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Static and Time-Resolved Terahertz Measurements of Photoconductivity in Solution-Deposited Ruthenium Dioxide Nanofilms

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Abstract

Thin-film ruthenium dioxide (RuO₂) is a promising alternative material as a conductive electrode in electronic applications because its rutile crystalline form is metallic and highly conductive. Herein, a solution-deposition multi-layer technique is employed to fabricate ca. 70 ± 20 nm thick films (nanoskins) and terahertz spectroscopy is used to determine their photoconductive properties. Upon calcining at temperatures ranging from 373 K to 773 K, nanoskins undergo a transformation from insulating (localized charge transport) behavior to metallic behavior. Terahertz time-domain spectroscopy (THz-TDS) indicates that nanoskins attain maximum static conductivity when calcined at 673 K ($\sigma = 1030 \pm 330 \text{ S} \cdot \text{cm}^{-1}$). Picosecond time-resolved Terahertz spectroscopy (TRTS) using 400 nm and 800 nm excitation reveals a transition to metallic behavior when calcined at 523 K. For calcine temperatures less than 523 K, the conductivity increases following photoexcitation ($\Delta E < 0$) while higher calcine temperatures yield films composed of crystalline, rutile RuO₂ and the conductivity decreases ($\Delta E > 0$) following photoexcitation.

Introduction

Metallic thin films are useful for a variety of applications including as electrocatalysts,¹ sensors,² and as transparent conductive electrodes in light emitting diodes (LEDs) and photovoltaics.³ Ruthenium dioxide (RuO₂) has been investigated as an alternative material for these applications^{4–7} because its rutile phase is metallic with high conductivity as single crystalline ($\sigma > 10^4$ S cm⁻¹) and polycrystalline ($\sigma \approx 10^2$ S cm⁻¹) forms.^{8,9} Due to the high cost of ruthenium, it is important to not only minimize the amount of active material required to generate functional performance but also utilize low cost and low-temperature fabrication techniques. To this end, a sub-ambient thermal, solution-based deposition technique was developed that allows fabrication of nanoscale disordered RuO₂ ("nanoskins") on porous supports (fibrous SiO₂ papers¹⁰ or aerogels¹¹), which provide high surface area for electrocatalytic applications, as well as onto planar substrates such as SiO₂,⁷ CaF₂, and Si, which are useful for optical applications.^{7,12–14}

Although RuO₂ nanoskins are initially deposited at low temperature, further heating (calcining) is required to generate films with optimal conductivity. The as-deposited material was previously classified as X-ray amorphous, having a nanoparticulate morphology and exhibiting lower conductivity than comparably thick rutile RuO₂.^{10,11} Nanoskins deposited on aerogels, SiO₂ paper, and planar substrates at thicknesses from ca. 2 nm to 30 nm exhibit maximum conductivity upon heating in air to a calcine temperature (T_{cal}) of 473 K. At this temperature, the film remained X-ray amorphous and retained the as-deposited close-packed particulate network. Further increases in T_{cal} lead to dewiring as the particulates coarsen and interrupt particle–particle contiguity within the film. This physical discontinuity results in reduced conductivity but also coincides with the formation of X-ray–observable crystalline rutile RuO₂.^{10,11,15}

The insulating to metallic classification of RuO₂ nanoskins on planar SiO₂ substrates has been evaluated in multiple ways. In one case, a metal-to-insulator transition was observed in temperature-dependent resistivity measurements for 20 nm and 30 nm thick nanoskins with T_{cal} ranging from 393 K to 473 K.¹⁶ A progression was observed where the films calcined at the lowest temperature exhibited the behavior of localized insulators to that of weakly localized conductors and finally moving towards metallic behavior at $T_{cal} \approx 473$ K. Films calcined at the lowest temperatures exhibit a negative temperature coefficient of resistivity (TCR) while a comparably thick film of rutile RuO₂ generated by reactive sputtering showed the expected metallic response with TCR > 0. Secondly, the metallic behavior was also evaluated by optical pump-probe spectroscopy in the visible/NIR and THz ranges.¹⁷ In this case, a localized surface plasmon resonance (lspr) band appeared in the NIR optical spectrum for ca. 20 nm thick

nanoskins treated at T_{cal} > 473 K, which was attributed to thermal generation of nanocrystallites of metallic RuO₂. Higher T_{cal} also led to a concomitant reduction in the electrical conductivity due to dewiring of the film.

