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Tunable hyperbolic metamaterials utilizing phase change heterostructures

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We present a metal-free tunable anisotropic metamaterial where the iso-frequency surface is tuned from elliptical to hyperbolic dispersion by exploiting the metal-insulator phase transition in the correlated material vanadium dioxide (VO2). Using VO2-TiO2 heterostructures, we demonstrate the transition in the effective dielectric constant parallel to the layers to undergo a sign change from positive to negative as the VO2 undergoes the phase transition. The possibility to tune the iso-frequency surface in real time using external perturbations such as temperature, voltage, or optical pulses creates new avenues for controlling light-matter interaction. © 2014 AIP Publishing LLC.

Correlated oxides that show metal-insulator transition are of great interest in condensed matter physics, oxide electronics, and photonics as their physical properties can be altered considerably by applying a perturbation in the form of heat, electric field, or optical pulses. At room temperature, vanadium dioxide (VO2) is an insulator with a monoclinic structure. Upon heating beyond a critical temperature, its structure changes to tetragonal rutile form accompanied by a drop in electrical resistance by several orders of magnitude. Applying electric field or optical pulses can also trigger a similar effect.

Tunable metamaterials and plasmonic switches have been realized in the past using the phase transition in VO2 by integrating the VO2 layer with metallic nanostructures. The change in refractive index of the VO2 upon undergoing phase transition shifted the resonance of the metamaterial/plasmonic structure, which in turn was used as a probe to study the phase transition. In this work, we exploit the insulator to metal phase transition in VO2 to tune the dispersion of the metal-free anisotropic metamaterial from elliptical to hyperbolic.

One of the most common geometries used to realize hyperbolic metamaterials is the one-dimensional layered structure. In such metamaterials, the dielectric tensor is uniaxial: $\tilde{\varepsilon}(\mathbf{r}) = \text{diag}(\varepsilon_{xx}, \varepsilon_{yy}, \varepsilon_{zz})$, where $\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{||}$ and $\varepsilon_{zz} = \varepsilon_{\perp}$. The optical iso-frequency surface for the TM-polarized waves propagating in such a metamaterial is given by

$$\frac{k_x^2 + k_y^2}{\varepsilon_{\perp}} + k_z^2/\varepsilon_{||} = \frac{\omega^2}{c^2}. \quad (1)$$

Here, $\varepsilon_{||}$ and $\varepsilon_{\perp}$ are the effective dielectric constants of the structure in mutually orthogonal directions. When $\varepsilon_{||}\varepsilon_{\perp} > 0$, the optical iso-frequency surface is an ellipsoid. On the other hand, when $\varepsilon_{||}\varepsilon_{\perp} < 0$, the optical iso-frequency curve takes

Metamaterials are engineered nanocomposites composed of building blocks of length scales much smaller than the wavelength of electromagnetic waves they interact with. They have attracted much attention over the last decade owing to their potential applications ranging from super- and hyper-lenses, optical cloaking, stealth elements to frequency tuning that occurs in transition metal oxides to tune the effective dielectric constant in a heterostructure.

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the form of a hyperboloid and the metamaterial is said to exhibit strong anisotropy. Because of the unbound nature of the optical iso-frequency curve, such a material can support electromagnetic states with large wave-vectors. This forms the basis of applications of hyperbolic metamaterials in enhancing photon density of states and diffraction-free optical imaging.

The metamaterial studied in this work consists of alternating layers of VO2 and titanium dioxide (TiO2) as shown schematically in Fig. 1(a). The layered geometry in addition to being the simplest to realize hyperbolic dispersion using a heterostructure also allows us to tune the degree of anisotropy by controlling the fill fraction of the constituent layers. The TiO2 and VO2 layers were deposited by magnetron sputtering in a pure Ar atmosphere onto c-plane sapphire from TiO2 and V2O5 targets, respectively. The substrate temperature and growth pressure were kept constant at 550 °C and 5 mTorr during the deposition. The growth rate of TiO2 and VO2 were calibrated by x-ray reflectivity and ellipsometry measurements.

The in-plane electrical properties of VO2 were measured using a Keithley 2635A instrument with samples placed on a temperature-controlled stage. The resistance values were calculated by linear fitting of the voltage-current curves. Fig. 1(b) shows the normalized in-plane resistance versus temperature curves of VO2 films on c-plane sapphire and on a TiO2/VO2/sapphire structure, respectively. The VO2 thin films on sapphire exhibit a metal-insulator transition with more than three orders of magnitude change in its resistivity at a transition temperature of ~72 °C as determined by the Gaussian fit of the d ln R/dT curve. VO2 thin film deposited on a TiO2/VO2 1-period structure on sapphire also shows similar electrical properties.

