

Article

Anisotropy of 3D columnar coatings in mid-infrared spectral range

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Abstract: Polarisation analysis in the mid-infrared fingerprint region was carried out on thin ($\sim 1 \mu\text{m}$) Si and SiO₂ films evaporated via glancing angle deposition (GLAD) method at 70° to the normal. Synchrotron-based infrared microspectroscopic measurements were carried out on the Infrared Microspectroscopy (IRM) beamline at Australian Synchrotron. Specific absorption bands, particularly Si-O-Si stretching vibration, was found to follow the angular dependence of $\sim \cos^2 \theta$, consistent with the absorption anisotropy. This unexpected anisotropy stems from the enhanced absorption in nano-crevices, which have orientation following the $\cos^2 \theta$ angular dependence as revealed by Fourier transforming the image of the surface of 3D columnar films and numerical modeling of light field enhancement by sub-wavelength nano-crevices.

Keywords: Polarisation, IR, fingerprint region, birefringence, dichroism, sculptured thin films, anisotropy

1. Introduction

Glancing angle deposition (GLAD) [1] can be used to make highly anisotropic thin films for light polarisation control, namely waveplates suited for the linear and circular polarisations [2,3] and polarizers for zero angle of incidence [4], by utilising complex arrangements of sample's tilt and rotation [5]. It becomes possible to make strongly birefringent thin films by GLAD using optically isotropic Si and SiO₂ materials [6]. It was recently demonstrated that such films have larger visible and near-infrared (near-IR) laser damage thresholds in J/cm² compared to polished surfaces or coatings made out of the two different materials [7]. GLAD deposited thin films can also act as an anti-reflection coating [8,9]. Recently, numerous investigations have been reported regarding the simulations and analysis of the GLAD coatings nanostructure [10,11] and constant morphology changes during growth [12] or in time [13]. All results indicate, that deeper understanding is required in order to fully understand the properties of nanostructured thin films, especially when stoichiometry changes [14]. How such anisotropic films behave at longer wavelengths in mid-IR fingerprint region needs clarification for applications in high-intensity laser optics, as well as in surface enhanced Raman scattering (SERS) sensors [15]. Also, the birefringent films and optical elements made by GLAD are porous and possess high surface area. The key question on whether surface defect absorption can



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compromise the performance of such GLAD coatings due to increased absorption deserves deeper analysis.

The mid-IR spectral range of 400-4000 cm^{-1} is indispensable for material characterisation. In this study, we used the IR radiation produced by a synchrotron source that offers 100-1000 times higher brightness than that of a thermal IR source commonly used in a laboratory-based FTIR instrument. This highly intense and highly collimated synchrotron-IR beam enhances spectral quality, in terms of signal to noise (S/N) ratio, and enables acquisition of high-quality FTIR spectra at diffraction-limited spatial resolution ideal for analysis of these micro-films.

We showed previously [16] that separate contributions to anisotropy due to birefringence and dichroism related to the real and imaginary parts of the refractive index ($n + i\kappa$), respectively, can be revealed from the angular dependence of transmittance or absorbance $A = -\lg T$. Indeed, an absorbing dipole has minimum and maximum A (and T) within an orientation change of π . Transmitted power through a linear polariser (e.g., mesh grid absorber) is given by the Malus law $T \propto \cos^2 \theta$. However, a change of T due to birefringence doubles the angular frequency since min-max of T occurs twice within an orientation change of π . The angular dependence of transmittance $T(\theta)$, when reflectance and absorbance are negligible $R \rightarrow 0$, $A \rightarrow 0$ for the crossed (\times) polariser-analyser setup ($T \rightarrow 1$ since $A + R + T = 1$), is given by:

$$T_{\times}(\theta) = \sin^2 2(\theta - \theta_R) \sin^2(\pi \Delta n d / \lambda), \quad (1)$$

where θ is the orientation angle; θ_R is the slow or fast axis direction (i.e. the slow axis is usually aligned to the main molecular chain or along a polymer stretch direction); Δn is the birefringence of the sample/object at the wavelength λ , for thickness d . Hence, $T \propto \sin^2(2\theta)$ angular dependence, which is double the angular frequency 2θ , rather θ for the absorber (Malus law).

Here we reveal optical anisotropy in the mid-IR fingerprinting region of 3D columnar films deposited by GLAD using the polarised synchrotron-IR microspectroscopy. Structural characterisation by scanning electron microscopy (SEM) was used and numerical modeling was applied for qualitative analysis.

2. Results

Polarisation analysis of thin columnar films deposited by GLAD was carried out in transmission T and reflection R modes (Fig. 1(a)) depending on transparency of the substrate in the 600-4000 cm^{-1} spectral window (16.7 - 2.5 μm wavelength). To ensure that the region on the substrate from which the orientational dependence of transmittance $T(\theta)$ and/or reflectance $R(\theta)$ was measured is consistent, wire grid KRS-5 (thallium bromo-iodide) and ZnSe polarisers were rotated with sample at a fixed position. The orientation angle θ corresponds to the angle between polariser and sample orientations. This ensured measurement from the very same focal spot, typically $\sim 17 \mu\text{m}$ in diameter (on the sample). Figure 1(b) shows one polariser and crossed polariser-analyser transmission. Due to the linear and isotropic (circularly polarised) contributions of the dipole and edge emission from the synchrotron source, it was not possible to extinguish transmittance with one polariser. With a pair of crossed polariser and analyser, it was possible to reach near-zero transmittance.

