Investigation of the near fields of sputtered Au thin films used for SERS, using the AFM and DDA

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Introduction

Surface enhanced Raman spectroscopy (SERS) is a powerful technique that uses metal nanostructures (Au, Ag, Cu) to gain in the best case single molecule sensitivity [1]. Most of the enhancement is attributed to the increase of the electric field near the surface of the metal nanostructure, because the Raman signal in this case scales approximately proportional to the fourth power of the electric filed strength [2]. A combination of AFM and the discrete dipole approximation (DDA) is a promising approach for a better understanding of solid SERS substrates. Using the AFM the geometry of a nanostructure on a flat substrate or a structured surface can be measured very accurately and the DDA is a well-established method for solving scattering problems for arbitrary shapes, which makes little assumptions about the sample other than the target geometry [3]. With your own matlab implementation of the DDA that calculates the nearfield from a given AFM image we are trying to predict the SERS enhancement factors of sputtered thin films.

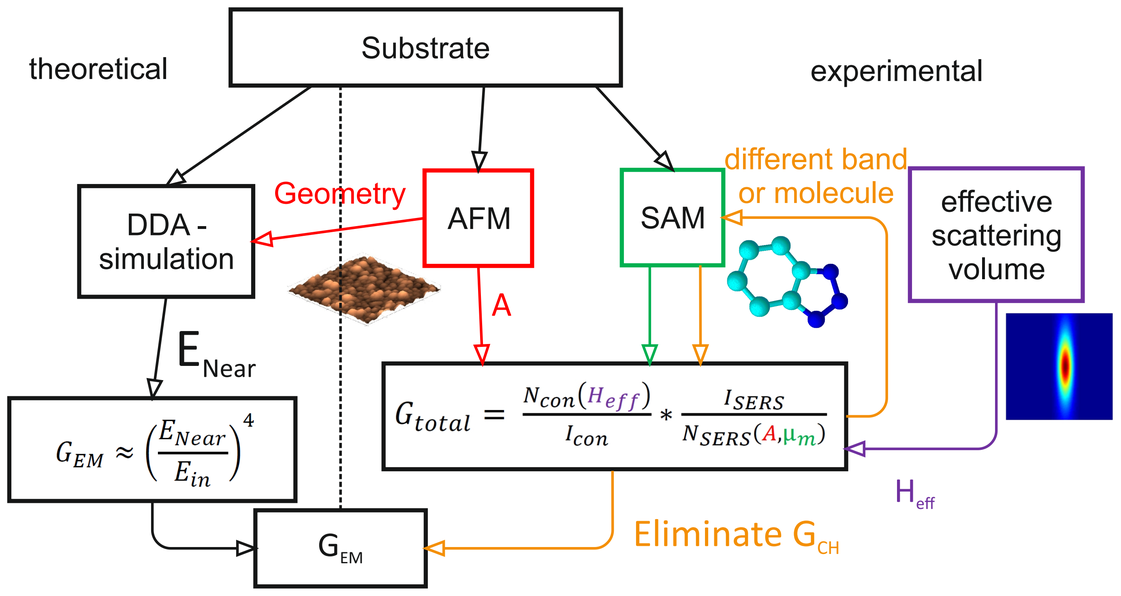


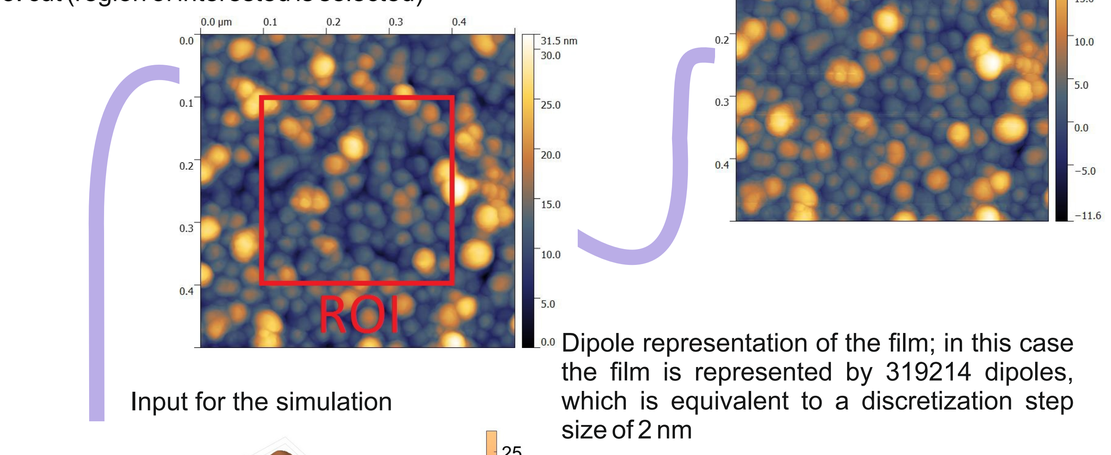
Fig.1: Flow chart of different approaches to determine SERS enhancement factors; this poster focuses on the theoretical (left) part

From AFM measurements to the final results

1. filtered (to avoid spiky features, discontinuities between lines and „nano-roughness" due to noise)

2. corrected (median plane subtracting and setting zero point)

3. cut (region of interested is selected)



Dipole representation of the film; in this case the film is represented by 319214 dipoles, which is equivalent to a discretization step size of 2 nm

