Enhanced Nonlinear Optical Response of One-Dimensional Metal-Dielectric Photonic Crystals

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We describe a new type of artificial nonlinear optical material composed of a one-dimensional metal-dielectric photonic crystal. Because of the resonant nature of multiple Bragg reflections, the transmission within the transmission band can be quite large, even though the transmission through the same total thickness of bulk metal would be very small. This procedure allows light to penetrate into the highly nonlinear metallic layers, leading to a large nonlinear optical response. We present experimental results for a Cu/SiO_2 crystal which displays a strongly enhanced nonlinear optical response (up to $12X$) in transmission.

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Metals are known to possess a fast, extremely large, nonlinear optical response. In particular, the third-order susceptibility of the noble metals can be as much as 10^6 times larger than that of fused silica, with relaxation times in the subpicosecond range [1]. However, being nontransmitting for optical radiation, metals have often been dismissed as candidate materials for nonlinear optical interactions. Most previous uses of metals as nonlinear photonic materials have dealt with colloidal solutions of metal nanoparticles [2], glasses doped with metal nanoparticles [1], and granular metal films [3]. It is noteworthy that the optical properties of metallic nanocomposite materials can be quite different from those of bulk metals. For instance, it has been shown that discontinuous metal-dielectric composites behave as saturable absorbers, whereas continuous metal films manifest induced absorption at the same wavelength [4]. Nonetheless, to a large extent, most previous work has entailed the fabrication of metal-dielectric composite materials containing a very small concentration of the metallic component in order to render the composite material reasonably transparent to optical radiation. While these approaches have proven reasonably successful, it would be desirable to develop a means of accessing the intrinsically large nonlinearity of metals in a more direct manner.

The propagation of light through bulk materials could be altered in photonic-crystal media [5]. Recently, one-dimensional metal-dielectric photonic crystals (MDPC) have been shown to be highly transmissive (50% and greater) within a certain controllable spectral range, even when the total thickness of metal significantly exceeds the conventional skin depth [6]. The central wavelength and width of the transmission windows can be altered by changing the number of metal layers and spacing between them, leading to optical properties that are controllable and are very different from those of bulk metal [6]. Theory predicts that such composite structures can be designed to enhance the nonlinear optical response of the metal while remaining reasonably transparent [7]. In this Letter, we report our experimental findings on the nonlinear optical response of 1D metal-dielectric photonic crystals. We find a large enhancement of the nonlinear transmission response for the metal-dielectric photonic-crystal in agreement with the earlier prediction [7].

It should be noted that the nonlinear optical properties of layered *dielectric-dielectric* composite structures of layer thicknesses much smaller than an optical wavelength have been studied previously both theoretically and experimentally and, in some cases, shown to display an enhanced nonlinear optical response [8]. However, we are unaware of previous experimental investigations of the nonlinear optical response of photonic crystals that contain a metallic component.

Thin films of noble metals (Au, Ag, Cu) are relatively transparent within a transmission window located at the onset of the interband transitions from d band to the conduction band. In copper, this onset occurs at 2.15 eV [9,10]. Figure 1 shows the linear transmission spectrum of 40 and 80 nm thick films of copper deposited on a glass

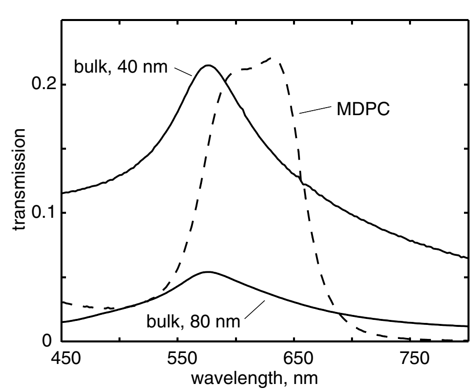

FIG. 1. Measured transmission spectra of the 40 and 80 nm thick bulk copper samples and the metal-dielectric photonic-crystal (MDPC) sample.

substrate. The films have a maximum transmission of about 20% and 6%, respectively, at 575 nm (2.16 eV). The transparency window is limited at the high-frequency side by absorption due to the interband transitions and is limited at the low-frequency side by strong reflection from the metal surface (as described by the Drude model of free electrons in metal). In our experiments, these films were used as bulk reference samples.

