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Optical constants of crystalline WO_3 deposited by magnetron sputtering

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Crystalline WO_{3-x} is an infrared (IR) electrochromic material having possible applications in satellite thermal control and IR switches. Optical constants of electrochromic materials change upon ion intercalation, usually with H^+ or Li^+. Of primary concern for device design are the optical constants in both the intercalated and deintercalated states. *In situ* and *ex situ* ellipsometric data are used to characterize both the deposition process and the optical constants of the films. *Ex situ* data from a UV-Vis-NIR ellipsometer are combined with data from a mid-infrared Fourier-transform-infrared-based ellipsometer to provide optical constants over a spectral range of 0.031–6.1 eV. © *1999 American Vacuum Society.* [S0734-2101(99)04905-2]

I. INTRODUCTION

Satellite thermal control is based on emissivity modulation. Thermal loads from satellite electronics must be balanced with earthshine and radiated energy to maintain the satellite temperature at an appropriate level, usually around 30 °C. Traditional thermal control devices are mechanical, using a ''venetian blind'' or similar arrangement. One side of the radiator is reflective while another is emissive. The radiator is mechanically actuated to switch between the emissive or the reflective side.[1]

Solid state emissivity modulators offer possible advantages over mechanical ones. Low weight, lack of moving parts, and the potential to coat irregular surfaces are the most intriguing benefits. In these devices, a stack of thin films would replace the mechanical apparatus. One or more films in the stack must have variable optical properties to allow for thermal control. Ideally, the stack should be switchable with minimal power consumption in either state. Switching power should also be minimized both in terms of peak power and total energy required.

Electrochromic materials have potential to act as emissivity modulators. WO_3 is probably the most widely studied electrochromic material, especially in an amorphous state.[2] Though less studied, crystalline WO_3 displays a change in optical constants over a wide spectral range in the visible and infrared (IR) regions when intercalated with Li^+ or H^+ ions.[3] The peak of the room temperature (RT) blackbody spectrum is at 9.7 μm and 94.5% of radiated power from a blackbody falls between 2 and 40 μm. Hence, for thermal control of a RT satellite, the emissivity modulator should be optimized for operation in this range. Some IR devices have been reported, but are usually used in a fairly limited range in the near infrared (NIR).[4]

Contrast this requirement to that for optical switching in the visible and NIR. Substantial work has been done on these devices, due to the large potential commercial interest for window applications.[5,6] For this application, the emphasis lies on performance in the 0.35–2.5 μm range.[6] Additionally, commercial window applications have aesthetic concerns and require larger areas for economic viability.[7] A variety of devices optimized for visible operation are described in the literature.[8–11]

II. EXPERIMENT

For the proposed solid state emissivity modulator, an optimized deposition scheme is required. Sputtered WO_3 films are often oxygen deficient and are better represented as WO_{3-z} with z typically ranging from 0 to 0.5 depending on deposition conditions.[12] Many parameters, including the optical switching upon ion intercalation in Li_xWO_{3-z}, vary with oxygen content. To investigate mid-IR switching applications, films were deposited under various oxygen partial pressures via direct current (dc) magnetron sputtering. Only the oxygen pressure was varied, as all other deposition parameters were held constant. Base pressures for the depositions were all about 2×10^{-6} Torr. Deposition power was 35 W in an Ar and O_2 environment with a total pressure of 15 mTorr. Quartz lamps radiatively heated the substrates to a temperature of approximately 375 °C. The substrates were 5 cm diameter Si wafers doped to 8 mΩ cm. These substrates act as a conductive electrode to supply electrons to the electrochromic film and as an adequately reflective substrate for infrared radiation.[13] The substrate reflection is lowest (about 30%) at short wavelengths but increases to beyond 50% at 40 μm. While the resistivity is much higher than a typical indium tin oxide (ITO) or metallic film, the macroscopic thickness of the wafer yields an overall resistance that is comparable to or lower than that of a metallic thin film. More importantly, properties of the Si wafer are well known both structurally and optically and are thus easily characterized for ellipsometric analysis.