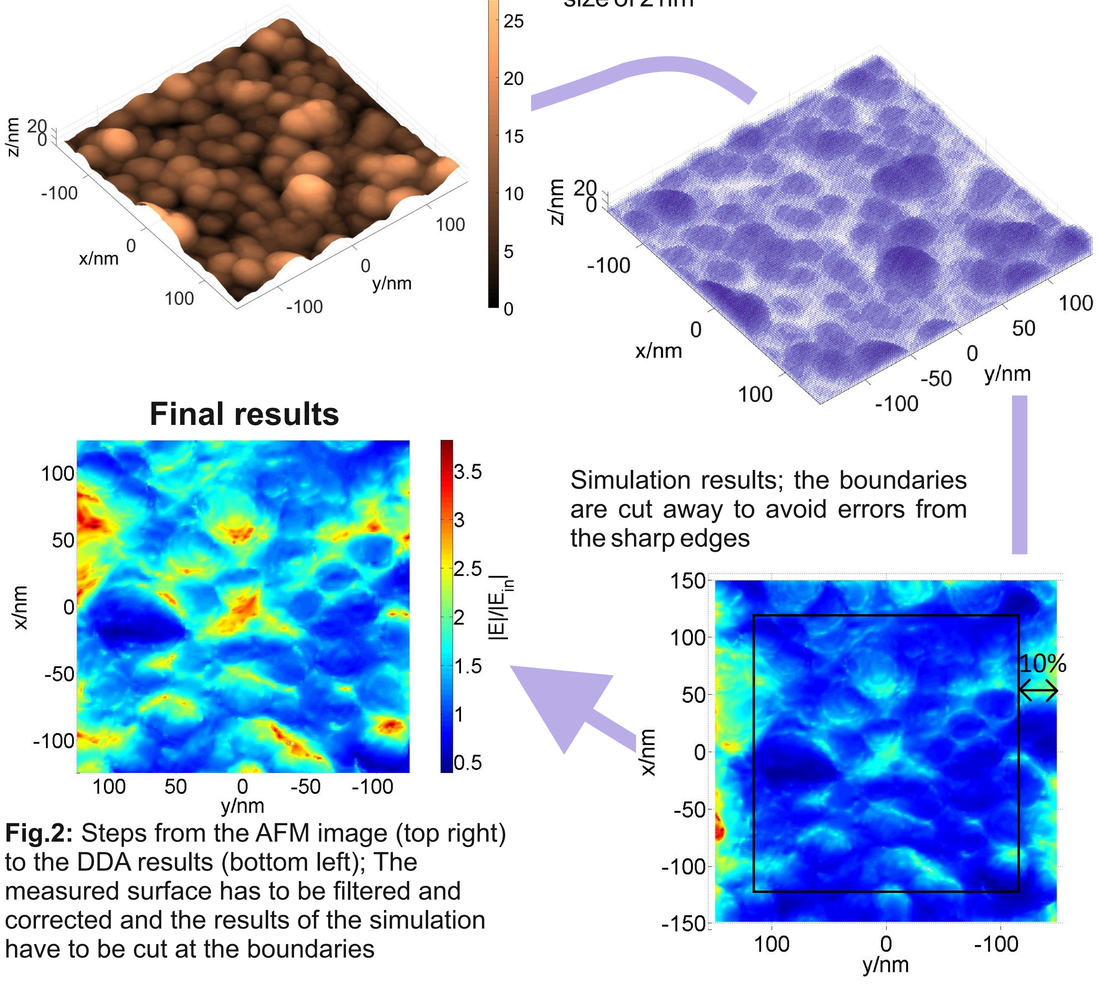


Fig.2: Steps from the AFM image (top right) to the DDA results (bottom left); The measured surface has to be filtered and corrected and the results of the simulation have to be cut at the boundaries

Results for a sputtered Au film

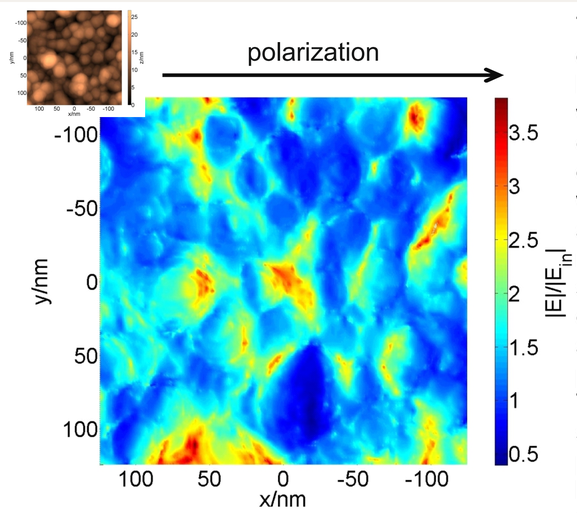


Fig. 3: Large scale simulation of the substrate; the discretization step size is 2 nm, which is too large for quantitative predictions, but the locations of the hotspots is visible

The electric field strength is always shown 2 discretization steps away from the surface, because a comparison of our DDA program with Mie Theory showed that the error of the electric field strength is smaller than 5% 2 discretization steps away from the surface for a wide range of discretization step sizes. This also means that, given the size of common test molecules (about 1-2 nm), a discretization step size of 0.5 nm or smaller is necessary for quantitative results. The enhancement factors are calculated as the average of the fourth power of the electric field strength.

The figure on the left shows a qualitative simulation of a large area to depicting the position of the „hot spots", which have the largest contribution to the signal. The hot spots were found to be in cracks and valleys oriented perpendicular to the polarization of the incoming field. The figures below show quantitative simulations of different hot spot positions.

