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Reduced Photoconductivity Observed by Time-Resolved Terahertz Spectroscopy in Metal Nanofilms with and without Adhesion Layers

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Abstract

Non-contact, optical time-resolved terahertz spectroscopy (TRTS) has been used to study the transient photoconductivity of nanometer-scale metallic films deposited on fused quartz substrates. Samples of 8 nm thick gold or titanium show an instrument-limited (*ca.* 0.5 ps) decrease in conductivity following photoexcitation due to electron-phonon coupling and subsequent increased lattice temperatures which increases charge carrier scattering. In contrast, for samples of 8 nm gold with a 4 nm adhesion layer of titanium or chromium, a *ca.* 70 ps rise time for the lattice temperature increase is observed. These results establish the increased transient terahertz transmission sign change of metallic compared to semiconductor materials. The results also suggest nanoscale gold films that utilize an adhesion material do not consist of distinct layers.

Keywords

Metal nanofilms; Gold; Chromium; Titanium; Time-resolved Terahertz Spectroscopy; electron-phonon coupling; carrier dynamics; alloy; adhesion layer

Films of metallic materials are commonly used as electrodes in devices such as chemical sensors,¹ molecular electronics,² and as transparent conductive electrodes³ in LEDs and photovoltaics. The function of these devices relies on the electrode to be highly conductive and a metallic material. However, the amount and type of material used as the electrode is also important towards development of devices that are both useful and cost effective. Thinner metal films have cost advantages and can be used as semi-transparent electrodes but the use of thinner films also lowers the electrical conductivity.⁴ As new materials are developed for these purposes, it is worthwhile to evaluate potential candidates for their conductivity and metallic classification.

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Supporting Information

See supplemental material at [url] for: Materials and experimental methods, AFM images for the gold films with and without adhesion layers (Figure S1), a comparison of UV-visible transmission spectra of the 8nmAu/4nmTi film and to a sum of 8nmAu and 4nmTi films (Figure S2), Terahertz electric field transmission through each film (Figure S3), a comparison of the static and differential electric field transmission through semiconductor and metallic samples (Figure S4), Fluence dependence of the measured TRTS signals (Figure S5), TRTS measurements using 400 nm excitation (Figure S6).

One way the conductivity of metal films can be measured is based on the percent transmission of terahertz frequency light through the material, a non-contact technique. This has been done in the steady state, where terahertz time-domain spectroscopy (THz-TDS), was used to directly measure the conductivity of doped semiconductors^{5,6} and gold thin films.^{7,8} This approach has also been used to measure the change in conductivity with time following photoexcitation, time-resolved terahertz spectroscopy (TRTS).⁹ TRTS experiments have been performed on a variety of semiconductor materials to determine their charge carrier dynamics and mobilities⁹ but surprisingly, THz studies of metallic samples are extremely limited. Despite this, it is expected that metallic materials exhibit a vastly different TRTS response compared to semiconductors. Considering direct current conductivity, the relation $\sigma = eN\mu$ (σ = conductivity, e = electron charge, N = charge carrier density, and μ = charge carrier mobility) suggests an increase in the number of charge carriers leads to an increase in conductivity. Band gap photoexcitation in a semiconductor can lead to changes in the sheet carrier density on the order of 1×10^{12} to $1 \times 10^{15} \text{ cm}^{-2}$. In TRTS, a change in N of this magnitude dominates the TRTS response and leads to a positive change in the photoconductivity. Conversely, photoexcitation of an intraband electronic transition in a metal would not lead to a significant change in the number of free charge carriers. Any conductivity changes would then be dominated by changes in mobility that results from the new electronic configuration in the photoexcited material.

