Subwavelength Structures for Interference Enhanced Attenuated Total Reflection Spectroscopy and its Application for Blood Analysis

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Attenuated total reflectance (ATR) infrared absorption spectroscopy is a well-established analytical method. However, the sensitivity is limited compared to transmission measurements by the penetration depth of the evanescent wave. Innovative ATR Crystals with subwavelength pillars were made from silicon. First experiments show an enhancement factor of up to 20 compared to a standard single reflection diamond ATR element. Calibration curves were made for fructose, glucose, mannitol, sorbitol and urea. For blood analysis the surface structure acts like a micro-sieve, separating blood cells from plasma. This signal-enhanced ATR crystals opens an opportunity for a disposable sample carrier for clinical analysis and diagnostics by infrared spectroscopy.

INTRODUCTION

In order to bring infrared spectroscopy to the clinic, a cost-effective sampling approach, high sample throughput, small sample sizes (<10 µl) and a low detection limit are required. We developed a new disposable and high sensitive ATR crystal that also makes the blood centrifugation redundant.

The high sensitive ATR crystals are micro-machined from silicon [1]. In contrast to usual ATR sample carriers, the sample side of the silicon ATR crystal is covered with subwavelength pillars. These pillars form together with the analyte an effective medium, which enhances at defined spectral regions the absorption signal due to an interference effect. It was already shown that thin dielectric films made from frozen nobel gases can enhance the absorption up to 100 times [2]. We derived a compact formula to investigate the essential parameters of the enhancement. Electromagnetic simulations were made, the novel ATR Crystals were fabricated and tested.

EFFECTIVE MEDIUM THEORY

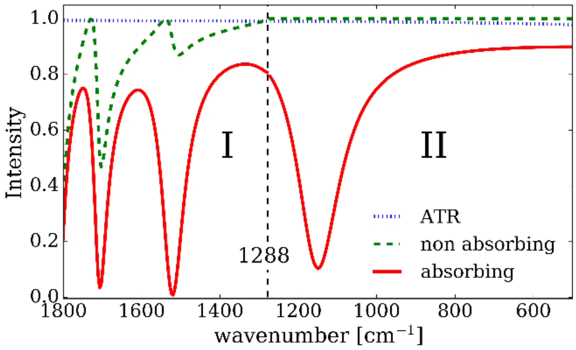
It is well known, that sub wavelength structures can be used to engineer the refractive index of an interface. The dimensions of the pillar structures must be smaller than the wavelength. A good estimator for the largest period p is the angle α dependent grating equation, whereby θ_m is the refracted angle of order m.

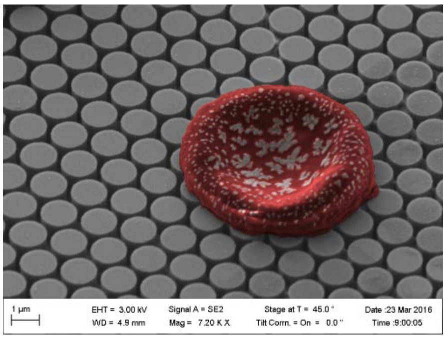
$$p(sin\theta_m + \sin\alpha) = m\,\lambda$$

The condition for an effective medium is that the first order m = 1 is refracted under an angle of 90°. The largest period p_{max} must be smaller than the minimal vacuum wavelength λ_{min}, so just the 0th order can propagate in the effective medium.

$$p_{max} = \frac{\lambda_{min}}{\mathrm{n}_1\,(1 + \sin\alpha)}$$

The optical response of the sub wavelength structures can be approximated by an effective refractive index n_{eff}. The fill factor f and the morphology control the optical properties. Square silicon pillars in a square lattice surrounded by a homogeneous absorbing material were simulated with RODIS. The spectral response is comparable to the analytical approximation. It shows the expected cut-off wavenumber at 1288 cm-1.





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KEY WORDS

effective medium; subwavelength structures; ATR infrared spectroscopy; mid infrared