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Transient Optical and Terahertz Spectroscopy of Nanoscale Films of RuO₂

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Abstract

Solution-deposited nanoscale films of RuO₂ (“nanoskins”) are effective transparent conductors once calcined to 200 °C. Upon heating the nanoskins to higher temperature the nanoskins show increased transmission at 550 nm. Electronic microscopy and X-ray diffraction show that the changes in the optical spectrum are accompanied by the formation of rutile RuO₂ nanoparticles. The mechanism for the spectral evolution is clearly observed with ultrafast optical measurements. Following excitation at 400 nm, nanoskins calcined at higher temperatures show increased transmission above 650 nm, consistent with the photobleaching of a surface-plasmon resonance (SPR) band. Calculations based on the optical constants of RuO₂ substantiate the presence of SPR absorption. Sheet resistance and transient terahertz photoconductivity measurements establish that the nanoskins electrically de-wire into separated particles. The plasmonic behavior of the nanoskins has implications their use in a range of optical and electrochemical applications.

Introduction

Thin-film ruthenium dioxide (ruthenia, RuO₂) has emerged as a useful material for a variety of electrochemical applications[1,2] including as an electrocatalyst for oxidation of water, chloride,[3,4] and when functionalized with Pt nanoparticles, methanol.[5] More recently, RuO₂ films have received considerable attention as a transparent conductor material.[6–10]

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The scarcity and high cost of ruthenium have motivated the development of RuO₂ thin-film preparation by various approaches, including sol–gel synthesis, metal–organic chemical vapor deposition, and magnetron sputtering,[6,11–17] in order to maximize the active form of this material while minimizing weight loading.

One such process, developed by Rolison and coworkers, employs a low-temperature solution-phase deposition of ultrathin films of disordered, nanometric RuO₂ (“nanoskins”). [13,12] This fabrication method was first reported on 3D substrates (silica aerogels[18] and silica fiber paper[13,12]) and then adapted to produce conformal, electrically conductive coatings on planar substrates at ~10 nm per deposition cycle ($n\times$).[19] The electrical, electrochemical, and optical properties of RuO₂ nanoskins are sensitive to film thickness and calcining temperature, which changes the morphology and crystallinity of the films. The as-deposited films are amorphous[13] and oxygen deficient.[19] While this disordered form of RuO₂ reaches maximum electrochemical capacitance after calcining at 150 °C, it achieves its highest electronic conductivity after calcining at 200 °C.[12,13] The nanoskins are less metallic than sputtered RuO₂ films of similar thickness as substantiated by their higher sheet resistance, lower four-terminal DC conductivity, and because the real component of their optical permittivity is positive,[19] not negative as for rutile RuO₂. [20]

The optical extinction of the nanoskins is flat, near 0.1 OD per ~10-nm layer, and extends from the visible to microwave wavelengths.[9] Chervin, *et al.* demonstrated that RuO₂ deposited on SiO₂ fibers visibly bleaches when calcined at or above 250 °C, turning from black to pale green; this optical signature is accompanied by growth of nanocrystalline RuO₂ and disruption of the electrical connectivity within the film.[13,12] The steady-state optical spectra of $3\times$ -RuO₂ nanoskins (~30-nm thick) deposited on planar substrates evolve with calcination temperature from featureless for nanoskins heated at 200 °C to development of an increased transmission near 550 nm upon heating to 250 °C, giving rise to the green color. In this study, we use transient optical spectroscopy and time-resolved terahertz spectroscopy (TRTS) to determine the origin of this spectral evolution in particularly thin (~20 nm) RuO₂ nanoskins. Because plasmonic forms of RuO₂ and other metal oxides have been reported,[21,22] we specifically use these methods to determine if plasmonic phenomena lead to the spectral evolution.