TRTS experiments on graphene reflect the notion that metallic materials behave very differently than semiconductors. In one report, photoexcitation of graphene lead to a transient reduction in the photoconductivity (*i.e.* an increase or “bleach” in the percent transmission at terahertz frequencies).¹⁰ The transient signal consisted of an instrument-limited rise, characteristic of lattice heating from electron-phonon coupling, followed by a 1 ps to 2 ps decay associated with cooling of the hot charge carriers assisted by phonon emission. Conversely, another graphene study assigned the same dynamics at room temperature but reported the opposite sign change in the TRTS response.¹¹ This ambiguity arises from the fact that graphene is a semi-metal, and can have both semiconductor and metallic properties depending on the intrinsic doping level and exposure to atmospheric adsorbates.^{12–14} If the intrinsic doping level is high, a change in the number of charge carriers by photoexcitation in a semi-metal will not necessarily dominate the sign change of the photoconductivity signal. Instead, the TRTS response is dominated by an increased charge carrier scattering rate (reduced mobility) that accompanies the elevated lattice temperature that follows photoexcitation and subsequent electron-phonon coupling.

Based on this ambiguity, it is worthwhile to fully establish the expected TRTS response, in transmission configuration, for conventional metallic nanofilm samples. In this Letter, metal nanofilms (e.g., gold and titanium <8 nm thick) are shown to undergo a transient decrease in electrical photoconductivity (increased terahertz transmission) upon photoexcitation with visible light. This is contrasted with bulk semiconductors, which undergo a transient increase in electrical conductivity and increased absorption due to a large change in the number of charge carriers. With this understanding, the effect of adhesion layers on the transient properties of metal nanofilms is also considered. The inclusion of adhesion layers (e.g., titanium and chromium < 4 nm thick) in metal films can affect the carrier dynamics,

have a strong influence on film properties, and potentially affect the end-performance of devices.

Thin metal films used in these experiments were fabricated by electron-beam deposition onto fused quartz (FQ) substrates and characterized by atomic force microscopy (AFM), Figure S1 (see SI for details). Multiple, equivalent samples were prepared side-by-side during the same deposition. The samples examined include 8 nm of gold on fused quartz ("8nmAu") or 8 nm of gold with a 4 nm adhesion layer of titanium or chromium ("8nmAu/4nmTi" or "8nmAu/4nmCr" respectively). A comparison between pure metals was made by studying an 8 nm film of titanium ("8nmTi"). An 8 nm gold sample was chosen to ensure the layer in each sample was above the percolation limit and of high electrical conductivity⁷ while the steady state terahertz transmission remained high enough to obtain reasonable signal-to-noise in the TRTS experiments. Lastly, a sample denoted "4nmCr" was prepared by exposing an 8nmAu/4nmCr sample to aqua regia.

Steady state visible absorption spectra of the metal films are shown in Figure 1(a). The 8nmAu spectrum contains two prominent absorption regions; one at wavelengths below ~ 500 nm from interband electronic transitions (d-band to s/p band above the Fermi level), the other between ~ 500 nm to the NIR from an intraband transition that excites the metallic electrically conductive electrons of the s/p band (surface plasmon resonance, SPR).^{15–17} This is consistent with previously published spectra for a high electrical conductivity gold film at a thickness greater than the percolation limit.^{18,19} Less information has been published about the optical properties of titanium nanofilms, but the absorbance spectrum of 8nmTi is qualitatively similar. Although the broad feature between 300 nm and 1000 nm rolls off into the NIR above 800 nm it is believed to be the intraband transition of conductive electrons in metallic titanium.

8nmAu/4nmTi and 8nmAu/4nmCr are qualitatively similar to 8nmAu except the onset of the intraband transition is shifted to longer wavelength with the largest shift occurring for the chromium adhesion layer sample. It is noteworthy that the spectrum of 8nmAu/4nmTi cannot be reproduced by adding the 8nmAu and an approximated 4 nm titanium film spectra (Figure S2). This suggests that for films deposited with adhesion layers the observed properties are interdependent, possibly due to the gold layer filling voids within or improved wettability on the Cr or Ti layer.^{20,21} The implications of this towards the final properties of the films utilizing adhesion layers are discussed in more detail in reference to the TRTS results. However, we surmise the 4nm adhesion layer provides extended conductive channels (increased fill factor) in the thin gold film which improves the conductivity and shifts the observed SPR to lower frequency. Lastly, the 4nmCr spectrum consists of a broad feature centered at 500 nm. When 8nmAu/4nmCr was exposed to aqua regia, the chromium remaining in the film likely oxidized in air to form Cr₂O₃,²² although some trace amounts of gold could also remain, giving rise to this feature.

