

Switchable Optical Nonlinearity at the Metal to Insulator Transition in Magnesium Thin Films

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ABSTRACT: We report resonantly enhanced and switchable third order nonlinearity in magnesium thin films. Utilizing an optical parametric oscillator as a tunable broadband light source, we find a highly wavelength dependent third harmonic conversion efficiency, exhibiting a 40- to 50-fold signal increase over the investigated wavelength range between 1300 and 1800 nm. We relate this unusually strong increase of the intrinsic magnesium material nonlinearity to resonant sp-interband transitions around 0.7 eV or 1770 nm in the fundamental wavelength range, multiplying their impact on the conversion efficiencies. Moreover, we make use of the drastic change in the optical properties of magnesium at the phase transition between metallic magnesium and dielectric magnesium hydride by in situ hydrogenation. We are able to cyclically switch



the nonlinearity and the efficiency of the third harmonic conversion process. The time-dependence of the nonlinear signal is complex and is a consequence of several contributions, including the hydrogen concentration-dependent change in the intrinsic nonlinear susceptibility, the change in the surface morphology during hydrogenation and dehydrogenation, as well as the volume change of the material. While shedding new light on the structural and morphological changes in such magnesium thin films, we envision that the switchable and large resonant third-order nonlinearity in magnesium will find applications in nanostructured systems, unlocking additional degrees of freedom in design and implementation, such as wavelength dependency and switchable material nonlinearities.

KEYWORDS: nonlinear optics, third harmonic generation, phase transition, magnesium, hydrides

onlinear frequency conversion has been studied in different systems, ranging from dielectrics and metals to semiconductors, in bulk form as well as micro- and nanostructured.¹⁻⁷ Nonlinear plasmonics, that is, the use of resonant metallic structures, has proved particularly useful for optical signal processing,^{8,9} all-optical switching,^{10–12} manipulation of emitted higher harmonic light,^{13–17} optical microscopy,¹⁸⁻²⁰ and surface science.²¹⁻²³ The reason lies with the nearly free choice of structure shape, size, and orientation, and thus tunability of the resonances, polarization properties, enhancement factors, as well as radiation patterns of the plasmonic excitations.²⁴⁻²⁷ Apart from the geometrical properties of such nanostructured systems, the used materials are another degree of freedom, in particular, as the nonlinear conversion takes place inside the material volume.²⁸⁻³⁰ For most applications, the materials used are transparent for the fundamental as well as the converted wavelength, ensuring spectrally flat responses and nearly wavelength-independent conversion efficiencies of the bare material.³¹ This is, for example, true in case of frequency doubling in tunable laser systems where broadband operation is required. Other examples include nanoscale plasmonic nonlinear converters which use gold or similar plasmonic materials in the infrared wavelength range.¹ Additionally, practical applications in most cases require chemically and physically stable systems, severely limiting in situ tunability of the linear as well as nonlinear optical properties. Consequently, the most common plasmonic

material is gold (Au),³² as it possesses favorable optical properties, while other materials have been used as well.^{33,34} In the case of Au, it was in fact recently shown that its absorption associated with transitions between the d- and sp-band results in an increased nonlinear conversion if the energies of the higher harmonic match these absorption bands.^{35–37}

These findings motivate the search for improved material properties. On the one hand, absorptive bands in the fundamental wavelength range would have significantly stronger influence on the nonlinearity. Moreover, for many applications switchable nonlinear properties are highly desirable, which Au cannot offer. Depending on the application, a partial reduction of the intrinsic nonlinearity allows to manipulate the absolute conversion efficiency, while a vanishing nonlinearity is required to switch the nonlinear conversion off entirely, for example, in routing applications. Magnesium (Mg) is a material that, so far, has not been studied as a candidate in nonlinear plasmonics, despite the fact that its reactivity allows to manipulate its optical properties.

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Apart from its apparent application in hydrogen (H_2) storage,³⁸⁻⁴⁰ first investigations show that Mg is a promising candidate for active plasmonics.^{41,42} Interestingly, Mg possesses a strong absorption peak in the near-infrared,⁴³ where resonant sp-sp-interband transitions are probably the cause.

