Construction of a setup for Ultrafast Electron Diffraction

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Chapter 3 Interface dynamics of a Cr/Au bilayer foil probed by Ultrafast Electron Diffraction

This chapter is in preparation for publication\(^1\).

Ultrafast Electron Diffraction (UED) was employed to investigate the structural dynamics of a Cr/Au bi-layer foil after photo-excitation by a near-infrared femtosecond laser pulse. By monitoring the electron diffraction intensities on a sub-picosecond time-scale we directly followed atomic disorder caused by the generation of hot electrons, the subsequent transfer of energy to phonons and the diffusion of both electrons and phonons through the Cr/Au interface. Our UED experimental data, which has an overall temporal resolution of 600 fs and a signal-to-noise ratio of less than 1 % in diffraction intensity changes, shows a bi-exponential decay of the Au diffraction intensities: a short 5 ps decrease in signal followed by a longer 30 ps decay. To explain our experimental data, we have performed detailed simulations that include the laser intensity profile within the foil, electron-diffusion, phonon-diffusion, electron-phonon coupling as well as interface interaction between the two metals. The simulations match the experimental observations and testify to the necessity of taking into account electron and phonon interface-diffusion as well as electron-phonon coupling to explain the two-step process observed.

3.1 Introduction

Over the last decade Ultrafast Electron Diffraction (UED) has proven to be a powerful technique to probe structural dynamics initiated by femtosecond pulsed laser excitation [1-5]. The experimental results of ultrafast laser heating of metal foils has been well explained theoretically with the two-temperature model in which energy from the excited charge carriers is transferred to the lattice by means of electron phonon coupling. High lattice temperature (after laser excitation) corresponds to increased atomic disorder in the foil that culminates in

a decrease in the intensity of the electron diffraction peaks, commonly described by the Debye-Waller factor. For mono-metallic Al, Au and Cu foils this phenomenon has been shown and described in [6,7]. In the reported experiments, the penetration depths of the excitation laser and the probing electrons are similar and therefore it was shown that the decrease in intensity of the diffraction peaks can purely be described by the Debye-Waller factor; the different observed decay time constants for Au and Cu being consistent with the theoretical prediction of the two-temperature model.

In this work we build upon this description by studying the Debye-Waller factor in a bi-metallic foil of chromium (Cr) and gold (Au). This is a very relevant system since Cr is frequently used as an adhesion layer for growing Au films on many substrates because of its high binding strength with oxygen and with Au, as well as its ability to favour the growth of smooth films. To model this system, a simple Debye-Waller factor in conjunction with the two-temperature model does not suffice, since the behaviour of the interface between the Au and Cr films is of crucial importance in governing the distribution of heat through the entire sample.

### 3.2 Experimental procedure and Results

A polycrystalline metal bi-layer foil was produced by consecutive sublimation of Cr (purity 99.999%, Sigma Aldrich) and Au (purity 99.999%, Sigma Aldrich) onto a NaCl window (Sigma-Aldrich Z267724-1EA) in a homemade deposition system operating at a pressure of $10^{-7}$ mbar, equipped with a digital control system for regulating the temperature and sublimation times. The resultant foil was floated onto deionized, distilled water [8] and transferred onto a 100 µm TEM aperture to produce a free-standing foil with thickness of 45 nm (5 nm Cr, 40 nm Au) and a diameter of 100 µm.