The degree of linear polarisation from synchrotron radiation [18,19] reaching the beamline is defined by the powers of linear P_L and isotropic P_I components, respectively, as $Lin = P_L / (P_L + P_I) = 11/14 \approx 78.6\%$ (Fig. 1(b)). This is consistent with the 22% previously measured for linearly polarised radiation at the THz beamline, which uses the other half of the synchrotron-IR beam extracted by the first IR mirror, with a larger portion of the isotropic emission [20]. With the strong linearly polarised synchrotron radiation at the Infrared Microspectroscopy (IRM) beamline, polarisation dependence of absorbance and transmittance can be analysed at an enhanced S/N ratio. Orientation of the slit of the

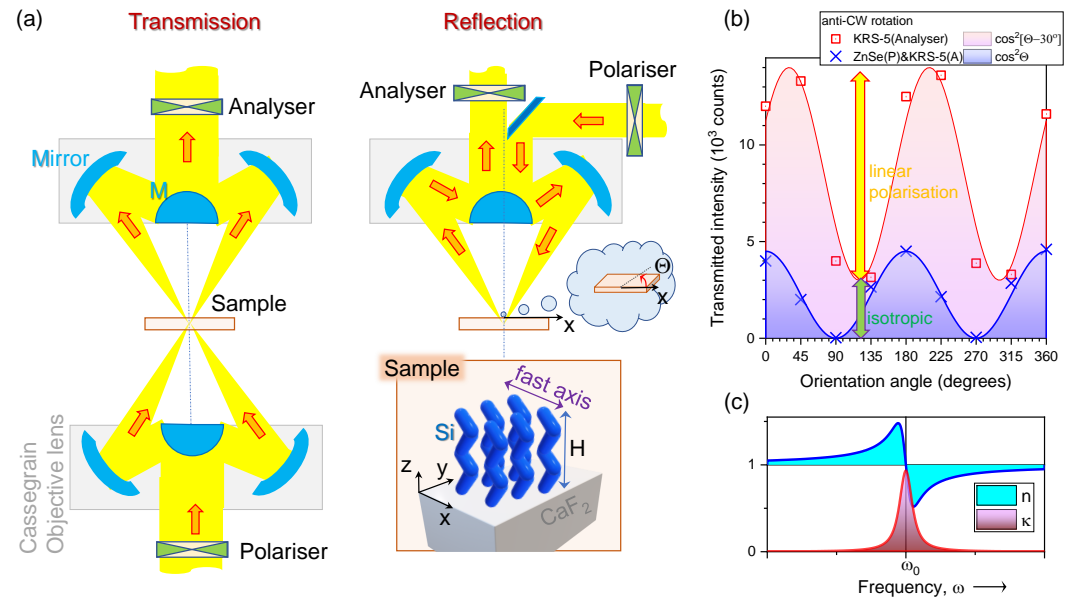


Figure 1. (a) Transmission and reflection modes with the possibility to set polarisation of the incident IR beam and analysis at the transmitted (or reflected) light; θ is sample's orientation angle with $\theta = 0^\circ$ corresponding to x-axis. Samples were Si and SiO₂ columnar structures of $H \approx 1 \mu\text{m}$ height deposited by GLAD at $\phi \sim 70^\circ$ on a substrate (silica, CaF₂, Si). Sketch shows Si columnar structures deposited via zig-zag folding (6 s deposition switch) along the x-axis during GLAD on IR transparent CaF₂; folding direction defines the optical fast-axis with refractive index $n_e < n_o$ due to structural anisotropy. (b) Transmitted power through one (red) and two (blue) crossed polarisers used in experiments. A crossed polariser (P) - analyser (A) eliminated transmitted power; measurements were carried out in transmission mode with a $5.6 \mu\text{m}$ aperture pinhole, which was contributing to a better axial resolution. (c) Lorentzian lineshapes for absorption $A(\omega) = \frac{\tau}{1 + (\omega - \omega_0)^2 \tau^2}$ and dispersion $1 - D(\omega) = 1 - \frac{(\omega - \omega_0)\tau^2}{1 + (\omega - \omega_0)^2 \tau^2}$, where ω is the cyclic frequency and τ is the relaxation time [17]; $\kappa \propto A(\omega)$ and $n \propto D(\omega)$ where refractive index is $\sqrt{\epsilon} = (n + i\kappa)$.

first IR mirror defines the orientation of a linearly polarised component, which was along x-axis in our experiments.

Polarisation analysis in the mid-IR spectral range can be carried out with the described polariser-analyser setup in direct transmission as well as in attenuated total reflection (ATR) modes [21]. Less explored polarisation dependencies are at the vicinity of the absorbance bands where the Lorentzian absorption $A(\omega)$ and dispersion $D(\omega)$ lineshapes are interrelated [17] (Fig. 1(c)).

2.1. Polarised synchrotron-IR spectra of anisotropic columnar Si micro-films

Figure 2(a) shows polarised synchrotron-IR spectra of 3D columnar Si deposited on an IR-transparent CaF₂ substrate. A single polariser (analyser) was rotated through 180° in 15° intervals and changes in spectral features are shown for each orientation θ . Figure 2(b) shows the same sample, but measured with an aligned polariser-analyser setup. The strongest absorption was found at $\sim 1100 \text{ cm}^{-1}$ attributable to Si-O-Si stretching vibration [22]. A Si-C band at $\sim 1620 \text{ cm}^{-1}$ was observed close to the adventitious carbon band at $\sim 1640 \text{ cm}^{-1}$ (i.e. C=C stretching mode) [23]. The doublet peaks centred at 2250 and 2120 cm^{-1} are assignable to Si-H and Si-H₂ vibrations, respectively [24]. Their positions are located adjacent to the CO₂ peaks ($\sim 2330 \text{ cm}^{-1}$) [25], which are recognisable as an atmospheric interference (the reference sample used for background measurement in this study was CaF₂). Due to inherent porosity of 3D columnar Si film, a perfect cancellation of the gaseous CO₂ bands was not achieved, even though samples were held in a nitrogen-purged enclosure throughout the experiment. Distinct CH₃ and CH₂ stretching bands

