Dynamically Reconfigurable Metadevice Employing Nanostructured Phase-Change Materials

Zhihua Zhu,* Philip G. Evans,** Richard F. Haglund, Jr.,§ and Jason G. Valentine*∥

†Department of Electrical Engineering and Computer Science, Vanderbilt University, Nashville, Tennessee 37212, United States
‡Computational Sciences and Engineering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States
§Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee 37235, United States
∥Department of Mechanical Engineering, Vanderbilt University, Nashville, Tennessee 37212, United States

ABSTRACT: Mastering dynamic free-space spectral control and modulation in the near-infrared (NIR) and optical regimes remains a challenging task that is hindered by the available functional materials at high frequencies. In this work, we have realized an efficient metadevice capable of spectral control by minimizing the thermal mass of a vanadium dioxide phase-change material (PCM) and placing the PCM at the feed gap of a bow-tie field antenna. The device has an experimentally measured tuning range of up to 360 nm in the NIR and a modulation depth of 33% at the resonant wavelength. The metadevice is configured for integrated and local heating, leading to faster switching and more precise spatial control compared with devices based on phase-change thin films. We envisage that the combined advantages of this device will open new opportunities for signal processing, memory, security, and holography at optical frequencies.

KEYWORDS: Metadevice, metamaterials, perfect absorber, vanadium dioxide, plasmon, nanoantenna

Metadevices—artificial electromagnetic media comprising plasmonic or dielectric nanostructures and active functional materials—have attracted interest for a wide range of applications, including sensing,8 memory or data storage,3,4 communications,5,6 and imaging.5,9 A number of techniques have been proposed for achieving dynamic control of metadevices at near-infrared (NIR) and visible frequencies, including carrier injection,5,6,7,10–14 mechanical actuation,15,16 liquid crystals,17,18 chemical activation,7,9 and the deployment of phase-change materials.10–21 However, all of these techniques face roadblocks that must be addressed in order to move toward commercialization of specific metadevice technologies. For instance, while carrier injection can be quite fast, it is difficult to achieve optical frequency modulation because of the large carrier concentrations and high voltages required.10–14 Even with sufficient voltage, the changes in the effective optical constants are small, which can limit the modulation depth. Thermal and electromechanical metadevices generally work at lower speeds, and while the modulation depth can in theory be large, to date reversible depths on the order of 10% have been achieved16 at optical frequencies.

Phase-change materials (PCMs) such as chalcogenide glass (GST) (nonvolatile) and vanadium dioxide (volatile) have been used for decades in memory storage and dynamic optical elements such as tunable absorbers and polarizers.3,4,9–27 Upon undergoing a phase change, these materials exhibit a large change in their optical properties, providing a means for modulation. Vanadium dioxide is particularly interesting, as it has a reversible phase transition at low temperatures (∼340 K) which is critical for realizing low-power devices. As a comparison, the transition threshold for GST is higher, and repeated cycling is limited by degradation associated with repetitive amorphous–crystalline phase changes. The majority of previously demonstrated PCM-based metadevices have employed PCM films that can be readily incorporated into structured metal resonators.19–21,23–26 However, in thermal switching, the large thermal mass of continuous films necessitates a large switching power per bit while also requiring an external heating element. At the same time, this limits the switching speed, as this thermal energy must then be dissipated to recover the device.

Here we present a metadevice that integrates VO2 nanocrystals with plasmonic metamaterials. By designing the unit cells so that each nanocrystal is in the feed gap of a bow-tie antenna, we have achieved strong field concentration within the VO2 nanocrystals. This allows the metadevice to be more sensitive to the optical properties of the VO2 while also utilizing a small thermal mass for reduced switching power and time. In

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addition, the metallic unit cells serve as the heating element, minimizing the volume that must be heated and improving integration. This results in an integrated device with a modulation depth of 33% within the telecommunications band and a recovery time of 1.27 ms.

The metadevice is based on the perfect absorber (MPA) architecture, with each unit cell consisting of a gold bow-tie antenna with a small VO$_2$ patch placed in its feed gap. This layer is separated from a thick gold backplane by a thin Al$_2$O$_3$ dielectric spacer layer (Figure 1a,b). Fabrication began with thermal deposition of 100 nm of gold (Au) on fused silica to form the backplane (see the material selection in section S1 in the Supporting Information). This was followed by atomic-layer deposition of 37 nm of Al$_2$O$_3$ to form a transparent dielectric spacer layer. The VO$_2$ patterns (120 nm × 120 nm × 37 nm) were then defined on the Al$_2$O$_3$ film by electron beam lithography. After development, the VO$_2$ was sputtered using a vanadium metal source, followed by a standard lift-off procedure and then annealing for 5 min to crystallize the VO$_2$ (see details in Methods). Figure 2a shows an atomic force microscopy (AFM) and scanning electron microscopy (SEM) images of the fabricated MPA structure. (a) AFM image of the uniform VO$_2$ nanocrystals. The AFM data indicates that the VO$_2$ nanocrystal height is 37 nm. (b) Measured optical properties for both semiconducting and metallic VO$_2$. Solid lines correspond to refractive index (left axis) and dashed lines correspond to absorption coefficient (right axis). (c) False-color SEM image of the final device. (d) Magnified SEM image of the final device. The VO$_2$ nanocrystals (purple) are located in the feed gaps of the bow-tie antenna (yellow).

