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Research paper

Ultrafast lattice dynamics of single crystal and polycrystalline gold nanofilms

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ABSTRACT

Ultrafast electron diffraction is employed to spatiotemporally visualize the lattice dynamics of 11 nm-thick single-crystal and 2 nm-thick polycrystalline gold nanofilms. Surprisingly, the electron-phonon coupling rates derived from two temperature simulations of the data reveal a faster interaction between electrons and the lattice in the case of the single-crystal sample. We interpret this unexpected behavior as arising from quantum confinement of the electrons in the 2 nm-thick gold nanofilm, as supported by absorption spectra, an effect that counteracts the expected increase in the electron scattering off surfaces and grain boundaries in the polycrystalline materials.

1. Introduction

The coupling of electrons and phonons in materials plays a key role in determining many physical properties of interest, such as superconducting transition temperatures [1], phase transitions [2,3], and energy transport [4,5]. Since the advent of femtosecond lasers, ultrafast optical spectroscopy has been widely used to investigate the electron-phonon dynamics in various materials [6,7]. Unlike ultrafast optical spectroscopy, where the electronic dynamics are probed, ultrafast diffraction techniques, that use either X-ray or electron pulses, are sensitive to the atomic motion. Hence they provide information on the lattice dynamics driven by electron-phonon coupling [8–11], and these complementary pump-probe techniques provide valuable insights into the interactions between electrons and lattices.

Gold is one of the most studied materials using either ultrafast optical spectroscopy or diffraction techniques [6–9,12–14]. The effect of the sample morphology on the electron-phonon coupling rate of gold has been widely studied as a function of the sample thickness and grain size(s), and interpreted using models that include the effects of additional scattering from surfaces and grain boundaries [15]. However, the possible impacts of quantum confinement on the electron-phonon coupling in few nm-thick polycrystalline (PC) gold nanofilms (AuNFs) have yet to be studied. Here we investigate the electron-phonon coupling dynamics in 2 nm PC and 11 nm gold single-crystal (SC) AuNFs using ultrafast electron diffraction (UED). In contrast to the predictions of the bulk film model [15], the electron-phonon coupling is found to be much less efficient in the thinner sample. Indeed, the comparison of experimental results with simulations, that treat the photo-generated electron and lattice temperatures independently, unambiguously show that the hot electrons in the SC AuNF interact much more efficiently with the lattice than in the case of the PC AuNF. We suggest that the reduction of the coupling rate in the PC AuNF is due to the quantum confinement of the electrons, as supported by the measured absorption spectra of the films.

2. Experimental methods

The samples investigated here, TEM images of which are shown in Fig. 1a and d, are [001]-oriented SC and PC AuNFs on TEM copper grids (Ted Pella Inc.) with thicknesses of ~11 nm and ~2 nm, respectively. The PC AuNF has a transverse grain size of 20–50 nm, surrounded by amorphous grain boundaries [13], while the SC AuNF has a much larger grain size (up to hundreds of μm).

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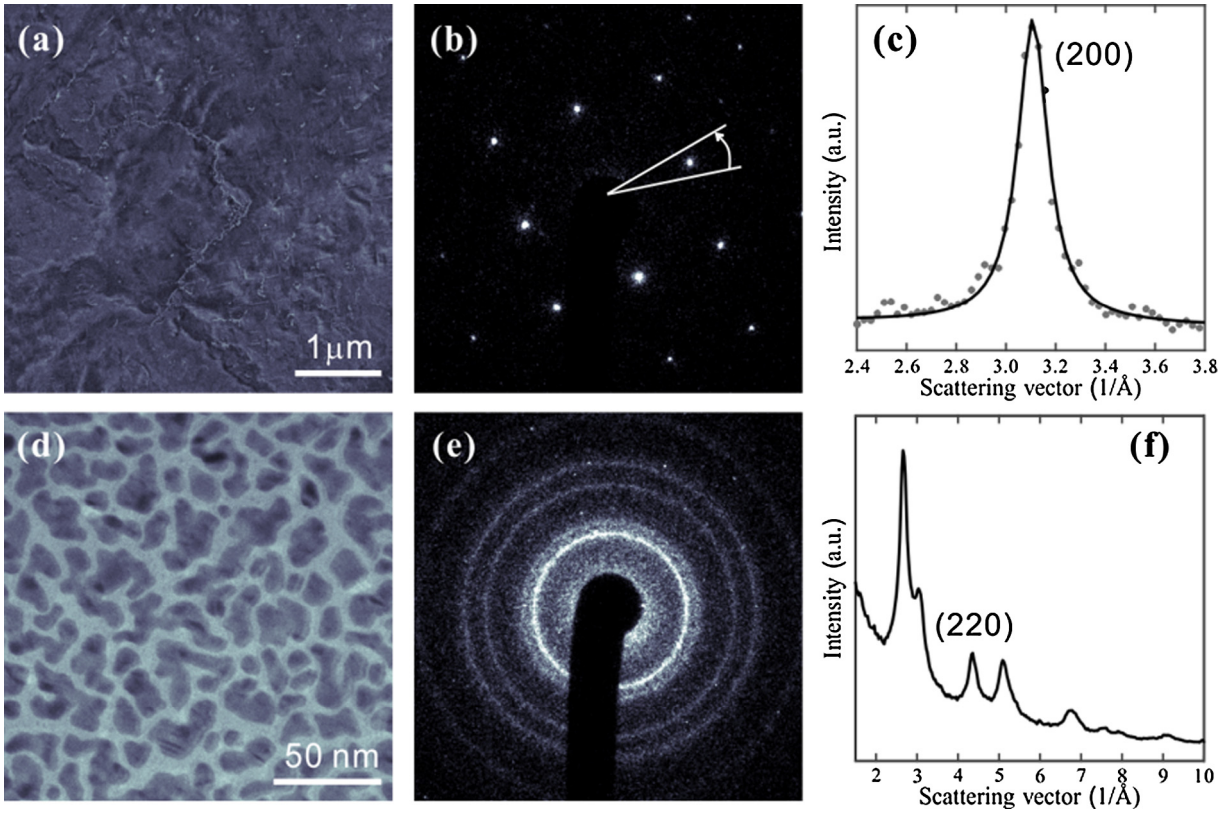

Fig. 1. TEM characterization and electron diffraction patterns for the gold films studied. (a) TEM image and (b) static electron diffraction pattern of the SC AuNF. (c) Diffraction intensity peak (200) obtained by azimuthally averaging the cone section indicated in (b) and its curve fitting (solid line). (d) TEM image and (e) static electron diffraction pattern of the PC AuNF. (f) One-dimensional diffraction curve obtained by azimuthally averaging the diffraction pattern of the PC AuNF. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article)

As observed from the Bragg diffraction patterns shown in Fig. 1b, the probed area ($130 \times 80\ \mu m^2$) on the SC AuNF can be attributed to a single domain, while the PC AuNF yields diffraction patterns composed of Debye-Scherrer rings (Fig. 1e).

The ultrafast electron diffraction (UED) experiments are performed in transmission. For details of the UED setup, see Refs. [2,16]. Briefly, a laser-pump/electron-probe scheme is employed to detect the light-induced *real-time* changes of the electron diffraction pattern. The pump beam (800 nm, 120 fs), generated by a Ti:Sapphire amplifier (Spectra Physics) at a repetition rate of 2 kHz, is used to excite the sample at an incidence angle of 45°. The electron pulses are produced by focusing the 266 nm UV third harmonic from the amplifier onto a LaB_6 photocathode in a 30-keV photoelectron gun (Kimball Physics, Inc.), and used to probe the sample by recording the diffraction images at different time delays. To eliminate space charge effects, the electron pulses contain no more than 300 electrons, with a duration of <1 ps [17]. The pump-probe beam time delay is precisely controlled by a motorized linear stage inserted into the optical path of the pump beam. The spatial overlap of two beams on the sample position is determined by maximizing the transmission of both beams through a 100 μm diameter copper aperture. The electron diffraction patterns are recorded on a gated microchannel plate/phosphor screen/CCD image intensifier.

In order to compare the dynamics, the absorbed pump fluence is tuned to yield nearly the same amplitude change of the diffraction intensity for the two samples, corresponding to 0.69 mJ/cm^2 and 0.49 mJ/cm^2 for the SC and PC AuNFs, respectively. Although the sample thicknesses are different, any such effects on the dynamics can be ignored because the ballistic transport (or scattering) of electrons occurs in tens of femtoseconds, thus ensuring the region probed is homogeneous along the propagation direction of the electron beam [7].

3. Results and discussion

Azimuthally averaging the diffraction pattern gives a one-dimensional diffraction curve as a function of the scattering vector, as shown in Fig. 1c and f. The temporal evolution of the diffraction pattern can therefore be obtained by fitting the location and area of the diffraction peaks at various pump-probe time delays. Here, the peaks of interest are fit by a piecewise-linear background and a Lorentzian function. In the case of the PC AuNFs, only the well separated {220} peak can be quantitatively analyzed.

Fig. 2a and b show the temporal change of the diffraction intensity of the {220} and {200} Bragg peaks for the SC and PC AuNFs, respectively. The intensity change of both samples exhibits a fast decay immediately after the laser excitation and then reaches a plateau. This behavior can be well attributed to the heating of the lattice via electron-phonon coupling following electron excitation by the femtosecond laser pulses, which results in an electron diffraction intensity decrease due to the Debye-Waller effect. The plateau is due to the slow pace of heat dissipation, on the order of microseconds from the ~100 μm diameter sample region probed, to the surrounding film. Fitting the dynamics with an exponential function gives decay lifetimes of 4.8 ± 0.2 ps and 17.1 ± 1.1 ps for the SC and PC AuNFs, and indicates more efficient electron-phonon coupling in the SC AuNFs. Although the fitted values are consistent with those reported in the literature [9,13,14], the phenomena observed here stand in contrast to previous experimental and theoretical results on thicker films that show grain