We also recently showed that time-resolved terahertz spectroscopy (TRTS), a non-contact probe of electrical conductivity (at THz frequencies), can be used to classify metallic materials and nanofilms.¹⁸ This technique serves as a direct probe to extract the TCR sign by measurements of the change in electric-field transmission, ΔE , following photoexcitation. For metallic-like materials, the photoexcitation pulse transiently heats the sample through rapid electron–phonon coupling, leading to decreased conductivity ($\Delta E > 0$).^{18–20} Our prior TRTS examination of a 20 nm thick metallic RuO₂ film generated by reactive sputtering and an 8 nm thick gold film exhibited the expected TRTS sign change. However, the lack of electrical conductivity that occurred upon dewiring at T_{cal} > 473 K prevented us from observing the same TRTS sign change for the 20 nm thick solution-deposited nanoskins.¹⁷ Herein, we use TRTS to investigate the insulator-to-metallic transition in solution-deposited RuO₂ nanoskins but now focus on thicker (70 ± 20 nm) films. This improved film growth allows the nanoskins to retain a sufficient degree of particle-to-particle contiguity despite the required thermal ripening when heating the nanoskins to T_{cal} > 473 K such that improved conductivity is achieved compared to the thinner films calcined above this temperature.

Experimental

a. Nanoskin Fabrication

The RuO₂ nanoskins were deposited on fused quartz substrates (GM Associates, Inc.)²¹ using a solution-phase deposition technique from the decomposition of RuO₄ precursor as previously described.¹⁷ The procedure for generating RuO₂ nanoskins is a layer-by-layer technique involving 373 K heating steps between depositing each ~10 nm thick layer from solution at sub-ambient temperature. For this work, seven layers (7×) were deposited) the coated substrate was then sectioned into individual pieces that were calcined at temperatures ranging from 373 K to 773 K to generate the final sample set. The entire nanoskin sample set was generated by two separate 7× depositions. One deposition comprised films calcined to 473 K, 523 K, 573 K, and 773 K while the second provided nanoskins calcined at 373 K and 673 K. For comparison of the nanoskins to a standard metallic film, a 20-nm-thick RuO₂ film fabricated by room-temperature DC reactive sputtering from a ruthenium target in an Ar/O₂ as previously described^{7,17} was also studied.

b. General Nanoskin Characterization

Ultraviolet–visible-Near Infrared (UV–Vis-NIR) transmission measurements were collected using Perkin Elmer Model Lambda 2 and 870 spectrometers with 2 nm resolution and were referenced to a bare fused silica substrate to correct for substrate surface reflections. Estimates of film ($T_{cal} = 373$ K and 673 K) reflectivity were determined using an integrating sphere accessory in diffuse and specular reflectance configurations. Four-point sheet resistance measurements were conducted using a contact-probe apparatus; average resistance values were derived from multiple measurements at various positions across the nanoskin film area. Scanning electron microscopy (SEM) was performed with a LEO Supra 55 field emission microscope at an accelerating voltage of 15 kV. Grazing incidence X-ray diffraction (GI-XRD) scans were collected in parallel-beam mode with a Rigaku SmartLab X-ray diffractometer operated at 40 kV and 44 mA with an incident beam angle of 0.4° and a 0.5° min⁻¹ scan rate. Diffraction peak fitting and Scherrer analysis were performed with the PDXL software (Rigaku).

The thickness of the RuO₂ nanoskins was measured by scanning probe microscopy (SPM in intermittent-contact mode, Bruker Dimension 6100, Santa Barbara, CA) where scratches were made by applying pressure to the apex of an unused razor blade. Two scratches were prepared across each film and imaged by SPM at two sites per scratch. Rectangular probes (OTESPA-R3, 26 N/m, 300 kHz, Bruker, Camarillo, CA) were used with a scan rate of 0.5 Hz for thickness profiles. Abraded film regions were imaged with the fast scan axis oriented normal to each scratch, sampling 512 points along each scan line while each region was imaged with 64 lines. Height data were offset to zero and leveled by subtracting a tilted plane fit to the raw topography of exposed bare quartz regions. Film thickness was measured as the difference between averaged RuO₂ and bare quartz height values taken from segments of entire scratch profiles using the Step measurement tool in NanoScope Analysis (ver. 1.5, Bruker, Santa Barbara, CA). In cases where minor abrasion was observed in the center of exposed quartz, we analyzed flanking profile segments that were both level and reflected the roughness of measured bare quartz. Three profiles from each imaged region were analyzed for a total of 12 measurements from each RuO₂ nanoskin. This analysis indicated an average film thickness of 70 ± 20 nm across the nanoskin sample set. Representative atomic force microscopy (AFM) images and height profiles of the scratched films are shown in the supporting information (Figure S1).