Figure 1. Schematic of the MPA structure. (a) Schematic of the multilayer MPA structure array and integrated local heater. (b) Schematic of a unit cell with $p_x=264$ nm, $p_y=300$ nm, wire width $w=100$ nm, and gap width $g=34$ nm.

Figure 2. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) images of the fabricated MPA structure. (a) AFM image of the uniform VO$_2$ nanocrystals. The AFM data indicates that the VO$_2$ nanocrystal height is 37 nm. (b) Measured optical properties for both semiconducting and metallic VO$_2$. Solid lines correspond to refractive index (left axis) and dashed lines correspond to absorption coefficient (right axis). (c) False-color SEM image of the final device. (d) Magnified SEM image of the final device. The VO$_2$ nanocrystals (purple) are located in the feed gaps of the bow-tie antenna (yellow).

shown in Figure 3a. The measured resonant position shifts from 1590 to 1230 nm as the stage temperature increases from 21 to 87 °C. This results in a figure of merit (FOM) of $\Delta\lambda/\lambda_{\text{fwhm}} = 82\%$. The reversible modulation depth (defined as $h(\lambda) = |A_{\text{max}}(\lambda) - A_{\text{min}}(\lambda)|$) was experimentally measured to be 27% at 1232 nm and 33% at 1588 nm. These are the highest values measured in free space within this wavelength regime to the best of our knowledge. It should also be noted that compared with VO$_2$-film-based metadevices, we observe a change in the switching temperature range resulting from the small size of the VO$_2$ nanocrystals (Figure 3d). The modulation starts earlier at about 40.3 °C and finishes at 86 °C, which provides greater dynamic range for grayscale control.

From a materials perspective, VO$_2$ has a lower switching threshold than PCMs like GST due to the near-room-temperature phase transition. In order to electrically switch the device, a current is applied to the antenna layer through the bus bars, heating the metal. In contrast to external heating, this technique generates heat only where it is required, reducing power consumption. The measured optical properties as functions of current injection are shown in Figure 3b. Local Joule heating of the device results in the same modulation depth as using the temperature-controlled stage. The threshold current to switch the entire 24 μm × 24 μm sample was found to be 56 mA (2.2 V), yielding a power consumption of 123.2 mW, which agrees well with the calculated switching threshold (see section S4 for the theoretical model).

The performance of the metadevice agrees well with full-wave finite-difference time-domain (FDTD) simulations (Figure 3c). In these simulations, the VO$_2$ properties were extracted from the experimentally measured optical properties shown in Figure 2b. On the basis of the simulated absorption spectrum, when the VO$_2$-based metadevice is in the semiconducting state (25 °C), the device exhibits almost unity absorption (99.7%) at a resonant frequency of 1590 nm. At an
Figure 3. Measured and simulated dynamic absorption spectra and temporal responses. (a) Experimental absorption spectra as a function of the device temperature. (b) Experimental absorption spectra as a function of input current. (c) Simulated MPA absorption in the semiconducting, intermediate, and metallic states. (d) Resonant wavelength (blue, left axis) and absorption amplitude (red, right axis) as functions of temperature. (e) Reflective power within one modulation cycle (blue circles) and the fitted exponential decay curve (red solid line). The decay time is 1.27 ms based on the fit. (f) Trigger signal (red, right axis) and monitored reflection (blue, left axis) over multiple modulation cycles.

Table 1. Comparison of Near-Infrared Free-Space Optical Modulators

<table>
<thead>
<tr>
<th>approach</th>
<th>material</th>
<th>trigger type</th>
<th>$\Delta \lambda$ (nm)</th>
<th>modulation depth</th>
<th>speed</th>
<th>switch energy per pixel</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEMS Si$_3$N$_4$</td>
<td>thermal</td>
<td>NA</td>
<td>2%</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>carrier doping</td>
<td>graphene</td>
<td>electrical</td>
<td>250</td>
<td>8%</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Lorentz force</td>
<td>ITO</td>
<td>electrical</td>
<td>NA</td>
<td>&lt;2%</td>
<td>250 ps</td>
<td>180 pJ</td>
</tr>
<tr>
<td>phase-change</td>
<td>GLS</td>
<td>electrical</td>
<td>150</td>
<td>15%</td>
<td>10 ms</td>
<td>NA</td>
</tr>
<tr>
<td>materials</td>
<td>GST</td>
<td>optical</td>
<td>200</td>
<td>30%</td>
<td>100 ns</td>
<td>2 pJ</td>
</tr>
<tr>
<td></td>
<td>VO$_2$</td>
<td>electrical</td>
<td>NA</td>
<td>80%</td>
<td>500 ms</td>
<td>1 pJ</td>
</tr>
<tr>
<td></td>
<td>(ours)</td>
<td>electrical</td>
<td>360</td>
<td>33%</td>
<td>1.27 ms</td>
<td>21 nJ</td>
</tr>
</tbody>
</table>