THz-TDS and TRTS measurements were conducted using an amplified femtosecond Ti:Sapphire laser system described in the supporting information. Without photoexcitation, transmission of the THz electric field through each sample, $E_{\text{sample}}(\omega)$, compared to the transmission through the bare substrate, $E_{\text{substrate}}(\omega)$, is a measure of the electrical

conductivity (THz-TDS). This is shown in Figure S3 for each sample scaled to a representative substrate. Fourier transform analysis allows the real, $\sigma_1(\omega)$, and imaginary, $\sigma_2(\omega)$, parts of the frequency-dependent conductivity to be determined, as shown in Figure 1(b).⁷

$\sigma_1(\omega)$ is relatively constant with a slight negative slope towards highest frequencies. For gold-containing films, the frequency-averaged values of $\sigma_1(\omega)$ were determined to be 35,000 S/cm, 60,000 S/cm, and 90,000 S/cm for 8nmAu, 8nmAu/4nmCr, and 8nmAu/4nmTi, respectively. These values show the gold films exhibit high conductivity above the gold percolation limit but are not at the bulk limit (DC conductivity of 410,000 S/cm).²³ 8nmTi and 4nmCr film conductivities are much lower: 1500 S/cm and 1700 S/cm, respectively. The 8nmTi film value is much lower than the bulk Ti conductivity (45,000 S/cm)²³ and further suggests that the films involving adhesion layers cannot be considered as distinct layers. An extra 4 nm layer of titanium cannot account for the 2- to 3-fold increase in conductivity of 8nmAu/4nmTi compared to 8nmAu. Instead, the films with adhesion layers likely have increased fill factor, which improves the real conductivity compared to 8nmAu. This, as well as the observed shifts in the SPR, is corroborated by AFM images (Figure S1), which show 8nmAu/4nmTi and 8nmAu/4nmCr are more continuous films with RMS roughness of 0.4 nm and 0.8 nm, respectively, due to improved wettability of the substrate by the Cr and Ti adhesion layers. This results in higher conductivity compared to the 8nmAu film, which consists of interconnected nanoparticulate islands with a RMS roughness of ~ 1.7 nm.

Conversely, $\sigma_2(\omega)$ is negative and decreases with increasing frequency. The presence of domain boundaries between the areas of gold and the adhesion metal (or particle boundaries in 8nmAu) could give rise to this type of Drude-Smith behavior. This is generally due to significant carrier scattering at particle boundaries and results in reduced conductivity.^{9,24} Alternatively, any small (~ 10 fs) errors in the measured phase, which can arise from variation in the substrate thickness or sample orientation relative to the THz probe propagation direction, could also result in artificially negative contributions to $\sigma_2(\omega)$.²⁵ This possibly explains the disagreement between $\sigma_2(\omega)$ for our gold film on a quartz substrate with that of Walther, et. al.,⁷ which used a silicon substrate with more uniform thickness. Nonetheless, the large, real, $\sigma_1(\omega)$, which is not as strongly affected by phase shifts, suggests the gold films studied here are still highly conductive and above the percolation limit.

Photoexcitation of the films at 800 nm leads to changes in the terahertz electric field transmission proportional to the change in conductivity (monitored by TRTS). In TRTS, the electric field transmission changes, E , are measured directly but relate to the electric field transmission through the photoexcited, E_p , and unphotoexcited, E_0 , sample by $E = E_p - E_0$. If $E_p < E_0$, the measured E will have an inverted phase compared to the unexcited sample. This is shown in Figure S4 for 8nmAu, 4nmCr and a reference sample of high-resistivity silicon (Si). From the measurement of E it is clear that the 8nmAu sample produces an increase in transmission of the THz electric field (bleach) and decrease in conductivity following photoexcitation. This is opposite to the sign of E for conventional semiconductor materials.