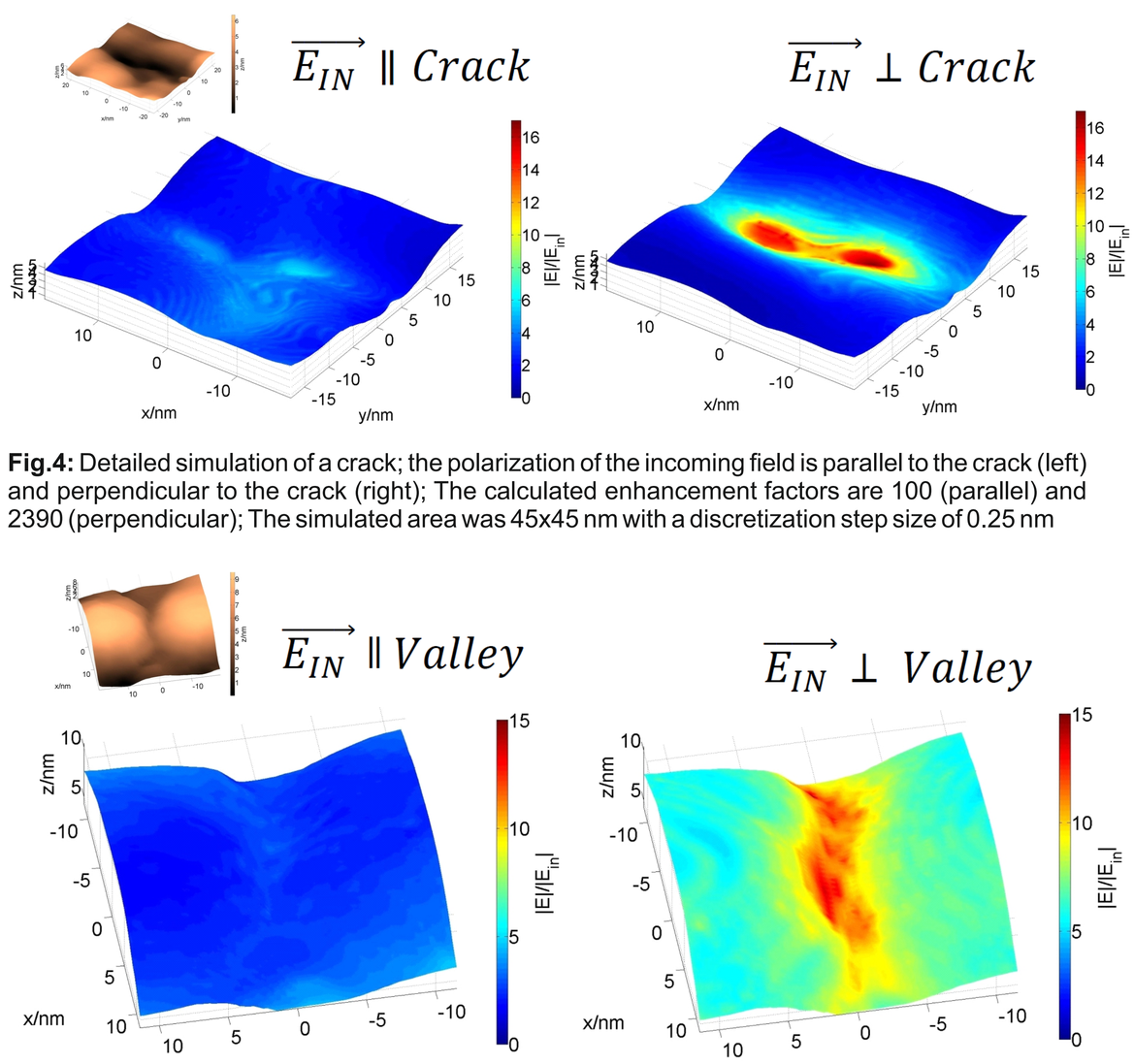


Fig.4: Detailed simulation of a crack; the polarization of the incoming field is parallel to the crack (left) and perpendicular to the crack (right); The calculated enhancement factors are 100 (parallel) and 2390 (perpendicular); The simulated area was 45x45 nm with a discretization step size of 0.25 nm

Fig.5: Detailed simulation of a valley; the polarization of the incoming field is parallel to the valley (left) and perpendicular to the valley (right); The calculated enhancement factors are 70 (parallel) and 5020 (perpendicular); The simulated area was 40x40 nm with a discretization step size of 0.5 nm

Conclusion

We have developed a matlab based implementation of the DDA, which is able to simulated electric fields from an AFM image of a metal nanostructure, with a discretization step size comparable to the resolution of an AFM. The qualitative simulations of sputtered Au thin films (SERS substrates used in this investigation) show high field strengths in cracks and valleys oriented perpendicular to the polarization of the incoming electric field. Quantitative simulations of these cracks and valleys predict enhancement factors of some 10^3, which is in approximate agreement with our measurements. However, in order to make a true comparison between simulation and experiment, we still need to address the issues of tip convolution, which is particular important when measuring narrow cracks, and the chemical enhancement factor, which is present in all measurements of SERS enhancement factors.

References/ Literature

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Acknowledgements

The authors are deeply grateful to the Graz Centre for Electron microscopy (ZFE) and the Graz University of Technology (TU Graz) for financial support.

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