Laser Structuring for Control of Coupling Between THz Light and Phonon Modes

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Modification of surface and volume of sapphire is shown to affect reflected and transmitted radiation at THz spectral range. Structural modifications were made using ultra-short 230 fs laser pulses at 1030 and 257.5 nm wavelengths forming surface ripples of ~250 nm and 60 nm period, respectively. Softening of the transverse optical phonon TO1 mode due to disorder was most pronounced in reflection from laser ablated surface. It is shown that sub-surface periodic patterns of laser damage sites have also modified reflection spectra due to coupling of THz radiation with phonons. Application potential of laser structuring and disordering for phononic engineering is discussed.

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1. Introduction

Spectral properties at sub-1 mm wavelengths at around terahertz (1 THz = 10^{12} Hz) frequencies are important for understanding weak interaction in peptides and proteins [1,2], material response at vicinity of phase transitions [3,4], glass formation where low frequency Raman spectra exhibit the low frequency 10-50 cm^{-1} boson peak due to rearrangement of density of states in amorphous materials [5]. In silk, amorphous and crystalline structural components with proteins forming a 3D network of random and α-coils together with a crystalline β-sheet phase can be distinguished in the THz spectral window [6-11].

Control of phonon spectrum is a new frontier in material science for growth and deposition of layered structures of usually incompatible materials with different thermal expansion coefficients. Materials’ optical properties at IR range can be engineered through control of the phonon spectrum. For example, surface phonon polaritons (SPP) are shown to control directionality of black body emission when coupled with surface gratings [12]. By introducing patterns with period Λ satisfying the grating equation:

$$\frac{2\pi}{\lambda} \sin \theta = k_i + m \frac{2\pi}{\Lambda},$$

(1)

where λ is the wavelength of emitted light (black body radiation), θ is the angle of emitted light, k_i is the surface wave component parallel to the surface (SPP), and m is an integer. It is thereby possible to create a strong directional out-coupling of the IR emission into free space out of the sample [12]. With a surface grating Λ = 0.55λ directional emission was observed at λ = 11.36 μm from SiC surface with intensity 20 times larger as that from a flat surface at the same temperature [12]. This is called Wolf’s effect: at the angle, θ, of the largest emissivity, the reflectivity, R, has a dip. This corresponds to Kirchhoff’s law: the polarized directional spectral emissivity ε is equal to the absorptivity α and is given by ε = α = 1 − R.

Surface nanotexturing of sapphire by fs-laser ablation is shown to enhance light extraction efficiency in light emitting diodes [13]. Surface patterns with periods about 1-5 μm with different duty cycles are used for epitaxial lateral overgrowth (ELO) for GaN to reduce the density of threading dislocations. A better understanding of nanotexturing effects at the T-ray spectral range (phonon modes) is required for future material engineering. Nano-/micro-scale surface modifications can be readily made by direct writing with ultra-short fs-laser ablation.

Here, laser modifications on/in sapphire are identified in reflection at the THz spectral range. Such nano-/micro-scale patterns can be used for controlling the phonon spectrum on the surface and in the bulk of polar semiconductors and dielectrics, hence, affecting heat transport, emissivity, coupling mechanisms between surface excitation in layered structures [14].

2. Samples and procedures

The THz/Far-IR Beamline at the Australian synchrotron was used to characterize laser modified samples at 40 – 800 cm^{-1} spectral range. The beamline is equipped with a Bruker IFS 125/HR Fourier Transform (FT) spectrometer and Opus software was used for initial data analysis. Up to
of charge $q$ (hence $q$-plate) for the azimuthal patterning of the optical axis. The azimuthal dependence of the slow axis is given by $\Psi = q\phi$, where $q$ is the half integer and $\phi$ is the polar angle. The laser ablated regions have a nanoscale pattern of ripples with periods scaling with wavelength and the refractive index, $n$, as $\lambda = \lambda/(2n)$ on dielectric (transparent material) surfaces. Hence, through variation of wavelength different nano-structures can be formed. At tight focusing below the surface, voids can be created inside dielectric host materials when a single pulse irradiance is $I_p > 10$ TW/cm$^2$ (Fig. 1(b)). Such surface and bulk modifications can be patterned with high precision and their use for tailoring optical, mechanical, and thermal properties are of interest. Optical characterization of such patterns at T-ray region was carried out. Sapphire can be used as a substrate for optical elements due to its high transparency (Fig. 1(a) and (b)) and performance of laser inscribed optical elements in T-ray region was to be well understood.