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During deposition, *in situ* ellipsometric data were acquired over a spectral range of 280–763 nm, with the primary goal of determination of the film thickness and sputter rate. *Ex situ* data would provide more accurate optical constants over a wider spectral range. After deposition, ellipsometric data were acquired in both the mid-IR and UV-Vis regions. The films were then intercalated electrochemically with Li^+ ions from a 1 molar solution of $LiClO_4$ in propylene carbonate. The equipment used for intercalation was an EG&G Princeton Applied Research Model 273A potentiostat utilizing a saturated calomel reference electrode (SCE). A platinum foil electrode of about 6 cm^2 served as the counter electrode. The potentiostat controls the voltage at the working electrode (sample) by varying the counter potential. All voltages are measured with respect to the SCE reference electrode allowing for a reproducible experiment by precisely controlling the solution potential. Intercalation potentials of −650 and +350 mW, respectively, colored and uncolored the films. All films were cycled three to four times to reach the ''full'' intercalation state.

After intercalation, the samples were mounted on the IR ellipsometer. Data were acquired repeatedly over a 75 min period to both quantify the optical constants and to observe any spontaneous bleaching as a function of time in the laboratory atmosphere. Electrochromic films, especially those intercalated with H, may exhibit a charge loss, and corresponding optical constant change, over time. In the case of Li intercalation, there was no detectable difference in the ellipsometric data over the 75 min period, suggesting that charge loss was not a concern in this experiment. Finally, the films were electrochemically deintercalated followed by ellipsometric measurements over the entire visible and infrared spectral range.

III. RESULTS

As is the case with most ellipsometric data, modeling and regression analysis are required to extract meaningful parameters from the measured Ψ and Δ spectra.[14] The fundamental ellipsometric equation is

$$\rho = \frac{r_p}{r_s} = \tan(\Psi) e^{i\Delta}, \tag{1}$$

where Ψ and Δ are the measured values.[15] A mathematical model based on Jones matrices is constructed to produce the Fresnel reflection coefficients and resulting Ψ and Δ values. A Levenberg–Marquardt regression algorithm was used to determine the film optical constants (ε_1 and ε_2, or n and k) from the measured and mathematically generated data.[16]

As previously noted, the primary goal for the *in situ* data was the determination of the film thickness for use when analyzing the *ex situ* data. Hence, the simple model of a single film on a semi-infinite substrate, was assumed. Window effects and high temperature optical constants for the Si substrate were also included. Film thickness ranged from 179 to 248 nm. Accurately knowing these thicknesses was vital for analysis of the *ex situ* data taken over a range of 0.031–6.1 eV. Generally fits of the *in situ* data are reasonable, especially considering the simple model used, and the fits have a high sensitivity (high measurement accuracy) to the film thickness.

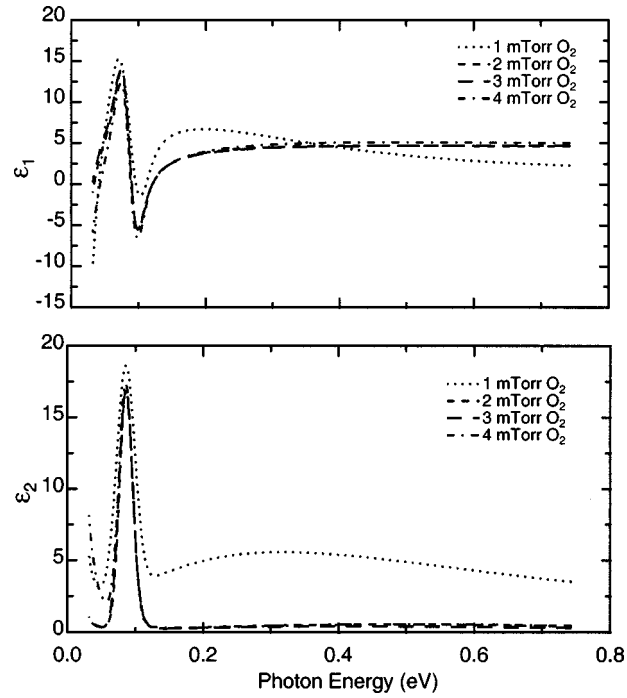

FIG. 1. IR optical constants of sputtered, as-deposited WO_{3-z} thin films.

