

LabRAM Soleil Nano for the chemical analysis of thin film solar cell interfaces

■ Background and Challenges

In the past few years, research on material for energy conversion has been focused on thin film solar cells. These consist of multilayered structures where a p-n junction is formed between a semi-conductor that acts as a “window”, to let the light pass, and a photosensitive material that works as an “absorber”. These two layers are separated by a buffer and sandwiched between two electric contacts, but the overall thickness is restrained within a few microns or less making these systems much thinner than the conventional silicon-based solar cells.

Among the possible materials studied for the role of the absorber layer, Sb_2Se_3 has stood out thanks to its broad band gap of 1.0-1.2 eV, high absorption coefficient and easy/cost-effective availability. However, its experimental performance as absorber did not meet the theoretical

expectations, thus arising the suspicion of a potential contamination from the adjacent buffer layer.

In this note, we present the first successful attempt of confirming this hypothesis by measuring a Sb_2Se_3 -based solar cell via Tip-Enhanced Raman Spectroscopy (TERS) by Kumar and coworkers at ETH Zurich, Switzerland^[1]. In TERS, or nano Raman, a sample-scanning probe coated with a plasmonic metal allows to collect simultaneously topographic and chemical information on the sample surface with an extraordinary resolution down to the nanometric scale. TERS analysis at ETH Zurich, carried out in a HORIBA's LabRAM Soleil Nano, made it possible to observe a partial inter-layer penetration at the Sb_2Se_3 -buffer interface, which is presumed to be responsible for the decrease in the photovoltaic performances of the solar cell.

■ Solution from HORIBA

HORIBA's LabRAM Soleil Nano (Figure 1) is a multi-modal system consisting of the coupling of a true confocal Raman microscope (LabRAM Soleil) with an atomic force microscopy (AFM) setup. For nanoscale measurements, the laser source is redirected towards an integrated optical platform to be focused on the apex of the AFM probe. Thanks to a combination of lightning-rod effect and localized surface plasmon resonance, the probe's apex amplifies both the incoming laser and the scattered Raman light up to a factor of 10^5 - 10^6 with respect to classic Raman. Moreover, the high signal confinement allows breaking the limits of the optical diffraction and reaching a spatial resolution in the nanometre scale. Its wide range of functionalities and ease of use make the LabRAM Soleil Nano a powerful tool for spectroscopic analysis in numerous application fields.



Figure 1. LabRAM Soleil Nano

Results

Figure 2a shows an optical image taken along the layered structure of the solar cell. The red line spans the section including the absorber layer Sb_2Se_3 layer, the buffer CdS and the interface between them. This same zone was subjected to a TERS mapping analysis, shown in Figure 2b. The map is colour-coded according to the main bands of the two expected compounds, which fall at $\sim 190 \text{ cm}^{-1}$ for Sb_2Se_3 (Ag vibrational mode, in orange), and at $\sim 300 \text{ cm}^{-1}$ for CdS (1 LO vibrational mode, in blue). The characteristic spectra, extracted from the points A and B in Figure 2b, are illustrated in Figure 2c.

While on the two extremities of the TERS map of Figure 2b the orange and blue colours are quite uniform, in the middle part they mix in a pink-coloured zone. To understand the contribution of both Sb_2Se_3 and CdS in this zone, the intensity of their characteristic bands, extracted from the pixels, were plotted as a function of their position along the line map (Figure 2d). The “interfacial region” was therefore defined as the zone where both bands show an intensity equal or superior to 1/3 of the most intense signal in their bulk zones. This proves that a partial inter-layer penetration occurs between the absorber and the buffer layers within the cell. Repeated measurement on different zones of the Sb_2Se_3 - CdS interface allowed estimating the average length of this region at $295 \pm 70 \text{ nm}$. This value, higher than what observed on $\text{Cu}(\text{In,Ga})\text{Se}_2$ -based solar cells, was attributed to the significant surface roughness of Sb_2Se_3 , which shows a needle-like structure in SEM experiments.