The dynamics of the photoinduced changes in E measured at the peak of the transmitted probe electric field as a function of pump-probe delay time are shown in Figure 2(a) for the pure metal films (8nmAu and 8nmTi) compared to the silicon reference and the 4nmCr samples. For each sample these signals are linear with respect to excitation power (Figure S5). The charge carrier dynamics of bulk semiconductors has been previously studied by TRTS and is shown here only as a comparison to establish the sign of E .⁹ Notably, E for 4nmCr has the same sign as that for the Si sample. The instrument-limited rise is attributed to an increased charge carrier density following photoexcitation and subsequent dynamics are consistent with other nanoscale semiconductor materials.^{26,27} Conversely, 8nmAu and 8nmTi yield the opposite sign of E . The time-dependent TRTS response of both pure metal films is characterized by a fast, instrument-limited rise. For 8nmAu, the rise is followed by a slower rise component that achieves maximum E by ≈ 20 ps and a longer-lived decay (lifetime > 200 ps). 8nmTi is characterized by only a long-lived decay component that also has a lifetime greater than 200 ps.

The time-dependent changes in E for the metallic films can be explained within the context of the photothermal effect and heat transfer through the metal films. Photoexcitation of electrons within the conduction band of gold (and other metals) generates hot electrons characterized by an effective electron temperature based on the amount of energy absorbed.²⁸ Electron-phonon coupling allows the hot electrons to equilibrate with the lattice atoms in less than a picosecond.¹⁵ At elevated lattice temperatures, the hot conductive electrons experience increased scattering from the lattice phonons which leads to decreased mobility and conductivity (increased THz transmission, $E > 0$).²⁹ In order to return to the ground state, the lattice must undergo heat transfer to the substrate or surroundings. This requires phonon-phonon coupling between the metal film and the substrate,³⁰ and likely accounts for the long-lived decays for these samples. A second possibility for the long-lived decay component is that the photoexcited sample equilibrates with the remaining unexcited part of the film. The decay rate would then be controlled by how quickly heat transfers through the film which depends on the thermal conductivity of the material. The ~ 20 ps rise component in 8nmAu is also consistent with photoinduced heat generation and transfer and has been observed by transient reflectivity measurements for other gold films.³¹

The effect of adding adhesion layers to the gold film is clearly evident from the 8nmAu/4nmTi and 8nmAu/4nmCr TRTS results. As shown in Figure 2(b), E is still positive indicating a transient decrease in conductivity, but there is no longer an instrument-limited rise. Instead, both 8nmAu/4nmTi and 8nmAu/4nmCr exhibit slow rise times that do not maximize until a delay time of approximately 70 ps. This slow rise time suggests the electron-phonon coupling is weaker in the mixed-metal system compared to the pure metals, resulting in a longer time required to convert the photoexcitation energy into heat and an increased lattice temperature. That both the 8nm Au and 8nmTi films have fast rise times but the 8nmAu/4nmTi does not is a possible further indication that the mixed metal films do not consist of distinct layers. There is also a longer-lived decay component with lifetime greater than 200 ps similar to the long-time response of 8nmAu assigned as before.

Excitation of the metal films at 400 nm produced similar results (Figure S6) for both the observed dynamics and the sign of E . This is noteworthy given that 400 nm excitation of

gold can promote both the intraband transition in the s/p band as well as the interband transition of d-band electrons above the fermi level.¹⁵ Contributions from the interband transition can lead to generation of new charge carriers which on its own should result in increased conductivity ($\sigma > 0$) following excitation. However, for low excitation fluence such that the concentration of excited d-band electrons is much less than the free carriers in the s/p band (which is the case for our experiments), the overall response will still be dominated by the reduced conductivity that follows the intraband s/p excitation and this agrees with our observation.

