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Disentangling topographic contributions to near-field scanning microwave microscopy images

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Abstract

We develop empirical models to predict the contribution of topographic variations in a sample to near-field scanning probe microwave microscopy (NSMM) images. In particular, we focus on $|\mathcal{S}_{11}|$ images of a thin Perovskite photovoltaic material and a GaN nanowire. The difference between the measured NSMM image and this prediction is our estimate of the contribution of material property variations to the measured image. Prediction model parameters are determined from either a reference sample that is nearly free of material property variations or directly from the sample of interest. The parameters of the prediction model are determined by robust linear regression so as to minimize the effect of material property variations on results. For the case where the parameters are determined from the reference sample, the prediction is adjusted to account for instrument drift effects. Our statistical approach is fully empirical and thus complementary to current approaches based on physical models that are often overly simplistic.

Keywords

Atomic force microscopy; GaN nanowire; Near-field scanning probe microwave microscopy; Perovskite materials; Statistical methods; Signal extraction

1. Introduction

To develop nanoscale components of electrical devices for supercomputers, communications and health care technologies, a quantitative understanding of material properties at the nanoscale scale is required. Near-field scanning probe microwave microscopy (NSMM) is a particularly promising experimental method for nanoscale electronic characterization. In NSMM, a microwave field is confined in the nanometer-scale apex of a scanning probe tip that provides simultaneous microwave and topographic measurements with nanometer spatial resolution [1–9]. Variations in microwave measurements can be produced by either material property variations or topographic variations [2]. Measurements are typically performed by integrating a one-port microwave signal with a conventional atomic force microscope (AFM) operating in contact mode. Our setup is based on a commercial system (Keysight) where the complex-valued $\tilde{S}$ signal is measured with a vector network analyzer

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Supplementary material

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(VNA). As described previously [10], the measured $\tilde{S}$ signal is directly related to the complex tip-sample admittance $\tilde{S} \propto \tilde{Y} = G + i\omega C$ where G , C and ω are tip-sample conductance, tip-sample capacitance and the operating frequency respectively. Measurements of the capacitive signal are of particular interest because (neglecting the contribution of topographic variations) they monotonically increase with sample conductivity. However, decomposition of $\tilde{S}$ into real and imaginary parts requires knowledge of a phase offset. Since we lack this knowledge for the samples studied here, we analyze $|\mathcal{S}_{11}|$ measurements. Spatial variations in $|\mathcal{S}_{11}|$ are primarily due to spatial variations in the imaginary term $i\omega C$ where C depends on topography and sample conductivity [10].

In typical experimental studies, the primary goal is to determine the component of $|\mathcal{S}_{11}|$ variations due to material property variations. Here, we regard the contribution due to topographic variations in the sample as a background that obscures the signal of interest. Hence, estimation (and ideally removal) of this topographic contribution to any NSMM measurement is a key challenge in NSMM. For some applications, topographic contributions to the signal of interest can be estimated based on physical finite element modeling [11], or based on approach curve measurements and additional modeling and measurements [12]. For many applications of interest, these approaches may not be practical due computational cost or their inability to accurately model the full complexity of the cantilever geometry. In this work, we focus on empirical statistical models to predict the topographic contribution to any $|\mathcal{S}_{11}|$ measurement that require neither numerical modeling nor additional measurements beyond $|\mathcal{S}_{11}|$ and topography measurements from the sample of interest or from an electronically homogenous (or nearly electronically homogenous) reference sample.

Recently, we developed an empirical model to predict the topographic contribution to $|\mathcal{S}_{11}|$ for photovoltaic thin film material samples based on observed topography and an estimate of the Laplacian of the observed topography image [10]. We determined the model parameters from the full NSMM image corresponding to the sample of interest by robust multiple regression [13] so as to suppress the influence of material property variations on results. Here, we extend our earlier work in two ways. First, we predict the contribution of topographic variations to the $|\mathcal{S}_{11}|$ image based on observed topography and the Laplacian of the smoothed topography image. As discussed in [14], the smoothing step is recommended for experimental data because it suppresses the effects of additive noise on results. The degree to which the topography image is smoothed depends on the choice of the Gaussian smoothing kernel standard deviation (bandwidth). Here, we present an empirical method to select this bandwidth parameter. Second, we determine the topographic prediction model from a reference sample that is nearly free of material property variations, and then apply it to a sample of interest where material property variations are more significant. To account for instrumental effects that vary from experiment to experiment, we adjust the model prediction determined from the reference sample before applying it to the second sample of interest. Determination of prediction model parameters from a reference sample is important because it may not be possible to determine these parameters directly from all samples of interest like we did in our earlier work [10]. For instance, the direct (“self-calibration”) method may fail if the fraction of the surface area of the sample of interest affected by