Figure 1(a) shows a pattern of grooves comprising an inhomogeneous birefringent plate with a topological defect

3. Results and discussion

Figure 1(a) shows a pattern of grooves comprising an inhomogeneous birefringent plate with a topological defect
from Table 5.2 of Ref. [17]. However, the best numerical fit of experimental reflectivity of sapphire was achieved for LO4 at 906 cm$^{-1}$ (not shown here). Figure 3(b) shows a strong alteration of reflectivity from laser ablated pattern of ripples at the TO 1 mode at two different polarizer orientations. Self-organized ripple structures with period of $\approx 250$ nm (Fig. 3(a)) or $\Lambda \approx \lambda_l/(2n)$ were recorded at the $\lambda_l = 1030$ nm laser wavelength used, and where refractive index of sapphire is $n = 1.7$. Strong relative reflectivity increase at the position of LO2 can be partially caused by a very low value of $R$ for the c-plane sapphire sample (small values of denominator used in normalization) which turn the overall minor mode softening by laser structuring appear as a large ratio. However, the value of this peak remained consistent throughout the measurements at all different polarizations, hence, it being a numerical artifact appears unlikely. There is an observable change in $R$ at the spectral location of TO4 mode. Reflection from the laser ablated surface shows spectrally broader TO 1,4 bands (Fig. 3(b)), a sign of mode softening. Reflectivity interrogated at different linear polarizer angles showed a consistent change in $R$ values of the TO1,4 bands (Fig. 3(c)).

Figure 4 shows transmission and reflection spectra from the pattern of laser inscribed lines with period $\Lambda \approx 24$ $\mu$m. In the reflectance spectrum a broad band around $\lambda_R = 294$ cm$^{-1}$ was observed (or $\lambda_R = 34$ $\mu$m in free space with refractive index $n = 1$). The reflected wavelength is also the same which is effectively absorbed, hence, coupled into the structure/sample. The momentum conservation for the wavevectors of reflected light $k_R$, structure/sample mode $k_s$, (could be a surface wave, SPP, TO-mode), and a grating $k_g$, is given by $k_R = k_s - k_g$. This is the simplest grating mediated two wave mixing scenario. One can find the corresponding wavelength $\lambda_s$ from the definition $k_s \equiv 2\pi/\lambda_s$, at which the energy is deposited (absorbed) from the right triangle rule:
\[
\left( \frac{2\pi}{\lambda_s / n} \right)^2 = \left( \frac{2\pi}{\lambda_i / n} \right)^2 - \left( \frac{2\pi}{\Lambda} \right)^2.
\]

Equation 2 allows to calculate the wavelength and energy of the mode which efficiently absorbs incoming IR light and, hence, effectively reflects it. One would find \( \lambda_s = 30.94 \mu m \) (323 cm\(^{-1}\)) with \( n = 3.2 \) in sapphire for the high transmission region (Fig. 2). This did not fit the TO\(_1\) mode. The second reflectivity peak at 366 cm\(^{-1}\) (or \( \lambda_s = 27.3 \mu m \) in free space) corresponds to \( \lambda_s = 26.43 \mu m \) or 378 cm\(^{-1}\), which is also close to the TO\(_1\). For the opaque region (shaded in Fig. 1(a)), \( \approx (4.5-5.5) \) for the TO\(_{1,2}\) region and the same analysis using Eqn. 2 suggests the 366 cm\(^{-1}\) peak being close to the TO\(_1\) mode; similarly, the broad 294 cm\(^{-1}\) feature has no match with phonon mode. The broad 294 cm\(^{-1}\) reflection band can be due to a coupling with acoustic modes [14] and would require future experiments for different \( \Lambda \) values matching the phonon modes.

Even though the reflectivity changes are very weak in the normalized spectrum (Fig. 4), they are discernable on a Rayleigh scattering slope (approximated by a line in this narrow spectral window). This proves that a designed periodic pattern can be used to couple energy into a specific phonon mode.

4. Conclusions and outlook

It is demonstrated that surface and volume structuring of sapphire has direct impact on softening TO phonon modes and changing reflectivity at specific modes. Laser induced damage and structural disorder is the reason of this modification of the phonon spectrum. Control over phonon spectrum is strongly required for the growth of layered structures where different optical and acoustical modes are coupling with the interface waves [14]. Among other possible applications are surface micro-texturing for ELO solutions in GaN-based LEDs, an electron mobility control in structures with strong phonon scattering, and in thermo-electrical materials for enhancement of difference between electron and phonon mean free path. Also a fast growing field of applications is in the design of flat optical elements using surface patterning [18] where fs-laser surface and bulk structuring has been well developed [19-21].

Acknowledgments and Appendixes

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