plots. Each cluster corresponds to a particular BS structure visualized by a corresponding multi-spectral Raman map. By performing PC analysis of a combination of the reference spectral database with the NIRA spectrum of an unknown sample we can determine a geometric position of the sample on the PC plot and relate it to a certain BS structure from the library of Raman maps. The identification was successfully validated on a test collection of 45 selected BSs of different types as well as shown to be feasible for the field deployment. The entire procedure can be potentially automatized and applied for an non-intrusive high-throughput analysis of the BS structure of PV modules in the field by using only NIRA measurements.

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CONFLICT OF INTERESTS
The authors declare no conflict of interests.

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

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