By employing multiple Bragg reflections, a 1D metal-dielectric photonic-crystal allows one to create an additional transmission window (passband) at a frequency below the interband transition edge [6]. To calculate the optical properties of such a composite structure, we modeled the propagation of a plane wave through the sample by solving Maxwell equations using a numerical procedure similar to the one described in Ref. [7]. The values of the linear dielectric constant of copper and of SiO_2 were taken from Ref. [10]. We designed a composite sample consisting of alternating layers of copper and silica with the maximum in transmission shifted to 640 nm. We chose this resonance wavelength of the photonic-crystal structure to minimize the absorptive losses in the Cu layers [10]. This wavelength is also far enough from the interband transition threshold so that the rapid changes in intrinsic nonlinearity of Cu associated with the onset of the interband transitions would not obscure the photonic-crystal effect. The design procedure and fabrication restrictions yielded a geometry of five 16 nm thick layers of copper separated by 98 nm (that is, approximately a quarter wavelength) of silica. Our numerical modelling showed that the use of more than five layers produces no appreciable improvement in the nonlinear optical response. Such a sample was built to our specifications on a 1-mm thick glass substrate by using electron beam vapor deposition [11].

The linear transmission spectrum of the composite sample is also shown in Fig. 1. The effect of the periodic photonic-crystal structure is evident in the modified shape of the transmission window and in the increased transmission per amount of metal thickness. In the absence of the periodic structure, the linear transmission of a 80 nm thick copper film is less than 6%. Although it seems logical to compare the photonic-crystal sample with a 80 nm thick bulk layer of copper, such a sample produces virtually no additional nonlinear effect over a 40 nm layer because the exponential decay of the field causes the field in the additional 40 nm to be too weak to contribute to the nonlinear response. The numerically calculated field distribution within the samples confirms this assumption as shown in Fig. 2. Additionally, a 40 nm sample was more experimentally suitable, as its damage threshold is higher and its linear transmission is comparable to that of the MDPC structure. Our experimental observations showed no measurable nonlinear response in transmission or reflection from SiO_2 layers of the thickness used in the MDPC sample and from the substrate in the range of intensities and wavelengths used in our experiments. Thus, in this Letter we compare the nonlinear optical response of the MDPC sample with that of the 40 nm thick bulk sample.

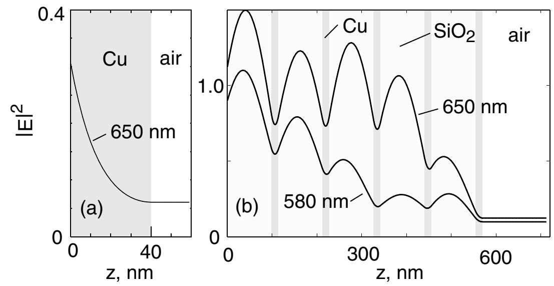

FIG. 2. Numerically calculated E-field distribution within the bulk 40 nm sample at 650 nm (a) and the MDPC sample at a wavelength of 580 nm (out of resonance) and 650 nm (in resonance) (b). The field distribution is normalized to the incident field.

Nonlinear transmission and reflectivity measurements were taken with 10 Hz 25 ps pulses from an EKSPLA optical parametric generator, spatially filtered and focused by a lens to a spot of approximately 100 μm diameter. A data acquisition system was used to record the energy of the pulses passed through and reflected from the sample as the sample was moved along the optical axis of the system across the focal point. Far away from the focal point the intensity was low and the detectors measured the linear transmission and reflectivity; in the vicinity of the focus, the intensity-dependent deviations ΔT and ΔR from the linear values T and R were recorded. In general, this experimental procedure was very similar to the well-known Z-scan technique [12]. The Z-scan technique is used primarily to determine the nonlinear cubic susceptibility $\chi^{(3)}$ of materials from the fractional change in transmission measured with a variable-size aperture in the far field. The concept of nonlinear cubic susceptibility does not apply well to resonance structures such as our MDPC sample. The nonlinear susceptibility characterizes the intensity-dependent change in the dielectric function of the material. However, it does not account for the resonant response of the structure. In our experiments we measured the intensity-dependent fractional transmission and reflectivity changes $\Delta T/T$ and $\Delta R/R$. A typical example of the experimental data for nonlinear transmission is shown in Fig. 3. The change in dielectric function $\delta\epsilon$ of the metal needed to produce such deviation from the linear values of T and R was deduced from the numerical calculations of the optical properties of the samples.

In the 550–680 nm spectral range studied in this Letter, two processes contribute predominantly to the third-order optical nonlinearity (light-induced change in the dielectric function) of bulk copper. The strongest

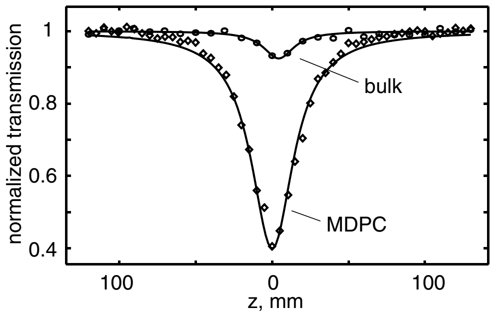

FIG. 3. Z-scan traces showing the normalized transmission of the bulk (circles) and MDPC (diamonds) samples at $\lambda = 650$ nm as a function of the distance from the focal point. The intensity at the focus was 500 MW/cm^2. The solid lines represent the fit obtained by numerical calculations.

source of optical nonlinearity in noble metals is usually attributed to the Fermi smearing mechanism, the modification of the Fermi distribution of the conduction electrons heated up by laser pulses [2]. Unlike most thermal processes responsible for nonlinear optical response, Fermi smearing is a fast process with a sub-ps response time and a relaxation time typically on the order of 1 ps, determined by the electron-phonon energy transfer time [13,14]. This effect leads to sharp, resonancelike features in the thermomodulation transmission and reflection spectra of Cu at the wavelength λ_{th} corresponding to the onset of the interband transitions from the d band to the conduction band [13,15,16]. In our work, we study self-action nonlinear effects of a single laser pulse propagating through the sample without additional temperature modulation. Laser pulses with energies on the order of 1.0 μJ are able to raise the temperature of the free electrons by thousands of degrees K and change the value of the dielectric function of Cu samples by as much as 10%. The other contribution is also thermal in nature but comes from the temperature dependence of the relaxation time in the Drude model of free electrons in the conduction band [17]. This effect is not as wavelength sensitive as the Fermi smearing and, in our range of wavelengths, could be well approximated by a constant. Both of these two processes influence mostly the imaginary part ϵ_2 of the dielectric function so that for any given incident intensity, the light-induced change in the dielectric function $\Delta\epsilon$ averaged over the metal layer could be approximated as

$$\Delta\epsilon_2(\lambda) = \Delta\epsilon_{\rm free} + \Delta\epsilon_{\rm FS}(\lambda). \qquad (1)$$

The exact wavelength dependence of the Fermi smearing term is rather complex and for our purposes we model it with a phenomenological Gaussian functional form

$$\Delta\epsilon_{\rm FS}(\lambda) = \Delta\epsilon_{\rm FS} e^{-(\lambda-\lambda_{\rm FS})^2/\Delta\lambda_{\rm FS}^2}. \qquad (2)$$

Our measurements with 25 picosecond pulses showed that the spectral features associated with the Fermi smearing in the nonlinear transmission and reflectivity spectra of the bulk Cu sample extend only about 30 nm from λ_{th} towards longer wavelengths. At 650 nm, the MDPC resonance wavelength, nonlinear response of the bulk copper film is much smaller than that at λ_{th} and almost flat with respect to the wavelength. This result is in good agreement with the thermomodulation experiments [13,15,16] on thin metal films. By fitting the data taken at an incident intensity of 200 MW/cm^2 with the functional forms (1) and (2) we found the parameters to be $\Delta\epsilon_{\rm free} = 0.18$, $\Delta\epsilon_{\rm FS} = 0.7$, $\lambda_{\rm FS} = 585$ nm, $\Delta\lambda_{\rm FS} = 22$ nm, as shown in Fig. 4. The values of these parameters represent the intrinsic nonlinear optical response of copper which the MDPC structure enhances.

A rigorous prediction of the nonlinear optical response for a MDPC structure requires that the phase accumulation within each layer be evaluated numerically and then summed over all layers. However, Bennink *et al.* [7] have found that to very good approximation the enhancement of the nonlinear optical response can be understood as the product of an intensity enhancement factor with a phase sensitivity factor.

The intensity enhancement factor, $F(\lambda)$, is defined as the ratio of the spatial average of the square of the electric field within the metallic component for the MDPC structure compared to that for the bulk metal sample containing 40 nm thickness of copper, $F(\lambda) = \langle E_m^2\rangle_{\rm MDPC}/\langle E_m^2\rangle_{\rm bulk}$. This enhancement factor was theoretically predicted to be as high as 2.5 at 650 nm for the MDPC sample as illustrated in Fig. 2. Assuming the nonlinear correction to the dielectric function of the metal $\delta\epsilon_2$ to be proportional to the intensity of the field within the metal

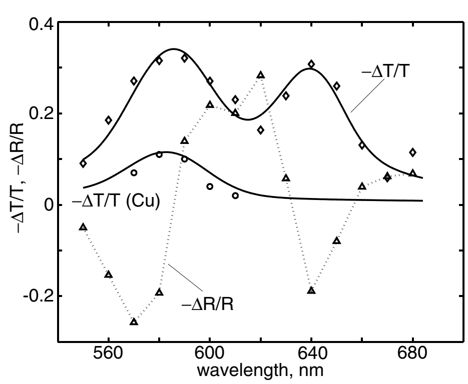

FIG. 4. Measured nonlinear fractional change in transmission (diamonds) and reflectivity (triangles) as functions of wavelength for the MDPC sample. The fractional change in transmission of the bulk Cu (circles) is shown for comparison. The intensity at the focus was 200 MW/cm^2. The solid lines represent the phenomenological model described in the text. Note the minus sign on the vertical axis; the transmission decreases with intensity.

layer, one may expect $\delta\epsilon_2$ averaged over all the layers of the MDPC sample to be

$$\Delta\epsilon_{2\mathrm{MDPC}}(\lambda) = [\Delta\epsilon_{\mathrm{free}} + \Delta\epsilon_{\mathrm{FS}}(\lambda)]F(\lambda). \qquad (3)$$

In a resonance structure, the observable nonlinear response (for instance, fractional change in transmission $\Delta T/T$ of the sample) induced by a certain value of $\delta\epsilon_2$ shows a strong resonant dependence on the wavelength. This enhancement of the nonlinear response is what we refer to as the phase sensitivity factor. The rigorous definition of the phase sensitivity factor is given and discussed in our earlier paper [7]. Our numerical calculations estimated the phase sensitivity factor of the MDPC sample as a function of wavelength and, combined with (3), produced the nonlinear transmission change which is in good agreement with the experimental data as shown in Fig. 4.

The measured $\Delta T/T$ and $\Delta R/R$ spectra shown in Fig. 4 were taken at a relatively low intensity of $200\ \mathrm{MW/cm^2}$ to avoid possible damage to the samples at the onset of the interband transitions. The smallness of the intrinsic nonlinearity of copper did not allow us to get reliable measurements for the bulk Cu sample throughout the entire spectral range at this intensity. At 650 nm, the absorption of Cu is lower than that at λ_{th}, and measurements could be taken at a higher incident intensity without risk of damaging the samples. In Fig. 3, two z-scan traces taken at $500\ \mathrm{MW/cm^2}$ with the bulk Cu and MDPC samples under the identical experimental conditions are presented. At this particular wavelength and power, the fractional nonlinear change in transmission of the composite sample is close to 60% whereas in the bulk sample it only reaches 7%. Thus, our measurements indeed demonstrate significant enhancement of the nonlinear response in transmission of the MDPC structure. The nonlinear change in transmission can be related to the (complex) phase shift $\Delta\phi$ experienced by the light wave in passing through the material. One finds that $\Delta\phi = -0.458i$ for the composite structure and that $\Delta\phi = -0.036i$ for the pure metal sample, corresponding to an enhancement factor of 12.7. The spectral region of measurable nonlinear transmission extends much farther from the onset of the interband transitions in the composite sample, up to 670 nm. The magnitude of the effect is greatly enhanced at all frequencies, starting from 550 nm ($\lambda < \lambda_{\mathrm{th}}$) to 670 nm. The $\Delta T/T$ spectrum of the composite sample has two prominent features; the one close to 590 nm, we believe, is due to the Fermi smearing at the interband threshold. This feature is present in the nonlinear spectra of both the bulk and MDPC samples. The other peak at 640–650 nm results from the intensity and phase sensitivity enhancement and is present only in the metal-dielectric sample. Note that the amplitude of the nonlinear transmission change is almost the same at 640 nm as it is at 580 nm, in the Fermi smearing region.

In conclusion, we have experimentally demonstrated how to utilize 1D metal-dielectric photonic-crystal materials to enhance the intrinsic nonlinearity of metals. We have found that the nonlinear change in transmission of the composite sample is enhanced by an order of magnitude with respect to that obtainable from bulk metal. The linear transmission in the same spectral range is also improved severalfold. These results suggest that metal-dielectric photonic-crystal materials may prove quite useful for various photonics applications. We also point out that the wavelength of the maximum enhancement is determined by the separation between the metal layers and thus could be changed. This property leads to increased flexibility of such composite materials to be tailored for particular applications.

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