

Femtosecond Trapping of Free Electrons in Ultrathin Films of NaCl on Ag(100)

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Supplementary Information

Dosing Calibration and Film Characterization:

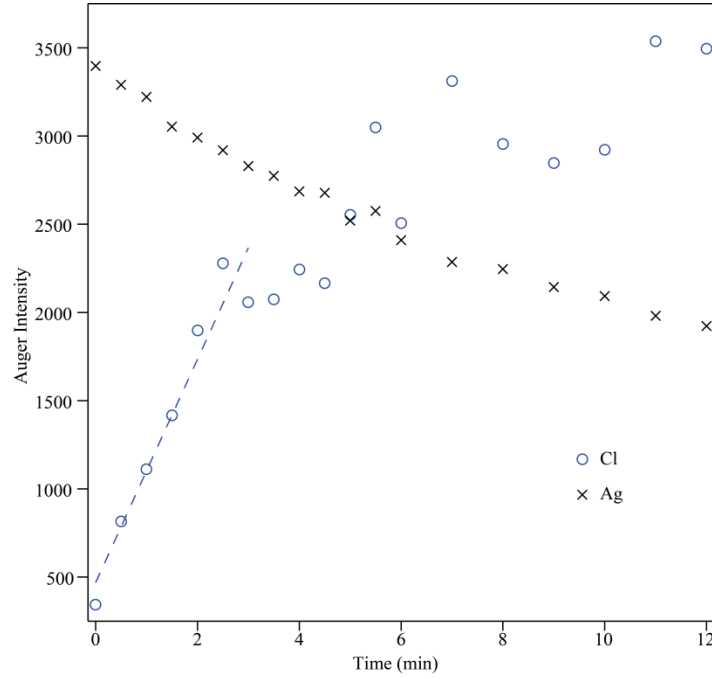


FIG S1. Dosing calibration rate for NaCl dosed at 810 K and Ag substrate held at 125 K for dosing and spectra. Auger intensity (Peak-to-Peak height) normalized against I_E emission current for Ag and Cl peaks. Beam energy = 1000 eV.

Dosing calibration was measured by slope changes in Auger electron spectroscopy of the Cl peak-to-peak height intensity (Fig. S1). The Ag substrate was held at 125 K in order to minimize NaCl diffusion and induce growth of 1 ML height islands rather than 2 ML height. These conditions lead to a more uniform coverage of NaCl on the Ag silver surface in order to determine dosing rate. Figure S1 shows a change in slope in Cl Auger intensity at approximately 3 ± 0.5 min leading to a dosing rate of ~ 0.3 MLE / min (monolayer equivalent). Using this definition of a MLE, we find that the $n=1$ of Ag(100) becomes nearly extinguished around 6 – 7 MLE, in good agreement with [1] that reported under their definition of 6 MLE, 98% of the silver surface was covered by NaCl films. This is further supported by calculating the adsorbate thickness by correlating the Ag peak intensity to the inelastic mean free path (IMFP). The Ag auger intensity can be described by,

$$I_{Ag} = I_{Ag}^0 e^{-d/\lambda_{eff}} \quad (1)$$

where I_{Ag} is the auger intensity, I_{Ag}^0 is the auger intensity of the bare Ag substrate, d is the NaCl thickness, and λ_{eff} is effective the IMFP. The effective IMFP determined by

$$\frac{1}{\lambda_{eff}} = \frac{1}{\lambda_{355}} + \frac{1}{\lambda_{1000}}, \quad (2)$$

which accounts for the IMFP of the 355 eV electrons (16 Å) and IMFP of the attenuated beam at 1000 eV (36.8 Å) through the NaCl film, yielded $\lambda_{eff} = 11.15$ Å [2]. Application of equation (1) yields the MLE occurs at 4.5 ± 0.5 min, by setting d to 2.82 Å, the distance between NaCl planes. Given that this latter method is prone to underestimate the rate of growth, we consider this be good agreement with the defined 3 MLE in this work. Application of equation (1) to calibrate growth rate is applicable to layer by layer growth, whereas NaCl shows much more complex island growth, and thus this method only serves as qualitative agreement. The slope change in the Cl peak showed to be the most sensitive and reproducible method, and is therefore taken to calibrate the dosing rate. The Auger data unambiguously demonstrates the film thicknesses studied herein are of ultrathin dimensions.

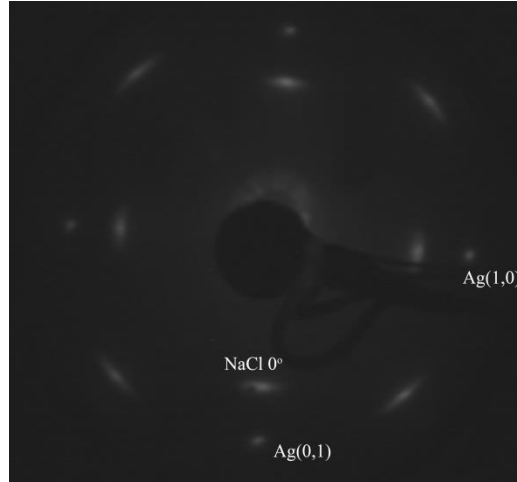


FIG S2. LEED of 2 MLE grown at Ag=400 K. Spectra taken at 120 K with beam energy of 54 eV. Ag(100) and NaCl spots corresponding to 0° islands are labeled.

Surface characterization was verified by LEED measurements as shown in Fig. S3. LEED measurements confirm crystalline material, and that NaCl islands are aligned 0° with respect to Ag(100). These images agree well those taken in references [1, 3-4].

Multiple State Determination:

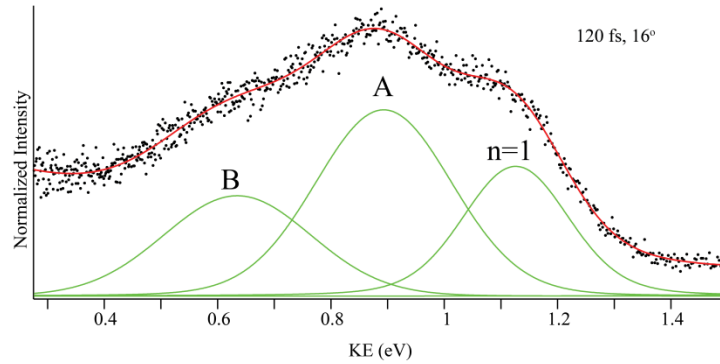


FIG S3. Fits of localized and delocalized states to 3 Voigts of 16° spectra at 120 fs time delay. Solid red line shows total fit, which includes an exponential multiplied by a Fermi Dirac to represent the hot electron distribution background (not shown).

At high dispersion angles at intermediate delays three separate states are observed. This can clearly be observed in Fig. S3, where the spectra in the region of interest are fit to three Voigts corresponding to the localized states A and B and the delocalized $n=1$ IPS.

Nonane Overlayers:

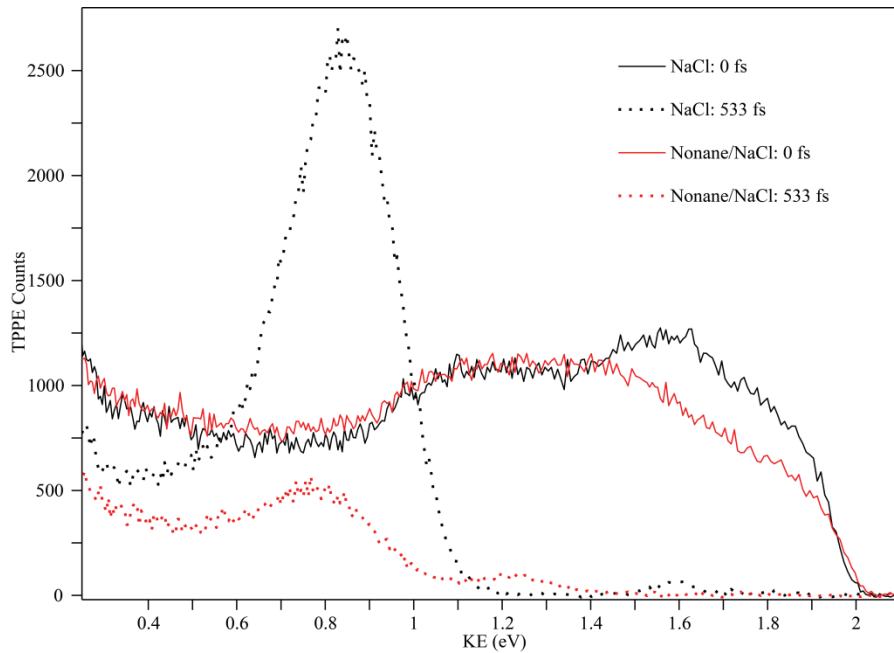


FIG S4. TPPE spectra 6 MLE NaCl (black) and 1 ML nonane / 6 MLE NaCl (red) at 52 K. Solid lines correspond to 0 fs delay, and dashed lines to 533 fs delay.