We perform nonlinear spectroscopic measurements on Mg thin films in transmission geometry between 1350 and 1800 nm wavelength, corresponding to the third harmonic (TH) radiated between 450 and 600 nm wavelength. We find that the radiated TH signals do in fact show a dramatic 40- to 50fold increase at the onset of interband transitions, that is, as soon as the fundamental wavelength becomes resonant with interband transitions, resulting in a highly wavelength-dependent nonlinear third order susceptibility of Mg in the near-IR wavelength range. This significant increase for Mg provides additional evidence of the role of interband transitions in the large absolute values of the third order nonlinearity of several metals.

The large reactivity of Mg allows the control of the intrinsic nonlinearity and thus opens up completely new possibilities in realizing switchable nonlinear optical systems. When Mg reacts with H_{22} a phase transition from the metallic Mg to the dielectric magnesium hydride (MgH₂) leads to a drastic change in the optical properties, which is expected to also massively influence the nonlinear response.⁴⁴ Moreover, this metal to insulator phase transition is theoretically nearly fully reversible under oxygen (O_2) exposure, leading to a dehydrogenation of the thin films and a transition to metallic Mg. This cyclic behavior is only limited by experimental constraints and Mg film degradation. We show that indeed the phase transition can be observed in the nonlinear response of the system and thus allows a strong and prominent modification of the nonlinear optical response of the metallic system.

Our experimental setup is sketched in Figure 1a. A 44 MHz repetition rate femtosecond Yb:KGW solid-state oscillator⁴⁵ is used to pump a fiber-feedback optical parametric oscillator (ff-OPO).^{46–48} The tuning range of the ff-OPO signal wavelength extends from 1330 to 1800 nm with an approximately constant pulse duration of about 200 fs. The nearly Fourier-bandwidthlimited pulses show a Gaussian shape with constant spectral width over the entire tuning range. As a compromise between TH signal strength and possible sample damage, the output power of the ff-OPO and thus the incident fundamental intensity at the sample is set to a constant value of 20 mW for all wavelength using a neutral density filter wheel. The ff-OPO signal beam is focused onto the Mg film, and the TH signals generated in the forward direction are collected using a second lens, separated from the remaining ff-OPO signal and finally coupled into a grating spectrometer with an attached chargecoupled device (CCD) for spectrally resolved detection (for further details, please refer to Figure S2 in the Supporting Information). We spectrally integrate the TH spectra and obtain a scalar value describing the overall TH enhancement at each measured wavelength point. These values are then normalized to the TH signal generated at the bare substrate to eliminate all possible wavelength dependences of the setup (filters, detector, fundamental intensity, etc.). The transmitted signal at the fundamental wavelength is coupled out via a beam splitter, and the intensity is measured with a power meter and serves as an in situ reference.



Figure 1. (a) Sketch of the experimental setup, utilizing a tunable broadband fiber-feedback optical parametric oscillator. For details, see the main text. (b) Photograph of the used gas cell with gas inlets and outlets in blue on top. (c) Scanning electron microscopy (SEM) image of the surface of a 25 nm thick Mg film before hydrogenation. The film is composed of single crystallites that cause a rough surface. The scale bar is 200 nm.

The sample is positioned inside a custom-made gas flow cell, as shown in Figure 1b. The cell is connected to a gas mixture system, giving control over the concentration of H_2 in nitrogen (N_2) as well as the flow rate, which in our experiments are 0.2% H_2 in N_2 at a flow rate of 2 l per minute. Also, an air flow with an O_2 concentration of 21% of the same flow rate can be set. The H_2 concentration is significantly below the explosive limit of around 4% in air; in our case it is additionally buffered in N_2 , further eliminating any immediate danger. The samples are fabricated by thermal evaporation on an ultraviolet (UV) transparent glass substrate (Suprasil, Heraeus). The thickness and evaporation rate are checked in situ with a quartz crystal monitor.

