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Mid- to Far- Infrared Sensing: SrTiO₃, a Novel Optical Material.

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Lattice dynamics and Crystal Structure

To study the lattice dynamics of the SrTiO₃ (STO) bulk crystal, we performed ellipsometric measurements in the range of 0.03 – 1 eV (250 – 8000 cm⁻¹) at three angles of incidence (65°, 70°, and 75°) using a Woollam IR Variable Angle Spectroscopic Ellipsometer. We also performed ellipsometric measurements at the same angles of incidence in the range of 0.7 – 5.2 eV (M2000 Woollam) to ensure continuity of the optical constants across the whole range of wavelengths from the far infrared to the ultraviolet (Fig. S1).



Fig. S1 Dielectric permittivity of $SrTiO_3$ measured by IR (solid lines) and near IR-Vis-UV (dashed lines) spectroscopic ellipsometry.

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The two spectra illustrate continuity of the optical constants. The combined spectra are shown as pseudo functions in Fig. S1 (note that since the STO crystal is bulk, there is no dependence on the angle of incidence in this case, so we only show data taken at 70°).

The raw ellipsometric data (ellipsometric angles Psi and Delta) are shown in Fig. S2 (green and blue lines respectively). The red solid lines represent the modelled Psi and Delta functions.



Fig. S2 Ellipsometric angles ψ (green solid, dashed and dotted lines) and Δ (blue solid, dashed and dotted lines) at three angles of incidence. The red solid lines are the simulations following eq. S2.

STO is a perovskite crystal with cubic symmetry (XRD data are shown in Fig. S3). Since it is an ionic crystal, each normal phonon mode will split into a Transverse Optical (TO) mode and a Longitudinal Optical (LO) mode. The energies of the normal phonon modes for STO have been determined elsewhere¹ employing hyper-Raman scattering and are presented in Table S1.

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	то	LO
Sr	0.0108 eV (87 cm ⁻¹)	0.0222 eV (179 cm ⁻¹)
Ti	0.0222 eV (179 cm ⁻¹)	0.0585 eV (472 cm ⁻¹)
0	0.0677 eV (542 cm ⁻¹)	0.0982 eV (792 cm ⁻¹)

Table S1 Location of the normal phonon modes of $\ensuremath{\mathsf{SrTiO}_3}$

Only the highest energy TO mode is apparent in our measured spectra, represented by a high absorption peak located exactly at 0.0677 eV. Interestingly the decrease of the real permittivity at lower photon energies, while maintaining negative values, points out that one or more additional strong peaks occur below our spectral range (since STO is a dielectric it cannot be assumed any Drude-like behaviour, *i.e.* contribution from free carriers, which would dictate the real permittivity to remain negative). Additional LO modes can be demonstrated when plotting the loss-function $(-1/\varepsilon)$, which we present in Fig. S4. The LO_{Titanium} mode and the LO_{Oxygen} mode can be clearly seen.



Fig. S3 X-ray diffractogram of the STO crystal. The inset depicts the structure of SrTiO₃: Sr: green sphere, Ti: blue spheres: O: red spheres.

Typically, to fit the ellipsometric data of polar dielectric crystals the following factorised form of the phonon response is employed:

$$\frac{\varepsilon(\omega)}{\varepsilon_{\infty}} = \prod_{i=1}^{3} \left(\frac{\omega_{i,LO}^2 - \omega^2 + i\gamma_{i,LO}\omega}{\omega_{i,TO}^2 - \omega^2 + i\gamma_{i,TO}\omega} \right)$$
(S1)

Equation S1 relates the dielectric function $\varepsilon(\omega)$ to the eigenfrequencies $\omega_{i,LO}$ and $\omega_{i,TO}$ (longitudinal and transverse optical phonons respectively) and assigns different broadening factors γ_i for the LO and TO phonons. When the broadening factors are equal, the usual Lorentz model is recovered.² However, our measured spectra, shown in Fig. S1, can be accurately reproduced by just two Lorentz oscillators:

$$\varepsilon(\omega) = \varepsilon_{\infty} + \sum_{i=1}^{n} \frac{A_{i}\omega_{i}^{2}}{\omega_{i}^{2} - \omega^{2} + i\gamma_{i}\omega}$$

Journal of Materials Chemistry C

We follow Zollner *et al.*³ and we fix the lower energy at 0.0108 eV (to represent the $TO_{Strontium}$) and we let free all the other parameters to best describe the measured IR spectrum. The resulting parameters are shown in Table S2. We notice that the two broadening factors are almost equal which also validates our model of choice.

Table S1 Location of the normal phonon modes of SrTiO₃

ε_{∞}	5.86
A1	1731 eV ²
ω_1	0.0108 eV
¥1	0.002 eV
A ₂	0.099 eV ²
ω2	0.067 eV
¥2	0.0019 eV

The TO_{Oxygen} phonon energy is accurately reproduced and the cross-over points (typically used as a criterion for the LO modes) at 0.057 eV and 0.098 eV is in agreement with references 1 and 2 of the supporting information document. A different way of representation of the dielectric function is by demonstrating the loss function ($1/\varepsilon$), which reveals all the modes of vibration within our measured spectral range (Fig. S4).



