

M. LISOWSKI  
P.A. LOUKAKOS  
U. BOVENSIEPEN  
M. WOLF<sup>✉</sup>

# Femtosecond dynamics and transport of optically excited electrons in epitaxial Cu films on Si(111)-7 × 7

Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin–Dahlem, Germany

**Received: 29 September 2003/Accepted: 29 October 2003**  
**Published online: 26 July 2004 • © Springer-Verlag 2004**

**ABSTRACT** Time-resolved two-photon photoemission spectroscopy is used to study ultrafast electron dynamics of epitaxial Cu films grown in situ on a Si(111)-7 × 7 substrate with 6 to 44 nm thickness. For excitation with femtosecond laser pulses at  $h\nu = 2.35$  eV a pronounced increase of the electron relaxation rates is observed with increasing film thickness and even further in comparison to bulk data. This is attributed to an enhanced energy dissipation in thicker films due to transport of excited carriers into the bulk.

**PACS** 73.50.Gr; 73.90.+f; 78.47.+p; 79.60.-i

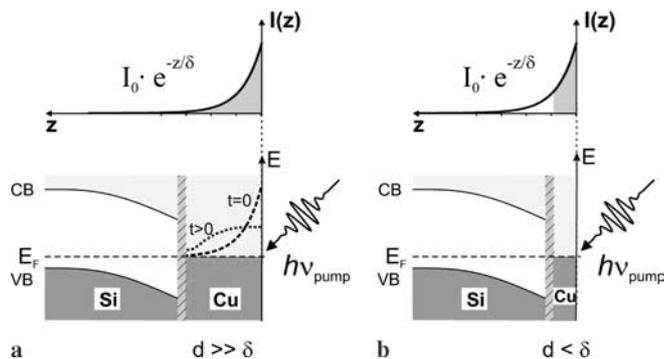
## 1 Introduction

The dynamics of energy dissipation in optically excited materials is of fundamental importance for applications in material processing and laser ablation. In metals, light is absorbed near the surface within the optical penetration depth of typically 10–20 nm. This leads to creation of electron–hole pairs, which relax predominantly by electron–electron (e–e) scattering on a femtosecond time scale. Subsequent energy transfer to the lattice by electron–phonon (e–ph) scattering is a first step towards ablation. However, the nascent carrier distribution is also depleted by transport of excited carriers into the bulk. Thus, transport processes decrease the energy density at the surface and distribute the deposited energy into the depth of the bulk.

A number of ultrafast time-resolved techniques have been applied to study the influence of transport on the energy relaxation dynamics in thin metal films after optical excitation [1–5]. Transient reflectivity measurements on Au films [1–3] revealed clearly a contribution of ballistic transport of energetic (unscattered) electrons whereby the majority of thermalized electrons are cooled by diffusive transport into the bulk in parallel to lattice heating. For example, Hohlfield et al. found a pronounced dependence of the relaxation time on film thickness, which could be well described by a modified two-temperature model assuming an increased optical penetration depth due to fast ballistic transport within

the laser pulse duration [3]. Further insight can be expected from time-resolved two-photon photoemission (2PPE) spectroscopy which accesses directly the dynamics of the electron energy distribution. The high surface sensitivity due to the short electron mean free path in the photoemission final state should make this technique even more suitable to study transport effects [6]. However, 2PPE studies of the hot electron relaxation dynamics in Au and Ag films were so far not conclusive. Cao et al. observed no thickness dependence between 15 and 300 nm for epitaxial grown Au films [4], whereas Aeschlimann and coworkers reported pronounced transport effects for thin Au and Ag films and bulk samples [5]. In both experiments the samples were not always kept in situ between preparation and measurements. However, it remains unclear if this is related to the observed differences.

In this paper we study the ultrafast electron dynamics in epitaxially grown Cu(111) films on Si(111)-7 × 7 as a function of layer thickness. Both preparation and 2PPE measurements are performed in situ. We have chosen copper because we have previously investigated the bulk electron dynamics and performed simulations of transport effects [6]. Figure 1 illustrates the principle of our experiment. For a homogeneous sample light absorption leads to an exponential gradient in the excitation density along the surface normal. For a film much thicker than the optical penetration depth  $\delta$  ( $d \gg \delta$ , Fig. 1a) transport of excited carriers subsequently dis-