Experimental

Nanoskin Fabrication and Characterization

Ruthenia nanoskins were deposited onto planar SiO₂ substrates (GM Associates, Inc. fused silica)[23] using a sub-ambient temperature, solution-phase deposition procedure as described previously.[12,13,19] Ruthenium tetroxide (RuO₄) is extracted from a 10-mL aqueous solution (STREM chemicals, 0.5%)¹ with two 15-mL aliquots of petroleum ether at dry ice/acetone temperature. **Hazard Warning:** The RuO₄ precursor is a strong oxidant, highly volatile, and toxic and should always be handled in a fume hood with appropriate personal protective equipment. The cold organic RuO₄ solution is gently warmed in an aqueous-ice water bath for 2 min and then decanted over the SiO₂ substrate(s) and allowed to warm to room temperature under ambient conditions for several hours. The RuO₄ thermally decomposes to RuO₂ and O₂(g) forming a ~7–10 nm thick layer of disordered

RuO₂ on the substrate. In this case, three-layer (3×) films with total thickness ~20 nm (determined *via* atomic force microscopy) were deposited and calcined in a furnace under static air at the indicated temperature (100 – 500 °C) with a 3 hour dwell time and 3 °C min⁻¹ heating and cooling ramps.

Parallel studies were carried out for 20-nm-thick RuO₂ films fabricated by room-temperature DC reactive sputtering from a ruthenium target in an Ar/O₂ mixture as described in more detail elsewhere.[19] Additionally, a 8-nm-thick gold film was prepared by electron beam sputtering onto a GM Associates quartz substrate.²³

Grazing-incidence X-ray diffraction scans were collected with a Rigaku SmartLab X-ray diffractometer²³ in parallel-beam mode using a scintillating detector and fixed CuK α radiation ($\lambda = 1.5406$ nm). The incident-beam grazing angle was set to 0.5° and the goniometer was operated in a continuous mode with 0.02 2 θ step size and 1-s dwell time. Scanning electron microscopy (SEM) was performed using a LEO Supra 55 field-emission microscope. Four-point sheet resistance measurements were conducted using a contact probe apparatus which yields average resistance values from several measurements of each sample.

Steady-State and Time-Resolved Visible to Near-Infrared Spectroscopy

Steady-state, visible to near-infrared transmission spectra were measured on Perkin Elmer Model Lambda 2 and 870 spectrometers²³ with 2 nm resolution and are reported with the substrate contribution subtracted. Picosecond transient absorption studies were carried out with visible excitation (400 nm) and white-light probe pulses. Visible-probe measurements were made using a high repetition rate regenerative amplifier (Coherent RegA 9000)²³ that provides a 100-kHz train of 130-fs, 6- μ J pulses centered at 800 nm. The reflected pulses from a 50% beamsplitter are focused into a beta-barium borate (BBO) crystal to generate 350-nJ excitation pulses at 400 nm. The transmitted pulses generate a white-light supercontinuum in a 5-mm-thick sapphire window. A computer-controlled delay stage varies the time delay between probe and excitation pulses and a chopper modulates the excitation pulse train. An off-axis parabolic reflector (e.f.l. = 100 mm) achromatically focuses the probe pulse into the sample and a lens (f.l. = 150 mm) focuses the excitation pulse into the sample at a small angle to the probe. After interrogating the sample, the probe pulses are analyzed by a 1/8th meter monochromator configured to give about 1 nm resolution. A photomultiplier tube connected to a lock-in amplifier detects the modulated probe pulses. A LabVIEW²³ program controls the delay stage, measures the differential transmission, and calculates a differential extinction at each time point in a scan. Error bars for the optical densities (A) shown in each trace below were obtained from the standard deviation of 10-scan averages yielding uncertainties on the order of 1%.