In the UV-visible-NIR range (0.73–6.1 eV), the optical constants were determined from a wavelength-by-wavelength regression fit, with no assumptions about the spectral form of the dielectric function. A parametrized model was used for fits in the 0.031–1 eV range. This model consisted of a sum of Gaussian and Lorentzian oscillators of the form given in Eqs. (2) and (3), and a Drude term [Eq. (4)] to account for free carrier-like absorption below about 0.04 eV.[13,17] The equations given are those used in our analysis software; several slightly different formulations are possible.[18]

$$\tilde{\varepsilon}_{\text{Lorentz}}(E) = \varepsilon_1 + i\varepsilon_2 = \frac{ABE_c}{E_c^2 - E^2 - iBE}, \tag{2}$$

$$\text{Im}\{\tilde{\varepsilon}_{\text{Gaussian}}(E)\} = \varepsilon_2 = Ae^{-[(E-E_c)/B]^2} + Ae^{-[(E+E_c)/B]^2}, \tag{3}$$

$$\tilde{\varepsilon}_{\text{Drude}}(E) = \varepsilon_1 + i\varepsilon_2 = \frac{-AB}{E^2 + iBE}. \tag{4}$$

The IR optical constants of pristine WO_{3-z} for various deposition conditions are shown in Fig. 1. A large Gaussian absorption was found at 0.086 eV and a smaller, broad Lorentzian absorption was found near 0.68 eV for all samples. In the analysis, the amplitude (A), breadth (B), and position (E_c) of the 0.68 eV absorption were mathematically correlated, a common behavior of broad absorptions. Thus, the center energy was fixed at 0.68 eV to fit the UV-Vis data and the other fit parameters were A, B, and E_c for the 0.086 eV absorption, and A and B for the long wavelength Drude term.

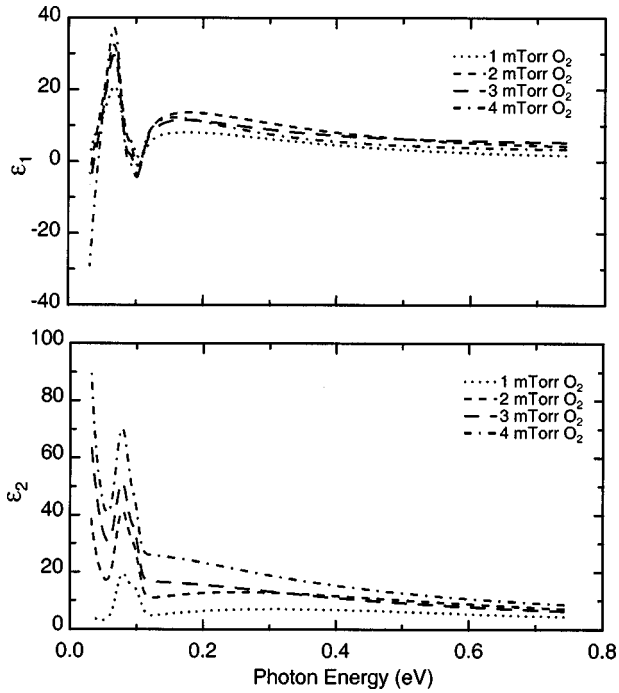

FIG. 2. IR optical constants of Li intercalated, WO_{3-z} thin films.

The optical constants of three samples with higher O_2 content displayed similar behavior in their as-deposited states. The 1 mTorr O_2 sample, in contrast, had a much larger broad absorption centered at 0.68 eV and a somewhat smaller contribution from the absorption at 0.086 eV.

Shown in Fig. 2, the optical constants of intercalated samples display a general increase in ε_2 with oxygen content. Absorption increases in all regions of the spectrum: the