material property variations is large (relative to a fraction of 0.5), and one cannot identify sufficiently large subregions of the sample where material property variations are negligible and the range of topographic variations is sufficiently broad. Hence, this work serves as a first step in demonstrating that prediction models determined from reference samples can be applied to samples of interest where “self-calibration” is not feasible. We quantify the difference in the predicted topographic contribution to $|\mathcal{S}_{11}|$ for the two ways of determining the prediction model. For quantitative imaging, comparison of predictions determined by these two methods may facilitate quantification of the component of uncertainty due to imperfect modeling. We also develop an empirical nonparametric smoothing model to predict topographic contributions to $|\mathcal{S}_{11}|$ for a GaN nano wire [15]. In the interior region of the nano wire, our empirical model yields more accurate results than an alternative approach based on a simple physical model.

2. Methods

2.1. Microwave near-field microscope

Our NSMM is based on a commercial instrument (Keysight 5400) All measurements shown here are taken around 18.7–18.8 GHz with an acquisition intermediate frequency bandwidth (IFBW) of 100 Hz used for VNA-based detection of the $|\mathcal{S}_{11}|$ signal. The AFM is operated in contact mode with commercial cantilevers (Rocky Mountain Nanotechnology) with an apex radius ≈ 20 nm. These cantilevers are engineered with a large (80 μm) cantilever height to minimize the stray capacitance.

2.2 Photovoltaic material

In this study, we re-analyze NSMM images acquired from two thin film samples of a perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ (Methylammonium Lead Iodide, MAPI) material produced and aged under different conditions [16] as described in [10]. A “reference” sample was fabricated under dry humidity conditions and measured prior to its deterioration (see Fig. 2 of [10]). For this sample, our scientific judgement is that the contribution of material property variations to observed $|\mathcal{S}_{11}|$ is very small relative to the contribution due to topographic variations. The other sample is electronically inhomogeneous and was fabricated under identical conditions but allowed to deteriorate for ~ 12 h under ambient conditions exhibited significant material property (conductivity) variations (see Fig. 4 of [10]). Following [10], we sometimes refer to the reference sample and the electronically inhomogeneous sample as “pristine” and “deteriorated” in this work.

Although the signal originating from the tip-sample admittance vary only weakly, spatial trends in $|\mathcal{S}_{11}|$ and (to a lesser extent) topography often vary erratically line-to-line due to short-term drift in the signal offset. Hence, instead of determining a smooth spatial 2d-trend in topography and $|\mathcal{S}_{11}|$ images as in [17], we determine a linear spatial trend (and associated residuals about the trend) for each scan line with a robust regression method. For the reference material, we predict the topographic contribution to $|\mathcal{S}_{11}|$ as $|\widehat{\mathcal{S}_{11}}|_{\text{topo}}$ where

$$|\widehat{\mathcal{S}}_{11}|_{topo} = \alpha_0 + \alpha_1 z + \alpha_2 LoG * z, \quad (1)$$

and $\alpha = (\alpha_0, \alpha_1, \alpha_2)$ are model parameters. Above, $LoG * z$ denotes the convolution of a discrete representation of the Laplacian of a Gaussian smoothing kernel $G(LoG)$ and the observed topography image z . Since $LoG * z$ is equivalent to the Laplacian of the $G * z$, the third term on the right hand side of Eq. (1) is proportional to the Laplacian of the smoothed topography image. (For details regarding the relationship between the Laplacian and mean curvature of a surface, see the Appendix.) The continuous representation of LoG is [14]

$$LoG = \frac{-1}{\pi\sigma^4} \left[1 - \frac{r^2}{2\sigma^2} \right] \exp\left(\frac{-r^2}{\sigma^2}\right), \quad (2)$$

where $r^2 = x^2 + y^2$ and x, y are Cartesian coordinates and σ is an adjustable bandwidth parameter. Next, we describe our method for selecting σ for a discrete representation of LoG . We denote the value of LoG for the selected value of $\sigma, \hat{\sigma}$, as $\widehat{LoG}$.