Al$_2$O$_3$ and had a height of 37 nm. These films were deposited at the same time, but shadowing by poly(methyl methacrylate) (PMMA) reduces the height of the nanoparticles. The different substrate and thickness can affect both the grain size and the grain boundaries, leading to deviations with the simulations. The VO$_2$ phase transition also depends on the nanocrystal size, and it has been shown that nanocrystals exhibit a broader hysteresis loop and phase transition compared with thin films. Lastly, inhomogeneities in the fabricated bow-tie antennas will broaden the resonances of the metadevice compared with the simulations.

The temporal response of the device was measured by using a function generator to modulate the applied current while the reflectivity at 1107 nm was monitored (see Figure S6). The results are presented in Figure 3e,f. First, it should be noted that the modulation contrast of the temporal intensity measurements is 37%, matching the steady-state measurements in Figure 3b and indicating that the device is fully switched. Second, the reflected power follows the trigger signal and has a rise time of 2.3 ms, which could be further reduced by increasing the applied current. The relaxation time was measured to be 1.27 ms, which is a function of the thermal conductivity of the substrate and the thermal capacitance of the VO$_2$. When plasmonic structures are fabricated on or under continuous VO$_2$ films, the absorption associated with the continuous VO$_2$ film increases the insertion loss, reduces the modulation depth, and lengthens the response time. Here the patterned nanocrystals have a thermal mass that is 18% of that for a thin film of the same thickness. The substantially reduced thermal capacitance of the system results in a response time 400 times shorter than that of film-based metadevices while also lowering the power consumption of the device.

Overall, the modulator compares favorably to past work in this wavelength regime, as shown in Table 1. Furthermore, the switching speed observed here is by no means a lower limit. VO$_2$ switching times on the order of 600 ns have been observed in waveguide-based structures in which current is passed directly through the VO$_2$. In this case, the higher speed is due to the fact that only the region between the electrodes is heated, further reducing the thermal capacitance and collateral heat generation. This technique could in principle be readily translated to the device presented here to realize a several orders of magnitude decrease in switching time. We also note that our metadevice was modulated for over 24 000 cycles and showed no degradation in the either the modulation depth or the speed, consistent with tests of current-driven VO$_2$ devices, which have been operated up to 260 million cycles without failure, far greater than the cycling reversibility of other phase-change materials such as GST.
One application of this approach could be in infrared and visible identification tags and coding. To demonstrate how one could employ the device for such applications, VO₂ nanocrystal arrays were patterned to form the letters “V” and “U” and then overlaid by a uniform, unpatterned, bow-tie antenna layer (24 μm × 24 μm) (Figure 4a,d). The array was imaged at a wavelength of 1010 nm, corresponding to the point where the bow ties with semiconducting VO₂ in the feed gap (30 °C) have the same reflectivity as the bare bow-tie antenna array. In this case, the array appears completely uniform. However, heating the metadevice to 82 °C switches the VO₂ into the metallic state and shifts the absorption maximum to shorter wavelengths, resulting in a reflection contrast of 23% (see the measured spectrum in Figure S7). As shown in Figure 4c–f, this causes the “V” and “U” to become visible, revealing the previously hidden image.

In summary, by fabricating unit cells with strong field concentration in a region occupied by nanocrystalline phase-change elements, we have significantly reduced the required switching time and power compared with thin-film-based spatial light modulators. The device exhibits a tuning range as large as 360 nm and a modulation depth of up to 33% with a switching time and power compared with thin-film VO₂ that was grown using a supercontinuum light source (Fianium), and the reflected signal from the sample was analyzed using a grating spectrometer with an InGaAs detector (Horiba iHR320).

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.7b01767.

Thin film design considerations, gap size dependence of the metadevice, VO₂ thin film characterization, calculation of local heating, simulated results with intermediate VO₂ states, time response measurement, and spatial performance contrast characterization (PDF)

AUTHOR INFORMATION
Corresponding Author
*E-mail: jason.g.valentine@vanderbilt.edu.

ORCID
Philip G. Evans: 0000-0002-9612-2031
Jason G. Valentine: 0000-0001-9943-7170

Notes
The authors declare no competing financial interest.

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