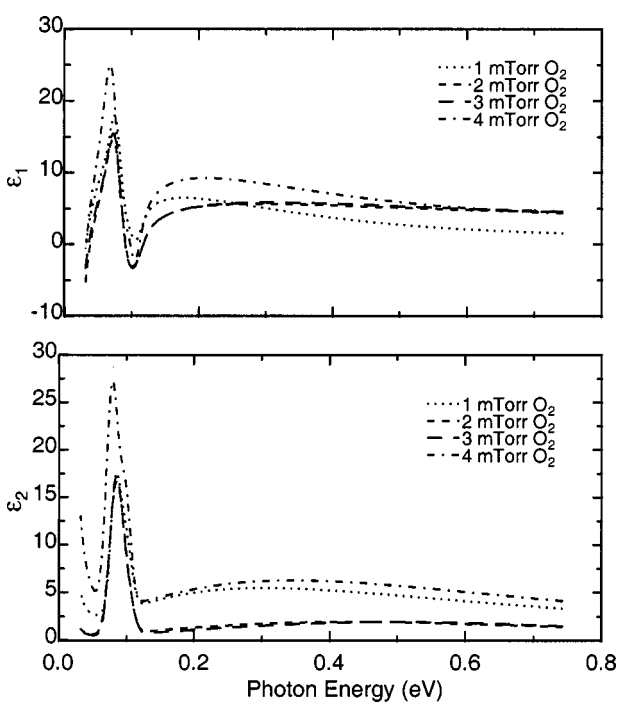

FIG. 3. IR optical constants of deintercalated, WO_{3-z} thin films.

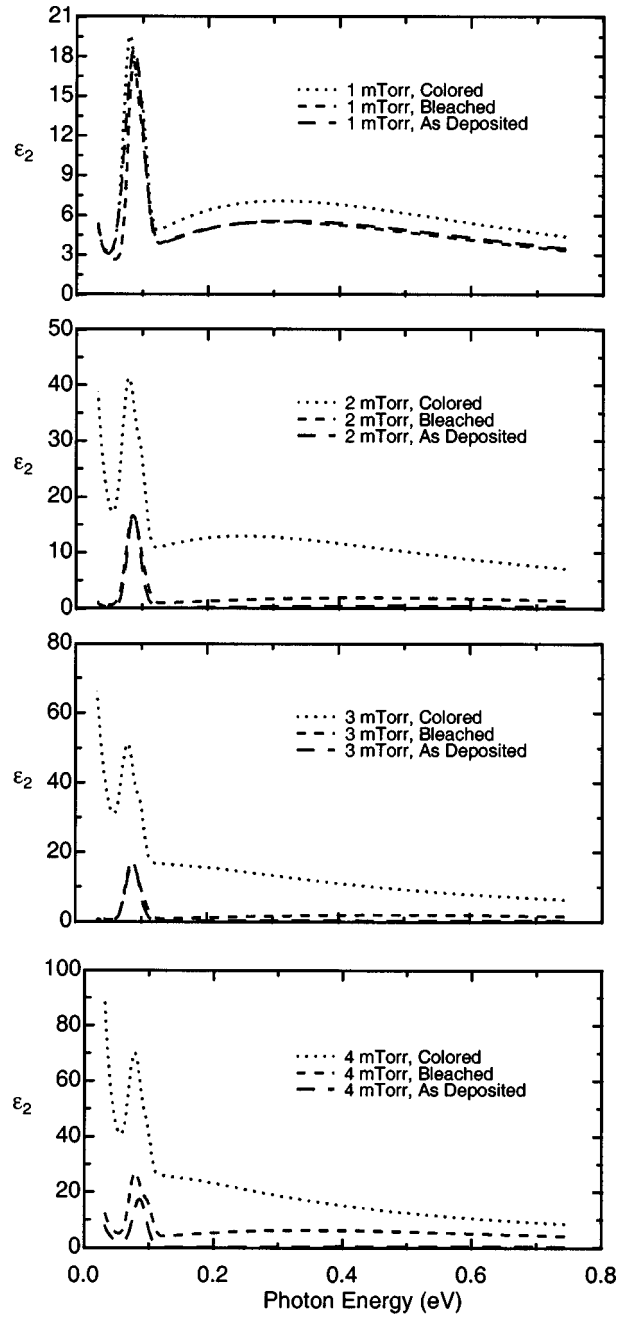

FIG. 4. IR optical constants summary.

Drude-like low energy tail, the main absorption, and the broad, higher energy absorption. In terms of relative change, though, the film deposited with lowest O_2 pressure displayed the lowest optical modulation, while the sample made at the highest O_2 partial pressure (4 out of 15 mTorr) changed most.