For each of many values of σ on a grid, we estimate α by robust regression by minimizing $\sum_i^n \rho(e_i)$ where ρ is the Huber loss function [18] and e_i is a scaled residual defined as

$$e_i = \frac{y_i - \hat{y}_i}{s}. \quad (3)$$

The i th observed and predicted values of the quantify of interest (in our case $|\mathcal{S}_{11}|$) are y_i and $\hat{y}_i$. s is a scale factor, and

$$\rho(x) = \begin{cases} \frac{1}{2}x^2, & \text{if } |x| \leq k \\ k\left(|x| - \frac{k}{2}\right), & \text{other wise.} \end{cases}$$

The threshold parameter k in the Huber penalty function is adjustable but often set to 1.345 for reasons we discuss later.

For the ideal case where residuals associated with observations affected solely by topographic variations are identically distributed according to some distribution with a known standard deviation, we would equate s to this standard deviation. In practice, one determines s from data with a robust method that suppresses the influence of outliers (in our case large magnitude residuals produced by material property variations) on the estimate of s . In particular, after each iteration of an optimization algorithm, the scale factor s is equated to 1.4826 times the median absolute deviation (MAD) between observed and predicted ($y_i - \hat{y}_i$) values (Eq. (3)). (The MAD is scaled by 1.4826 so that the asymptotic value of s agrees with the true standard deviation of the residuals for the special case where each residual is a

realization of a normal (Gaussian) random variable with expected value 0 and the same variance.) Since the Huber penalty function is quadratic for small deviations between observed and model prediction values, but linear in the magnitude of deviations for larger ones, the influence of outliers (in our case observations due to strong material property variations) are down-weighted.

We select the bandwidth parameter σ (Eq. (2)) by minimizing the MAD of the deviations $|\mathcal{S}_{11}| - |\widehat{\mathcal{S}}_{11}|_{topo}$ determined from the full NSMM image. Given $\hat{\sigma}$ our estimate of σ is

$$\hat{\sigma} = (\hat{\alpha}_0, \hat{\alpha}_1, \hat{\alpha}_2). \quad (4)$$

We implement robust regression and determine $LoG * z$ in R [19] with the functions **r1m** [20] and **applyFilter** [21] respectively.

In this work, we set $k = 1.345$ (the default value in the R function **r1m**). To understand why this choice is reasonable, consider a toy problem where one estimates the theoretical mean (expected value) of a Gaussian random variable from multiple realizations of the random variable. When $k = 1.345$ and the scale factor β is set to estimated standard deviation of the random variable, the asymptotic (large sample limit) variance of the robust estimate of the theoretical mean is only 1.05 times the asymptotic variance of the sample mean (which corresponds to choice of $k = \infty$.) However, realizations of e (Eq. (3)) with magnitude greater than 1.345 are down-weighted [18]. Thus, for many problems of interest, the choice of $k = 1.345$ down-weights a significant fraction of possible outliers without dramatically inflating random uncertainties of estimated model parameters. As a caveat, other choices of k would yield different results. Finally, there are other implementations of robust regression based on other choices of the loss function $\rho(x)$ [13]. Although worthwhile, studies of how other choices of k in the Huber loss function affects results, as well as how the choice of other loss functions affects results, are beyond the scope of this work.

Instrumental effects that vary from experiment-to-experiment significantly affect $|\mathcal{S}_{11}|$ measurements but not topography measurements. Hence, estimates of the model parameters in Eq. (1) determined from the pristine reference sample do not directly apply to the deteriorated sample unless they are corrected for instrument drift. Below we describe our correction method.

Given that we determine α and LoG from the pristine reference sample, and the measured topography image for the deteriorated sample is $\tilde{z}$, we predict the topographic contribution to the $|\mathcal{S}_{11}|$ image for the deteriorated sample as

$$|\widehat{\mathcal{S}}_{11}|_{topo} = \gamma_0 + \gamma_1 \tilde{\Theta}, \quad (5)$$

where

$$\tilde{\theta} = \hat{\alpha}_0 + \hat{\alpha}_1 \tilde{z} + \hat{\alpha}_2 \widehat{LoG} * \tilde{z}, \quad (6)$$

and γ_0 and γ_1 are determined by fitting the Eq. (5) model to measured $|\mathcal{S}_{11}|$ for the deteriorated sample by robust regression.

2.3. Nanowire

For the GaN nanowire, the effect of material property variations on measured $|\mathcal{S}_{11}|$ depends on an applied bias voltage [15]. We analyze data corresponding to an applied bias voltage of $-5V$ where the nanowire is locally depleted and the conductivity is below the detection limit of the NSMM instrument. Thus, the effect of material property variations (in this case variations of charge carrier concentration) is negligible. We develop a model for the topographic contribution to measured $|\mathcal{S}_{11}|$ with a robust implementation of a non-parametric local regression method LOCFIT [22,23]. We implement this approach in R.

As the probe moves along a scan line, the tip of the probe maintains contact with the sample. That probe is tilted with respect to surface normal. Thus, the axis in which the probe tip moves is not orthogonal to the surface of the sample. Hence, the functional relationships between $|\mathcal{S}_{11}|$ and x is not symmetric about the center of the nanowire. To account for this asymmetry, we partition the location coordinate x for each scan line into two non-overlapping intervals. The break point for the intervals is approximately the location of the center of the nanowire. We determine separate prediction models for each interval. As a side remark, for the thin photovoltaic material sample, the morphology of the sample is irregular and spatially random. We neglect possible topographic asymmetry effects when constructing prediction models for the photovoltaic samples.

3. Results

3.1 2d photovoltaic material

3.1.1 Pristine sample—Based on analysis of the reference sample, we determine the bandwidth parameter σ that defines the *LoG* term (Eq. (2)) to be 20.6 nm (1.05 times the pixel side length (19.6 nm) in our image). In Fig. 1a–d, we show topography, the Laplacian of smoothed topography and measured $|\mathcal{S}_{11}|$ and $|\widehat{\mathcal{S}_{11}}|_{topo}$ images for the pristine reference sample. In Fig. 2a–c, we show scatterplots of measured $|\mathcal{S}_{11}|$ versus topography, Laplacian of smoothed topography and $|\widehat{\mathcal{S}_{11}}|_{topo}$. In Fig. 3a and b, we show the residual image,

$|\mathcal{S}_{11}| - |\widehat{\mathcal{S}_{11}}|_{topo}$, and its denoised version respectively. We determine the denoised image with the Adaptive Weight Smoothing (AWS) method [24]. For more discussion of AWS and its application to other NSMM images, see [17]. In our implementation of AWS, the degree of the local polynomial is 2, the maximum neighborhood size is 8 pixel lengths, and smoothing parameter I_{adjust} is 1. Both the residual and denoised residual images exhibit spatially correlated features. Although the RMS deviation of the denoised residuals ($7.9e-07$

dB) is not large relative to the range (max - min) of $|\widehat{\mathcal{S}}_{11}|_{topo}$ values ($3.8\text{e-}05$ dB), the observed structure suggests that the reference sample is affected by material property variations or that the prediction model is imperfect (Fig. 3a and b). Scatterplots of residual and denoised residual versus $|\widehat{\mathcal{S}}_{11}|_{topo}$ do not reveal any obvious pattern (Fig. 3c and d).

3.1.2 Deteriorated sample—We first determine the topographic prediction model parameters $\alpha = (\alpha_0, \alpha_1, \alpha_2)$ and the bandwidth parameter for *LoG* based on analysis of the reference sample as discussed in the previous section. Based on these and observed topography image of the deteriorated sample, we predict the topographic contribution to $|\widehat{\mathcal{S}}_{11}|$ for the deteriorated sample as $\tilde{\theta}$ (Eq. (5)). We then adjust this prediction for instrumental drift to get our final prediction $|\widehat{\mathcal{S}}_{11}|_{topo}$ (Eq. (5)) as discussed in Section 2.1.

The estimates of the affine transformation parameters in Eq. (5) are $\hat{\gamma}_0 / \text{dB} = (6.7 \pm 5.3)\text{e} - 08$ and $\hat{\gamma}_1 = (0.668 \pm 0.012)$. (The intervals for parameter estimates have nominal coverage probability of 0.68. The intervals are based on random uncertainties determined from robust regression. Since we neglect uncertainty in topography measurements and our estimate of the Laplacian of the smoothed topography image as well as possible systematic effects, the nominal 68 percent intervals are likely to be optimistic.) In Fig. 4a and b we show measured z and the Laplacian of smoothed topography for the deteriorated sample. In Fig. 4c and d, we show measured $|\mathcal{S}_{11}|$ and the predicted contribution to $|\mathcal{S}_{11}|$ due to topographic variations ($|\widehat{\mathcal{S}}_{11}|_{topo}$) as determined by Eq. (5).

In Fig. 5a–c, we show scatterplots of measured $|\mathcal{S}_{11}|$ versus topography, Laplacian of smoothed topography and the predicted contribution to $|\mathcal{S}_{11}|$ due to topographic variations. The residual and denoised residual images shown in Fig. 6a and b correspond to estimates of the contribution of material property variations to measured $|\mathcal{S}_{11}|$. We attribute the skewness of the scatterplots in Fig. 6c and d and the histogram of denoised residuals in Fig. 7b to material property variations. In contrast, for the pristine sample, we attribute the apparent symmetric shape of the scatterplots (Fig. 3c and d) and the histogram of denoised residuals (Fig. 7a) to the lack (or weakness) of material property variations.

When we determine the prediction model directly from the deteriorated sample, the selected bandwidth parameter σ that defines the *LoG* term (Eq. (2)) is 40.38 nm (2.06 times the pixel side length (19.6nm) in our image). In Fig. 8, we compare predictions of the topographic contribution to measured $|\mathcal{S}_{11}|$ from this “self-calibration” method to the Eq. (5) prediction.

The agreement appears generally good visually. However, there may be systematic differences between the two model predictions (particularly at larger values).

3.2 Nanowire

Our primary data consists of eight scans of the nanowire where the location of each scan is approximately the same. For each topography scan, we determine a linear spatial trend by robust regression and calculate residuals about the trend based on analysis of data

corresponding to $x < 82$ nm and $x > 618$ nm. Each $|\mathcal{S}_{11}|$ scan is corrected for an offset by subtracting the maximum value in each scan from all other values in that scan. We then denoise the resulting $|\mathcal{S}_{11}|$ and the topography images with the Adaptive Weights Smoothing method. In our implementation of AWS, the degree of the local polynomial is 2, the maximum neighborhood size is 24 pixel lengths, and smoothing parameter I_{adjust} is 1. We index the scans as 1, 2, 3, ...8. In Fig. 9a and b, we display topography and $|\mathcal{S}_{11}|$, before and after denoising, for one of the eight scans. In Fig. 9c and d, we show the difference between not-denoised and denoised results. Note that denoising has a very small effect on the topography scan but a dramatic effect on the $|\mathcal{S}_{11}|$ scan. For this scan line, the root-mean-square difference between denoised and not-denoised results for topography and $|\mathcal{S}_{11}|$ are 0.34nm and 2.7e-06 dB respectively.

We determine our scatterplot prediction model from the even scans and predict results for the odd scans with a robust implementation of LOCFIT (Figs. 10 and 11). In this approach, a locally linear model is fit to the scatterplot of $|\mathcal{S}_{11}|$ versus z in the neighborhood of each point of interest in a robust manner. The parameter in LOCFIT that controls the size of the neighborhood about any point is 0.05. The value of the fitted locally linear model at the point of interest is the prediction. In Fig. 12, we show how well our method predicts results for the (odd) scans.