Figure S4 shows TPPE spectra of 6 MLE NaCl and a corresponding 6 MLE NaCl covered with ~ 1 ML of nonane as calibrated with temperature programmed desorption. Nonane serves as a dielectric overlayer to distinguish whether states reside in the vacuum or inside the material. For an electron residing in the material, the electronic state should remain largely unaffected by the overlayer, but for states residing at the sample/vacuum or in the vacuum, they should be changed by the negative electron affinity of the nonane and ‘quenched’. This technique was used to show that the electron resided inside the NaCl for the case of a small polaron [5]. Our results show the populations of the initial states are similar in magnitude, but the localized state is largely decreased by the nonane overlayer, further supporting this state resides at the NaCl surface/vacuum interface. Some intensity of the localized state likely remains due to incomplete uniform coverage by the nonane.

Preliminary KCl and NaF Results:

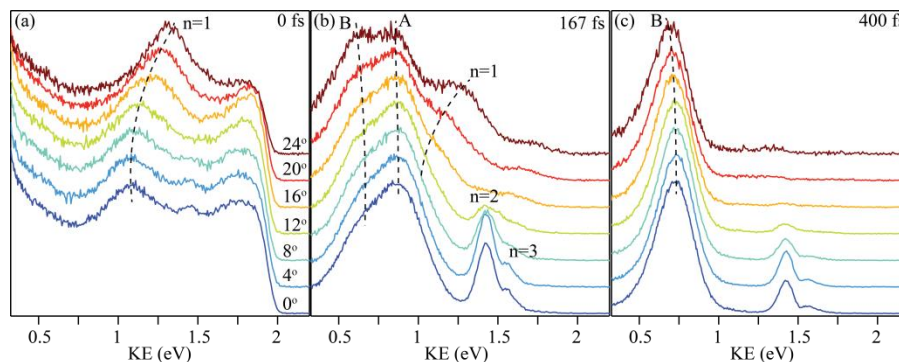


FIG S5. TPPE spectra of KCl dosed for 16 min at 773 K and Ag(100) at 400 K. Spectra taken at ~ 130 K with pump = 3.67 eV and probe = 1.84 eV. Dispersion spectra taken at time delays of (a) 0 fs, (b) 167 fs, and (c) 667 fs.

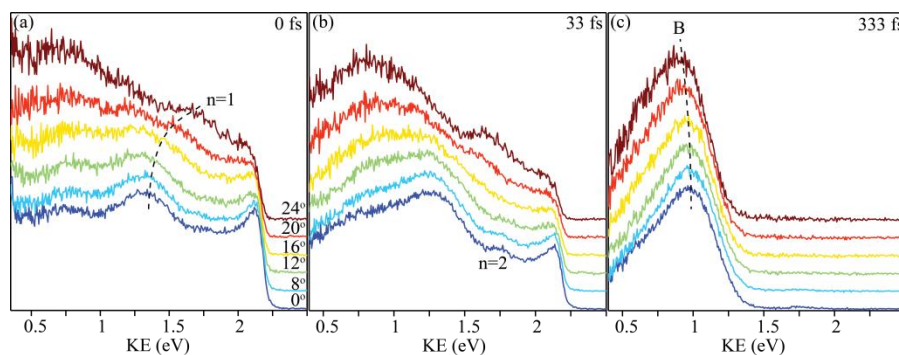


FIG S6. TPPE spectra of NaF dosed for 52 min at 900 K and Ag(100) at 400 K. Spectra taken at 120 K with pump = 3.79 eV and probe = 1.89 eV. Dispersion spectra taken at time delays of (a) 0 fs, (b) 33 fs, and (c) 333 fs.

Preliminary studies of KCl and NaF, shown in Fig. S5 and Fig. S6, are presented as a qualitative comparison to NaCl/Ag(100). A similar phenomena is observed, where the

delocalized $n = 1$ IPS (0 fs, dotted line to guide the eye) undergoes population transfer to localized state with an apparent negative effective mass after a few hundred femtoseconds. The KCl data at intermediated delays (Fig. S5 (c)) clearly show the presence of both delocalized and multiple localized states. This behavior agrees well with that observed for NaCl, and as mentioned, the band gap of NaF would exclude the conduction band from being observed in our measurements.

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