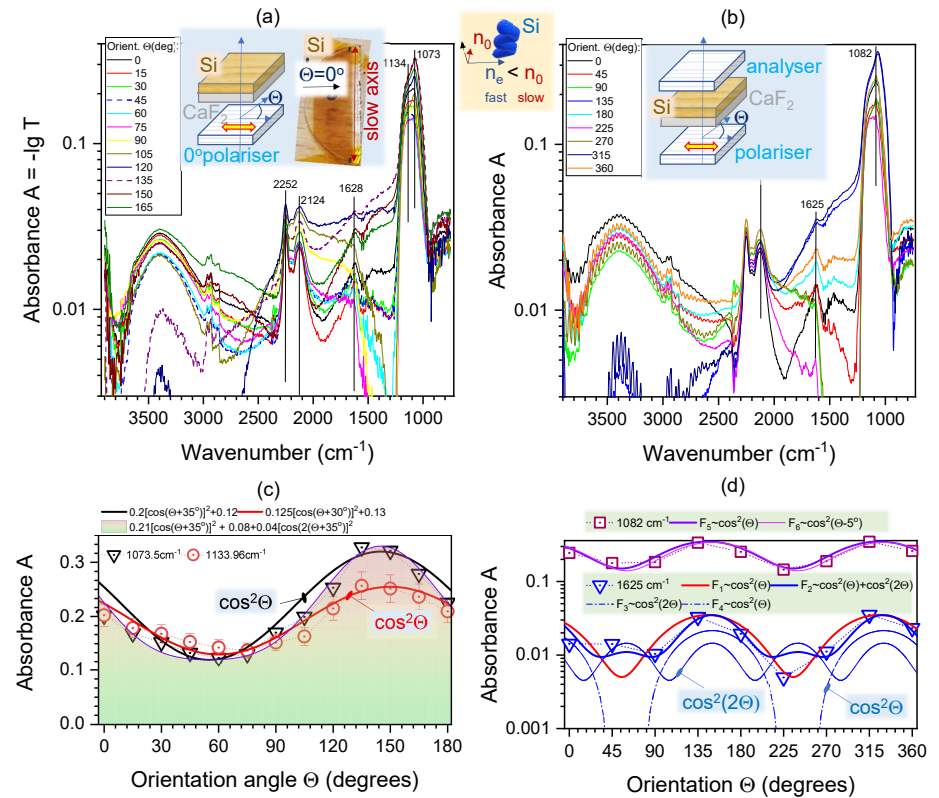


Figure 2. Polarisation analysis of the absorption bands. (a) Spectra at various polarisation orientations of θ for an analyser only setup. Inset shows geometry of experiment and a top-view photo of the sample with $\theta = 0^\circ$ along the fast-axis (n_e index); slow-axis (n_o) is at $\theta = 90^\circ$. Positive θ corresponds to the anti-clockwise rotation around the z-axis. (b) Spectra at various orientations of θ polarisation for an aligned polariser-analyser setup. (c) Orientational dependence of absorbance $A(\theta)$ of a columnar Si of $H \approx 1 \mu\text{m}$ height measured at the polarised irradiance; reference was CaF_2 substrate. Error bars mark $\pm 10\%$ uncertainty band. (d) The dependence $A(\theta)$ and spectra measured through an aligned polariser-analyser pair (high transmission mode). Focal spot size $16.7 \mu\text{m}$; Polariser is KRS-5 and Analyser ZnSe (see insets and Fig. 1); spectral resolution 4 cm^{-1} . See details in the text. Note the lg-scale.

in $2950\text{--}2850 \text{ cm}^{-1}$ spectral region are identifiable and observed next to the broad -OH stretching band at $\sim 3400 \text{ cm}^{-1}$ as a result of the Si-OH structure. Interestingly, there is a similarity of spectral profile of absorbance between 3D porous columnar Si film deposited by GLAD and 3D porous Si made by electrochemical wet etching of (poly)crystalline Si [26].

We selected several spectral positions within specific absorption bands of Si-O-Si and some other spectrally distinct locations to investigate anisotropy of birefringence and dichroism at the corresponding wavelengths.

2.2. Orientation dependence of IR absorption bands

In order to measure polarisation dependence of absorbance $A \propto \Delta\kappa$, one polariser is required. For measurement of birefringence $\Delta n = n_e - n_o$, usually a cross-polarisation setup is used and transmittance T_\times (Eq. 1) is measured. However, such determination of birefringence is not applicable to absorbing samples or at spectral positions close to absorption bands. In the visible spectral range, where most polarisation optical elements are used ($T \rightarrow 1$), absorption is not important and optical losses are mostly due to reflection and scattering (related to Δn rather $\Delta\kappa$). It is possible, however, to determine the dichroism $\Delta\kappa$ contribution in the case of polariser-analyser transmission measurement when they are both aligned to the maximum transmittance (\parallel). This condition is related to the cross-polarisation alignment by simple algebraic expression $T_\parallel = 1 - T_\times$ (see Eq. 1).