In a first step we investigate the spectral dependence of the intrinsic third order Mg nonlinearity. We evaporate a 2 nm titanium (Ti) wetting layer to promote the growth of the subsequent 20 nm thick Mg film. Figure 1c depicts a scanning electron microscopy (SEM) image of the surface of a 25 nm thick bare Mg film. The Mg thin film is composed of single crystallites, which has been reported earlier, 49-52 and can be clearly seen in the SEM image of the Mg surface shown in Figure 1c.41,53-55 This surface morphology is in stark contrast to the commonly studied plasmonic materials such as Au and silver (Ag).⁵⁶ These materials possess a smooth surface and are seemingly amorphous. This unique feature of Mg renders the nonlinear response of these films highly interesting as the structure of the surface is expected to play a major role in the nonlinear light generation process.^{57,58} The influence of surface-to-volume ratios and the morphology of interface has not been investigated in detail.

We first turn to the measurements on TH generation from bare Mg thin films. The measured relative wavelengthdependent TH intensity for Mg is shown in Figure 2a on the left. Tuning the laser from shorter to longer wavelengths, the TH intensity increases nearly exponentially. The largest TH intensity is found at 1800 nm, which corresponds to an energy of 0.7 eV. The TH intensity in the longer wavelength range is about 40–50-fold larger compared to the short-



Figure 2. (a) On the left, the measured wavelength-dependent thirdorder microscopic nonlinearity of a 20 nm thick Mg film (referenced to a blank Suprasil substrate) is shown which increases when tuning the wavelength from 1340 to 1800 nm about 40-fold. On the right, the absorption spectrum is depicted where the maximum at 2000 nm corresponds to 0.62 eV. (b) Sketch of the band structure of Mg. Interband transitions between sp bands below and above the Fermi energy are possible in the blue shaded area with 0.7 eV and can enhance TH processes as photons with sufficient energy can excite electrons to the upper band. The resonant emission of TH photons is illustrated by the blue arrow. (c) Energy diagram of the THG for Mg on the left and Au on the right. The interband transition is resonant with the fundamental wavelength for Mg, whereas it is resonant with the TH for Au.

wavelength end. As previous measurements for Au have shown.^{35-37,59,60} the intrinsic material third-order susceptibility $\chi^{(3)}$ is influenced by interband transitions and therefore possesses a dispersive behavior, however, much smaller absolute changes are observed. Thus, we expect that similar effects are responsible for the observed strong wavelength dependence. Indeed, we find that the increase in TH signal is accompanied by an increase in the linear absorption, as displayed in Figure 2a on the right. The absorption spectrum has been measured ex-situ with a Fourier transform infrared (FTIR) spectrometer (Bruker Vertex 80, equipped with a Hyperion microscope) and is calculated from the measured transmission and reflection spectra. The maximum in absorption occurs at around 2000 nm, a wavelength that cannot be reached with our current nonlinear optical spectroscopy setup. In fact, in Mg interband transitions are possible near the H-point, as illustrated in the band structure diagram in Figure 2b. The energetic splitting between the fully occupied sp band below the Fermi energy and the partially filled sp band above the Fermi energy is roughly 0.7 eV and thus corresponds to the observed maximum in the linear absorption as well as the TH increase. Since the bands are parallel between the H- and the L-point, the transition is associated with significant absorption (for a full band structure diagram, please refer to Figure S1 in the Supporting Information). According to the empirical Miller's rule, originally formulated for second harmonic generation (SHG) yet generalizable for TH, the third order nonlinear susceptibility $\chi^{(3)}(\omega)$ can be estimated as the product of the cubed linear susceptibility $\chi^{(1)}(\omega)$ at the fundamental frequency ω and the linear susceptibility $\chi^{(1)}(3\omega)$ at the TH frequency 3ω :