c. Terahertz Spectroscopy

The apparatus for terahertz spectroscopy is based on a kilohertz repetition rate, amplified femtosecond Ti:sapphire laser system that has been previously described in detail.²² Briefly, the amplified 800 nm output is split into three arms and used for the visible pump, THz probe, and gated electro-optic detection. This system was used for both static THz-TDS (visible pump beam blocked) and TRTS measurements (pump pulses at 400 nm and 800 nm with beam diameter ≈ 5 mm, ≈ 50 fs FWHM pulse duration, and fluence $\approx 1 \times 10^{15}$ photons-cm⁻²). Samples were mounted

on an aperture larger than the THz and visible pump beam sizes in a purged dry air box at room temperature. For THz-TDS, electric-field waveforms transmitted through the film/substrate (E_{sample}) and bare substrate (E_{substrate}) were scanned 10 times and averaged (Type B, k=1 analysis—extracted frequency-dependent spectra discussed below are derived from averaged scans). For TRTS measurements, the pump delay was scanned while holding the delay between the gate and THz probe pulses fixed at the position that gives the maximum differential electrooptic response (ΔE) to yield the TRTS decay dynamics. The pump scans were collected 10 times, averaged, and then used to calculate the pump-induced change in conductivity (see below). Spectral changes to the photoconductivity were also collected by holding the delay between the visible pump and THz probe fixed and scanning the delay of the THz probe relative to the gate. The sign of the TRTS signal was referenced to a silicon wafer response. Ten sweeps of the differential electric field waveforms were collected, averaged, and used to determine the frequency dependent photoconductivity.

d. THz Spectroscopy Data Analyses

All films studied here were considered to fall within the thin-film limit because their thickness (70 \pm 20 nm) is less than the wavelength of THz probe radiation (1 THz = 300 μm). 23 From the UV–Vis absorption spectra (see below), the optical penetration depth of the visible pump beam is larger than the film thickness, so the films are considered to be uniformly excited. The conductivity of a thin-film sample on an insulating substrate is related to the amplitude of electric-field transmission through the sample, $T_{s}(\omega)$, by use of the thin-film approximation according to equation (1):

$$T_s(\omega) = \frac{E_s(\omega)}{E_i(\omega)} = \frac{2}{1 + N + Z_0 d\sigma(\omega)},$$
(1)

where $E_i(\omega)$ and $E_s(\omega)$ are the complex-valued Fourier transform of the time-dependent electric field incident upon and transmitted through the sample/substrate, respectively, N is the substrate index of refraction, Z₀ is the free space impedance, d is the thin-film thickness, and $\sigma(\omega)$ is the complex-valued photoconductivity.²³ For an insulating substrate $\sigma(\omega) = 0$,²¹ and the THz transmission is given by $T_{sub}(\omega) = E_{sub}(\omega)/E_i(\omega) = 2/(1+N)$, which represents amplitude losses in the THz electric field due to reflections from the substrate surfaces. For measurements of the static, non-photoexcited conductivity, it is conventional to consider the THz transmission of the sample relative to that through the blank substrate $T_s(\omega)/T_{sub}(\omega)$, which can be rearranged to yield equation (2):

$$\sigma(\omega) = \left(\frac{1+N}{Z_0 d}\right) \left(\frac{E_{sub}(\omega)}{E_s(\omega)} - 1\right).$$
(2)

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This equation is typically used to relate the measured electric field waveforms to the conductivity of a thin-film sample and was used here to calculate the static conductivity in the RuO_2 nanoskins.²⁴

In a similar fashion, equation (1) can be used to calculate the conductivity of a photoexcited sample in TRTS experiments by considering the THz transmission relative to that of the non-photoexcited sample, equation (3):

$$\frac{T_s^p(\omega)}{T_s^{np}(\omega)} = \frac{E_s^p(\omega)}{E_s^{np}(\omega)} = \frac{1+N+Z_0 d^{np}\sigma^{np}(\omega)}{1+N+Z_0 d^p\sigma^p(\omega)},$$
(3)

where the superscripts p and np indicate the photoexcited and non-photoexcited samples, respectively. In TRTS, the differential THz transmitted waveform is measured directly by chopping the pump beam, where $\Delta E = E_s^{p} - E_s^{np}$. Making use of this relation and rearranging equation (3) for $\sigma^{p}(\omega)$ yields equation (4):

$$\sigma^{p}(\omega) = \left(\frac{d^{np}\sigma^{np}(\omega)}{d^{p}}\right) \left(\frac{E_{s}^{np}(\omega)}{\Delta E(\omega) + E_{s}^{np}(\omega)}\right) - \left(\frac{1+N}{Z_{0}d^{p}}\right) \left(\frac{\Delta E(\omega)}{\Delta E(\omega) + E_{s}^{np}(\omega)}\right).$$
(4)

With the assumption that $\sigma^{np}(\omega) = 0$, equation (4) reduces to the right-hand side and is equivalent to the expression developed by Hegmann, et al., for semiconductor thin film samples of low intrinsic conductivity.^{23,25} Further simplifications similar to those made by Hegmann, et al., assume the photoinduced conductivity changes are small, i.e., $\Delta E << E_s^{np}(\omega)$ or $\Delta E/E_s^{np}(\omega) < 20\%$. Given that the RuO₂ nanoskins studied here have $\sigma^{np}(\omega) \neq 0$, Equation (4) was required to properly calculate the conductivity under photoexcitation conditions. As written, equation (4) generates the frequency-dependent conductivity spectra from the measurements of the time-dependent electric field waveforms. However, equation (4) can also be used to determine the dynamics of the photoinduced conductivity by replacing the complex-valued frequency-dependent electric fields by the peak magnitudes of the time-dependent electric field (E₀) and differential electric field (ΔE) waveforms. This procedure represents the frequency-averaged, real part of the complex conductivity. Equation (4) was used to analyze the time-dependent and frequency-dependent photoconductivity of the RuO₂ nanoskins and the sputtered 20 nm thick rutile RuO₂ film.

Results and Discussion

a. UV–Visible Spectroscopy

The UV–vis spectra derived from transmission measurements are shown in Figure 1 for the 70 \pm 20 nm thick RuO₂ nanoskins calcined between 373 K to 773 K and compared to the 20 nm thick sputtered film. It should be noted these extinction spectra do exhibit significant contribution (<

10%) from specular reflection but they are very similar to thinner, \approx 20 nm thick, nanoskins studied previously.¹⁷ At T_{cal} < 473 K, the spectra are broad and relatively featureless across the visible range, giving rise to their black appearance while still being \approx 30% transmissive. Calcining the nanoskins to > 473 K results in the emergence of a transmission feature with a minimum at \approx 600 nm. This feature was previously determined to arise from a distribution of irregularly shaped crystalline rutile RuO₂ nanoparticles that thermally ripen within the 20 nm thick nanoskins and give rise to a broad plasmon resonance absorption band in the NIR. Supporting GI-XRD/SEM analyses of these 70 ± 20 nm thick nanoskins corroborate the same conclusions. The GI-XRD (Figure S2) pattern is consistent with rutile RuO₂ for T_{cal} ≥ 523 K and scanning electron micrographs (Figure S3) clearly show formation of distinct nanoparticles for T_{cal} = 773 K.

Band-structure calculations and optical reflectivity measurements on single-crystal rutile RuO₂ suggest a low energy electronic transition arises from an intraband transition within the d-electron t_{2g} manifold, while a higher energy transition arises from a p-to-d interband transition,²⁶ which agrees with the observed spectra for the nanoskins with $T_{cal} > 473$ K. Further support for the rutile RuO₂ classification is obtained by comparison of the spectra with the 20 nm thick sputtered film, which was previously characterized as metallic rutile RuO₂.^{7,16,27} The sputtered film is a polycrystalline, contiguous film and provides a broader plasmon resonance band compared to the nanoparticulate nanoskins. Nonetheless, the nanoskins progress towards similar spectral features consistent with rutile RuO₂ as the calcine temperature is increased. Overall, improved transmission across the visible, especially in the window from \approx 500 nm to 800 nm was achieved by calcining above 473 K while also allowing for the 70 ± 20 nm thick nanoskins to be electrically conductive (see below).



Figure 1: Extinctionspectra from transmission measurements of the 70 \pm 20 nm thick RuO₂ nanoskins calcined to 373 K (orange), 473 K (purple), 523 K (green), 573 K (red), 673 K (teal), and 773 K (blue), and the 20 nm thick sputtered RuO₂ film (black).

b. Static THz-Time Domain Spectroscopy

The THz-TDS measurements were collected for the nanoskins and sputtered film. The electricfield waveforms transmitted through representative films and corresponding bare insulating substrate exhibit no measureable phase delay between the sample and substrate (Figure S4), suggesting the samples fall within the thin film limit. This absence of sample–substrate phase delay validates the use of equation (2), therefore Fourier transforms of these data were used to generate frequency-dependent real, $\sigma_1(\omega)$, and imaginary, $\sigma_2(\omega)$, conductivity spectra for each nanoskin and the sputtered film (Figure 2).

For all of the films, $\sigma_1(\omega)$ is positive and relatively frequency independent between 0.3 THz to 1.8 THz, Figure 2(a). For the sputtered film, $\sigma_2(\omega)$ is positive and increasing towards higher frequency. Similarly, for the nanoskins with $T_{cal} \leq 673$ K, $\sigma_2(\omega)$ is either close to zero or positive and slightly increasing towards higher frequency. Combined, the observed frequency dependence for these 70 ± 20 nm thick nanoskins is consistent with free charge carriers that move under an applied electric field and have a characteristic scattering time, τ , as described by the Drude model.²¹ That $\sigma_1(\omega)$ is essentially frequency-independent and $\sigma_2(\omega)$ is close to zero makes using the Drude model to fit the data difficult but suggests that $\omega \tau \ll 1$ and $\sigma_1(\omega) \approx$ σ_{DC} .²³ As shown in Figure 2(c), a comparison of the frequency-averaged $\sigma_1(\omega)$ to four-point probe contact measurements yields very good agreement, within error, across the set of nanoskins and reflects this point.