Time-resolved electron diffraction experiments were performed [8] in transmission geometry, with the femtosecond laser pulse (wavelength $\lambda = 780$ nm, pulse duration $\tau = 50$ fs, fluence $F = 7 \pm 1$ mJ/cm$^2$, s-polarized light) impinging onto the sample at an angle of 40º. The sample was rotated 15º with respect to the incoming electron beam to compensate for the non-synchronous pump time on the “left” and “right” of the laser beam due to the extreme incident angle (see Figure 3.1 (a)). The FWHM of the laser beam at the sample was 500 µm, ensuring
uniform excitation of the 100 µm sample. For the probe arm of the experimental setup, the third harmonic of the laser light was generated. The electron pulses were generated on a front-illuminated solid Cu cathode and accelerated to 30keV. The electron pulses containing roughly $10^5$ electrons/pulse were collimated using a solenoid magnetic lens and then focused through the sample onto the detector using a second solenoid lens. Coulombic expansion of the bunches in the propagation direction was compensated by a RF-cavity compressor [9-12]. The FWHM of the electron beam was 300 µm at the sample and the duration was measured with an ultrafast photo-triggered streak camera [13] to be 600 fs. The experiment was performed at a repetition-rate of 2 kHz. Diffraction patterns were detected with a Princeton Instruments PI-MAX fibre coupled CCD camera equipped with a gated multi-channel plate (MCP) amplification system synchronized with the laser for signal to noise optimization.

Time zero ($T_0$) was determined by measuring the distortion of the shadow image of a TEM mesh due to the local field created by photoelectrons from the pump laser in a separate experiment, as described in [14,15]. The spatial overlap of the electron bunches and the laser pulses was optimized using a blank 100 µm TEM aperture. For each time-step a pumped (pump laser open) and unpumped (pump laser blocked) diffraction image was recorded; each diffraction image results from an accumulation of 10000 shots, which corresponds to an exposure time of 5 s.

To extract the changes in diffraction intensity, radial intensity integration of each diffraction image was performed, as well as a subtraction of the background.
scattering. The resultant change was calculated with $\Delta I(r,t)/I_0(r,t) = [I_p(r,t)-I_u(r,t)]/I_u(r,t)$. From the definition it follows that if there is no change in diffraction intensity between optically pumped and unpumped, the corresponding value for $\Delta I(r,t)/I_0(r,t) = 0$. The values corresponding to a doubling and complete suppression of the diffraction intensity are $+1$ and $-1$, respectively. The radial coordinate can be converted to a scattering vector $S$, where $S=(2/\lambda_s)\sin(\theta_{\text{diff}}/2)$ where $\tan(\theta_{\text{diff}})=r/L$ with $L$ the distance between the sample and detector and $r$ the diffraction ring radius on the detector. The resultant $\Delta I(S,t)/I_0(S,t)$ is shown in Figure 3.2 (a). The time-traces (i.e. horizontal cuts taken along Figure 3.2 (a)) for three selected diffraction rings are shown in Figure 3.2 (b). Decreases in diffraction peak intensity between 9 and 20 % are observed and fitting the data with a double exponential is possible, identifying a fast process ($\tau_1 = 3\pm0.5$ ps) comparable with what is expected for an Au foil [6], and a considerably slower process ($\tau_2 = 26 \pm 4$ ps).

### 3.3 Simulation procedure and Results

To explain the appearance of a two-step process (deviating from the predicted behaviour of the standard two temperature model) a detailed simulation of the experiment was done. The simulation comprises: (1) calculating the laser intensity profile within the film instantaneously after $T_0$, (2) using the laser intensity to calculate the initial electron gas temperature profile within the foil, (3) following the evolution of the system through electron-diffusion, electron-phonon coupling and phonon-diffusion. The simulation also incorporates the interface interaction (interlayer diffusion of electron and phonons) between the two metals. It uses the
initial excitation profile in the depth coordinate to calculate the electronic system state at \( T_0 \) and simulates how our system evolves using the well-known two-temperature model [16,17] with an added interface interaction between the two layers.

For sub-picosecond pulses, the laser energy is primarily absorbed by the free electrons in the skin depth of the metal foils accessible to the excitation. The excitation profile in the plane of the foil was assumed to be homogenous since the size of the laser beam on the sample was five times larger than that of the sample (see Experimental Method section). However, the penetration depth of near-infrared light varies from around 7-17 nm depending on the wavelength and the metal in question [18]. For extreme incident angles and s-polarized light, which is the case in this study, there are also substantially large reflectivities at the interfaces to be considered. Taking into account the experimental geometry, wavelength, polarization and metals involved, the excitation profile in the depth coordinate was calculated and the result is shown in Figure 3.3 (a). Reflectivity at the Vacuum/Cr and Cr/Au interfaces as well as multiple reflections within the Cr layer were also included to calculate the total light absorbed by the Cr and Au layers.

