Materials and Methods:

Sample fabrication:

Highly oriented VO₂ thin films on Al₂O₃ (0001) substrates were deposited by reactive sputtering from a vanadium target through reactive bias target ion beam deposition using an Ar + O₂ gas mixture. Metamaterials (MM) on VO₂ films were made by stencil deposition technique. The 200 nm gold metamaterial arrays were deposited onto the 75nm VO₂ film using a single step process with a SiN shadow mask: electron-beam gold evaporation at a deposition rate of 1Å/s. No chemical cleaning is needed afterwards.

Electromagnetic Simulations:

Figures 2a and S2d were created using a 2D electric field monitor at 0.41 THz; the VO₂ film was assumed to be in its initial state. The result was then normalized to the excitation signal, yielding the values shown.

Figures 2b and 2c were created using the temporal profile of the real pulse as the excitation source, then calculating the temporal profile of an electric field probe defined at the center of the gap in real space. The resulting curves were Fourier transformed and normalized to the excitation signal to calculate field enhancement in the frequency domain.

For Fig. 2e we specified a region within the SRR gap consisting of VO₂ where the conductivity could range over the values obtained through the phase transition, while maintaining the conductivity in the remaining portions of the VO₂ film at the value for the initial temperature. We obtained those data sets by sweeping the electrical conductivity across the values shown in the Fig. 2.
Theoretical analysis:

There are several possible mechanisms which could be responsible for the THz-induced IMT. One possibility is impact ionization whereby carriers accelerated by the electric field acquire sufficient kinetic energy to create additional carriers through collisions. Although impact ionization plays an important role in the high-field THz response of semiconductors, it cannot be the origin of the IMT in our experiment because of the low carrier mobility in the insulating state of VO₂ (~1 cm²/Vsec). For impact ionization, the carrier kinetic energy should be larger than the ionization threshold (>0.67 eV), which requires that electrons are accelerated to a speed > 3x10^7 cm/s. Model calculations based on a simple rate equation approximate the critical field strength to be ~25 MV/cm, which is greater than the highest enhanced field strength in our experiments. The related parameters of VO₂ are listed in table S1 as summarized from previous experimental data.

<table>
<thead>
<tr>
<th>VO₂</th>
<th>Insulating state (room temperature)</th>
<th>Metallic state</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carrier mobility</td>
<td>0.1~1 cm²/Vsec</td>
<td>1~10 cm²/Vsec</td>
</tr>
<tr>
<td>Effective mass of electron</td>
<td>1.6~7</td>
<td>1~3</td>
</tr>
<tr>
<td>Electron density</td>
<td>10^{19}~10^{20} cm⁻³</td>
<td>1~3x10^{21} cm⁻³</td>
</tr>
<tr>
<td>Energy gap</td>
<td>0.6~0.7 eV</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table S1 | The properties of VO₂ in the insulating state and metallic state.

Since impact ionization could not have initiated the phase transition, other possibilities must be considered. The THz photon energy (~ 3 meV) is far lower than the bandgap (0.7 eV) and the
lowest-frequency IR active mode\textsuperscript{35} (23.4 meV), ruling out direct electron-hole creation or coherent vibrational excitation by the THz pump pulse\textsuperscript{36-39}.

The Poole Frenkel (PF) effect and thermal effects are the two obvious choices for an induced conductivity change (see refs. 40-41, also see equations 1 and 2 in the paper). Since the initial conductivity at \sim 320K is quite low (\sim 10 (\Omega \text{ cm})\textsuperscript{-1}), pure thermal heating (\sigma E^2) cannot solely explain the phase transition behavior. An in-gap field of \sim 1 MV/cm with the initial low conductivity yields a temperature rise less than 1 Kelvin in the two-temperature model (see equation 2 in paper), which is clearly insufficient to explain the measured change in transmission. Thus, an initial conductivity change must occur before the thermal effects take over. The PF effect lowers the potential barrier arising from on-site coulomb repulsion in VO\textsubscript{2}, yielding additional carriers. When the carrier density approaches a critical value, typically \sim 10^{21} \text{ cm}^{-3}, a phase transition occurs. With a DC field, this requires a critical field of a few hundred kV/cm\textsuperscript{42-47}. Dynamically with ultrafast THz pulses, we found the critical field to be on the order of 1 MV/cm. Accompanied with the initial conductivity rise induced by the PF effect, heating described by \sigma E^2 raises the electron temperature, then relaxation through electron-phonon scattering takes place and heats the lattice on the ps timescale.