Figure 2: (a) Real, $\sigma_1(\omega)$, and (b) Imaginary, $\sigma_2(\omega)$, parts of the complex photoconductivity determined from room temperature THz-TDS measurements of $E_{sub}(\omega)/E_s(\omega)$, equation (2), for the 20 nm thick sputtered RuO₂ film (black, circle) and the 70 ± 20 nm thick RuO₂ nanoskins calcined at 773 K (blue, diamond), 673 K (teal, circle), 573 K (red, circle), 523 K (green, circle), 473 K (purple, diamond), and 373 K (orange, circle). (c) Comparison of the frequency-averaged real part of the conductivity measured by THz-TDS (red, square) and four-point probe resistivity (blue, diamond). The error bars reflect the standard deviation in film thicknesses as measured by AFM.

The measured conductivity of the series of nanoskins also compares well with contact-probe measurements on the previously studied 20 nm and 30 nm thick films, which had conductivity of 575 S·cm⁻¹ and 600 S·cm⁻¹, respectively, when calcined to 473 K.⁷ Previous nanoskins less than 20 nm thick, however, achieve maximum conductivity at $T_{cal} = 473$ K to 523 K and suffer from reduced conductivity with further heating due to dewiring.^{10,15,17} The nanoskins studied here, however, achieve maximum conductivity at a higher calcination temperature of 673 K before the onset of dewiring effects take place. This maximum can be explained by considering

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two ways in which the calcination procedure tends to improve conductivity. One, rutile RuO₂ crystallizes out of the amorphous, as-deposited material at $T_{cal} = 523$ K, as evidenced by the XRD results (Figure S2). Two, calcining to higher temperature tends to increase the crystalline domain size, which is also indicated by the sharpening of the XRD peaks (Figure S2) and substantiated by SEM (Figure S3) for the nanoskins calcined at 673 K and 773 K. The increased crystalline domain size leads to higher conductivity, so long as it does not coincide with dewiring. Therefore, improvement of the conductivity at $T_{cal} = 673$ K is attributed to this film withstanding higher thermal excursions without dewiring due to the larger 70 ± 20 nm thickness compared to thinner films.

Increasing the calcination temperature to 773 K apparently reduces the conductivity of the nanoskin. The micrographs for this film reveal it comprises a distribution of large particles and contains visible bare patches of the fused silica substrate, Figure S3(a). These features indicate electrical dewiring occurs within the film in keeping with its reduced conductivity compared to the nanoskin calcined at 673 K. Physical dewiring in this film is electrically substantiated by the static THz-TDS spectrum, which shows the sign of $\sigma_2(\omega)$ is negative and the magnitude decreases with increasing frequency. This response is characteristic of charge transport that is strongly affected by localization, which may arise from charge scatter at nanoparticulate boundaries formed in the dewired film and is better described by the Drude-Smith model or the localization-modified Drude model.²³ This rationale is a common explanation for the observed changes in $\sigma_2(\omega)$, but, it should be kept in mind that the sign and shape of $\sigma_2(\omega)$ also strongly depend on the measured phase, which can be erroneously affected by differences in the substrate thickness between the sample and bare substrate spots.^{28,29} These localization effects that arise due to formation of nanoparticulates could also explain the statistical difference in the conductivity observed between THz-TDS and four-point probe measurements for the nanoskin calcined at 773 K. Terahertz spectroscopy operates on the picosecond timescale and probes carrier transport over comparatively shorter length scales whereas fourpoint probe measurements require charge transport between physically separated contacts, increasing the likelihood that detrimental film discontinuities are encountered that lead to reduced conductivity.²³

Note that all of the 70 \pm 20 nm films exhibit conductivity consistent with free charge carriers over the entire range of calcination temperatures. We attribute the observed Drude-like behavior as arising from the fabrication of thicker, 70 \pm 20 nm, films, which sustain film contiguity at each calcination temperature. These nanoskins do not, however, necessarily meet all the qualifications to classify them as metallic by THz spectroscopy. Clearer distinctions can be made between the set of nanoskins from the TRTS results which follow.

c. Time-Resolved Terahertz Spectroscopy

Each of the calcined nanoskins and the sputtered film were also studied by TRTS to measure the time-dependent change in conductivity following 400 nm excitation (Figure 3) and 800 nm excitation (Figure S5). The percent change in THz transmission, $\Delta E/E_0$, measured at the peak of the THz probe waveform is shown in Figure 3. In general, the measured changes in ΔE relate to the change in conductivity that occurs following photoexcitation according to equation (4). These changes in conductivity are also related to the charge-carrier density, N, and mobility, μ , at low frequency (direct current, DC, conductivity) by the relation $\sigma = eN\mu$, where e = electron charge. Therefore, the sign of ΔE indicates the change in conductivity resulting from photoexcitation and arises either from changes in N or μ (or both) following photoexcitation.