The electronic system, modelled as a hot electron gas, gives rise to two competing processes: the ballistic motion of the excited electrons into deeper parts of the metal with velocity close to the Fermi velocity \( (10^6 \text{ m/s}) \) and the collision between the excited electrons and electrons in states around the Fermi level. The hot electrons are cooled by transferring their energy to the lattice through electron-phonon coupling [19]. This process can be described by the two-temperature model, which was originally proposed by Anisimov et al. [16] and considers heat transfer through and between electronic and lattice subsystems. Assuming that the heat conduction for electrons and phonons is based on the Boltzmann transport equation, the energy equations of the systems are [20]:

\[
C_e(T_e) \frac{\partial T_e}{\partial t} = -\nabla q_e - G(T_e - T_l) + S \tag{1}
\]

\[
C_l(T_l) \frac{\partial T_l}{\partial t} = -\nabla q_l + G(T_e - T_l) \tag{2}
\]

\[
\nabla q_e = -K_e \nabla T_e \tag{3}
\]
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\[ \nabla q_l = -K_l \nabla T_l \]

(4)

where \( T \) denotes temperature, \( q \) the heat flux vector, \( t \) time, \( C \) heat capacity, \( K \) thermal conductivity, \( G \) the electron-lattice coupling factor, and \( S \) the laser heating source. The quantities with subscripts \( e \) and \( l \) are associated with electrons and lattice respectively. The electron-lattice coupling factor, \( G \), accounts for the rate of energy exchange between electrons and phonons and can be estimated by the following expression [21]:

\[ G = \frac{9}{16} \frac{n_e k_B^2 T_D^2 v_F}{\Lambda(T_e)(T_e - T_l) \mu_F} \]

(5)

where \( T_D \) is the Debye temperature, \( v_F \) the Fermi velocity, and \( \Lambda \) the electron mean free path. The values of all constants in the equations are given in Table 3.1.

Table 3.1: List of constants used in the simulations.

<table>
<thead>
<tr>
<th>Constant</th>
<th>Cr</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat Conduction</td>
<td>93.7 W/(m*K)</td>
<td>317 W/(m*K)</td>
</tr>
<tr>
<td>Density</td>
<td>7190 kg/m³</td>
<td>19320 kg/m³</td>
</tr>
<tr>
<td>Specific Heat</td>
<td>450 J/(kg*K)</td>
<td>128 J/(kg*K)</td>
</tr>
<tr>
<td>( K_{eq} )</td>
<td>94 W/(m*K)</td>
<td>317 W/(m*K)</td>
</tr>
<tr>
<td>( A_e )</td>
<td>195 J/(m³*K²)</td>
<td>70 J/(m³*K²)</td>
</tr>
<tr>
<td>( G )</td>
<td>( 4.2 \times 10^4 ) J/(ps)/(m³*K)</td>
<td>( 2.6 \times 10^4 ) J/(ps)/(m³*K)</td>
</tr>
<tr>
<td>Thickness</td>
<td>5 nm</td>
<td>40 nm</td>
</tr>
</tbody>
</table>

Figure 3.3: (a) Relative intensities of laser light inside the Cr and Au layers; multiple reflections within the Cr layer were included in the simulation. (b) Temperature of the hot electron gas inside the respective layers calculated from the light intensity and used as input (i.e. first column of Figure 3.4 (a)) for the simulations.
To simulate the system using these equations a finite difference method was used. A grid was implemented to model the Cr/Au film and to incorporate the Cr/Au interface the thermal conductivity is scaled by the interfacial thermal resistance whenever the heat flux vector was between a Cr and Au point on the grid. For the thermal conductance of the interface we did not find exact values in literature and therefore a value for which the simulation best fitted the observed experimental time constants was used (650 MW/(m$^2$*K) at 300 K). This value is similar to those of other metal-metal interfaces reported in literature [22-24]. For each time point the energy exchange between neighbouring points was calculated; both inside the two metals and through the interface. The time $\Delta t$ between time steps was chosen to be small (10 fs) in order to have a good approximation of the continuous time scale. The simulation was carried out in Matlab.

The results of the simulations, indicating the temperatures of the electron gas and the lattice as a function of time, are shown in Figure 3.4 (a) and (b). The time-dependent temperature generated by the simulations was used to calculate the time-dependent decrease in diffraction intensity due to the varying Debye-Waller factor. The resultant curve is plotted in Figure 3.5 (b) superimposed on the experimental data.
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Figure 3.5: (a) Simulated Au lattice temperatures as a function of the depth at fixed times (i.e. vertical cuts along Figure 3.4 (b) at selected times). (b) Comparison between the drop in diffraction intensity, extracted from the lattice temperature simulation, and experimental data for diffraction ring 220.

3.4 Discussion

In Figure 3.5 (b) the time evolution of normalized intensity difference between the pumped and unpumped is plotted for the (220) diffraction peak together with the results of the simulation explained in the previous section. The excellent signal-to-noise ratio allows for a straightforward comparison between experimental data and simulation. Before $T_0$ the intensity of the peaks is the same for the pumped and the unpumped images (resulting in $\Delta I(0)/I_0(0) = 0$). This is indicative of the fact that the sample recovers fully in the 500 μs between the laser pulses (no accumulative heating observed). After $T_0$ the intensity of the peaks decreases. The sharp edge at $T_0$ confirms the sub-picosecond time resolution. From the relative amplitude of the drop of the peak intensities, one can estimate the final temperature of the film to be between 410 and 460 K. This measured value is in good agreement with the simulation presented in the previous section (440 K). In the simulation the used value for the laser fluence was 6.5 mJ/cm$^2$ in order to obtain a final temperature that matches the experimental results. This value is in accordance with the experimental fluence within the experimental error (7±1 mJ/cm$^2$).

Based on the simulation and the experimental data for the (220) ring presented in Figure 3.5 we can describe the energy transfer processes after laser excitation as follows: due to the different optical properties of Cr and Au [18] much of the energy deposited by the laser is absorbed in the amorphous chromium film where it creates hot electrons. The fast intensity drop corresponds to the spreading of
these hot electrons into the gold and subsequent excitation of phonons via electron-phonon coupling. The slow process corresponds to the heating of the Au film due to the transfer of energy between Cr and Au. Setting the thermal conductance of this interface \( G_i \) as a free parameter we fitted the experimental data using simulation parameters as described above. An excellent result was obtained for \( G_i = 650 \text{ MWm}^{-2}\text{K}^{-1} \) (at 300 K). We can therefore conclude that the slow dynamics of the system is indeed guided by the energy transfer at the interface. The value obtained from the simulation for \( G_i \) is similar to what is reported for other metal-metal interfaces [22-24].

### 3.5 Conclusion

Ultrafast heating of mono-metallic foils is well understood theoretically and has experimentally been observed in several UED experiments as a decrease in diffraction intensity as a function of time, corresponding to an increased atomic disorder in the foil (Debye-Waller factor). Here we have demonstrated that this well-known theoretical two temperature model is insufficient to explain the structural dynamic behaviour of bi-metal foils possessing a metal-metal interface. The effects of the interface, being optical (reflection at the interface), electronic (hot electrons diffusing through the interface) and thermal (phonon transfer through the interface), all contribute to the dynamics of the structure observed using UED. We have added these contributions in our simulations thereby providing a new and complete theoretical support for the observed behaviour of the transient diffraction.

### References

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