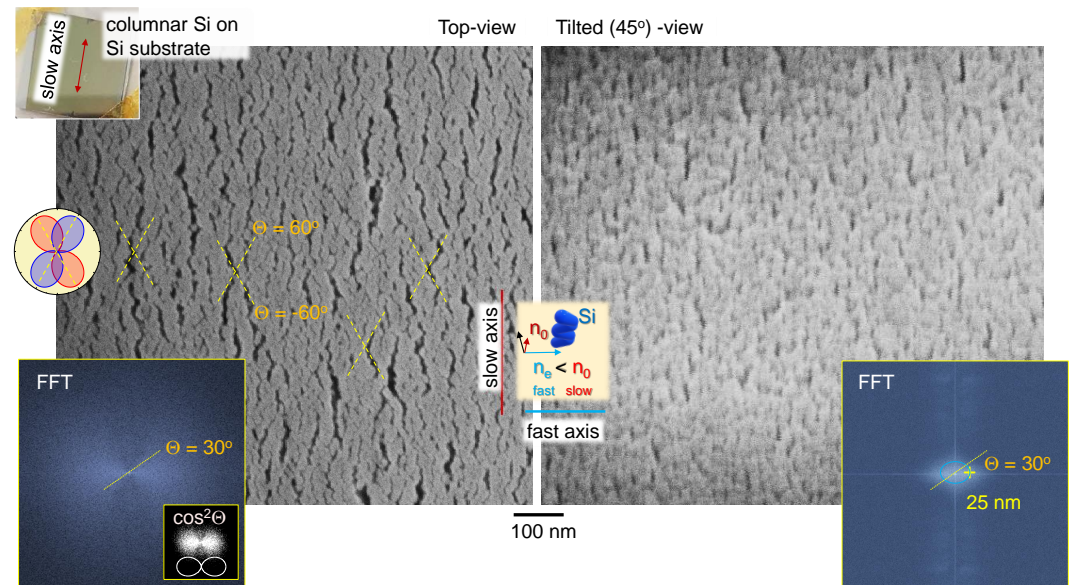


Figure 3. SEM images of a $\sim 1 \mu\text{m}$ -thick columnar Si on Si substrate (top-left inset photo of $1 \times 1 \text{ cm}^2$ sample); no metal coating was used for SEM imaging; side-insets show fast Fourier transform (FFT) images of top and slanted view images. High-contrast FFT image (top-view SEM) shows an overlaid $\cos^2 \theta$ polar plot. Center-inset shows orientation of the columnar Si coating. The cross-markers (dashed lines) on top-view image shows orientations of crevices at $\pm 60^\circ$ orientations and corresponding dipole profiles $\cos^2(\theta \pm 60^\circ)$.

Indeed, for determination of optical losses due to absorption (and its anisotropy $\Delta\kappa$), a high transmission measurement setup is required in contrary to the measurement of birefringence Δn where crossed polarisation (zero transmission) is implemented.

It was shown that separation of anisotropy due to birefringence Δn and dichroism $\Delta\kappa$ can be obtained using a fit to the transmittance $T(\theta)$ (or absorbance $A(\theta) = -\log T(\theta)$) by the $\cos(2\theta)$ and $\cos \theta$, respectively [16]. Such analysis is presented in Fig. 2(c) and (d). Different fits are shown for qualitative understanding of anisotropy components measured with analyser and aligned polariser-analyser (hence T_{\parallel}).

With only the analyser, one could reveal anisotropy in absorbance if there is ordering and alignment of the absorbing dipoles. However, if the sample is isotropic, there should be no angular dependence in $A(\theta)$. For example, the absorption band, e.g., Si-O-Si at $\sim 1100 \text{ cm}^{-1}$ should follow $T(\theta) \propto \cos^2 \theta$ in the presence of the simplest case of anisotropy. Experimental data of $A(\theta)$ were fitted and the orientation angle was $\theta_D = 35^\circ$: $\cos^2(\theta + \theta_D)$. It was different from the orientation of the transmission maximum shown in Fig. 1(b) by $\sim 65^\circ$. The sample of columnar (normal to the substrate) Si film has a form-birefringence at visible wavelengths, i.e., there is an alignment due to a specific material distribution with extraordinary refractive index smaller than the ordinary $n_e < n_o$. How such a structure can affect the anisotropy property in mid-IR region has never been reported and requires further investigation. Structure of a pristine surface of columnar Si film without metal coating is shown in Fig. 3. This film was deposited on a Si substrate (not CaF_2) to eliminate surface charging during SEM imaging and the as-fabricated structure of columnar Si film can be visualised.

The $\cos^2 \theta$ fits of columnar Si on CaF_2 (see detailed expressions in the legend of Fig. 2(c)) closely match $A(\theta)$. However, a slightly better fit can be achieved with two contributions. Namely, for the 1073 cm^{-1} experimental measurements of $A(\theta)$ with $\Delta\theta =$

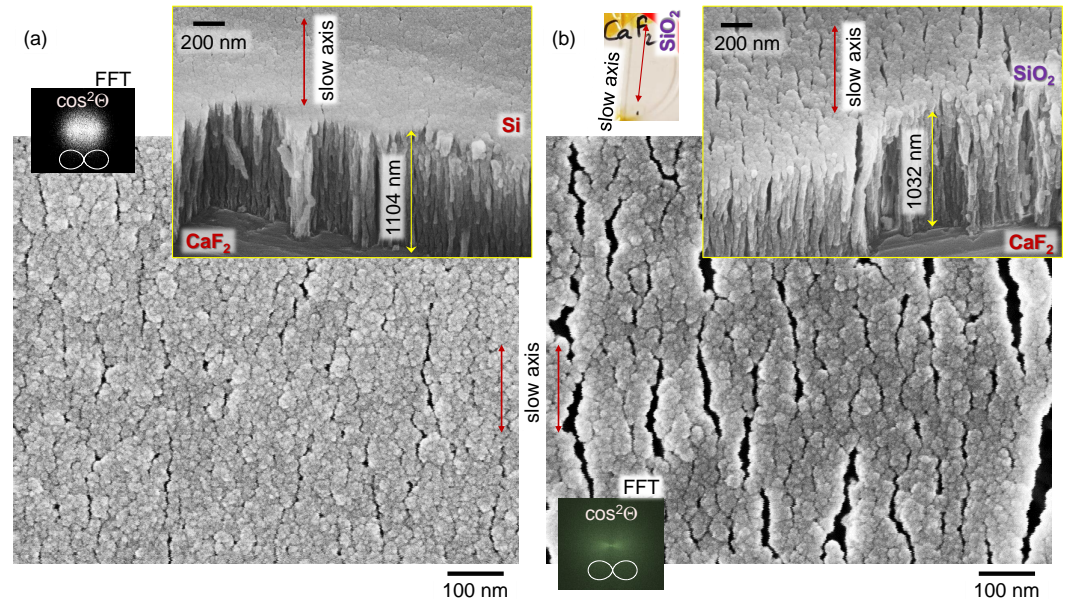


Figure 4. SEM images of a $\sim 1 \mu\text{m}$ -thick columnar Si (a) and SiO₂ (b) on CaF₂ substrate. A coating of Cr 20 nm was used for SEM imaging (columnar Si film without Cr coating is shown in Fig. 3). Top-insets were taken at $\pi/4$ tilt and film thickness is calculated with a factor $\sin(\pi/4)$ as $H = y/\sqrt{2}$ where y is the vertical length on the image.