In our experience, semiconductor materials undergo large increases in N following photoexcitation of the band gap transition given by the laser fluence, sample absorbance, and free carrier photogeneration efficiency, which in turn results in large increases to the conductivity ($\Delta E < 0$).^{22,30,31} These increases in N can be on the order of 1×10¹⁵ photons/cm³ to 1×10¹⁸ photons/cm³ in TRTS experiments and therefore typically dominate the observed sign of ΔE . However, observation of $\Delta E < 0$ does not necessarily identify the studied material as a semiconductor. This same sign change could be observed in the limit of small changes in N if photoexcitation leads to increases in carrier mobility via thermally activated electron transport.³² For metallic materials, photoexcitation of an intraband transition, as in the s/p band of gold, does not produce a change in N. Rather, lattice heating is generated through electron–phonon coupling which generally increases carrier scattering and reduces the mobility.^{33,34} This interaction leads to decreased conductivity and $\Delta E > 0$.¹⁸

The responses displayed in Figure 3 are therefore associated with changes in the conductivity and are related to these processes according to equation (4). It is notable that the nanoskins calcined at \leq 473 K exhibit $\Delta E < 0$, indicating *increased* conductivity following photoexcitation, while the sputtered film and the nanoskins calcined at > 473 K yield $\Delta E > 0$, indicating *decreased* conductivity. We associate the progression in ΔE from negative to increasingly positive values with the transformation of the initially deposited material from a weakly conductive, "amorphous" RuO₂ to the highly conductive, crystalline, rutile form of RuO₂ that is generated upon calcining to higher temperatures. The TRTS measurements on the high-temperature calcined nanoskins and on the sputtered film are consistent with RuO₂ in these films exhibiting the intraband electronic transition expected of a metal. Although excitation at 400 nm could potentially directly excite an interband transition leading to a change in carrier density, the spectra in Figure 3, especially for the metallic nanoskins with T_{cal} > 473 K, are dominated by the intraband transition in metallic rutile RuO₂. This assignment is supported by parallel experiments on the same samples using 800 nm excitation, which is well below the interband pto-d transition in rutile RuO₂ and shows the same trends as with 400 nm excitation (Figure S5).



Figure 3: TRTS measurements of the time-dependent percent changes in THz transmission, $\Delta E/E_0$, following 400 nm excitation at room temperature for the 20 nm thick sputtered RuO₂ film (scaled by a factor of 1/4 for clarity) and 70 ± 20 nm thick RuO₂ nanoskins calcined at temperatures from 373 K to 773 K.

The time-dependent dynamics in $\Delta E/E_0$ for each of the films exhibit a fast, instrument-limited rise followed by subsequent decays. Each signal has a long-lived component with lifetime much greater than the 50 ps timescale of our experiment. Some films however also exhibit a markedly fast initial decay with lifetime ca. 1 ps to 2 ps that makes a small contribution to the overall magnitude at early delay times. For the metallic-like films with $\Delta E > 0$ (the 20 nm thick sputtered film and the 70 ± 20 nm thick nanoskins with $T_{cal} \ge 523$ K), the instrument-limited rise is associated with the electron–phonon coupling time. In most metals, photoexcitation of an intraband transition and the electron–phonon coupling process that leads to lattice heating occurs in less than a picosecond and therefore occurs beyond our time resolution.³⁵ The system is already prepared in a state that has undergone lattice heating with reduced conductivity at our earliest detectable delay times. The subsequent longer-time dynamics are associated with heat transfer and equilibration with the surroundings. This longer delay could arise due to heat transfer out of the probed film region and equilibration with the unexcited part of the film and/or equilibration with the substrate.³⁶

Although $\Delta E/E_0$ is negative for the nanoskins calcined at ≤ 473 K, the time-dependent dynamics are very similar to those just discussed. They also consist of a fast, instrument-limited rise followed by subsequent decays and the persistent response. For $T_{cal} = 473$ K, only the persistent response with $\tau >> 50$ ps is observed, while for $T_{cal} = 373$ K, an additional 1 ps to 2 ps initial decay is evident. In both cases, the instrument-limited rise is due to placing the nanoskin in a state of increased conductivity at earliest delay times following photoexcitation. The origin of increased photoconductivity is due to either an increase in charge carrier density and/or an increase in charge carrier mobility.

