

# Research Report

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# Local thickness determination of thin insulator films via localized states

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We propose measuring the lifetime of localized states below the conduction band to determine the local thickness of thin insulating films using scanning tunneling microscopy (STM). The lifetime, which is a characteristic fingerprint of the film thickness, is inversely proportional to the saturation value of the tunnel current through the localized state at close tip-sample separation and is readily measured using scanning tunneling spectroscopy. We demonstrate the method for 5–11 monolayer thick NaCl films grown on Cu(111).

The development of nondestructive methods for determining the thickness of epitaxial films is of fundamental interest in surface science and thin-film technology. If the film leaves the substrate partially uncovered and if no intermixing of substrate and adsorbate occurs, the layer thicknesses can be determined *directly* by layer counting or topographic measurements. With most systems, this is feasible up to coverages of a few monolayers (ML) without using special surface-masking techniques during deposition<sup>1</sup>. If the film is soft compared to the substrate, the application range of layer counting can also be extended by scratching the film<sup>2</sup>. On the other hand, film thicknesses can be determined *indirectly* by measuring macroscopic film properties that vary with the film thickness, e.g., the refractive index<sup>3–5</sup>. In the case of thin insulating films, the film thickness can be determined by recording so-called Fowler–Nordheim  $I(V)$  curves<sup>6</sup>. Using X-rays, the film thickness can be determined by various methods<sup>7</sup>, e.g., by using the Pendellösung interference fringes of x-ray rocking curves<sup>8</sup> or by analyzing the relative peak intensities of two peaks at different take-off angles<sup>2</sup>. In general, indirect methods allow the film thickness to be determined from a few tens to hundreds of nanometers with an accuracy on the order of a few atomic layers. Because most of the methods average over a larger area, nominal thickness values are obtained for the case of surface roughness. For systems that feature quantum-sized effects, indirect methods can also yield layer-by-layer resolution, as has recently been shown<sup>4,9,10</sup>.

Here, we propose a novel method for the local thickness determination of thin insulating films by scanning tunneling spectroscopy. The method consists of determining the lifetime of a localized state below the conduction band by measuring the tunnel current through the localized state as a function of the tip-sample distance. At close tip-sample distances, the tunnel current through the double-barrier tunneling junction (vacuum gap, tunnel barrier across the film) is determined by the lifetime of the localized state. We demonstrate the method for 5–11 ML thick NaCl films grown on Cu(111) using the vacancy state (VS) of single chlorine vacancies.

The experiments were performed in a custom-built ultra-high-vacuum (UHV) apparatus with a base pressure of  $1 \times 10^{-10}$  mbar. The apparatus contains means for substrate cleaning and film preparation as well as a combined low-temperature (LT) STM/ atomic force

microscope (AFM) with an internal, home-built current preamplifier (1 fA noise floor). We used Cu(111) and Cu(100) substrates, which were cleaned by repeated Ne<sup>+</sup> sputtering cycles (1 kV, 20  $\mu\text{A}/\text{cm}^2$ ) and short annealing periods at 900 K prior to film preparation. Thin NaCl films with a nominal thickness of 9–11 ML were deposited from a molecular beam evaporator onto the substrate held at 270 K at a rate of 2 ML/min. The evaporation rate was monitored using a quartz micro-balance. After deposition, the sample was annealed at 500 K for 3 min and then rapidly cooled down to 4 K. Cleanliness of the surface was checked after preparation using the *in-situ* LT STM/AFM.