Although the focus of this letter is to establish the sign change in TRTS experiments in thin metallic films, the magnitude of $\Delta\sigma/\sigma_0$ for the samples is also noteworthy. For example, the peak $\Delta\sigma/\sigma_0$ for 8nmAu is about five-fold larger than 8nmTi at equivalent excitation fluence. Within the context of electron-phonon coupling leading to increased lattice temperatures, the magnitude of $\Delta\sigma$ is related to the conductivity change that results from the increased temperature following photoexcitation. Given the specific heat and density of bulk gold and titanium, and known experimental parameters (excitation fluence, beam diameter, and absorption of the excitation pulse), the expected temperature rise can be calculated for the 8nmAu and 8nmTi films (assuming 100 % light-to-heat conversion). This was determined to be 117 K and 133 K for gold and titanium, respectively. Considering the electrical conductivity of metals is linearly dependent on temperature near room temperature and the temperature coefficient of resistivity is also nearly equivalent for gold and titanium,^{23,32} it is expected that the two bulk materials would yield a similar photoconductivity change in response to the temperature rise associated with photoexcitation. This is not the case for the films measured here and supports the idea that the metal films are not bulk. However, this analysis also highlights the idea that if temperature jumps in nanofilms were independently measured, TRTS measurements potentially determine the specific heat of nanoscale materials based on the magnitude and sign of the measured $\Delta\sigma/\sigma_0$ without the use of contact temperature probes.

In this letter, TRTS was used to monitor conductivity changes in several samples of metallic nanofilms on insulating, fused quartz substrates. Metal nanofilms of pure gold and titanium yielded an instrument-limited, transient *decrease* in conductivity following photoexcitation of the intraband transition at 800 nm. The decrease in conductivity was attributed to an elevated lattice temperature that results from electron-phonon coupling between the lattice and photoexcited electrons. This follows the expected temperature dependence of conductivity in conventional metals.²⁹ In contrast, for the semiconductor Cr₂O₃ and bulk silicon there was a photoinduced *increase* in conductivity. These experiments are a direct comparison of the expected transient conductivity response in TRTS and establish the idea that materials classified as metallic should also undergo this transient reduction in conductivity in TRTS experiments, so long as photoexcitation does not lead to a significant change in the number of free charge carriers. For nanoscale materials, this classification also depends on the thickness and morphology of the film. This study utilized metal films near, but above, the percolation limit with high conductivity, but the observed TRTS response may not necessarily be equivalent for low conductivity metal films below the percolation limit. The observed dependence of $\Delta\sigma$ on film thickness is beyond the scope of this letter but

planned for future studies. Metallic gold films incorporating adhesion layers were also studied using TRTS. It was shown that the metallic films cannot be considered as distinct layers but likely consist of a mixture of the two metals, which leads to smoother, more continuous, films and higher conductivity. In 8nmAu/4nmTi and 8nmAu/4nmCr, including both metals resulted in weaker electron-phonon coupling and slower temperature equilibration times between the photoexcited electrons and metal lattice. Overall, these results could have implications for the design and function of future devices which incorporate layers of thin metal films that utilize adhesion layers as well as offer opportunities for future non-contact measurements of the heat generation or specific heat of nanofilm materials.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

(a) UV-Vis absorption spectra for each film at room temperature. (b) Real ($\sigma_1(\omega)$, squares) and imaginary ($\sigma_2(\omega)$, circles) complex conductivity determined from $E_{\text{sample}}(\omega)/E_{\text{substrate}}(\omega)$. The symbols $\sigma_1(\omega) / 5$ indicates the real conductivity values are divided by 5 for clarity.

Figure 2.

TRTS measurements following the time-dependent changes in E following 800 nm photoexcitation at room temperature for (a) the pure metal films compared to semiconductor samples and (b) the films involving adhesion layers compared to the pure metal films.