In Fig. 13, we display observed and predicted (according to our scatterplot prediction model) $|\mathcal{S}_{11}|$ for the scan line shown in Fig. 12b. We also show predicted results determined from a physical model (Eqs. (7) and (8)) where we model the capacitance of our physical system as the series connection of two capacitors where one capacitor represents the probe tip and nanowire and the other represents a background SiO₂ dielectric layer. We assume that the cross-sectional areas of those two capacitors are the same. The approximate linear shape of scatterplot predictions for topography values between 10 nm and 80 nm (Figs. 10 and 11) indicates that this assumption is reasonable. In general, if the areas were significantly different, we could account for the difference by increasing the complexity of our model. Such an extension would increase the number of model parameters by 1. Our physical model for the expected value of observed $|\mathcal{S}_{11}|$, $< |\mathcal{S}_{11}| >$, is

$$< |\mathcal{S}_{11}|(h, V) > = < |\mathcal{S}_{11}|(h_0, V) > + k (C_{rel}(h, V) - C_{rel}(h_0, V)), \quad (7)$$

where h is the (theoretical) height of the probe tip above the background dielectric layer, V is the applied voltage, $< |\mathcal{S}_{11}|(h_0, V) >$ and k are intercept and slope parameters in our model, and $h_0 = 0$ nm. The model for relative capacitance C_{rel} (by relative, we mean that the actual capacitance would be C_{rel} times a scale factor) is

$$C_{rel}(h) = \frac{\epsilon_2 d_1}{\epsilon_1 h + \epsilon_2 d_1}, \quad (8)$$

where relative permittivities are set to $\epsilon_1 = 4$ and $\epsilon_2 = 8$, and the thickness of the dielectric layer is set to $d_1 = 500$ nm. The quantities $\langle |\mathcal{S}_{11}|(h_0, V) \rangle$ and k are model parameters determined by fitting the Eq. (7) model to scatterplots in observed $(C_{rel}(z, V) - C_{rel}(z_0, V), |\mathcal{S}_{11}|(z, V))$ space (where z is measured topography and $z = 0$ nm) by the method of least squares for two regions. The first region corresponds to $-4.5e-05 \text{ dB} \leq |\mathcal{S}_{11}| \leq -3.1e-05 \text{ dB}$ and $150 \text{ nm} < x < 350 \text{ nm}$. The second region corresponds to $-4.5e-05 \text{ dB} \leq |\mathcal{S}_{11}| \leq -3.1e-05 \text{ dB}$ and $350 \text{ nm} < x < 550 \text{ nm}$. For the first region, the estimated intercept and slope parameters are $(2.6 \pm 0.8)e-05 \text{ dB}$ and $(7.9 \pm 1.0)e-04 \text{ dB}$ respectively. For the second region, the estimated intercept and slope parameters are $-(1.9 \pm 0.1)e-05 \text{ dB}$ and $(3.7 \pm 0.1)e-04 \text{ dB}$ respectively. (For both regions, intervals for parameter estimates have nominal coverage probability of 0.68. The intervals are based on random uncertainties determined from ordinary least squares. Since we neglect uncertainty in topography measurements, the LOCFIT prediction model, and other possible systematic effects, the nominal 68 percent intervals are likely to be optimistic.) The physical model fails to account for the ripples in measured $|\mathcal{S}_{11}|$ in the interior of the nano wire. In contrast, the prediction of the nonparametric model is in good agreement with the observed ripples in the interior of the nanowire. However, the performance of the nonparametric model is not as good for the other regions. We attribute the lack of good agreement in these other regions to stray capacitance effects.

4. Summary

We determined topographic prediction model parameters from a reference photovoltaic sample that is nearly free of material property variations and applied it to a second electronically inhomogeneous photovoltaic material sample of interest after an adjustment for instrumental drift. In general, the resulting prediction model agreed well with a prediction model determined directly from the electronically inhomogeneous material sample. We attribute this success to the fact that the fraction of the samples affected by material property variation was small relative to 0.5. For cases where the fraction is larger than 0.5, our robust regression methods that are designed to down-weight the influence of material property variations on model parameter estimates, may break down unless there are identifiable subregions in the samples where topographic variations are sufficiently broad and material property variations are slight.

