Localized surface curvature artifacts in gap-mode tip-enhanced nanospectroscopy

Stepanichsheva D. [1], Sheremet E. [1,*], Kim L. [1], Kolchuzhin V. [2], Milekhin A. [3], Zahn D.R.T. [2], Rodriguez R. D. [1]

[1] *Tomsk Polytechnic University, Lenina ave. 30, 634034, Tomsk, Russia*

[2] *Chemnitz University of Technology, Straße der Nationen 62, 09111, Chemnitz, Germany*

[3] *Institute of Semiconductor Physics, Lavrentiev ave. 13, 630090, Novosibirsk, Russia*

Tip-enhanced Raman spectroscopy (TERS) allows for chemical analysis to exceed the limit of light diffraction and to reach nanoscale spatial resolution. The high-spatial sensitivity is provided by the metal substrate in the so-called gap-mode TERS. However, in this case, the connection between the tip and the sample could lead to distortions in the image of the nanostructure during visualization. The purpose of this work is to provide a generalized view of such image artifacts in TERS imaging and to find out whether these effects occur and to what extent. We used ultrathin molecular layers and self-assembly monolayers as Raman-active probes deposited on Au and Si films and Au nanostructures. In addition to the 6-fold amplification of the Raman signal, we found that the sample curvature in gap-mode induces imaging artifacts visible as distortions in the electromagnetic field distribution.

Our results show that the use of gap-mode significantly increases the signal strength, but that at the same time, the sample curvature makes an impact to the TERS image contrast which was not considered until now. Beyond metal nanoparticles functionalized with organic molecules, our conclusions impact the nanoscale chemical visualization of molecular and inorganic systems using vibrational spectroscopy.

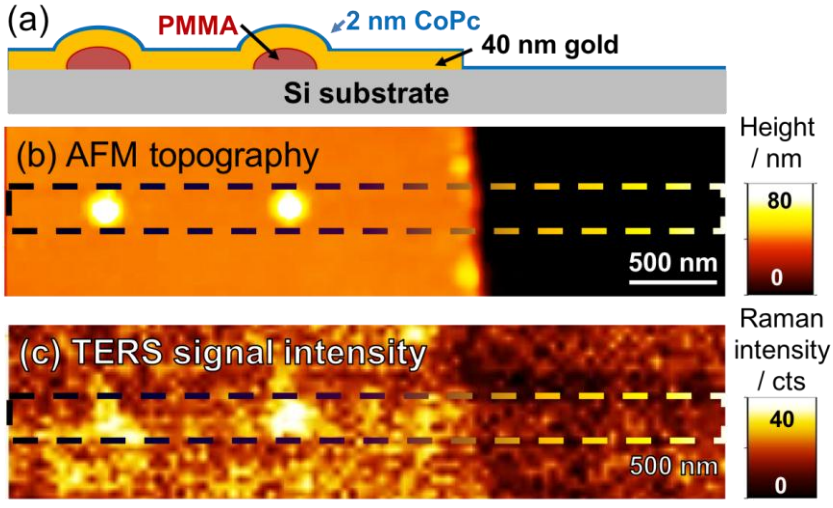

Figure 1. TERS imaging of the sample with different surface curvature . (a) Sample cross-section; (b) AFM image of the surface; (c) TERS image of the mode at 682 cm-1.

* Author for correspondence: jane.sheremet@gmail.com