Thanks to nano Raman, the loss of Sb_2Se_3 efficiency as an absorber in thin film solar cells could be hypothesized as related to the rather long interfacial region with the nearby buffer, where cross-contamination occurs. This information could be achieved thanks to the extraordinary spatial resolution (down to 10 nm) and great signal enhancement provided by TERS, confirming its emergence as a powerful analytical tool for investigation of functional thin films at the nanometer length-scale.

References

1. S. Bienz, G. Spaggiari, D. Calestani, G. Trevisi, D. Bersani, R. Zenobi, N. Kumar, “Nanoscale Chemical Analysis of Thin Film Solar Cell Interfaces using Tip-Enhanced Raman Spectroscopy”, *ACS Applied Materials and Interfaces*, 2024, 16, 14704-14711. Further permissions related to the material excerpted should be directed to the ACS
2. A. Rai, S. Bienz, V. F. Hansen, R. Zenobi, N. Kumar, “Nanoscale Structural Insights into Thermochromic VO_2 Thin Films Using Tip-Enhanced Raman Spectroscopy”, *ACS Applied Materials & Interfaces*, 2025, 17, 32625–32634
3. X. Liu, B. Erbas, A. Conde-Rubio, N. Rivano, Z. Wang, J. Jiang, S. Bienz, N. Kumar et al., “Deterministic grayscale nanotopography for strained MoS_2 FETs”, *Nature Communications*, 2024, 15, 6934

info.sci@horiba.com

USA: +1 732 494 8660
France: +33 (0)1 69 74 72 00
Germany: +49 (0) 6172 1396 0
UK: +44 (0)1604 542 500

Italy: +39 06 51 59 22 1
Japan: +81(75)313-8121
China: +86 (0)21 6289 6060
India: +91 (80) 4127 3637

Singapore: +65 (6) 745-8300
Taiwan: +886 3 5600606
Brazil: +55 (0)11 2923 5400
Other: +33 (0)1 69 74 72 00

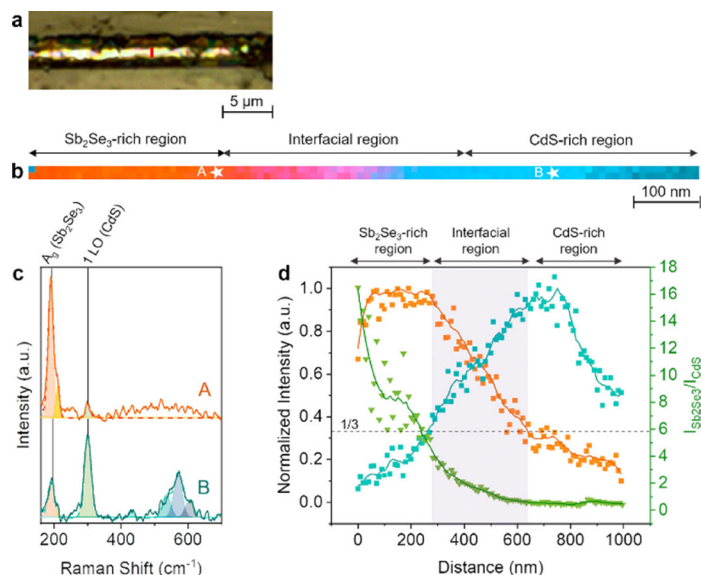


Figure 2. (a) Optical image of the thin film solar cell cross-section. The marked red line indicates the location of the TERS line map shown in (b), acquired with a step size of 10 nm. The point A and B refer to the spectra reported in (c), which evidence the bands of Sb_2Se_3 (190 cm^{-1} , orange) and CdS (300 cm^{-1} , blue); the colours were used to create the TERS map in (b). (d) Plots of the intensity variation of the 190 and 300 cm^{-1} bands and of their ratio ($I_{\text{Sb}_2\text{Se}_3}/I_{\text{CdS}}$) along the section.

The same LabRAM Soleil Nano system at ETH Zurich has also been successfully employed for nanoscale structural characterization of thermochromic thin films^[2] and strain-engineered single-layer MoS_2 on nanopatterned substrates^[3].