15° steps, the fit as a sum of θ (dichroism) and 2θ (birefringence)¹ is better (Fig. 2(c)). This hints that 3D form-birefringent Si films (Fig. 3) can have a contribution to the pure absorption band (atomic/molecular level dipole alignment) due to a larger microscale material alignment and reorganisation.

2.3. Transmittance through an aligned polariser-analyser setup T_{\parallel}

Fit of experimentally measured absorbance $A(\theta) = -\log T$ in the aligned polariser-analyser setup can separate contributions due to the birefringence and dichroism when the following fit is used [16]:

$$A_{\parallel}(\theta) = [Amp_D \times \cos^2(\theta - \theta_D) + Offset_D] + [Amp_R \times \cos^2 2(\theta - \theta_R) + Offset_R], \quad (2)$$

where D index stands for contributions due to absorption dichroism and R is due to birefringence (real part of the refractive index). In order to check the above presented conjecture, that birefringence contribution to the absorption band should be considered due to sub-wavelength nano-structure of the 3D Si film, measurements were carried out with an aligned polariser-analyser setup by measuring $A_{\parallel}(\theta) = -\lg T_{\parallel}(\theta)$ shown in Fig. 2(b). This measurement is suitable to separate θ and 2θ dependencies using fit (Eq. 2). Fig. 2(b) shows that the strongest Si-O-Si band has the major contribution due to the component of the θ -dependence, which was the main contribution using the analyser setup (a). The $\cos^2(2\theta)$ contribution in one-polariser A measurement might be caused by the double action of the sample which has two high order structures: the form birefringent SiO₂ zig-zag structure and oriented nano crevices. One may act as a polariser and another as a retarder, so that one can observe two angular dependencies $\cos^2(\theta)$ and $\cos^2(2\theta)$ even under the single Nicole configuration.

Large orientation steps of $\Delta\theta = \pi/4$ does not allow for a reliable fit by $\cos^2(2\theta)$. The $\cos^2\theta$ -fits are reliable as demonstrated by a small $\Delta\theta_R = 5^\circ$ change in F_5 and F_6

¹ Terminology of θ and 2θ dependencies are used here for brevity. It should be remembered that the transmittance T (so also absorbance A) follows $T \propto \cos^2 \theta$ the θ -dependence (folding onto itself with cycle of π). However, for the A fits should not be confused with apparent 2θ dependence: $\cos^2 \theta = \frac{1}{2}(\cos(2\theta) + 1)$.

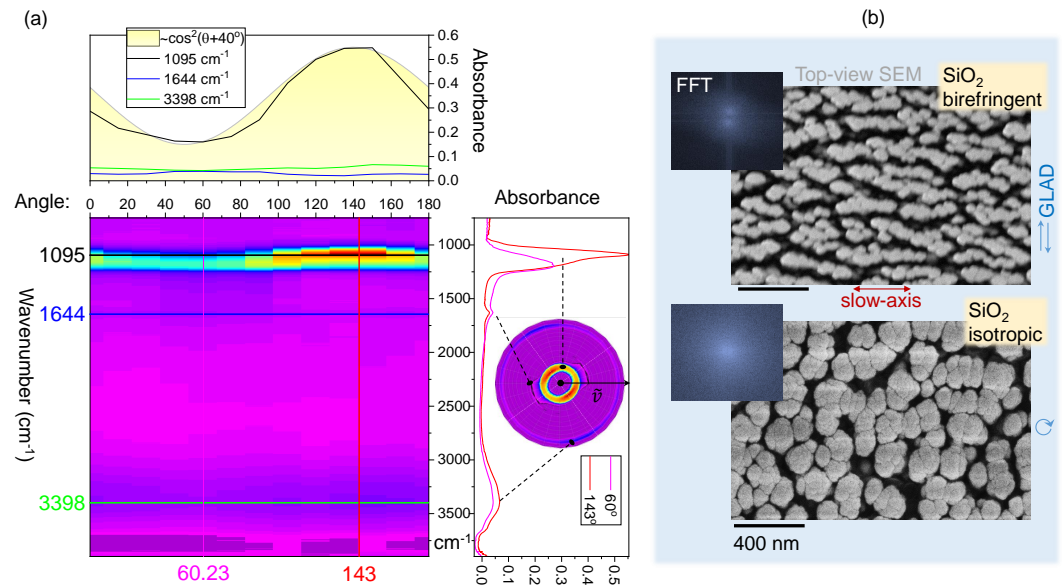


Figure 5. (a) The IR absorbance map of columnar SiO₂ on CaF₂ substrate with side-view cross sections of spectra at specific orientation angle θ ; measured with the aligned polariser-analyser rotated around the sample. The $\sim \cos^2(\theta+40^\circ)$ -fit is the best match to the angular dependence of the Si-O-Si band at $\tilde{\nu} = 1095 \text{ cm}^{-1}$. The inset in the absorbance spectrum cross section shows a 2π -folded angular dependence map to highlight angular correlations between bands. (b) Top-view SEM images of a birefringent SiO₂ columnar film (researched in another study and coated at 74° angle) and isotropic SiO₂ grown by GLAD at a constant rotation; see differences in FFT maps.

functions (Fig. 2(d)). Sampling at smaller angular steps is planned for future AuSy beamline experiments.

A shoulder band at 1625 cm^{-1} (Fig. 2(d)) can be fitted by Eq. 2 with a weak $\cos^2(2\theta)$ contribution, i.e., some birefringence orientational behaviour. For qualitative analysis it is instructive to show separate $\cos^2 \theta$ and $\cos^2(2\theta)$ contributions (D and R terms in Eqn. 2) to the fit. Asymmetric distribution of $A(\theta)$ can be fitted by adding $\pi/2$ -shifted angular dependencies (F_4 and F_3 in Fig. 2(d)) using the orientation angles θ_R and θ_D (with selected amplitude and offset values). The fits presented in (d) are qualitative only since a higher angular sampling is required to clearly distinguish the Δn -related high angular frequency contribution.