In the case of the former possibility, population dynamics, carrier transport, or carrier cooling could all contribute to the subsequent observed dynamics.^{37–39} Alternatively, the lattice heating effect could also lead to improved mobility in localized or weakly localized metals where transiently heating the sample could provide energy necessary to overcome a barrier to charge transport.³² In this case, the subsequent dynamics would also be controlled by heat transfer and depend on the temperature equilibration of the film with its surroundings, similar to that described for the metallic films. More detailed studies are needed to definitively assign the mechanisms responsible for the long-lived dynamics and are beyond the scope of this paper. We are more focused on the meaning of sign changes in ΔE following photoexcitation that distinguish the thicker nanoskins (i...e., 70 ± 20 nm rather than \leq 30 nm) calcined above and below 523 K.

The sign of ΔE is also indicated by measuring the THz probe waveform at a particular pumpprobe time delay, as shown in Figure S6. If $\Delta E < 0$, the measured phase amplitude will be inverted compared to the unexcited waveform. This inversion was observed for the nanoskin with T_{cal} = 473 K, Figure S6(a), at a pump delay of 10 ps. Conversely, for the nanoskins with T_{cal} > 473 K and the sputtered film (see Figures S6(b) and S6(c), respectively) the amplitude sign and phase of ΔE is the same as for the unexcited film. These waveforms were also Fourier transformed to produce frequency-dependent real and imaginary parts of the conductivity spectra for the sputtered film and nanoskins with T_{cal} = 473 K and 773 K following 400 nm photoexcitation (Figure 4). The differential response for the real conductivity, $\Delta \sigma_1(\omega)$, is negative across the detected frequency range for the metallic nanofilm (T_{cal} = 773 K) and sputtered film which further reflects that $\Delta E > 0$ (reduced conductivity). The opposite occurs for the nanofilm calcined at 473 K indicating increased conductivity following photoexcitation. Although the differential frequency-dependent spectra, $\Delta\sigma(\omega)$, are seemingly significantly changed due to the change in sign, they represent only ca. 2% change and the actual spectral characteristics of the photoexcited films, $\sigma^{p}(\omega)$, remain mostly the same as the unexcited films. The photoexcited films can therefore be classified under the same Drude or modified Drude models as discussed above to interpret the THz-TDS data.



Figure 4: Changes in the frequency-dependent photoconductivity, $\Delta\sigma(\omega)$ following 400 nm excitation at room temperature for the RuO₂ nanoskins calcined at (a) 473 K (b) 773 K and (c) 20 nm thick sputtered film.

The real conductivity determined from THz-TDS and TRTS for the nanoskins and sputtered RuO₂ film is summarized in Table 1. This Table shows that despite the small change in the conductivity of the nanoskins by photoexcitation, information about the temperature coefficient of resistivity and the metallic nature of the films is still accessible. Assuming bulk values of the density and heat capacity of rutile RuO₂ and known experimental parameters (excitation fluence, pump beam diameter, and pump beam absorption), the temperature jump resulting from photoexcitation is estimated to be ≈ 11 K for the metallic (nanoskins calcined at > 523 K) and ≈ 13 K for the sputtered, metallic film.⁴⁰ At these modest temperature jumps, the

resistivity is expected to depend linearly on temperature and have a positive temperature coefficient (TCR > 0) for metallic samples.⁴¹ In our experiment, the temperature is controlled by laser power and the measured ΔE is linear with respect to this parameter (Figure S7). The metallic RuO₂ films have a negative slope, indicating the conductivity decreases with temperature and TCR > 0. Conversely, the T_{cal} = 473 K nanoskin has a positive slope and TCR < 0. Of all the nanoskins, the 773 K-calcined nanoskin shows the biggest decrease in conductivity with photoexcitation (laser-induced heating). This photo-induced suppression of conductivity presumably arises because this film has the greatest rutile RuO₂ character (particles with largest crystalline domain size) while σ (TDS) is lower due to dewiring of the film as through-film contiguity is disrupted upon particle ripening at the highest calcination temperature.

Table 1: Summary of the frequency-averaged static conductivity, σ (TDS), and changes in the frequency-averaged conductivity, $\Delta\sigma$ (TRTS), determined from measurements of ΔE and E_0 measured at the probe waveform peak following 400 nm excitation of nanoskin and sputtered samples.