For a GaN nanowire where material property effects on $|\mathcal{S}_{11}|$ measurements are negligible, we developed an empirical model for the topographic contribution to $|\mathcal{S}_{11}|$ measurements. For the interior region of the nanowire, the prediction model was in very good agreement with observed values. We also predicted $|\mathcal{S}_{11}|$ measurements with a physical model with adjustable parameters that we determined empirically. For the interior region of the nano wire, the agreement between the simple physical model prediction and observations was poor. In all likelihood, this failure is due to the fact that the electronic fields within the nanowire change in a complicated way as the spatially extended probe moves along the facets of the nanowire. In contrast, our simple physical model prediction is based on a

parallel-plate approximation that neglects how electric fields depend on the shape of the facets and the probe and their points of contact.

Here, for each sample of interest, we analyzed NSSM data acquired at one particular frequency. In general, if data were acquired at each of many frequencies, our method could be applied to data acquired at each of frequencies. Certain adjustable parameters in our analysis algorithms were selected by scientific judgement. In future studies, given a sufficient number of repeat measurements at the same experimental conditions, we hope to explore machine learning methods such as cross-validation [25] to select adjustable parameters. Such additional data would also be useful for uncertainty analysis.

Although we focused on predicting the topographic contribution to $|\mathcal{S}_{11}|$ in NSMM, our general empirical approach may have application to other raster and scanning probe imaging experiments where variations in topography acquired with an AFM (or some other instrument) affect measurements simultaneously acquired with other instruments. Possible application areas include: laser microscopy [29–31], scanning coherent anti-Stokes Raman microscopy [32], and Raman spectroscopy [33–35], luminescence imaging [36–38], fluorescent imaging and single molecule spectroscopy [39,40], photo acoustic molecular imaging [41], nonlinear sum frequency generation imaging [42–44], and aberration-corrected scanning transmission electron microscopy [45].

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Appendix A. Curvature and the Laplacian

The mean curvature [26,27] of a surface defined as $z = s(x, y)$ where x, y, z are cartesian coordinates, is $H(x, y)$ where

$$H(x, y) = -\frac{1}{2} \nabla \cdot \hat{\mathbf{n}}(x, y). \quad (9)$$

Above, $\hat{\mathbf{n}}(x, y)$ is the unit normal to the surface at (x, y) and can be expressed as

$$\hat{\mathbf{n}} = \frac{\nabla \phi}{|\nabla \phi|}, \quad (10)$$

where $\phi = z - \mathcal{J}(x, y)$ [28]. Thus,

$$H(x, y) = \frac{(1 + \mathcal{J}_x^2)\mathcal{J}_{yy} - 2\mathcal{J}_x\mathcal{J}_y\mathcal{J}_{xy} + (1 + \mathcal{J}_y^2)\mathcal{J}_{xx}}{2(1 + \mathcal{J}_x^2 + \mathcal{J}_y^2)^{3/2}}, \quad (11)$$

where $\mathcal{J}_x = \frac{\partial \mathcal{J}(x, y)}{\partial x}$, $\mathcal{J}_y = \frac{\partial \mathcal{J}(x, y)}{\partial y}$, $\mathcal{J}_{xx} = \frac{\partial^2 \mathcal{J}(x, y)}{\partial x^2}$, $\mathcal{J}_{yy} = \frac{\partial^2 \mathcal{J}(x, y)}{\partial y^2}$, and $\mathcal{J}_{xy} = \frac{\partial^2 \mathcal{J}(x, y)}{\partial x \partial y}$. For the case

where $\mathcal{J}_x^2 < 1$, $\mathcal{J}_y^2 < 1$ and $2\mathcal{J}_x\mathcal{J}_y\mathcal{J}_{xy} < \min(\mathcal{J}_{xx}, \mathcal{J}_{yy})$, the mean curvature of the surface is well approximated as one half times the Laplacian. That is,

$$H(x, y) \approx \frac{\mathcal{J}_{xx} + \mathcal{J}_{yy}}{2}. \quad (12)$$

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Fig. 1. Pristine reference photovoltaic sample. (a). Topography image (z/nm). (b). Laplacian of smoothed topography image (a.u.). (c). $1000 \times |S_{11}| / \text{dB}$ image. (d). Predicted topographic contribution to $1000 \times |S_{11}| / \text{dB}$ image due to topographic variations in the sample.