X-ray diffraction data were acquired with Cu Kα radiation by 2θ-ω coupled scan using a triple-axis Bruker D-8 high resolution XRD diffractometer. Fig. 1(c) shows the 2θ-ω coupled scan of the 1 period TiO2/VO2 structure on sapphire. VO2 is found to be single phase epitaxial on sapphire with its (010) plane parallel to the c-plane of sapphire substrates. The two diffraction peaks from TiO2 indicate coexistence of (001) anatase and (100) rutile phases. Although rutile TiO2 is thermodynamically more favorable than anatase, the anatase phase is kinetically stabilized at 550 °C, consistent with previous studies of epitaxial TiO2 growth on c-plane sapphire at similar temperature.17 This indicates that the epitaxial VO2 layer on sapphire can serve as a buffer layer for the growth of TiO2. X-ray diffractions from multi-period samples show similar diffraction pattern and peak positions, indicating that the epitaxial relation is maintained in multi-period samples. However, the growth of a TiO2 layer on VO2 weakens the metal insulator transition possibly due to diffusion of Ti into VO2 at higher growth temperatures. This is discussed in greater detail in the last section.

![FIG. 1. (a) Schematic of the metamaterial; (b) Normalized electrical resistance of VO2 grown directly on c-plane sapphire and grown on TiO2/VO2 structure on sapphire spanning the phase transition. (c) 2θ-ω coupled x-ray diffraction scan from VO2/TiO2/c-sapphire. The four peaks (from left to right) correspond to (1) TiO2 Anatase (004), (2) TiO2 Rutile (200), (3) VO2 (020), and (4) Al2O3 (000 12) and (d) AFM image of the surface of a two-period TiO2/VO2 on sapphire sample. Sharp interface between VO2 and TiO2 is desired to achieve anisotropy and hyperbolic dispersion in the metallic phase of VO2. The surface roughness of the structure is 2.2 nm, while the total thickness of the structure is ~70 nm.](image-url)
broadening of VO₂ is characterized by nucleation, island formation, and a function of frequency. The transition temperature of VO₂ above the transition temperature. All three terms are required to model the dielectric constants of VO₂ at room temperature and at high-frequency electronic transitions. The second term is the Lorentz oscillator term that accounts for contribution from free electrons coupled to each other. The fit parameters were the amplitude and broadening of the Lorentz oscillators comprising the dielectric function of VO₂. Dielectric constant of TiO₂ as a function of wavelength is obtained by performing VASE measurements on a single layer deposited on a sapphire substrate.

Once the single layers were characterized, the metamaterial structure was fabricated by depositing alternating layers of VO₂ and TiO₂ on a sapphire substrate (Fig. 1(a)). The thicknesses of the individual VO₂ and TiO₂ layers estimated from X-Ray Reflectometry (XRR) measurements were found to be 23 ± 2 nm and 12 ± 1 nm, respectively. Ellipsometric measurements were then carried out on the multilayered sample as a function of temperature to obtain the dielectric constant of VO₂. While fitting the ellipsometry data, the individual VO₂ and TiO₂ layers were assumed to be coupled to each other. The fit parameters were the amplitude and broadening of the Lorentz oscillators comprising the dielectric function of VO₂. Dielectric constant of TiO₂ obtained from measurements on a single layer was used in modeling the multilayered structure. Ellipsometry data from the multilayered sample are then fitted to retrieve the dielectric constant of TiO₂ as a function of wavelength.

The individual VO₂ and TiO₂ thin films were characterized optically by Variable Angle Spectroscopic Ellipsometry (VASE) measurements using a Woollam M2000 ellipsometer. To obtain the optical properties of VO₂ film as a function of temperature, the sample was placed in a heat cell (HTC 100) during ellipsometric measurements. A Drude-Lorentz model was used to model the optical properties of VO₂ as a function of frequency:

\[
\varepsilon(\omega) = \varepsilon_{\infty} + \sum_{n=0}^{\infty} \frac{A_n \omega_n}{\omega^2 - \omega_n^2 - iB_n \omega} + \frac{-A_d \omega_d}{\omega^2 + iB_d \omega}.
\]

The first term is purely real and is the contribution from high-frequency electronic transitions. The second term is the sum of multiple Lorentz oscillators with amplitude \(A_n\) and broadening \(B_n\) centered at energy \(\omega_n\). The third term is the Drude term that accounts for contribution from free electrons when VO₂ becomes metallic. Here, the parameter \(A_d\) is related to the plasma frequency. The first two terms are used to model the ellipsometry data below the transition temperature. All three terms are required to model the dielectric function of VO₂ above the transition temperature. The dielectric constants of VO₂ at room temperature and at 130 °C retrieved from ellipsometry measurements are shown in Fig. 2(a). The dielectric constant of TiO₂ as a function of wavelength is obtained by performing VASE measurements on a single layer deposited on a sapphire substrate.