Under these growth conditions, we obtained small copper areas embedded into large, well-ordered NaCl terraces, as needed for calibrating the proposed method with absolute thickness values from layer counting. The four-fold NaCl film grows incommensurately on the three-fold Cu(111) substrate, giving rise to randomly oriented domains. Where several domain boundaries coincide, bare copper areas can be found. An example of such a region is shown in Fig. 1a; the Cu patch appears dark in the STM image. A line-scan taken at the position indicated by the blue line is shown in Fig. 1b. The height profile reveals a first tall step with an apparent height of  $\approx 10\text{\AA}$  followed by monoatomic steps of rather uniform apparent height. Comparison of the bias dependence of the apparent heights of bilayer NaCl islands shows that the initial

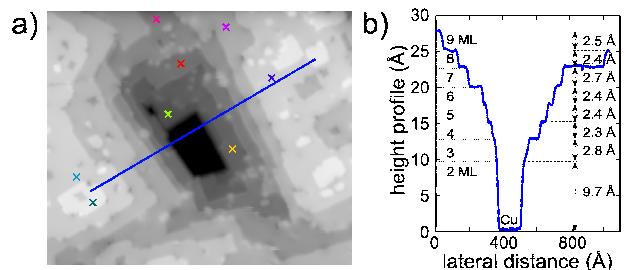


FIG. 1: (a) STM image of a patch of bare Cu (dark contrast) surrounded by NaCl terraces that are 2 to 9 ML thick. The colored crosses indicate the positions of deliberately created chlorine vacancies after recording the image. A height profile taken at the position indicated by the blue line is shown in (b). Imaging details:  $1200 \times 1000 \text{\AA}^2$ , sample bias  $V = 4.35 \text{ V}$ , tunnel current  $I = 1.5 \text{ pA}$ .

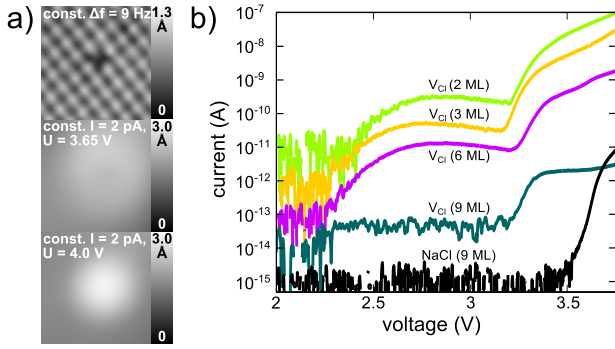


FIG. 2: (a) Appearance of a chlorine vacancy at typical imaging conditions. Top panel: constant- $\Delta f$  feedback ( $\Delta f = +9$  Hz), middle and bottom panels: constant-current feedback ( $V = 3.65$  V,  $I = 2$  pA, and  $V = 3.4$  V,  $I = 2$  pA, respectively). All images are of size  $30 \times 30 \text{ \AA}^2$ . (b) Semilogarithmic depiction of  $I(V)$  spectra of chlorine vacancies on a selection of NaCl layer thicknesses. The spectra have been recorded at the locations indicated by the colored crosses in Fig. 1a. An  $I(V)$  spectrum recorded on 9 ML NaCl is shown for reference. For the sake of clarity, the spectra have been shifted up by a factor of 10 from one spectrum to the next.

tall step corresponds to a bilayer NaCl terrace. We believe that the variations in step height in between 3 and 9 ML are due to imaging at elevated bias.

At the positions indicated by the colored crosses, we have created single chlorine vacancies, one per pulse, by ramping the bias voltage from the STM set point (4 V, 0.5 pA) up to 4.8–5.2 V. The bias was kept at the upper value until a sudden increase of the tunnel current indicated the formation of a Cl vacancy; the current increase is due to the VS that becomes available for tunneling. Chlorine vacancies created this way are easily identified by their appearance in STM and AFM, see Fig. 2a. The top panel depicts an atomically resolved image of the Cl lattice, which was recorded in AFM mode (const.- $\Delta f$  mode). The Cl vacancy appears as a dark depression. STM images of the same area obtained at 3.65 V and 4.0 V are shown in the middle and bottom panel, respectively. In Fig. 2b,  $I(V)$  spectra of chlorine vacancies on a selection of NaCl thicknesses are shown. An  $I(V)$  spectrum recorded on 9 ML NaCl is shown for reference. Two states localized at 2.3–2.8 (depending on the layer thickness) and 3.35 V are apparent, which we identify as the singly and the doubly occupied VS, respectively. On bilayer NaCl, we observe the VS at 2.8 V, in agreement with Ref. 11. The NaCl spectrum (black curve) reveals the onset of the conduction band at approximately 3.5 V. As the doubly occupied VS is only slightly below the conduction band, a fully-developed second plateau in the  $I(V)$  spectrum is only seen for chlorine vacancies on thicker NaCl films ( $\geq 9$  ML).

Next, we determined the lifetime of the VS by measuring the tunnel current through the VS as a function of the tip approach  $z$ , i.e., recording so-called  $I(z)$  spectra. Figure 3a shows the results for the singly occupied VS

measured at 2.6 V for NaCl thicknesses between 5 and 9 ML. All curves exhibit a similar behavior: At large tip-sample distance, starting from  $I = 1$  fA at  $z = 0$ , the tunnel current increases exponentially with decreasing tip-sample distance. Then, as the tip approaches the surface further, the tunnel current starts to saturate and eventually reaches a plateau. As the VS is the only occupied state at 2.6 V and electrons have to tunnel sequentially via this state, the maximum tunnel current is a direct measure of the lifetime (1 A corresponding to

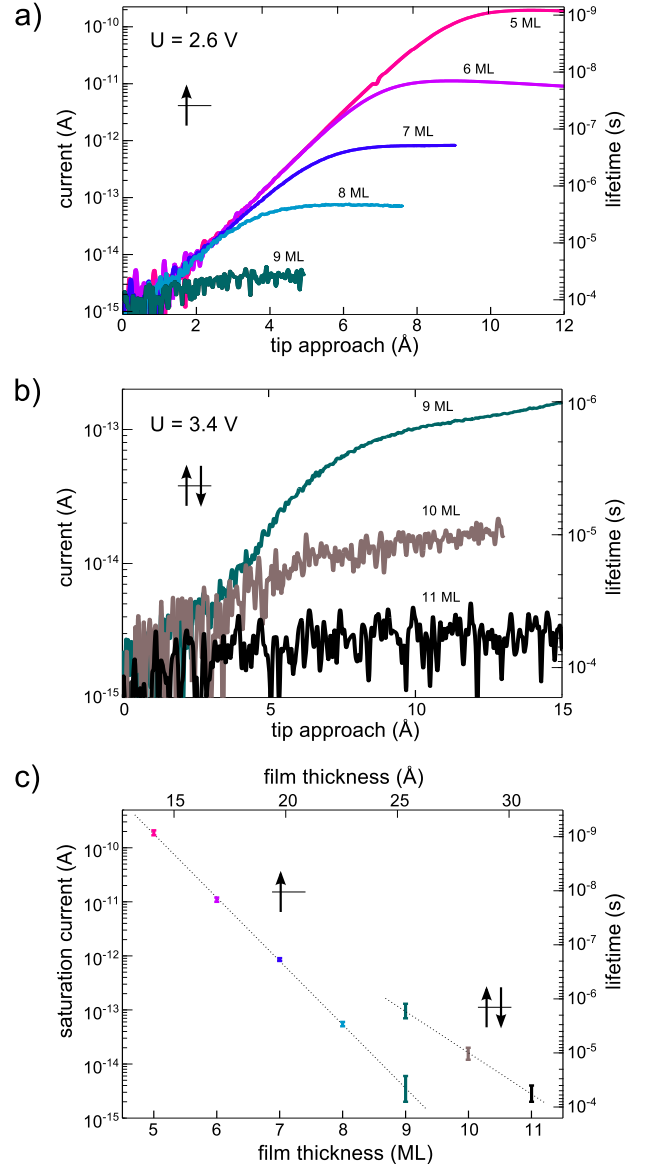


FIG. 3: (a, b) Semilogarithmic depiction of  $I(z)$  spectra of chlorine vacancies recorded at  $V = 2.6$  V on 5–9 ML thick NaCl films and at  $V = 3.4$  V on 9–11 ML thick NaCl films, respectively.  $z = 0 \text{ \AA}$  corresponds to an STM setpoint ( $V = 4.2$  V,  $I = 1$  pA) above NaCl. (c) Lifetime of the singly and doubly occupied chlorine VS as a function of NaCl film thickness. The dotted lines are a guide to the eye.

$6.241 \times 10^{18}$  electron charges per second as indicated on the right ordinate of Fig. 3a). A similar set of  $I(z)$  spectra, measured for the doubly occupied VS at 3.35 V on 9 to 11 ML thick NaCl layers, is shown in Fig. 3b. The  $z$ -dependence of the tunnel current can be understood from a simple resistor model consisting of a gap resistance and a film resistance connected in series. At large tip-sample distance, the gap resistance is much larger than the tunnel resistance across the film. In this distance regime, the total resistance is determined by the gap resistance, which thus decreases exponentially with decreasing tip-sample distance. At the other extreme, at close tip-sample distance, the gap resistance is negligibly small and the total resistance is determined by the tunnel resistance across the film, which is an inherent property of the film and depends strongly on the film thickness. Note that, if the influence of the electric field of the tip can be neglected, the saturation current is independent of the properties of the probe tip.

Figure 3c summarizes the lifetime measurements by showing the measured saturation currents (left ordinate) and the corresponding lifetime (right ordinate) as a function of the film thickness. An exponential decrease (increase) of the saturation current (lifetime) is observed with increasing film thickness. In the semilogarithmic depiction, the data points for the singly occupied VS fall onto a straight line (dotted line, shown as a guide to the eye) with a slope of  $10^{-1.17} \text{ ML}^{-1}$ . The fact that the lifetime changes by more than an order of magnitude from one layer to the next makes it an extremely sensitive parameter for thickness determination. The range of thicknesses that can be determined in this way depends on the dynamic range of the current preamplifier and on the relative change of the saturation current per layer. The lower limit in our case is 5 ML, which is because of the requirement of tunneling exclusively via the VS and film destruction if the current is too large. For ultra-thin films, the exponential decrease with increasing thickness of the tunnel current can be used as a measure of the thickness<sup>12</sup>. The relative change of the saturation current per layer depends on the barrier height for tunneling into the substrate. Note that, in general, the film will relax upon putting an electron into the localized state.

Indeed, Fig. 3c reveals a decreased relative change of the saturation current per layer for the doubly-occupied VS,  $10^{-0.78} \text{ ML}^{-1}$ . The higher saturation current of the doubly-occupied VS at 9 ML allows us to extend the range for NaCl thickness determination to 11 ML before reaching the noise level of our current amplifier. If thermally activated processes do not play a role, as in the case of the experiments presented here, the application range of the proposed method can be extended to thicker films by measuring the saturation current of a localized state with a very small barrier height, for example, by depositing a suitable adsorbate. This is important because thermal excitation of an electron from the localized state into the conduction band would open up a direct channel for tunneling and, therefore, would impede lifetime determination by the proposed method.

In conclusion, we have shown that the lifetime of localized states below the conduction band is a characteristic fingerprint of the film thickness. Depending on the barrier height for tunneling into the substrate, the lifetime can change by more than an order of magnitude from one layer to the next. This latter fact makes the lifetime a very sensitive quantity for thickness determination. Furthermore, the proposed lifetime determination by measuring the saturation current at close sample distance is not influenced by the properties of the probe tip. We have demonstrated the proposed method for 5–11 ML thick NaCl films grown on a Cu(111) substrate using the VS of single chlorine vacancies, but the method is of much broader applicability. The only requirement is that of a localized state below the conduction band, whereas the origin of the localized state (surface defect, adsorbate) does not matter. Like with most indirect thickness determination methods, the proposed method needs calibration. Aside from the practical aspects of the presented work, the characterization of the thickness-dependent lifetime of the VS could provide useful for conceiving novel experiments that exploit the increased lifetime of charged states on thicker NaCl films<sup>13</sup>.

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