**FIGURE 1** Comparison of optical excitation density in Cu films on *p*-doped silicon for thicknesses larger (a) and smaller (b) than the optical penetration depth  $\delta$ . For thicker films the initial exponential excitation profile expands rapidly into the bulk by transport of hot carriers. The copper–silicite interface layer is indicated as a grey hatched area

tributes the energy into deeper regions and thus reduces the excitation density at the surface. Simulations show that this process occurs on a 10–100 fs time scale, which is comparable to the time scale of energy redistribution by e–e scattering leading to thermalization and generation of low energy secondary electrons [5, 6]. For thin films with  $d < \delta$  (Fig. 1b), transport into deeper regions is inhibited by the band gap of the Si substrate. A more homogenous spatial profile at a higher excitation density is expected for constant incident fluence compared to thicker films. For film thickness  $< 4$  nm, we observe contributions of the Cu/Si interface and injection of carriers excited in the Si substrate above the indirect band gap becomes important. However, these data will be subject to another publication.

## 2 Experimental details

The sample preparation and 2PPE experiments were performed in a single ultra high vacuum (UHV) chamber combined with a tunable femtosecond laser system, as described previously [7].

Copper with a purity of 99.9999% was evaporated from a tungsten crucible at rates between 1 and 6 Å/min determined by a quartz microbalance onto a Si(111)-7 × 7 substrate (*p*-type wafers, resistivity 15 Ω cm) kept at 200 K [8]. To obtain good photoemission spectra with sharp surface states (see Fig. 2 inset), the Cu films were annealed at 300 K for several hours before measurement. Low energy electron diffraction showed sharp hexagonal patterns with sixfold symmetry [9].

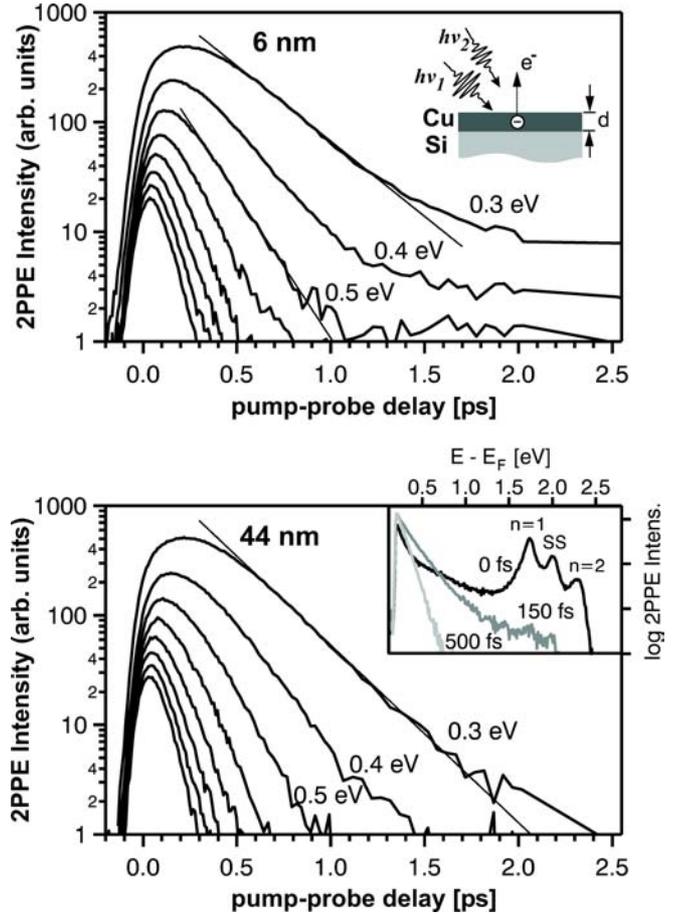
2PPE measurements were carried out at 300 K. Femtosecond laser pulses (55 fs FWHM) at 2.35 eV photon energy were generated in an optical parametric amplifier pumped by a 200 kHz amplified Ti : Sapphire laser system. The 2.35 eV pump pulses were focused onto the sample together with time delayed, frequency doubled probe pulses ( $h\nu_{\text{probe}} = 4.7$  eV) with both beams *p*-polarized at 45° angle of incidence. Photoemitted electrons were detected along the surface normal in a time of flight spectrometer. Zero time delay and pulse duration were determined from the 2PPE cross correlation signal of the Cu(111) surface state [6]. The absorbed pump fluence was below 30 μJ/cm<sup>2</sup>, which keeps the rise of the electronic temperature below 100 K.

## 3 Results and discussion

In 2PPE, electrons from an occupied initial state are excited by the pump pulse to an initially unoccupied intermediate state. After a time delay  $\Delta t$  a probe pulse excites the electrons into final states above the vacuum level where they escape from the sample and are detected by an electron spectrometer. The energy of the intermediate state relative to the Fermi level  $E - E_F$  is obtained from the kinetic energy by

$$E - E_F = E_{\text{kin}} + \Phi_{\text{TOF}} - h\nu_{\text{probe}},$$

where  $\Phi_{\text{TOF}}$  is the work function of the spectrometer. Time-resolved data were obtained by recording photo-electron spectra at various pump–probe delays. After subtraction of the background due to 2PPE induced by the probe pulse only, the cross correlation traces in Fig. 2 were obtained by averaging



**FIGURE 2** Cross correlation curves for 6 nm (*top panel*) and 44 nm (*bottom panel*) Cu films recorded at intermediate state energies  $E - E_F$  between 0.3 and 1.0 eV in steps of 0.1 eV. The *inset* (*bottom panel*) shows 2PPE spectra at 0, 150 and 500 fs delay on a logarithmic intensity scale. The  $n = 1$  and  $n = 2$  image potential states and the surface state (SS) appear in the spectrum at 0 fs

the 2PPE intensity in intervals of 50 meV for  $E - E_F$  between 0.3 eV and 1.0 eV.

In general, several processes contribute to the observed population decay in 2PPE. Relaxation out of a given energy interval above  $E_F$  is affected by e–e scattering, e–ph scattering and by transport out of the detection volume. The rate of e–e scattering (i.e., the inverse inelastic lifetime) is given by the screened Coulomb interaction and the available phase space depending on the energy above the Fermi level [10]. However, generation of secondary electrons by Auger decay of electrons and holes may also increase the population in particular in energy intervals close to  $E_F$ . For these reasons, the measured relaxation times can not be simply identified with electron lifetimes at least for energies close to  $E_F$ .

The relaxation times are determined by fitting the cross correlation curves with a convolution of the pump probe cross correlation with a single exponential decay. For energies ( $E - E_F$ )  $> 0.7$  eV the fit describes the data very well. For lower energies the electron population is more and more dominated by refilling processes with secondary electrons as can be seen from the initially flat region and a shift of the maximum in the cross correlation to later time delays. For these energies the fit was restricted to a range of delays with an

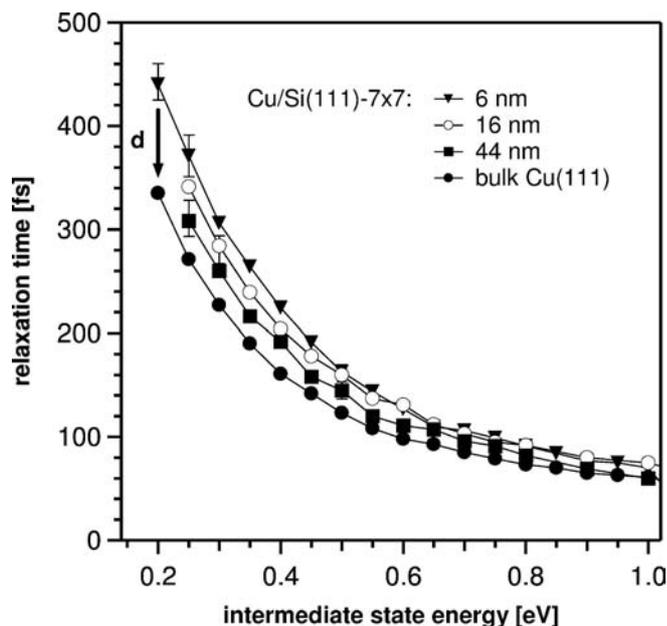


FIGURE 3 Relaxation times of photoexcited electron distributions in Cu/Si(111)-7 × 7 films and bulk Cu(111). For details see text

exponential decay. Relaxation times for films of 6 to 44 nm thickness including data taken on a Cu(111) single crystal with the same experimental setup are summarized in Fig. 3.

For all films the relaxation times clearly exceed the bulk values, whereby the largest differences are observed for low energies. The 6 nm film exhibits the highest relaxation times while for thicker films the values decrease systematically towards the bulk values. Two effects can explain this observation: (i) transport acts as a net loss channel of electron population in the near surface region. Therefore, hindering transport, by confining the energy to a comparably thin layer, will lead to a slower decay [11]. (ii) Quantization of the electronic states normal to the surface may reduce the available phase-space for e–e scattering. However, the latter effect is presumably very weak, as no quantum-well features are evident in our 2PPE spectra [8]. These results are consistent with observations of Aeschlimann et al. on Au and Ag [5] and in reasonable agreement with simulations [4–6]. We did not attempt modeling of our data, because scattering and relaxation at the Cu/Si interface hinders a quantitative treatment.