The Si-OH broad band at 3400 cm^{-1} shows interference features characteristic to measurement with two polarisers (mesh grids on KRS-5 and ZnSe). Those interference fringes can be filtered out by editing the Fourier interferogram, if required [27] (Suppl. Fig. A1 shows the performed fringe removal). For an isotropic homogeneous sample, there should be no orientational dependence due to adsorbed (and absorbed) water at this spectral range.

Next, anisotropic SiO₂-on-CaF₂ samples of the same height and GLAD deposition conditions as Si-on-CaF₂ are summarised in Fig. 5(a). Absorption color map with selected cross sections at the peak of absorption of Si-O-Si band at 1095 cm^{-1} shows almost an identical angular dependence of $\cos^2(\theta + 40^\circ)$ as was observed for Si-on-CaF₂ (Fig. 2). Such dependence is attributable to the nano-crack/planes of SiO₂ columns alignment along the optical slow-axis (for visible wavelengths). Fourier transform of SEM images shows the pattern anisotropy following the $\sim \cos^2 \theta$ angular dependence which is absent in the case of the same SiO₂ columnar film grown at a constant spinning during GLAD deposition. Other peaks at 1644 and $\sim 3400 \text{ cm}^{-1}$ showed almost no angular dependence. The band 1644 cm^{-1} was showing only a weak angular dependence, but has anti-correlation character with the Si-O-Si 1095 cm^{-1} absorption. The 1645 cm^{-1} band was determined from an isotropic absorption to be a combination of the phonons at 1160 cm^{-1} and at

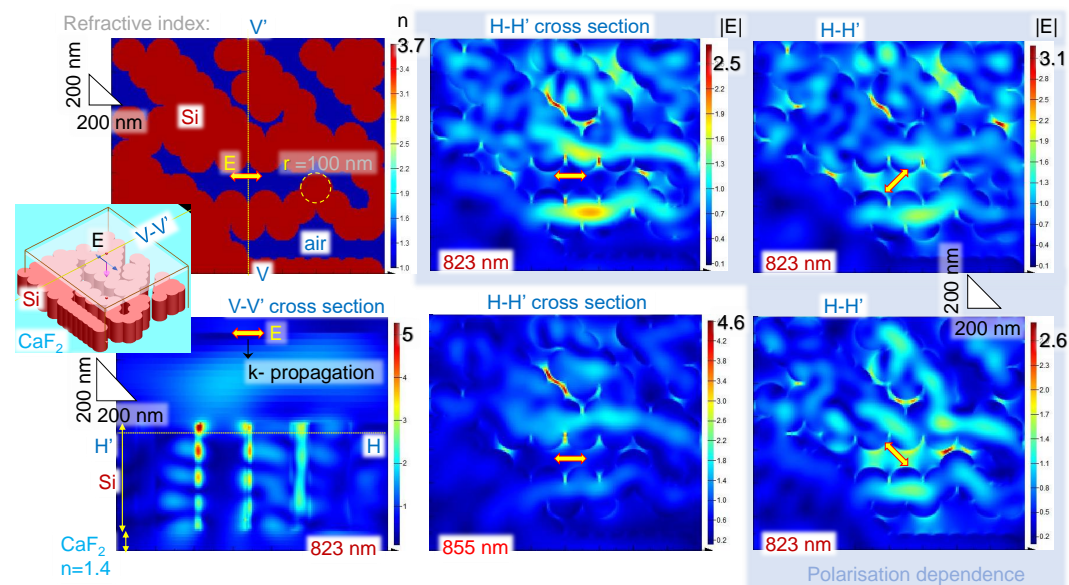


Figure 6. A numerical toy-model of light scattering and enhancement by a Si columnar pattern on CaF_2 for different orientations of incident linearly polarised E -field ($0; \pm\pi/4$) of light calculated by finite difference time domain (FDTD) solver (Lumerical). Transverse $V'-V'$ and longitudinal $H'-H$ cross sections show (E/E_0) -field enhancement for the incident plane wave $E_0 = 1$. Height of $r = 100$ nm Si cylinders was $0.5 \mu\text{m}$; perfectly matching boundary conditions were used. Inset shows 3D rendering of the calculation volume. Permittivity of Si at the selected wavelength was used from the Palik's database in Lumerical.

480 cm^{-1} [28]. Interestingly, there is no 811 cm^{-1} phonon band in 3D columnar silica which also contributes to a significant 2000 cm^{-1} absorbance band of SiO_2 [28]. A weak shoulder feature is recognisable at usually narrow Si-OH 3740 cm^{-1} peak while the related 3660 cm^{-1} broad band is not prominent.

3. Discussion

An unexpected result is that Si film which is expected to show absorption anisotropy due to its vertical columnar (isotropic) structure, in fact, shows an angular dependence of the strongest Si-O-Si absorption band following $A(\theta) \propto \cos^2(\theta - \theta_D)$ (measured in transmission; Fig. 1(b)). This measurement was carried out with a parallel polariser-analyser setup and was sensitive to the birefringence contribution, if any. However, Δn contribution with $\cos^2(2\theta)$ angular dependence was found to be negligible (finer angular sampling is required for definitive separation of θ and 2θ dependencies). The angle for the strongest absorption was $\theta_D \approx 65^\circ$ from the orientation when strongest linearly polarised synchrotron radiation was delivered onto the sample. Figure 3 reveals that the FFT image of top-view Si columnar coating has $\cos^2 \theta$ distribution; for an isotropic sample a disk or ring pattern is present (see Fig. 5(b)). The orientation of $\sim 60^\circ$ corresponded to some of the largest crevices which were formed at angle to the direction of slow-axis (Fig. 3).

These sub-wavelength (at IR wavelengths of incident light) structures will contribute to light field enhancement, hence, contributes to a stronger absorbance. This is an underlying reason why the structure/orientation of the surface features with angular dependence $\cos^2 \theta$ is transferred to the angular dependence of absorbance $A(\theta)$. Even for isotropic columnar Si films, the angular dependence of A is present due to nanoscale structure of Si film. Figure 4 shows 3D structure of Si and SiO_2 columnar films. Very similar structure of films was obtained at the same protocol of GLAD deposition. Slightly larger nano-crevices were observed on dielectric SiO_2 surface, which has stronger charging under SEM imaging even when coated by 20 nm of Cr for imaging.