Time-Resolved Terahertz Spectroscopy

Time-resolved terahertz spectroscopy (TRTS) and time-domain spectroscopic (TDS) data were collected using a 1 kHz femtosecond laser system (Coherent Mira and Legend).²³ For TRTS measurements, the amplifier output (800 nm, ca. 1.6 mJ/pulse and 40-fs FWHM) is split into three computer-controlled delay arms for generation of THz probe pulses, 400-nm excitation pulses (ca. 20 to 40 μ J/pulse focused to ca. 2-mm diameter spot size on the fixed

position sample), and weak 800-nm gate pulses for electro-optic detection of the THz probe. A 1-mm-thick ZnTe (110) crystal generates the THz probe pulses and a 2-mm-thick ZnTe crystal mixes the gate and probe pulses for electro-optic detection. Electric-field information contained within the transmitted THz probe pulse is encoded in the 800-nm gate pulse by the electro-optic detection system and collected by a pair of balanced silicon photodetectors.[24] An optical chopper synchronized to the laser output modulates the excitation pulse train at 167 Hz and a digital lock-in amplifier measures the excitation-dependent change in the THz transmission (T). TDS probe pulse only measurements were conducted in standard fashion (9-mm diameter collimated beam) by collecting nine probe pulse sweeps with averaging and comparing samples with nanofilms to a single substrate scanned before each sample.

To measure TRTS decay dynamics, we scan the delay between the excitation and probe pulse, keeping the delay between the gate and probe pulses fixed at the position that gives the maximum electro-optic response. An increase in THz transmission after excitation corresponds to a decrease in photo-induced conductivity while a decrease in transmission indicates increased conductivity. To unambiguously determine the sign of T/T , we calibrate the lock-in amplifier phase using the known decreased transmission response from a lightly doped Si wafer. Each TRTS trace is an average of 10 scans of the excitation delay. Similar results were obtained when using lower power 600-nm and 800-nm excitation pulses (data not shown).

Results and Discussion

Steady-State and Transient Visible Spectroscopy

As mentioned above, the visible extinction spectrum of RuO₂ nanoskins evolves with calcining temperature. Figure 1a shows the steady-state extinction spectrum of the films prepared for this study. The formation of a dip in the spectrum centered at 500 nm gives rise to the green color of the nanoskins. The spectra also suggest the formation of a broad absorption band centered near 850 nm, but the spectra are complicated by the flat, broad absorption of the nanoskins calcined at lower temperatures.

To further explore the evolution of the visible spectra with calcining temperature, we use transient absorption spectroscopy. Because the curvature of the steady-state spectra remains constant near 400 nm, we use 400-nm pulses to excite the RuO₂ nanoskins. The excitation pulse induces a small (<25 °C, estimated from the absorption coefficient, pulse energy, and heat capacity of other tetravalent metal oxides) temperature change in the nanoskin and a probe pulse interrogates the transmission of the sample after a variable time delay. Figure 1b shows the responses of three representative nanoskins probed at 600 nm and their evolution with time. Each nanoskin shows increased extinction (decreased transmission) that we associate with a temperature-induced change in the optical constants of the nanoskin. Films calcined at other temperatures up to and including 500 °C also show this response (see SI).

We emphasize that the effect of this small temperature jump is quite different from that of the high-temperature calcining. That the response of the nanoskins is zero before excitation shows that there is no residual response from the previous excitation pulse (10 μ s duty cycle). The heat introduced by the laser pulse dissipates in no greater than 10 μ s and the

highest lattice temperatures the nanoskins reach are much lower than even the lowest calcining temperature, 100 °C. The first tens of ps after excitation show a rapid decay that we surmise arises from diffusion of heat away from the excitation volume of the pump pulse. Afterward, the slow decay we observe is consistent with lattice cooling measured in other thin films.[25] To better examine the spectral evolution of the nanoskins, we construct transient spectra by measuring the response of the nanoskins at various probe wavelengths.