FIG. 2. (a) Dielectric constants (real and imaginary) of identical VO₂ samples determined using ellipsometric measurements in the insulator and metallic phases. The effective dielectric constants of the multilayered structure determined using ellipsometry and effective medium theory at (b) room temperature and (c) at 130 °C where the VO₂ has undergone phase transition to metallic phase causing the \(\varepsilon_{\infty}\) to become negative beyond 1560 nm and resulting in hyperbolic dispersion.

FIG. 3. Optical and electrical properties of the structure across the VO₂ phase transition. Left vertical axis corresponds to effective in-plane dielectric constant at 1650 nm, \(\varepsilon_{\infty}\) undergoes a sharp decrease and becomes negative beyond 95 °C. Right vertical axis corresponds to normalized resistance of VO₂ on a 1-period structure as a function of temperature. Inset shows \(\varepsilon_{\infty}\) at 1000 nm as a function of temperature where no transition into the hyperbolic regime is observed.
dielectric constant of VO₂ as a function of wavelength, at different temperatures. From the dielectric constants of VO₂ and TiO₂ as well as the thicknesses of the layers, effective dielectric constants of the structure are then determined using effective medium theory.

Fig. 2(b) shows the plot of the effective dielectric constants as a function of wavelength when the multilayered structure is at room temperature. Since both VO₂ and TiO₂ are non-metallic, both ɛ∥ and ɛ⊥ are positive throughout the spectrum and the optical iso-frequency curve takes the shape of an ellipsoid due to the slight anisotropy in the dielectric constants. However, when the metamaterial is heated to a temperature of 130 °C, due to the insulator-metal transition in VO₂, ɛ∥ < 0 for wavelengths beyond 1566 nm while ɛ⊥ > 0 in the entire spectrum, as shown in Fig. 2(c). Consequently, the optical iso-frequency surface transitions into a hyperboloid at wavelengths beyond 1566 nm.

In Fig. 3, we plot the effective in-plane dielectric constant as a function of temperature at 1650 nm to demonstrate the tunability of the dispersion. Here, ɛ∥, which is positive at lower temperatures, decreases sharply as the temperature increases and becomes negative for temperatures beyond 95 °C, with the largest change happening around 70 °C. This temperature dependence is identical to the decrease of electrical resistance of VO₂ (gray squares—Fig. 3). This similarity in the optical and electrical characteristics is due to the change in free carrier concentration as the sample is heated and transitions from a Lorentz regime to a Lorentz-Drude regime. Beyond 120 °C the free carrier concentration saturates and hence the optical and electrical properties show minimal change. On the contrary, at 1000 nm (inset—Fig. 3), which lies in the elliptical dispersion regime, even at higher temperatures there is hardly any change in ɛ∥. This is because, at 1000 nm, VO₂ does not exhibit metallic properties even at high temperatures.

We observed that the optical properties of VO₂ in the multilayered structures were different from that of a single layer. As the number of the TiO₂/VO₂ periods increase in the multilayered structure, VO₂ shows weaker plasmonic behavior. To understand this, we studied how the properties of VO₂ are affected when multiple layers are deposited on top. Fig. 4(a) shows the dielectric constants of VO₂ measured by ellipsometry, on a 1-period structure and a 3-period structure, at 130 °C. VO₂ behaves as a weaker metal on the 3-period structure. (b) d lnR/dT curve as a function of temperature to compare the metal-insulator transition of VO₂ films in different environments. Compared to a single VO₂ film, the transition is weaker on a VO₂/TiO₂/VO₂ structure. VO₂ film on a heterostructure after etching away the top TiO₂ layer shows a much weaker transition. This could be due to interdiffusion of Ti into VO₂ at high temperatures during growth as well as damage of VO₂ during etching.
dielectric constant shows a sharp transition from positive to negative values resulting in a change in the topology of the optical iso-frequency curve from closed ellipsoid to open hyperboloid (Eq. (1)). This transition results in modification of physical parameters such as dynamics of propagating waves supported by the system and the photon density of states as was noted previously. The possibility to dynamically tune the iso-frequency surface using external perturbations as shown here points to interesting research directions in contemporary efforts to control light-matter interaction.

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