Turning back to Fig. 2, we observe a double exponential decay for the 6 nm film. While the initial fast decay can be attributed to e–e scattering, the slow decay with a time constant of  $4.0 \pm 0.5$  ps must be of different origin. On a pico-second time scale the electronic system has already equilibrated with the lattice. In this case electrons at 0.3 eV above  $E_F$  arise from the tail of the Fermi–Dirac distribution of the electron gas at the elevated lattice temperature. This is consistent with observed exponential form of the 2PPE spectra at low ener-

gies (see inset in Fig. 2). The slow decay of these low energy electrons can be understood considering that they reside at an energy inside the band gap of the Si substrate and therefore energy transport by electrons is blocked. The remaining mechanism is transport mediated by phonons.

Comparison between the dynamics of the 6 and 44 nm films at delays  $\geq 2$  ps shows that the electron (and lattice) temperature is higher for thin films. This can be understood as follows: The intensity of the pump decays exponentially into bulk Cu with an optical penetration depth of  $\delta = 15$  nm (see Fig. 1). For films thicker than  $\delta$  (44 nm =  $3\delta$ ) excited electrons are subject to transport into the bulk due to a gradient in excitation density. For thinner films (6 nm =  $0.4\delta$ ) two effects are important: (i) Part of the pump radiation is reflected back into the metallic film at the substrate–film interface, thereby increasing the excitation density in the film. (ii) Excited electrons cannot escape as far into the bulk as in thicker films. Therefore, a higher population will remain in the near surface region. As a consequence, more energy is transferred to the lattice at the surface leading to a higher lattice and electron temperature, in agreement with our observation.

In summary, we have employed time-resolved 2PPE spectroscopy to investigate the electron dynamics in Cu(111) films on Si(111) and find that the relaxation rates increase with film thickness up to the bulk limit. We attribute these findings to efficient energy transport out of the probe volume into the bulk for films exceeding the optical penetration depth. This trend becomes even more pronounced at energies close to  $E_F$  which reveals that relaxation by transport competes with energy relaxation by e–e scattering, whereby the latter process dominates for  $E \gg E_F$ .

**ACKNOWLEDGEMENTS** We acknowledge financial support by the Deutsche Forschungsgemeinschaft through Sfb 290 and SPP 1093. P.A. L. also acknowledges EU financial support, contract no. MEIF-CT-2003-501826.

## REFERENCES

- 1 S.D. Brorson, J.G. Fujimoto, E.P. Ippen: Phys. Rev. Lett. **59**, 1962, (1987)
- 2 C. Suarez, W.E. Bron, T. Juhasz: Phys. Rev. Lett. **75**, 4536, (1995)
- 3 J. Hohlfeld, S.S. Wellershoff, J. Güdde, U. Conrad, V. Jähnke, E. Matthias: Chem. Phys. **251**, 237, (2000)
- 4 J. Cao, Y. Gao, H.E. Elsayed-Ali, R.J.D. Miller, D.A. Mantell: Phys. Rev. B **58**, 10 948, (1998)
- 5 M. Aeschlimann, M. Bauer, S. Pawlik, R. Knorren, G. Bouzerar, K.H. Bennemann: Appl. Phys. A **71**, 485, (2000)
- 6 E. Knoesel, A. Hotzel, M. Wolf: Phys. Rev. B **57**, 12 812, (1996)
- 7 M. Lisowski, P.A. Loukakos, U. Bovensiepen, J. Stähler, C. Gahl, M. Wolf: Appl. Phys. A **78**, 165, (2004)
- 8 K. Pedersen, T.B. Kristensen, T.G. Pedersen, P. Morgen, Z. Li, S.V. Hoffmann: Phys. Rev. B **66**, 153 406 (2002)
- 9 G. Gubbiotti, G. Carlotti, C. Minarini, S. Loreti, R. Gunnella, M. De Crescenzi: Surf. Sci. **449**, 218, (2000)
- 10 P.M. Echenique, J.M. Pitarke, E.V. Chulkov, A. Rubio: Chem. Phys. **251**, 1, (2000)
- 11 R. Knorren, K.H. Bennemann, R. Burgermeister, M. Aeschlimann: Phys. Rev. B **61**, 9427, (2000)