$$\chi^{(3)}(\omega) \propto [\chi^{(1)}(\omega)]^3 \cdot \chi^{(1)}(3\omega)$$

Consequently, the large linear susceptibility due to the interband transitions at the fundamental wavelength has a significantly stronger impact. This behavior can also be understood intuitively in the photon picture, which is illustrated in Figure 1c. A TH conversion process involves three photons at the fundamental frequency (here shown in red) and one at the TH (shown in blue). Consequently, an increase in the material interaction, that is, absorption at the fundamental frequency for Mg (on the left) is more important for the overall conversion process, as it increases the simultaneous absorption probability of three fundamental photons. In the case of Au (right panel of Figure 2c), the absorption of a photon at the TH frequency is resonantly enhanced due to interband transitions. While this also increases the overall conversion efficiency, the impact is smaller, explaining why earlier work on the enhanced and resonant material nonlinearity in Au reports smaller enhancement factors when compared to the Mg case.^{35-37,59,60} It should be noted that a transition at twice the fundamental frequency has no impact on the overall process as no photon of this energy takes part in the conversion. While second harmonic generation is possible due to the broken symmetry at the boundary,⁶¹ the cascaded process of second harmonic generation with subsequent frequency mixing, which also results in emitted photons at triple the fundamental energy and thus contributes to the measured nonlinear signal, is very unlikely.⁶² We would like to note that, in principle, one can approximate the third-order nonlinearity from the measured

linear optical properties in the entire relevant wavelength range between the fundamental and the higher harmonic.⁶³

As a next step, we will study the H2-dependent third-order nonlinear response of the Mg thin films. Since Mg is a comparably reactive metal, we can easily manipulate the linear response and thus also the nonlinear one. The hydrogenation of Mg leads to a phase transition from metallic Mg to dielectric MgH₂. This metal to insulator transition has two immediate consequences: During hydrogenation, the resonant absorption at the fundamental wavelength disappears almost completely as the sp-sp-band transition in Mg is no longer possible in MgH₂ due to band reorganization. This behavior can be seen in the time evolution of the linear reflectivity spectrum of a Mg thin film during hydrogenation, shown in Figure S3 in the Supporting Information. We also note that the transition is smooth in that no energetic shift of the resonance is observed, only a continuous amplitude decrease, as expected. Consequently, MgH₂ is expected to radiate less TH intensity. Furthermore, it is well-known that the intrinsic nonlinearities of dielectric media tend to be significantly smaller compared to those of metals.³¹ The measurements of the intrinsic Mg nonlinearity shown in Figure 2b show a strong increase toward longer wavelength. We thus choose 1770 nm fundamental wavelength as the working point for our hydrogen-dependent nonlinear measurements. While this guarantees large TH signal strength, it is also the most interesting working point for any application.

In Figure 3, we introduce step by step our H₂-concentrationdependent measurements of Mg thin films. The sample structure is depicted in Figure 3a. The samples consist of a multilayer structure of a 2 nm Ti wetting layer and the 20 nm Mg film, followed by a 2 nm Ti buffer layer and the 5 nm Pd catalytic layer,^{64,65} which facilitates the hydrogenation of the Mg film, on top of a UV transparent substrate (Suprasil, Heraeus). We chose a fundamental wavelength of 1770 nm in the spectral range of largest resonant enhancement. Our setup allows us to simultaneously measure a linear response as well as the third harmonic generation (THG), as sketched in Figure 3a. The linear signal here, in contrast to the FTIR measurement depicted in Figure 2a, is the transmitted fundamental laser intensity and thus offers information on the transmissivity of the sample at this wavelength.

The top panel of Figure 3b depicts the measured timedependent linear transmission of the fundamental light intensity at 1770 nm through the Mg film. An orange shaded background indicates a hydrogen flow of 0.2% O₂ in N₂, while a light blue background indicates an air flow with 21% O₂ concentration. In the beginning, most of the incident light is reflected from the metallic film, and consequently, the transmittance is low. H₂ molecules are split at the Pd layer and diffuse into the Mg layer, successively forming MgH₂, which is a transparent dielectric. We thus observe an increase in transmittance. The hydrogenation takes roughly 20 min. Switching the gas flow to O_2 , the film dehydrogenates, leaving metallic Mg. As expected, the transmittance drops, yet, on a much shorter time scale of a few minutes. The transmittance of the film reaches about the same value after the dehydrogenation as before. The diffusion dynamics and thus the temporal evolution of the transition from Mg to MgH₂ in polycrystalline thin films are very complex and depend on several independent properties, such as the graininess, the material interfaces, and the hydrogenation state of the Mg itself as MgH₂ is a diffusion barrier for hydrogen, rendering its general description and



Figure 3. (a) Sample structure. The thin films consist of a 5 nm thick Pd layer on top of a 20 nm thick Mg layer, separated by a 2 nm thick Ti buffer layer. The Pd layer acts as a catalyst for the splitting of the H_2 molecules and, thus, enables fast hydrogenation of the Mg layer. Another 2 nm of Ti are used as a wetting layer on top of the Suprasil substrate. (b) Hydrogenation of the Mg thin film structure shown in (a). In the upper part the intensity of the transmitted light at the fundamental wavelength of 1770 nm and in the lower part the intensity of the TH signal at 590 nm is shown as a function of time. An orange background color marks the time where the H_2 flow is turned on, a light blue background color marks the time where the O_2 flow is turned on.

modeling an unsolved problem. We note that the time scales for hydrogenation and dehydrogenation observed here are different than the ones reported in earlier work.^{54,66–68} The reason is most likely 2-fold: First, it has been shown that the exact dynamics depend significantly on the individual films and that considerable variation is observed for nominally identical films. Second, and most probably more importantly, the incident laser beam locally heats the sample. Consequently, the hydrogenation is prolonged while the dehydrogenation is accelerated.

The lower panel of Figure 3b depicts the THG response of the film. It has been shown in earlier work that the size of the nonlinear response can be estimated from the linear response.^{69,70} Taking the results of the top panel into account, we expect the TH signal to decrease with increasing transmittance during the hydrogenation as the film becomes less and less metallic and the resonant third order nonlinearity vanishes, leaving the expected smaller nonlinearity of the dielectric MgH₂. Conversely, the TH signal is expected to increase during dehydrogenation as the film transitions back to its metallic state. The measured nonlinear signal strength indeed follows this prediction. The TH signal decreases during hydrogenation, and the signal increases during dehydrogenation. This TH signal change also follows the time scales of the linear measurements. However, we observe one striking difference between this expectation and the measurements:

In the first few minutes, we measure a significant increase in the radiated TH signal. This finding is highly intriguing, as it demonstrates that an additional process of signal generation mechanism has to be present that goes beyond the mere modification of the absolute values of the material nonlinearities, that is, the linear response.

To further investigate this intriguing feature, we have measured the linear and TH response of the sample for subsequent hydrogenation and dehydrogenation cycles. Additionally, we developed a simple intuitive model in order to gain further insight in the origin of the additional TH signal. This data is shown in Figure 4. The fundamental wavelength was fixed at 1770 nm.



Figure 4. H_2 and O_2 cycle measurements for the film shown in Figure 3. The upper row shows the intensity of the transmitted fundamental signal at 1770 nm as a function of time, the middle row shows the intensity of the TH signal at 590 nm as a function of time, and the bottom row shows a remodeling of the nonlinear response based on the linear signal as a function of time with added delta functions to simulate the missing features. An orange background color marks the time where the H_2 flow is turned on, a light blue background color marks the time where the O_2 flow is turned on.

The linear response is shown in the uppermost panel. As for the single cycle shown in Figure 4, the transmittance of the film increases during the hydrogenation, while a decrease can be observed during the dehydrogenation. In general, a decrease in amplitude is visible, for which there may be several reasons. First, full saturation is not achieved because the hydrogenation,

and to a lesser extent the dehydrogenation, become slower after some time. As the hydrogenation and dehydrogenation speeds decline due to sample degradation, for example, due to regions of remaining MgH₂ inside the metallic Mg film, which forms a diffusion barrier for hydrogen, smaller amplitudes are reached. Additionally, possible mechanical degradation of the Mg layer and the palladium layer due to the formation of cracks and defects may also hinder the hydrogenation and diffusion.⁷¹ We suspect that the main reason for the mechanical degradation is related to the volume increase and decrease between the Mg and MgH₂ states.⁷² There are different strategies to try and overcome these issues, for example by alloying Mg with other materials to mitigate the volume increase. Alloying might in fact also help in avoiding or minimizing remaining hydrogenated material in the film. Additionally, it has recently been shown that the hydrogenation in Mg starts at the grain boundaries between the individual nanocrystallites and that the successive hydrogenation of adjacent nanocrystallites limits the overall diffusion speed and thus the switching times.⁵⁴ Tailoring the grain sizes and grain boundaries is thus also a promising route for decreased switching times. Moreover, these measures will result in reduced deterioration of the films and thus are expected to result in a larger number of hydrogenation and dehydrogenation cycles.

At first glance, the nonlinear signal in the same time frame does not seem to show a simple direct correlation. Nevertheless, most features are easily explained. During hydrogenation, the nonlinear intensity decreases during the predominant time, as previously observed and explained by the phase transition. Likewise, the signal increases during most of the dehydrogenation when the film switches back to the metallic state. Furthermore, it is clearly visible that the amplitude generally decreases. For the later cycles, the decrease in signal during hydrogenation and the increase in signal during dehydrogenation are barely identifiable as they are on the order of the noise level. Still, all main features are present that are expected when assuming a direct correlation between the linear and the nonlinear signal as a first-order approximation. As mentioned before, we observe an additional and unexpected feature in the nonlinear signal. The TH intensity not only decreases as expected during hydrogenation, but increases strongly at first, visible as a spike in the nonlinear signal at the beginning of the hydrogenation. Its height is on the order of magnitude of the decrease in signal, and since it does not decrease significantly over time, the spikes become the dominant feature for the last cycles. For these cycles, a strong decrease in the TH signal can also be observed, that is, spikes downward, which point in the opposite direction to the increase due to the phase transition back to metallic Mg.

So far it is unproven whether the TH signal follows, in general, the linear response, that is, whether most of the features can be explained by the linear response alone, which is naïvely expected. Moreover, the nature of the additional feature, appearing as a "spike"-like contribution, is unclear. To determine whether these spikes are the only difference between linear and nonlinear response, a simple modeling of the nonlinear response based on the linear response was performed. Such modeling is frequently applied in nonlinear plasmonic systems and known to be surprisingly accurate.^{29,70} For our model, we assume that the linear and nonlinear signals behave oppositely, that is, if the transmittance increases and thus metallicity decreases, the TH signal diminishes and vice

versa. As a most basic assumption, we thus model the TH signal to scale proportionally to the inverse of the linear signal. At the beginning of each hydrogen flow, a positive spike is added to this curve. Likewise, a negative spike is added at the beginning of each oxygen flow to mimic the observed spikes. The size of the spikes upward and downward is fixed and chosen to best match the nonlinear response. We would like to stress that the added spikes represent therefore an additional signal contribution, which is characterized by a much shorter time scale than the linear transmittance change due to the hydrogenation and dehydrogenation of the Mg film. Due to the simplicity of our model, we only expect qualitative predictions and no quantitative agreement.

The results of our very basic nonlinear model are presented in Figure 4 in the bottom row. When comparing the nonlinear measurement and the nonlinear model, it is evident that the general trend is well described by the model. There are a few smaller additional deviations visible, for example, the measured nonlinear response seems to saturate for the later cycles, whereas the model seems to predict a slight increase. There are several possible explanations for these differences. The degradation of the films, which is visible in the linear response, is suspected to have different consequences for the linear and nonlinear response as, for example, for later cycles, larger amounts of MgH₂ remain in the film, influencing the TH generation more severely. Also, the model uses as few assumptions and free parameters as possible; thus, certain deviations are to be expected. We therefore assume that these spikes are indeed the main difference between the linear and the nonlinear signal. We performed measurement on two additional samples, shown in Figure S4 in the Supporting Information, which confirm our interpretation. Additionally, Figure S5 and the accompanying text discusses and rules our trial measurements artifacts such as pressure spikes. One important point to notice is related to the top Pd and Ti layers. These layers hydrogenate close to instantaneously, as compared to the Mg film. The change in the transmission for the transition from Pd to PdH_x and Ti to TiH_x will slightly increase the fundamental intensity that reaches the Mg film. Yet, this minute effect is significantly too small to account for the observed response and can thus, if any, only be a minor contribution. Another point is related to the nonlinearities of Pd and Ti, in particular, as their transition to hydrides will mute their nonlinearity itself. However, the signal generated by the 5 nm Pd layer and the 2 nm Ti layers is very small, as can be seen in the control experiment shown in Figure S5 in the Supporting Information. Consequently, for simplicity, we have not taken them into account in our modeling of the nonlinear response of the Mg layer in our samples.