The transient visible spectra of 3×-RuO₂ nanoskins calcined at 200 °C show increased extinction across the visible spectrum 25 ps after excitation at 400 nm (Fig. 1(c)) while those calcined at 250 °C, the same temperature at which the transmissive feature appears in the steady-state spectra, show decreased extinction at probe wavelengths longer than 650 nm. Although omitted from Fig. 1(c) for clarity (see Supplemental Information), the excitation-dependent dynamics of films calcined at 100 °C resemble those calcined at 200 °C in that they exhibit transient absorption increases across the visible. The signals for films calcined at 400 and 500 °C are similar to those calcined to 250 °C and 300 °C in that they also exhibit a transient bleach (increased transmission or decreased absorption).

The negative transient extinction at longer visible wavelengths strongly suggests that calcining at higher temperatures leads to a new absorptive feature that bleaches upon excitation at 400 nm. Because single-crystal ruthenium dioxide is metallic and has a negative real part of the permittivity in the visible spectral region ($\epsilon_1 = -2$ near 1.5 eV or 800 nm), [11,16,19,22,26] we ascribe the negative transient response to photobleaching of a localized surface plasmon band (LSPR) in RuO₂ nanocrystallites.

Figure 1d shows the time evolution of the response of several nanoskins probed at 700 nm after excitation at 400 nm. The film calcined at 200 °C exhibits a response similar to its response at 600 nm, but the films calcined at higher temperatures clearly show a negative response with similar time-dependent behavior. This negative response is consistent with the response of other metallic nanostructures with LSPR bands, where lattice heating induces photobleaching. If the prevalent effect of the heating is stronger damping, the damping broadens the LSPR band, increasing absorption in the wings and decreasing absorption near the center of the band, as observed for Au.[27,28] In some cases, the band can redshift (if ϵ_1 is temperature sensitive), which will result in a bleach to the blue and an absorption to the red as observed for Ag.[28] In either case, the result is a negative signal near the center of the LSPR band. Because our instrument only measures transient signals between 450 and 800 nm, we cannot measure the response of the nanoskins in the near infrared, where the sign of the signal would reveal whether the LSPR band is shifting or broadening.

Structural Evolution and DC Conductivity of RuO₂ Nanoskins

The structural evolution of the nanoskins with calcining at and above 250 °C supports our assignment of the transient bleach to a LSPR. Characteristic rutile X-ray diffraction peaks appear (Fig. 2(a)) and these features sharpen and become more intense at higher calcining temperature, indicating that the nanoparticles within the film become more crystalline. The average crystallite size, calculated from the full-width half-maximum of the (110) reflection using the Scherrer formalism, increases with increasing calcination temperature: 11.5 nm for 250 °C and 13.8 nm for 300 °C. Scanning electron microscopy (Fig. 2(b–d)) also confirms

that the particles within the nanoskin coarsen at higher calcination temperature. The formation of metallic, rutile RuO₂ nanoparticles in the films measured here coincides with a drastic reduction in object conductivity, as has been reported for ruthenia nanoskins deposited on other substrates.[13,12] The film calcined at 100 °C has a sheet resistance of 6.4 kΩ/sq measured by four-point conductivity. Upon calcining to 200 °C, the sheet resistance drops to 0.8 kΩ/sq, but the nanoskins become highly insulating (>1 MΩ) after calcining to 250 °C or above. This dramatic loss in conductivity suggests that the samples electrically de-wire on a macroscopic scale, while the XRD results show that the crystalline character is preserved. We take this as evidence that the films comprise electrically isolated RuO₂ nanoparticles.

The spectral position of the transient bleach observed matches predictions for the location of RuO₂ LSPR bands. Traveling surface and bulk surface resonance phenomena have been recently studied for crystalline and near-crystalline RuO₂ films,[22] and so we use the optical constants established for crystalline RuO₂ to predict the characteristics of possible LSPR bands. The condition required for a localized surface resonance plasmon band for a sphere is $\epsilon_1 = -2\epsilon_m$, where $\epsilon_m (= n_m^2)$ is the dielectric constant of the surrounding medium, [29] which we previously determined is ~2 near 800 nm for amorphous RuO₂. [19] For crystalline RuO₂, [19,22,26] $\epsilon_1 = -2$ near 1.70 eV, which suggests that nearly spherical metallic RuO₂ nanoparticles in air should have an LSPR at ~1.7 eV or near 730 nm, in the vicinity of the transient bleach we observe. The LSPR band is shifted red due to the dielectric constant of the surrounding medium and because of the distribution of particle shapes.