In order to qualitatively explain the observed $\cos^2 \theta$ dependence of the main absorbance band at $\sim 1100 \text{ cm}^{-1}$ ($\lambda = 9.09 \text{ }\mu\text{m}$ wavelength), numerical simulation of light field enhancement inside random pattern of sub-wavelength crevices was carried out for Si nano-cylinders on CaF_2 . For simplicity, the finite difference time domain (FDTD) calculations were carried at several wavelengths around $0.9 \text{ }\mu\text{m}$ which are shorter by a factor of 10 as compared to the IR wavelengths used. With the same dielectric properties of structures ($n(\text{Si}) = 3.7$, $n(\text{CaF}_2) = 1.4$), a qualitative understanding can be obtained for light enhancement. Figure 6 shows summary of the results of E-field enhancement just 50 nm below the surface of Si cylinders which are all the same height. The diameter of cylinders were $2r = 200 \text{ nm}$ and do not correspond to the columnar structures, but were used to form the pattern of the Si-layer with different opening sizes (see refractive index cross section in Fig. 6).

The largest E-field enhancements are at the narrowest sub-wavelength grooves which are $\lambda/100$ and for polarisation orientation perpendicular to the nano-groove. The latter is related to the boundary condition for the E-field normal at the interface between two materials, i.e., $\epsilon_{\text{Si}} E_{\text{Si}} = \epsilon_{\text{air}} E_{\text{air}}$, where the permittivity is defined by the complex refractive index $\epsilon = \tilde{n}^2$. The intensity in the air gap is $I_{\text{gap}} \equiv |E_{\text{air}}|^2 = n_{\text{Si}}^4 E_{\text{Si}}^2$. This scaling qualitatively explains augmented intensity inside sub-wavelength gaps. It is noteworthy, the field enhancement exists inside Si as well since skin depth of evanescent field protrudes up to $\lambda/4$ into the volume below the interface. Also, there is always a strong wavelength dependence as illustrated by two panels for 823 nm and 855 nm wavelengths. For wider nano-gaps $\lambda/10$ there is almost no any E-field enhancement (central horizontal gap in panels of Fig. 6). For the columnar SiO_2 -on- CaF_2 sample of the same geometry as Si-on- CaF_2 (Fig. 4(b)), FDTD simulations predict a weaker enhancement and its localisation as shown in Supplement Fig. A2. However, the same orientational dependence of enhancement takes place. i.e., it is the strongest for the normal orientation of the field to interface.

The qualitative description of E-field enhancement inside sub-wavelength $\lambda/100$ grooves is valid for $\sim 10 \text{ }\mu\text{m}$ IR light at which the angular dependence of absorbance band was measured (Fig. 2(b) and (d)). The crevices in the columnar Si-on- CaF_2 sample (Fig. 4) are $\sim 100 \text{ nm}$ long and corresponds to the $\lambda/100$ at the $\lambda = 10 \text{ }\mu\text{m}$ ($\tilde{\nu} = 1000 \text{ cm}^{-1}$). Once such groove is aligned with the linearly polarised incident synchrotron radiation, field enhancement inside groove and its vicinity will occur. This enhancement is related to the stronger absorbance and naturally follows the same $\cos^2 \theta$ angular dependence as observed in FFT maps of SEM images of the surface of columnar Si films.

4. Conclusions and outlook

3D columnar form-birefringent (at visible spectral range $\lambda = 0.4 - 0.8 \text{ }\mu\text{m}$) Si micro-films were characterised at the IR finger printing spectral window $3 - 10 \text{ }\mu\text{m}$ using AuSy IR-microscopy beamline. Measurements were carried out from focal volumes which are sub-wavelength in thickness and with spot sizes 1-to-5 wavelengths in cross section laterally. It is shown that detailed polarisation analysis can be carried out from such small volumes comparable to the wavelength in the IR range. The known material IR absorption bands, e.g., Si-O-Si in Si and SiO_2 , are shown to obey the $\cos^2 \theta$ orientation dependence as determined by the 4-angle polarisation method. The very same dependence is observed in patterns of nano-crevices on the surface of the films as revealed by Fourier image analysis. By qualitative numerical modeling of light E-field enhancement, it is suggested that the orientational dependence of absorbance follows enhancement (hence stronger absorption) in sub-wavelength $\lambda/100$ crevices observed on the columnar Si films. Universal character of E-field enhancement by $\lambda/100$ gaps shown by numerical simulations is relevant for qualitative discussion of the observed orientational dependence of absorbance $A(\theta) \propto \cos^2 \theta$.

5. Experimental: samples and procedures

5.1. Samples

Samples for this study were made using electron beam evaporation technology equipped with two stepper motors for GLAD. Two sets of evaporation have been performed in order to form anisotropic silicon and silica thin films.

For Si coating, polycrystalline wafers of silicon was broken, melted and used as a source of evaporation. The deposition rate was constantly maintained at 3 Å/s and controlled using crystal quartz monitor. Silicon thin films were coated using a VERA 1100 (VTD, Germany) deposition plant.

For silica thin films, granules of SiO₂ were evaporated at the same 3 Å/s constant rate. Silica thin films were coated using SIDRABE (SIDRABE, Latvia) deposition plant.

In both cases, the thickness of thin films were 1 µm and the coatings were evaporated using the Serial Bi-Deposition (SBD) technique [29]. During SBD, the substrates were tilted at 70° angle between its normal and the vapour flux. At the same time, half-turn rotations were performed every 6 seconds in order to enhance the birefringence of the films and gain better thickness uniformity as well. CaF₂ and ⟨100⟩ orientation p-type Boron doped Si wafers were used as the substrates in both depositions.