This can be approximated using the two-temperature model\textsuperscript{41}. Calculations show that for a relatively moderate field strength (\sim 1MV/cm), the resulting conductivity change is \sim 200(\Omega \text{ cm})\textsuperscript{-1} and the lattice temperature rise is \sim 20 K.

For the numerical calculations, we used a value of 324 K for the initial temperature; 10 for insulating state relative permittivity; 10 (\Omega \text{ cm})\textsuperscript{-1} for the insulating state conductivity; 60 J/molK for the lattice specific heat; 4000 J/mol for latent heat (which can be included in specific heat
data as an input term); $1.4 \times 10^{-2}$ J/molK$^2$ for the electronic specific heat coefficient; $10^{18}$ W/Km$^3$ for the electron-phonon coupling coefficient; and 4.3 g/cm$^3$ for the density $^{48-50}$.

**THz Damage Threshold:**

The THz damage threshold was measured by gradually increasing the THz field strength while monitoring the SRR resonance change at 0.41 THz. Above a certain field strength (refer to Fig. S1), the on-resonance THz transmission no longer increases, nor does the transmission resonance fully recover upon decreasing the field. These signatures indicate film damage. The resulting cracking of the film (see Fig. 4 in the main paper and Fig. S2) forms an insulating gap which enhances rather than diminishes the SRR resonance. The second (Down1) and third (Up2) scans with varying pump fluences show that the resulting damage is permanent and that no further damage occurs after the in-gap VO$_2$ is cracked. At higher temperatures, the damage threshold is smaller due to larger THz absorption in the VO$_2$ thin film. After the in-gap VO$_2$ film was permanently damaged, optical microscopy (Fig. 4) and SEM (Fig. S2) were used to characterize the damage patterns at different positions relative to the THz illumination spot. Severe damage was found at the center of the beam and different patterns were found in the vicinity of the THz spot. Figure 4a and S2 indicate that the damage patterns are directly related to the THz intensity. Different SRR structures with different gap sizes fabricated on VO$_2$ thin films were also investigated and the results were in good accordance with our interpretation. For example, with simple SRRs with larger gaps deposited (4μm and 10μm), much smaller nonlinear effects were observed and no damage occurred under the highest field strengths.

At the highest THz fluence the temperature rise of the electrons is substantial but the absolute value is hard to estimate due to the extreme nonlinear nature of this process. The mechanism for
damage is still unclear at this stage and is worthy of further investigation. It appears that damage process is significantly different from dielectric breakdown since the damage is along the equipotential lines while typical dielectric breakdown is along the direction of the electric field. At room temperature, the transmission change is near the detection limit even when we probe the metamaterials resonance change with enhanced sensitivity provided by the metamaterials and no damage occurs at room temperature. This indicates the importance of the initial carrier density and electron-phonon coupling in the dynamics, which is consistent with our model calculation.
Supplementary Information Figures:

Figure S1 | Field strength-dependent THz transmission of VO₂ with metamaterials at 0.41 THz. The arrows indicate the directions in which the field is changed. Down1 and Up2 curves indicate that permanent damage to the film occurred above ~3.5 MV/cm THz field strength.
Figure S2 | Damage patterns of VO₂ metamaterials. a, THz-induced damage at the edge of the THz pump spot. b, THz-induced damage at the center of the THz pump spot. c, Damage pattern follows the equal potential lines of the induced high field in the MM gap. d, Simulated in-plane THz electric field in the vicinity of the MM SRR gap. The color scale indicates the THz field strength at the resonance frequency.
Supplementary Information References:


