Dynamical mean-field theory for correlated electrons
by Dieter Vollhardt
Probing the thermal response of a silicon field emitter by ultra-fast Laser Assisted Atom Probe Tomography

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The interaction between an ultrashort laser pulse and a subwavelength silicon tip under a high static electric field is investigated numerically and experimentally. Using an original autocorrelation setup of the laser-assisted atom probe tomography, the temporal evolution of the lattice temperature at the tip apex is experimentally monitored. An ultrafast cooling process, related to a confinement of the heating at the surface, is reported. This confinement is well predicted by a new model taking into account the free charges generation by photon absorption, their drift-diffusion motion under the electric field and their energy relaxation to the lattice.

The interaction between a laser beam and a nanometric tip under high electric field is of interest in many physical domains such as in near-field imaging of surfaces with the photon-assisted scanning tunneling microscopy (p-STM) [1], photon-assisted electron emission (p-EE) [2, 3] and, more recently, in the domain of materials imaging at atomic scale with the laser-assisted atom probe tomography (La-APT) [4]. For all these applications, the laser-tip interaction causes linear and nonlinear optical effects (field enhancement, second harmonic generation, optical rectification) [1, 2, 5] but it also induces a heating of the tip. The evaluation of the absorption and heating of the tip becomes a key factor in the estimation of the contribution of the thermal effects as compared to the optical effects. For example, the surface structuring by p-STM can be due to the strong field enhancement at the tip apex or to the thermal dilatation of the tip and the resulting mechanical contact of the surface [1]. Similarly, the electron or ion ejection in p-EE and La-APT can be thermally or optically assisted [2–5]. Recently it was shown that when HfC tips are used as electron emitters, due to the low work function, low laser intensity can be used, decreasing the thermal emission [6].

However, when the field emitter is non metallic (such as Si tips) the static electric field applied to the tip can strongly affect their optical properties, as theoretically studied by Tsong in 1979 [7] and more recently by authors [8]. Tsong suggested that the conduction and valence bands at the surface of a doped semiconductor at room temperature are bent under a huge positive electric field. As a result, the high density of holes at the surface changes the properties of the material at the surface, which becomes semi-metallic. However, all models developed in the different domains of laser-tip interaction to evaluate the contribution of the thermal and optical effects neglect the band-bending due to the static field, in band-gap materials.

In this Letter, we show, theoretically and experimentally, that the high static electric field can confine the absorption at the surface of a silicon tip, where the band bending takes place. This confinement of the absorption increases the contrast between the temperature of the surface and that of the bulk (tip apex and tip shank). This contrast is at the origin of an ultra-fast thermal pulse which is probed by time-resolved measurements using La-APT.

In La-APT analysis a fs laser is used to trigger a single atom emission from a tip under a high electrostatic field. Recent results have shown that the absorption of the laser energy increases the tip surface temperature enough to allow the evaporation of atoms [4,9]. Since this emission results from the optical and thermal response of the tip to the fs light pulse, light absorption and transient heating and cooling processes of the tip can be investigated [9]. Moreover, the ions are evaporated one by

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hence it can be approximated with a 1D model along the ∼250 nm. The tip can be considered as a cylinder whose diam-

electric field, x = 0 corresponds to the surface of the sample. Laser pulse parameters: I = 20 GW/cm², τp = 50 fs, the pulse profile is shown in the inset. External static field E = 2 V/nm.

one from the surface, hence the LA-APT gives information directly on the surface temperature evolution.

To describe the transient response of the silicon tip to the field during the interaction with the laser pulse, we use the drift-diffusion approach [10, 11]. The optical absorption depth of Si at a wavelength λ = 400 nm is > 250 nm. The tip can be considered as a cylinder whose diameter is ∼100 nm, smaller than this absorption depth, hence it can be approximated with a 1D model along the axial direction. The model consists of the solution of the continuity equation for hole density nh

\[ \frac{\partial n_h}{\partial t} = -\frac{\partial}{\partial x} \left( \mu_h n_h E + D_h \frac{\partial n_h}{\partial x} \right) = \frac{(1 - \Gamma) \alpha_{opt} I}{\varepsilon_{ph}} + S_h - R_h \]

where \( \alpha_{opt} = 4 \times 10^4 \text{ cm}^{-1} \) is the interband absorption coefficient of Si at λ = 400 nm at 80 K [12], \( \Gamma = 0.5 \) the reflectivity, \( S_h \) the impact ionization rate [10] and \( R_h \) the hole losses due to the Auger and surface recombination [8]. We consider the Gaussian temporal profile with the pulse width (FWHM) \( \tau_p = 50 \) fs as reported in the inset of Fig. 1a. At the laser intensity used in our analysis (\( I < 20 \text{ GW/cm}^2 \)) and a photon energy \( \varepsilon_{ph} = 3.1 \text{ eV} \) the multi-photon processes are negligible. The hole mobility \( \mu_h \) and diffusivity \( D_h \) account for the Fermi-Dirac statistics [13]. The electron density \( n_e \) is given by a similar equation. During the hole and electron density evolution the field \( E \) inside the tip changes self-consistently according to Poisson equation. Field is fixed at the surface of the tip (x = 0): \( E = 2 \text{ V/nm} \).