Figure 3 shows the calculated spectrum of RuO₂ nanospheres (black line), assuming the surrounding medium is the amorphous RuO₂ so that $\epsilon_m = n^2 \sim 4$ and using the optical constants reported by Hones, *et al.*, [20] as described in more detail in the supporting information. The band is quite broad because of the large imaginary permittivity. The thermally ripened RuO₂ nanocrystallites are not spherical but rather form as irregularly shaped particles (Fig. 2(b–d)), as has been previously observed for unsupported, cryogenic RuO₂ nanoparticles prepared from similar RuO₄ precursors.[30] A distribution of shapes and sizes for aspherical RuO₂ nanoparticles broadens and shifts the LSPR to longer wavelengths to satisfy changes in the resonance condition with changes in particle shape and size. With increasing aspect ratio for ellipsoids, the geometry factor G increases ($\epsilon_1 = -G\epsilon_m$) [29], shifting the LSPR band to longer wavelengths (Fig. 3, red). The distribution of particle shapes in the nanoskins leads to a smearing of the spectrum we observe. The blue edge of the band is sharper because the transverse band does not shift as much, which may account for the decreased extinction and increased transmission in the steady-state spectra near 550 nm that gives the films their green appearance.

Terahertz Spectroscopy

Time-domain (TDS) and time-resolved terahertz spectroscopy (TRTS) measurements were performed on the films to provide additional information on the low-frequency conductivity as a function of calcining temperature and to further characterize inherent material property changes pertinent to the visible transient absorption observations. The TDS results, tabulated

in SI, indicate that the spectrally averaged (0.5 – 2 THz) absorbance is about 0.15 OD for the 200 °C film and is much less (<0.05 OD) for all films calcined at other temperatures. Since lower dc conductivity results in weaker absorption, these results agree with our observation that the 200 °C film has the lowest sheet resistance (0.80 k Ω). While the absorption and conductivity increase after heating from 100 °C to 200 °C without any change to the XRD, upon calcining to 250 °C or above, the ~20 nm films break apart and lose sheet conductivity as previously observed for nanoskin-coated silica paper.^{11,12}

Time-resolved THz spectroscopy gives a measure of the excitation-dependent conductivity (photoconductivity) of the sample but is also sensitive to the steady-state THz absorption. After 400-nm excitation of 3 $\times$ -RuO₂ nanoskins calcined at 100 °C and 200 °C, the TRTS transmission decreases (T/T is negative; Fig. 4a), indicating that conductivity increases upon excitation, which is consistent with poorly conducting metallic films, where heating activates electron transport,[31] or with semiconductors, where the excitation pulse generates carriers.[32] For the films calcined to higher temperatures, the transient THz response is weaker; after calcining at 250 °C or higher, the films show no change in their THz transmittance after excitation. Because XRD shows that the higher temperature films contain metallic RuO₂, the TRTS of metal films is an important point of comparison. In good conductors like metals[33] and graphene[34], the excitation pulse transiently heats the sample, which increases the electron–phonon scattering rate thereby reducing the conductivity of the metal and increasing its THz transmission. The increased transmission expected for metallic films is demonstrated by the observations for a sputtered, 20 nm thick, high conductivity, metallic RuO₂ film and a 8 nm gold film prepared by electron-beam sputtering shown in Fig 4b.