Calcination	(AFM)	(THz-TDS) ^b	(TRTS) ^c
Temperature ^a	Thickness / nm	σ / S·cm ^{−1}	$\Delta\sigma$ / S·cm ⁻¹
373 K	73 ± 8	330 ± 42	+4.0 ± 0.2
473 K	73 ± 17	630 ± 150	+8.8 ± 0.6
523 K	78 ± 13	600 ± 100	-0.9 ± 0.6
573 K	61 ± 15	590 ± 150	-4.8 ± 0.6
673 K	72 ± 23	1030 ± 330	-8.3 ± 0.4
773 K	75 ± 16	500 ± 100	-12.5 ± 0.9
Sputtered ^d	20	5450 ± 160	-269 ± 5

^a Nanoskin (70 \pm 20 nm-thick) samples prepared by nonaqueous solution deposition; sputtered rutile RuO₂ prepared as a standard.¹⁵

^b The error bars reflect the point-to-point deviation across the THz spectrum and the thickness variation determined by AFM measurements.

^c Measurements of $\Delta E(\text{peak})$ were averaged from 40 ps to 50 ps time delay and applied to equation (4) to generate σ^{p} ; $\Delta \sigma$ (TRTS) was determined by subtracting σ (THz-TDS). The error bars indicate the standard deviation of the average.

^d Thickness measured by a quartz crystal balance. The error bars in conductivity for this film represent the standard deviation of the THz spectral conductivity (THz-TDS) and time-dependent conductivity from 40 ps to 50 ps time delay (TRTS).

Conclusions

Previous RuO₂ nanoskins less than 30 nm thick fabricated by solution-deposition methods were characterized as weakly localized conductors when heated to T_{cal} < 473 K.¹⁶ Heating to higher

calcination temperatures improves the film conductivity by generating X-ray–observable, crystalline, rutile RuO₂ but also eventually leads to dewiring and reduced conductivity when calcined at even higher temperatures. In this work, we deliberately fabricated thicker, 70 \pm 20 nm films and used static and time-resolved THz spectroscopy to evaluate the photoconductive properties as a function of calcination temperature between 373 K and 773 K.

The synthesis of thicker films improved our ability to probe the conductivity of the solution deposited nanoskins in two ways. One, nanoskins calcined at the lowest temperature show complex conductivity characteristics consistent with free charge carriers according to the Drude model. Two, the thicker films maintain contiguity at higher calcination temperatures, even after coarsened RuO₂ nanoparticles are formed. This retention of through-film contiguity allows conductivity to be measurable in the high-temperature calcined films such that the metallic classification can be made for nanoskins with $T_{cal} \ge 523$ K. This conclusion was clearly demonstrated by the TRTS results, which indicated that the nanoskins with $T_{cal} \ge 523$ K undergo reduced conductivity ($\Delta E > 0$) upon photoexcitation, consistent with a metallic classification with TCR > 0. This behavior could not be probed in our earlier study of ≈ 20 nm thick nanoskins because they dewired and became highly resistive for $T_{cal} > 473$ K.

It is interesting that the nanoskins calcined at T_{cal} < 473 K do not show fully metallic characteristics even though they exhibit Drude-like behavior. To reiterate, TRTS measurements following photoexcitation of the nanoskins with $T_{cal} \leq 473$ K show *increased* conductivity ($\Delta E <$ 0) while the nanoskins with T_{cal} > 473 K show *decreased* conductivity (ΔE > 0) upon laserinduced heating. This behavior is associated with the phase transformation from an insulating (localized conductor) to a metallic material that occurs within the nanoskins when calcined at increasing temperature. Previous studies^{7,10,11} show that rutile RuO₂ is not generated until T_{cal} = 523 K and here we have shown that further increases in T_{cal} lead to larger RuO₂ crystallites (SEM and XRD) resulting in greater metallic character and larger TCR (progression in TRTS $\Delta E/E_0$ response to larger values with increasing T_{cal}). More material characterization and identification is needed, however, to determine whether the observed TRTS response of nanoskins with $T_{cal} \leq$ 473 K is controlled by changes in charge carrier density or mobility. All together, we demonstrated improved conductive performance of solution-deposited nanoskin films deposited to 70 ± 20 nm thickness. Although the sputtered rutile RuO₂ film still exhibits superior optical and conductive properties, the solution-deposition technique could offer a less expensive means to fabricate metallic thin films using RuO₂ as an alternative material, particularly for flexible, transparent electronics.

Supporting Information

See **Supporting Information** with atomic force microscopy images and height profiles (Figure S1), grazing-incidence X-ray diffraction (Figure S2), and scanning electron microscopy images (Figure S3) of the nanoskin samples. THz probe waveform scans transmitted through the nanoskins compared to the blank substrate (Figure S4), TRTS measurements of $\Delta E/E_0$ using 800 nm excitation for the sputtered film and nanoskins with $T_{cal} = 473$ K and 773 K. (Figure S5), THz probe waveform scans transmitted through the photoexcited and non-photoexcited samples for the sputtered film and nanoskins with $T_{cal} = 473$ K and 773 K (Figure S6), Excitation power dependence of measured $\Delta E/E_0$ for the nanoskins with $T_{cal} = 473$ K and 773 K (Figure S7).

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