In the presence of a positive electric field, the photo-generated holes start moving toward the surface, whereas the electrons move in the opposite direction. This effect leads to a significant increase in the hole density at the surface with respect to its bulk value, as reported in Fig. 1a. The separation of holes from electrons generates space charge that results in the screening of the external field. When the carrier distributions reach a quasi-equilibrium, which is governed by the balance between drift and diffusion currents, the field becomes completely screened (Fig. 1b). At this time, the valence band maximum at the surface is significantly higher than the hole quasi Fermi level in the bulk and the hole density reaches \( n_h = 3 \times 10^{21} \text{ cm}^{-3} \), a value much higher than the carrier density in the bulk \( n_{bulk} = 4 \times 10^{19} \text{ cm}^{-3} \). The electrons are swept by the field away from the surface where their density decreases below \( 10^{17} \text{ cm}^{-3} \). At the surface, accumulated holes can significantly absorb laser energy. The change of the dielectric function \( \Delta \varepsilon \)

and, thus, hole absorption coefficient \( \alpha_h \) caused by the free-carrier response is described by the Drude model [10, 11, 14]

\[ \Delta \varepsilon_{fcr} = -\frac{n_e e^2}{\varepsilon_0 m_e^* \omega_p^2} \frac{1}{1 + i \omega \tau_D} \]

\[ \alpha_h = \frac{4 \pi}{\lambda \sqrt{2}} \left( \left| Re \Delta \varepsilon_{fcr} + Im \Delta \varepsilon_{fcr} \right|^{1/2} - Re \Delta \varepsilon_{fcr} \right)^{1/2} \]

where \( m_e^* = 0.5 m_e \) is the effective mass of a hole and \( \tau_D = 1 \text{ fs} \) is hole damping time. The free-carrier absorption coefficient for the surface hole density equals to \( \alpha_h = 2.8 \times 10^5 \text{ cm}^{-1} \) that is several times higher than the interband absorption coefficient \( \alpha_{opt} \).

The temperature at the surface of the tip is determined by the processes of heating and heat dissipation in the bulk. The heating is caused by the transfer of energy from the carriers to the lattice through carrier-phonon coupling and carrier recombination. Because of field-induced charge separation and very low density of electrons at the surface the surface recombination becomes negligible and the temperature time evolution is determined by the thermalization process between hot holes and the lattice. The energy transferred to the lattice depends on the hole temperature and its density. Thus, the hole temperature evolution is given by

\[ \frac{\partial}{\partial t} (C_h T_h) = (1 - \Gamma) I \left( \frac{\alpha_{opt}}{2 \varepsilon_{ph}} (\varepsilon_{ph} - \varepsilon_g) + \alpha_h \right) - \frac{C_h}{\tau_{ph}} (T_h - T_L) + \frac{\partial}{\partial x} K_h \frac{\partial T_h}{\partial x} \]

Figure 1 (online color at: www.ann-phys.org) Spatial profiles inside the Si sample at different times for (a) the hole density, (b) the electric field. x = 0 corresponds to the surface of the sample. Laser pulse parameters: I = 20 GW/cm², τp = 50 fs, the pulse profile is shown in the inset. External static field E = 2 V/nm.
where $C_h$ and $K_h$ are hole heat capacity and thermal conductivity, considered for Fermi-Dirac statistics [13] and $\varepsilon_{gap} = 1.15$ eV is the band gap energy. The evolution of the electron temperature $T_e$ is described by a similar equation. The electron and hole energy coupling to the lattice is described by the carrier-phonon energy relaxation time $\tau_{ph} = 240$ fs for Si [10, 11].

The change of the lattice temperature $T_L$ is calculated separately

$$\frac{\partial}{\partial t} (C_L T_L) = \frac{C_h}{\tau_{ph}} (T_h - T_L) + \frac{C_e}{\tau_{ph}} (T_e - T_L) + \frac{\partial}{\partial x} K_L \frac{\partial T_L}{\partial x}.$$  

(4)

The lattice heat capacity $C_L$ strongly depends on lattice temperature below 300 K, as well as thermal conductivity $K_L$ as reported in literature for Si nanowires, whose geometry is close to the APT tip geometry [15]. These dependencies are taken into account in the model. The initial lattice temperature is 80 K along the sample.

The results of the solution of the Eqs. (3), (4) for carrier and lattice temperature together with the Eq. (1) for the carrier density are presented in Fig. 2. At the surface, the tip temperature is higher than in the bulk due to the substantially higher surface hole density [Fig. 2a]. At the considered laser intensity (20 GW/cm²) the surface temperature reaches $T_L \approx 230$ K [Fig. 2b] and then decreases very fast due to the heating confinement within several nanometers.

To verify the confinement of the absorption at the surface, a linear 3D atom probe assisted by femtosecond laser pulses and equipped with a multi-hit position sensitive detector. Experiments are performed in ultrahigh vacuum ($< 10^{-7}$ Pa), and the sample is cooled down to cryogenic temperature ($T_0 = 80$ K). The laser system is an amplified Ti:sapphire laser (wavelength $\lambda = 800$ nm, frequency 1 kHz, pulse duration 50 fs, pulse energy up to 2.5 mJ/pulse). Using a nonlinear crystal the wavelength is shifted to $\lambda = 400$ nm by second harmonic generation. Using an autocorrelation setup, two laser pulses with a variable temporal delay are slightly focused onto the tip with a spot diameter of 0.2 mm to avoid any problem of alignment and their linear polarizations are set parallel to the tip axis where the field enhancement is the highest. More details on the experimental setup are reported in Ref. [16]. The energy of each laser pulse is set to 120 nJ.

The static field is set at about 70% of the evaporation field (33 V/nm [17]), hence $E_{out} = 0.7 \times 33 = 23$ V/nm $\sim \varepsilon E = 23.4$ V/nm, with $E$ the value of the field used in the model of 2 V/nm and $\varepsilon = 11.7$ the dielectric constant. Considering the field evaporation theory of a field emitter, surface atoms are emitted with an evaporation rate $\phi(t)$ given by [17]:

$$\phi(t) = N\nu \exp\left(\frac{-Q_n}{k_B T(t)}\right).$$  

(5)

with $N$ the number of kink site surface atoms, $\nu$ the surface atom vibration frequency, and $Q_n$ the activation energy ($\approx 0.1$–$1$ eV). The evaporation rate is measured by varying the delay from 1 ps to 350 ps at an equivalent displacement speed of 0.25 mm/s. It is worth noting that the smallest delay was set to 1 ps to avoid any optical interaction of the two laser pulses. Fig. 3 shows the evolution of the evaporation rate $\phi$ as a function of the delay $\tau$ between the pulses. To evaluate the effect of tip blunting due to the evaporation process, the measurements are performed successively in the two directions of the stage.

A very fast decay is observed experimentally as a function of the delay between pulses: the evaporation rate is divided by a factor two in less than 5 ps. To have more information on this fast decay, the evaporation rate was measured by varying the delay from 1 ps to 8 ps at an equivalent displacement speed of 0.025 mm/s. As reported in inset of Fig. 3 during the first 2 ps the evaporation rate is almost constant (only the fluctuations related to the evaporation process are visible) and then the evaporation rate is rapidly divided by a factor two, following the behavior measured on large delay scale with a faster displacement speed.

Considering that each pulse heats the tip, as described above, the temperature of the tip at each value
of the delay $\tau$ is: $T(t, \tau) = T(t) + T(t + \tau) - T_0$ where $T(t)$ is calculated theoretically and reported in Fig. 2b. The tip cooling can be adjusted using the following analytical expression:

$$T(t) = T_0' + \frac{T_{\text{rise}}}{\sqrt{1 + \frac{t}{\tau_{\text{cooling}}}}},$$

with $T_{\text{rise}}$ the temperature increase and $\tau_{\text{cooling}} = u^2/D$ the characteristic cooling time of a nanowire heated on the area $u$ with a thermal diffusivity $D$ [4]. This function fits well the theoretical evolution of the tip temperature, as reported in Fig. 2b for $T_0' = 110$ K and $T_{\text{rise}} = 124$ K. The temperature $T_0' = 110$ K is higher than the initial temperature of 80 K. These discrepancy is due to photon absorption into the bulk and the resulting heating of the lattice. Considering that the energy stored in the system due to the increase of the base temperature is equal to the energy relaxed from the hot electrons and holes in the bulk, a tip temperature of $T_0' = 110$ K is obtained, from the energy conservation law.

Because of the exponential behavior of the evaporation process most of the ions are emitted at the maximum temperature ($T_{\text{max}}$), hence, to fit our data, we can consider only the variation of the maximum temperature of the tip as a function of the delay: $T_{\text{max}}(\tau) = T_{\text{max}} + T(\tau) - T_0$, with $T(\tau)$ given by Eq. (6). Using Eq. (5) and Eq. (6), we can fit the experimental data with the values of $T_{\text{rise}}$ and $T_0'$ obtained by the fit of the theoretical curve reported in Fig. 2b and the same cooling time $\tau_{\text{cooling}} = 1.7$ ps. Then, only one parameter is adjusted: the activation energy. A barrier of $Q_n = 0.15$ eV is obtained by the fit, this value is similar to the values already reported in the literature [17]. The cooling time of only 1.7 ps is incredibly short and can only be related to a near-surface optical absorption and heating. Hence, the measurement of this short cooling time is an experimental evidence of the influence of the band bending due to the high electric field on the optical properties of the tip and its following heating and cooling process.

As a conclusion, the good agreement between the modeling results and experimental data validate the developed model as a versatile tool to improve and understand all techniques based on the interaction between a laser beam and a nano-metric tip under high electric field. In the field of ion or electron emission, this model can be used to properly evaluate the thermal contribution to the fast emission observed using fs laser excitation and it can be included in the tip expansion models for p-STM to clearly demonstrate the contribution of tip dilatation to the surface microstructuring.

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