Because the high-temperature nanoskins contain metallic, rutile nanoparticles, we expect a TRTS response similar to that for metals. The high-temperature nanoskins are already nearly completely transmissive to the THz probe pulse, and so we do not observe the increase in transmission we expect. We take this as further evidence that the nanoskins evolve from a disordered, somewhat poorly conducting film (negative T/T) to a structure containing electrically de-wired metallic nanoparticles (zero T/T) with increasing calcining temperature. We note that X-ray fluorescence measurements show that the RuO₂ in 100 and 200 °C-calcined nanoskins may be oxygen-deficient (i.e. are composed of other, non-stoichiometric forms of ruthenium oxide). If these forms are semiconducting, they would give responses similar to those we expect for activated transport in poorly conducting metals. Preliminary results on thicker (50 nm, not shown) nanoskins suggest that they retain DC conductivity and exhibit positive, metal-like TRTS responses upon calcining to 250 °C and above. Further studies of the structure and THz dynamics of RuO₂ nanoskins are underway to determine the origin of the TRTS response for films calcined 200 °C and further describe the changes in electrical properties of RuO₂ induced by calcining. The transient THz results reinforce our assessment the higher temperature films comprise electrically isolated rutile RuO₂ nanoparticles, which is consistent with the XRD results and supports the interpretation of the visible transient bleach in terms of the RuO₂ LSPR.

Conclusion

Our results demonstrate that the properties of solution-deposited RuO₂ nanoskins become more metallic and plasmonic upon calcining to 250 °C or above. A transient bleach observed at wavelengths longer than 650 nm arises from the photobleaching of a broad absorption that we attribute to an LSPR band. The appearance of this feature correlates with the growth of thermally ripened, rutile nanocrystallites, as confirmed by X-ray diffraction and electron microscopy, and is consistent with rutile RuO₂ optical properties. The TRTS measurements show that the nanoskins become less photoconductive when calcined at or above 250 °C, consistent with the development of metallic, rutile nanocrystallites and the appearance of the plasmonic feature. The plasmonic and transparent-conducting properties of the RuO₂ nanoskins treated at temperatures >250 °C are potentially advantageous for a variety of optical and electrochemical applications.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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FIG. 1.

(a) Visible absorption spectra of 3x-RuO₂ nanoskins deposited on fused silica after calcination at 100 °C, 200 °C, 250 °C, 300 °C, 400 °C, and 500 °C. The region accessed by the probe pulse is highlighted in blue. (b) Kinetics of the transient absorption probed at 600 nm for films calcined at 200, 250, and 300 °C as a function of time delay with respect to the 400 nm excitation pulse. (c) Transient visible absorption spectra of the nanoskins from (a) measured 25 ps after the 400-nm excitation pulse. The spectra are normalized for clarity. We measure differential absorption on the order of a few mOD at the wavelengths with the strongest transient response. Error bars represent uncertainties we estimate as the standard deviation of 10 measurements. (d) Kinetics of the transient absorption probed at 700 nm for films calcined at 200, 250, and 300 °C as a function of time delay with respect to the 400 nm excitation pulse.

FIG. 2.

(a) X-ray diffraction profiles of β - RuO_2 nanoskins deposited on fused silica after calcination at 200, 250 and 300 °C. Each scan has been arbitrarily offset vertically for clarity. Peak positions for rutile RuO_2 (110), (101), (200), and (211) are labeled. (b–d) Scanning electron micrographs of β - RuO_2 nanoskins calcined at (b) 200 °C, (c) 250 °C, and (d) 300 °C.

Figure 3.

The measured steady-state extinction of the nanoskin calcined at 300 °C (blue) and the calculated extinction for RuO_2 nanoparticles with varying aspect ratio. As the aspect ratio increases from 1 (black) to 2 (dark red) to 3 (light red), a longer-wavelength band appears in the spectrum.

FIG. 4.

Time evolution of the pump-induced THz transmission change after excitation at 400 nm of (a) RuO₂ nanoskins calcined at the indicated temperatures and (b) a 20 nm sputtered RuO₂ film and 8 nm sputtered Au film. The detected change in transmittance is integrated across the 0.5–3 THz spectrum of the THz probe pulse.