Samples were structurally characterised by scanning electron microscopy (SEM) using field-emission SEM mode of Raith 150-TWO electron beam lithography setup. Image processing was made by freeware ImageJ.

5.2. Polarised synchrotron-IR microspectroscopy in transmission mode

The Australian Synchrotron commenced operations for researchers in 2007, with IRM and THz beamlines included in the beamline suite. The details of the synchrotron-IR beam extraction and beamline configuration were previously published elsewhere [30]. The synchrotron-IR experiment was performed on the IRM beamline at the Australian synchrotron (Victoria, Australia), using a Bruker Vertex 80v spectrometer coupled with a Hyperion 3000 FTIR microscope and a liquid nitrogen-cooled narrow-band mercury cadmium telluride (MCT) detector (Bruker Optik GmbH, Ettlingen, Germany). In transmission mode, the IR microscope was operated with a matching 36× IR reflecting objective and condenser ($NA = 0.50$). All the synchrotron-IR spectra were recorded within a spectral range of 3800–700 cm^{−1} using 4 cm^{−1} spectral resolution. Blackman-Harris 3-term apodization, Mertz phase correction, and zero-filling factor of 2 were set as default acquisition parameters using OPUS 8.0 software suite (Bruker Optik GmbH, Ettlingen, Germany).

Polarisation of the synchrotron-IR radiation has a combination of linear (horizontal along the slit of the first IR-extraction mirror) and circular polarisations [20]. The two components originate from dipole emission inside the bending magnet and at its edge (at the entrance/exit) [18,19]. The IRM beamline receives a higher proportion of the dipole emission compared to the edge emission, which contributes to a larger portion on the THz beamline.

Polarisation is defined as x- and y-polarisations in room frame of reference (Fig. 1) along the direction of propagation (z-axis) in transmission mode. Data analysis was carried out with OPUS 8.0 software (Bruker Optik GmbH).

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Data Availability Statement: Data can be provided upon a reasonable request.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Light field enhancement calculations by FDTD for SiO₂-on-CaF₂ are shown in Fig. A2 (it is the same geometry as for Si case shown in Fig. 6.)

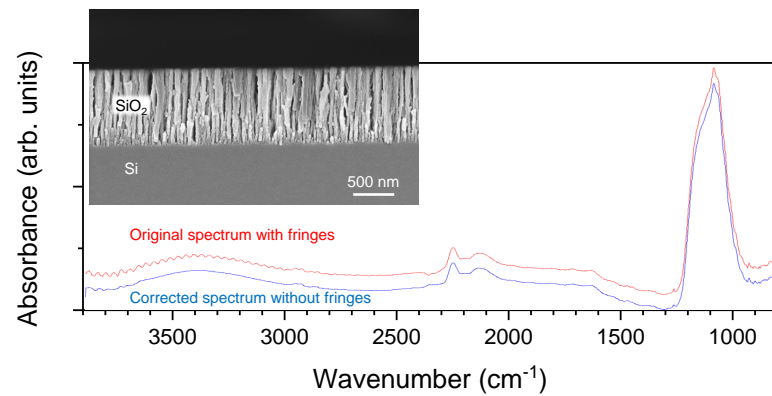


Figure A1. Fringe removal from Si-on-CaF₂ spectra by the method presented in ref. [27]; plotted with vertical offset for clarity. Inset shows cross sectional SEM view of SiO₂-on-Si prepared at the same conditions; a better quality cleaving of the sample can be achieved on Si substrate; sample was cleaved along the fast-axis.

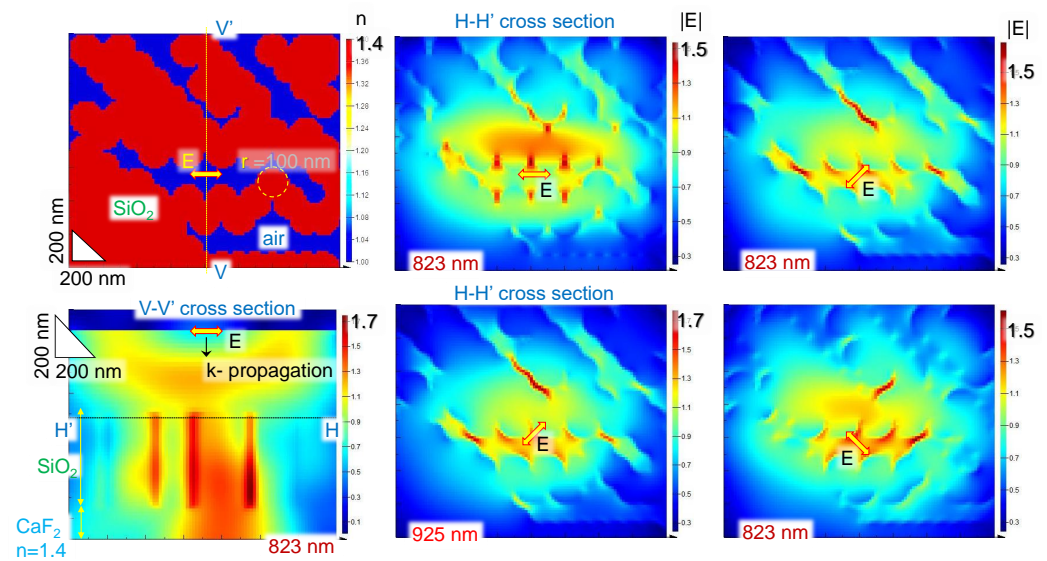


Figure A2. A numerical toy-model of light scattering and enhancement by a SiO_2 ($n = 1.4$) columnar pattern on CaF_2 for different orientations of incident linearly polarised E -field ($0; \pm\pi/4$) of light calculated by finite difference time domain (FDTD) solver (Lumerical). Transverse V - V' and longitudinal H - H' cross sections show (E/E_0) -field enhancement for the incident plane wave $E_0 = 1$. Radius of SiO_2 cylinders $r = 100$ nm; perfectly matching boundary conditions were used. Inset show 3D rendering of the calculation volume.

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