Finally, the IR optical constants of deintercalated WO_{3-x} are shown in Fig. 3. In this state, the samples display a slightly different grouping. The low oxygen samples of 1, 2, and 3 mTorr exhibit very similar behavior; the optical constants of deintercalated WO_{3-z} returned very nearly to their as-deposited values. However, the sample with the highest oxygen pressure during deposition did not return to its origi-

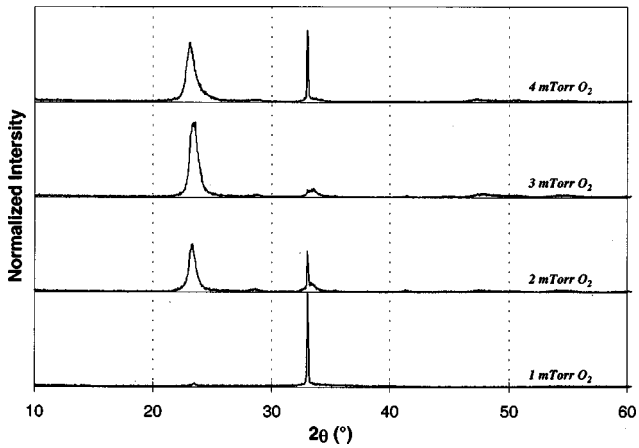

FIG. 5. XRD data of deintercalated WO_{3-z} thin films.

nal state; retaining instead an increased broad absorption near 0.68 eV.

From these IR measurements, we conclude that the optimum O_2 content for device performance is around 2–3 mTorr partial pressure in a 15 mTorr Ar environment (13%–20% O_2 in Ar). These films exhibit both a large broadband change in optical constants and a return to a near-pristine state. The film deposited with lower O_2 content shows very little optical change while the higher O_2 film colored irreversibly. These results are best shown by the optical constant summary given in Fig. 4. Here, only the ε_2 values are shown for clarity. For intercalated samples deposited with 2, 3, and 4 mTorr O_2, the main oscillator amplitudes near 0.086 eV are about 2.7 times the values found in the deintercalated state. For the 1 mTorr sample, this change is only a few percent. Similarly, the broader absorption increases by around 250%–600% for the more oxygenated films, while the sample deposited with 1 mTorr O_2 displays an increase in ε_2 of around 40%.

The O_2 deposition pressure also affected the crystallinity of the films. To investigate this possibility, x-ray diffraction data were acquired after deintercalation. These data are shown in Fig. 5. These data are normalized to the largest peak, the peak near 33° for the sample made with 1 mTorr O_2. This sample exhibits one strong, very narrow peak near $2\theta = 33°$, corresponding to a d spacing of 0.271 nm. The only other peak evident is much smaller and is centered at $2\theta = 23°$. Conversely, the three other films have large, broad x-ray diffraction (XRD) peaks near 23.3°, suggesting a d spacing of 0.381 nm. The peak near 33° is generally of lower amplitude and has a small, broad peak superimposed. The absence of the 23.3° peak correlates with the markedly different optical constants of the 1 mTorr sample. Previous studies have shown similar behavior near 23.3°, but lacked the sharp 33° peak.[19] We believe that the differences may be due to higher substrate temperature, greater target power density, and our use of magnetron sputtering. The physical and optical properties of WO_{3-z} thin films are known to be highly dependent on the deposition process.[20] Further investigation in this area is needed, especially since intercalation