Fig. 2.

Pristine reference photovoltaic sample. (a) Scatterplot of observed $|S_{11}|$ versus topography.

(b) Scatterplot of observed $|S_{11}|$ versus Laplacian of smoothed topography. (c) Scatter-plot

of observed $|S_{11}|$ versus predicted contribution due to topographic variations in the sample.

Reference line of equality shown. Units the same as in Fig. 1.

Fig. 3.

Pristine reference photovoltaic sample. (a) Predicted contribution due to material property variations ($|S_{11}| - |\widehat{S_{11}}|_{topo}$). (b) Denoised version of (a). (c) Scatterplot of (a) versus predicted contribution due to topographic variations. Nonparametric trend estimate (smoothing spline) shown. (d) Scatterplot of (b) versus predicted contribution due to topographic variations. Nonparametric trend estimate shown. Units the same as in Fig. 1.

Fig. 4. Deteriorated photovoltaic sample. (a). Topography image (nm). (b). Laplacian of smoothed topography image (a.u.). (c). $1000 \times |S_{11}| / \text{dB}$ image. (d). Predicted topographic contribution to $1000 \times |S_{11}| / \text{dB}$ image.

Fig. 5. Deteriorated photovoltaic sample. (a) Scatterplot of observed $|S_{11}|$ versus topography. (b) Scatterplot of observed $|S_{11}|$ versus Laplacian of smoothed topography. (c) Scatterplot of observed $|S_{11}|$ versus predicted contribution to $|S_{11}|$ due to topographic variations in the sample. Reference line of equality shown. Units the same as in Fig. 4.

Fig. 6. Deteriorated photovoltaic sample. (a) Predicted contribution to $1000 \times |\mathcal{S}_{11}| / \text{dB}$ due to material property variations. (b) Denoised version of (a). (c) Scatterplot of (a) versus $|\widehat{\mathcal{S}}_{11}|_{\text{topo}}$. Nonparametric trend estimate (smoothing spline) shown. (d) Scatterplot of (b) versus $|\widehat{\mathcal{S}}_{11}|_{\text{topo}}$. Nonparametric trend estimate shown. Units the same as in Fig. 4.

Fig. 7.

(a) Distribution of denoised residuals for the pristine sample (Fig. 3b). (b) Distribution of denoised residuals for the deteriorated sample (Fig. 6b). The medians of these distributions for the pristine and deteriorated samples are $8.6\text{e-}10\text{dB}$ and $1.1\text{e-}06\text{dB}$ respectively.

Fig. 8.

Deteriorated photovoltaic sample. (a) Prediction determined from sample of interest (self-calibration method) versus adjusted prediction determined from reference sample (Eq. (5)). (b) Difference of predictions. Nonparametric trend (smoothing spline) shown. Mean difference is $-1.2\text{e-}09$ dB. Root-mean-square difference is $3.8\text{e-}07$ dB.

Fig. 9. GaN Nanowire. Representative scan lines of topography and $|S_{11}|$. Denoised and not denoised results (a,b), Residuals (difference of not-denoised and denoised)) (c,d). The root-mean-square values of the residuals shown in c and d are 0.34nm and 2.7e-06dB respectively.

Fig. 10. GaN Nanowire. LOCFIT empirical prediction model (line) for contribution to $|\mathcal{S}_{11}|$ due to topography variations for $x < 350$ nm. Model is determined from data corresponding to four scan lines.

Fig. 11. GaN Nanowire. LOCFIT empirical prediction model (line) for contribution to $|\mathcal{S}_{11}|$ due to topography variations for $x > 350$ nm. Model is determined from data corresponding to four scan lines.

Fig. 12.
 Predicted contribution to $-|\mathcal{S}_{11}|$ due to topography variations. Results for odd scans (a–d) are predicted with a model determined from data corresponding to even scans.

Fig. 13.

Predicted contribution to $|\mathcal{S}_{11}|$ due to topography variations based on a physical model (Eqs. (7) and (8)) and our empirical scatterplot prediction model (Figs. 10–12) for the scan line shown in Fig. 12b. We determine adjustable slope and intercept parameters for the physical model from data within the box.