Fig. S4 Imaginary permittivity, ε_2 (red solid line) and loss function l/ε_l (blue solid line) of bulk STO, measured at 70° incidence.

Finite-Difference Time-Domain calculations

The calculations of the optical response of the designed STO structures were performed by time-integrating Maxwell's equations⁴ on a computational grid utilizing the FDTD method.⁵ In the computational process the material dispersion is introduced in the form of polarization equations coupled and solved concurrently with Maxwell's equations, where the various parameters defining the optical constants of the materials are obtained by performing a Lorentz fit⁶ to the experimental spectra of a STO perfect (100) crystal. The electromagnetic fields are extracted at every point in the structure in time domain, and by applying Fourier transforms we get the corresponding quantities (S_{2}^{2}) frequency domain. An in-house 3D FDTD simulator^{7,8} was used in all calculations.

^{2 |} Journal of Materials Chemistry C, 2018, 00, 1-3

Journal of Materials Chemistry C

The dielectric function of Fig. 1 (red thick solid lines) is utilised within the FDTD framework to evaluate the localised SPhR performance of STO. Thus, we calculate the reflection, transmission, absorption, the detailed spatial distribution of the enhanced electric field and the electric field lines to further understand the nature of the localised modes.

The system is discretized to 10 nm/grid at which results are already converged to <2% error. The input field is a broadband plane wave (narrow Gaussian temporal profile) at normal incidence. We get the optical response (reflection, transmission and absorption) in frequency domain by Fourier transforming the fields on suitably chosen monitor planes and taking the appropriate ratios with and without the particle array.

Size effect

Given the dielectric function of STO there is a lot of flexibility in the design of resonators that sustain localised surface phonon resonant modes (LSPhRs); from few nm to several microns in size. Here, we report the effect of the diameter of disks of 200 nm in thickness. For these calculations we have established a ratio of 1:2 between the diameter and pitch distance (periodicity) in order to maintain a filling ratio of 20%. We also restricted the diameter size in order to contain the maximum wavelength resonance within the upper limit of our measurement (40 μ m) and without the requirement to extrapolate the values of the dielectric function. However, as Sirenko *et al.*⁹ suggests the real part of the dielectric function remains negative until ~100 μ m so larger sizes (for this filling ratio) are still vaild.



Fig. S5 Global absorption map of STO nanodisks (200 nm thick) on Si substrate varying the diameter size. During the calculations a ratio of 1:2 between the diameter and pitch distance (periodicity) was maintained rendering a filling ratio of ~20%.

Periodicity (filling ratio) effect

We also examined the effect of the periodicity on 200 nm thick disks of 400 nm in diameter. We varied the periodicity in order to achieve filling ratios that span from 3% (sparse structure) to 45% (dense structure). The effect is illustrated in Fig. S6.



Fig. S6 Global absorption map of STO nanodisks (200 nm thick, 400 nm in diameter) on Si substrate varying the pitch distance (periodicity). The range of filling ratios achieved spans from \sim 3% to 45%.

Comparison with other polar crystals

We compare the performance of STO photonic resonators of the same exact geometry as with other polar dielectrics such as Sapphire, GaN and GaP. We illustrate the results in Fig. S5. Evidently, in all other cases the LSPhRs are restricted in the spectral range of the Reststrahlen band. In contrast STO's effective Sr-Ti Reststrahlen band dictates the ability of LSPhRs to tailor across the far-IR range. The maximum absorption is similar in Sapphire, STO and GaN and only GaP seems to perform poorly. This is also evident by the linewidth of the absorption band which is broader in comparison to the other three polar dielectrics.



Fig. S7 Global absorption map of nanostructures of various polar dielectric crystal on various substrates. Within the graph, the IR ellipsometric measurements of the polar dielectric's real permittivity (white dashed line) are superimposed. (a) The case of STO. (b) The case of Sapphire. (c) The case of GaN. (d) The case of GaP. All the simulations

Electronic Supplementary Information

Electronic Supplementary Information

were performed for the exact same nano-structuring arrangement (disks of 400 nm in diameter, thickness of 200 nm and pitch of 800 nm) for comparison.

Strong coupling effects

The sensing capability of the STO antennas was explored by calculating the reflectance, transmission and absorption spectra (Fig. S8) of the STO antennas on top of Si, covered by a 100 nm thin molecular film. Optically, the molecular thin film is described by a Lorentzian line shape, with its central wavelength varied so to scan the entire range between 30 - 40 µm, where the strongest dipole moment of the antennas is located.



Fig. S8 (a) Reflection, (b) Transmission and (c) Absorption of STO nanodisks on Si substrate (disk thickness is 200 nm, diameter is 400 nm and the pitch is 800 nm) with a 100 nm molecular thin film on top. The molecular thin film's response is described by a Lorenztian line shape whose centre is scanned across the entire range between 30 - 40 μ m.

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