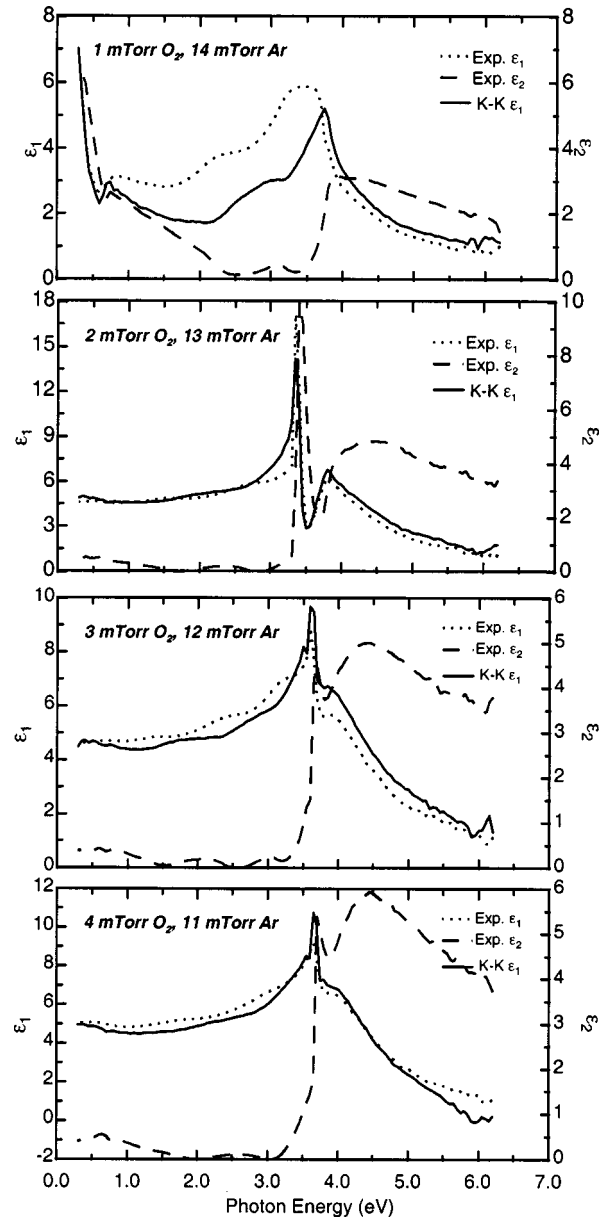

FIG. 6. UV-Vis optical constants of WO_{3-z} sputtered thin films and Kramers–Kronig comparisons.

is known to affect the crystallinity and structure of WO_3 thin films.[21]

While our primary interest lies in the IR region near the peak of the room temperature blackbody spectrum at 9.7 μm, we also acquired data in the visible and UV range from 0.73 to 6.3 eV. In this range, a direct inversion of the ellipsometric data yields the optical constants of the film. Here, we again assume a single uniform layer on a semi-infinite Si substrate with a thin native oxide. Thicknesses of the film and oxide were determined from *in situ* data. Figure 6 shows the optical constants resulting from the wavelength-by-wavelength fits. In this case, the optical constants of the film were determined at each energy independently, with no assumptions about the functional form of the dispersion. The three films with highest O_2 content during deposition behave

similarly. All exhibit a rapid onset of absorption near 3.3 eV, an exciton-like behavior between 3.64 and 3.84 eV, and a gradually decreasing ε_2 from a peak at 4.4 eV toward higher energies.

To confirm the accuracy of the resulting optical constants, a Kramers–Kronig consistency check was performed. This check confirms that determined optical constants obey causality.[17] The determined ε_2 value is used to generate an ε_1 spectrum for comparison with the ellipsometrically determined ε_1 values. The Kramers–Kronig relation is given as Eq. (5).

$$\varepsilon_1(E)-1=\frac{2}{\pi}\mathcal{P}\int_0^\infty \frac{E'\varepsilon_2(E')}{(E')^2-E^2}dE'. \tag{5}$$

Figure 6 shows the comparison between the two spectra for each sample. Only the 1 mTorr sample shows poor agreement, suggesting that the simple model used for this film was inadequate for the UV and visible ranges. The optical constants for the other samples are quite similar to the expected values from Kramers–Kronig analysis. The onset of absorption is accompanied by a sharp feature in ε_1. The ε_2 decrease in the ''exciton'' region is illustrated in ε_1 by a shoulder at slightly higher energy as predicted by causality. Finally, the general shapes of the ε_1 spectra in the slowly varying regions are quite similar to the Kramers–Kronig predictions. In any case, a strict Kramers–Kronig analysis requires measurements over an infinite spectral range, whereas spectroscopic ellipsometry yields both ε_1 and ε_2 over the measured spectral range. In this respect, any remaining differences in the data from the 2, 3, and 4 mTorr samples does not present a significant consistency problem. That is, the ellipsometrically measured dielectric function is accurate.

IV. CONCLUSION

Several thin films of crystalline WO_3 on Si were deposited via magnetron sputtering. Their optical constants were determined from 0.031 to 6.3 eV using spectroscopic ellipsometry. For device performance, a large, reversible increase in ε_2 over a broad spectral range was desired. An oxygen content of 13%–20% in Ar at an operating pressure of 15 mTorr yielded the best results for reproducible optical switching in the infrared.

ACKNOWLEDGMENTS

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