This finding underpins that there is indeed an additional contribution that is obviously linked to the linear response during hydrogenation and dehydrogenation of the Mg, but is not merely determined by the change in the absolute value of the nonlinearity due to this linear optical change.

One prominent consequence of the hydrogenation of Mg is a significant volume expansion of about 30% resulting in buckling due to the hydride formation in parts of the film. Recent work has demonstrated that this causes a significant increase in the surface roughness.^{54,55} The largest change in surface morphology, in fact, occurs in the first minutes of hydride formation. Even more striking, during the dehydrogenation, the surface roughness decreases again, yet, does not reach the initial roughness level. This behavior is once more rather intuitive: The film effectively "deflates", recovering in parts the original surface morphology.

Nonlinear optical processes are known to sensitively depend on symmetry and on the properties of interfaces.⁷⁴ Even though THG, in general, is considered a volume effect rather than an interfacial one, the studied films are too thin (in terms of the optical skin depth) to even fully distinguish between these two regimes. We estimate the skin depth in our wavelength range to be on the order of 20 nm, that is, close to the overall film thickness. One would assume that only from thicknesses on the order of several skin depths surface and bulk become well distinguishable. The strong influence of the surface roughness on $\rm SHG^{75}$ and $\rm THG^{76}$ has in fact been shown. We thus suspect that our observed "spike-like" additional signals are caused by the sudden increase in surface roughness. One can also argue that the larger interface gives rise to a larger nonlinear generation "volume". The observed signal dependence would thus be a competition between an increasing TH signal due to an increased surface area and a decrease due to the loss of metallicity and thus the resonant nonlinearity. Conversely, during dehydrogenation, the surface roughness suddenly decreases, resulting in a smaller interfacial volume and thus a decrease in signal. Again, this phenomenon competes with an increase in signal due to an increasing metallicity in the transition from MgH₂ to Mg.

Our nonlinear measurements are therefore offering additional insight into the surface morphology. These measurements are experimental evidence of the importance and influence of surface roughness on the nonlinear properties in such systems. It would be highly intriguing to tailor the surface roughness of Mg films and study the dependence on the signal strength. If properly calibrated, such measurements could serve as all-optical measures of surface morphology.

In conclusion, we have demonstrated that Mg is a promising candidate for complex and tunable nonlinear optical systems. Due to interband transitions between the sp bands, the microscopic third-order nonlinearity is drastically enhanced and reaches relative enhancement factors on the order of 40 to 50. The reason for this dramatic enhancement of the TH intensity are the absorptive material transitions in the spectral range of the fundamental laser intensity. Additionally, we demonstrated a switchable nonlinearity during hydrogenation and dehydrogenation for Mg thin films. Both in the linear and the nonlinear responses, the switching is easily observable. Remarkably, additional spikes pointing in the opposite direction to the naive expectation based on the linear optical properties are observed in the nonlinear signal. We suspect fast changes in surface roughness at the beginning of the hydrogenation and the dehydrogenation to be the reason. First indications point toward a strong influence of the surface roughness on the TH signal. Moreover, the strong TH signal in combination with a high versatility due to the reactivity make Mg a promising material for nonlinear plasmonics.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsphotonics.0c00409.

Full band structure of magnesium and imaginary part of the computed dielectric function; detailed sketch of the nonlinear spectroscopy setup; measured time-dependent reflectivity of a pristine magnesium film to the fully hydrogenated one; linear and nonlinear measurements as well as modeling for additional film; scanning electron microscope images of the measured thin films after the cycling, measured third harmonic spectra of palladium and titanium films (PDF)

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Notes

The authors declare no competing financial interest.

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