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Phononic Crystals and Applications

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Abstract:
Optical and acoustic band gap materials, so-called photonic and phononic crystals, belong to the group of metamaterials and provide a novel and alternative platform for sensing material properties in small cavities. The sensor employs specific transmission peaks to determine properties of a component that builds the photonic or phononic crystal. We here concentrate on phononic crystal sensors. One typical arrangement of band gap materials consists of periodically arranged holes in a solid matrix. The peak used for sensing is usually created by introducing a defect into the otherwise regular structure. Such a transmission peak results from a resonant mode created by the defect. The value of interest changes the acoustic properties of the defect and thereby wavelength or frequency of the resonant defect mode. Transmission or reflection coefficients are therefore appropriate parameters for measurement. A (micro)fluidic channel may act as a defect on the one hand and part of the analyte delivery system on the other.

Key words: Photonic crystals, phononic crystals, metamaterials, refractive index, speed of sound.

Introduction

Photonic crystals (PtC) are engineered optical composite materials with periodic spatial modulation of the dielectric constant on the scale of the optical wavelength [1,2]. The acoustic equivalent, so-called Phononic Crystals (PnC) are periodic composite materials with spatial modulation of elasticity, mass density and longitudinal and transverse speed of sound [3]. Photonic / phononic crystals are engineered optical / acoustic composite materials with periodic spatial modulation of the respective material constant on the scale of the optical / acoustic wavelength. The typical structure consists of scattering centers with optical / acoustic properties different to a homogeneous matrix surrounding the scatters.

Destructive interference of multiple scattered waves in periodic structures gives rise to the most prominent feature of photonic / phononic crystals - photonic / phononic band gaps. This is a range of frequencies, respective wavelengths, in which electromagnetic / elastic waves cannot propagate inside the crystal. Photonic and phononic crystals belong to the group of metamaterials with designed properties not known in nature like negative refractive index, sound focusing, wave confinement or wave guiding. The latter can be achieved introducing point or linear defects into an otherwise regular structure. Localized modes exhibit resonant characteristics. This feature can be used for sensing purposes. Defect modes can be designed to create a well separated mini-transmission band within the band gap or mini-stop band outside. They appear as transmission peak or transmission dip within the transmission spectrum of photonic and phononic crystals and therefore provide a simple measure, as long as the position of the respective mode on the wavelength-frequency scale, shortly called peak frequency, is sensitive to defect properties which can be changed by the measurement value of interest. Most literature dealing with sensor applications prove the sensitivity of the peak frequency on refractive index, *RI* [4-6], and speed of sound, *c* [7-9], of the defect material, respectively:

$$\lambda_p = f(n) \qquad f_p = f(c) \qquad (1)$$

If the defect is a *hole* or a slit filled with a liquid analyte (1) consequently describes the peak frequency as a function of *bulk* properties of the confined analyte. In case of a *solid* defect, realized in the simplest case by omitting scatter in the center of the crystal, the sensor becomes sensitive to *RI* and (surface) density of a material, ρ_s, acting on the *surface* of the defect. Sensitivity to external forces changing geometry is not considered here.

Sensitivity

In the following we concentrate on phononic crystal sensors. We believe that phononic crystal sensors can satisfy the high demand on very sensitive devices which require an ultralow analyte volume and can compete with their optical counterpart. However, the primary sensitivity, S_f, on changes in c or ρ_s depicted as Δx

$$S_f = \frac{\Delta f_p}{\Delta x} \qquad (2)$$

is perhaps less exciting. Instead, input parameters like concentration of a component in a complex mixture [10] or conversion rate during a chemical reaction, (bio)chemical activity or size of associates or molecule conformation e.t.c., would attract much more interest. The key point of the overall sensitivity analysis of the new sensor would therefore include the correlation between the parameter of the applicant's interest, y_i, and speed of sound:

$$S_f = \frac{\partial c}{\partial y_i}\frac{\partial f}{\partial c} \qquad (3)$$

The first derivative usually requires the introduction of a 'component' providing (bio)chemical sensitivity and selectivity into the complete transduction scheme. A phononic crystal sensor having a solid defect can resume the procedures of acoustic microsensors. The defect surface must be modified by a (bio)chemically sensitive material, i.e. by immobilizing receptor molecules. They interact with the analyte which results in changes in the interfacial acoustic properties. In the simplest and most common case the frequency is related to the mass of absorbed or adsorbed molecules. This value is usually related to the concentration of the respective molecule in the analyte. Sensitivity can be enhanced by increasing the resonance frequency, here the frequency of the defect mode. A scaling law applies similar to acoustic microsensors. Whereas dimensions in the mm-range correspond to frequencies around 1 MHz, dimensions typical for photonic crystals below 1 µm require acoustic frequencies in the GHz range. Indeed, it has been shown theoretically that photons and phonons can be confined simultaneously [11-14] resulting in an ultrahigh so-called phoxonic crystal sensor [15,16]. In case of a liquid analyte-filled cavity the confined liquid itself acts as resonator. Sensitivity and selectivity must be realized in volume. It requires completely new concepts; however, it opens the gate to a new sensing concept. The phononic cavity sensor specifically has the inherent advantage that biomolecules can be analyzed in their physiological environment. The challenging question unsolved so far is if the effect of an interaction, e.g. between an antibody and antigen sufficiently changes the overall properties of the solution. It therefore might become necessary to add labels to achieve sufficient sensitivity. On the other hand, the principle should allow for the analysis of real probes like blood or serum and effects like coagulation should not require any label. Again, sensitivity can be improved by increasing the probing frequency.

It has been shown previously that with nanoscale dimensions sensitivity of resonant devices can be pushed to its upper limits [17]. Hypersonic phononic crystals are possible as well [18]. However, ultrasonic wave propagation through liquids has to consider viscous losses. Just recently Holmes et al. have analyzed Millipore water by acoustic spectroscopy [19]. Experiments confirm theoretical predictions:

$$\alpha = \frac{\omega^2}{2\rho v^3}\left[\mu + \frac{4}{3}\eta + \frac{(\gamma-1)\tau}{c_p}\right] \qquad (5)$$

where α describes the dissipative term in the longitudinal wave number, μ is the bulk and η is the shear viscosity, γ is the ratio of specific heats, τ is the thermal conductivity and ρ the density of the fluid. Attenuation arising from thermal conductivity gives only a negligible contribution to the overall attenuation for most liquids. In the interesting frequency range up to 100 MHz attenuation (Np m^{-1}) can be fit by a single polynominal in frequency of the form af^b with a = 0.0215 and b = 2.0012 [19]. Since cavity size goes with f^{-1} the fundamental longitudinal acoustic mode attenuation can therefore be expected to increase linearly with f. Although experimentally proven only for frequencies up to 200 MHz for simple liquids and mixtures, one can conclude that bulk viscosity cannot be neglected at GHz frequencies. One should have in mind that at resonance the effective acoustic path length increases with the quality factor of the resonator, Q.

Figure 1 shows the consequences for a phononic crystal sensor with a slit cavity following the design in [8] for a working frequency close to 1 GHz calculated with a reduced one-dimensional model. The lattice constant is 0.54 µm, the hole diameter 0.46 µm, and the slit width 0.9 µm. The peak frequency decreases from about 0.982 GHz to 0.878 MHz when exchanging water in the slit by 1-propanol. The reduction is mainly caused by the decrease in speed of sound from 1483 m s^{-1} to

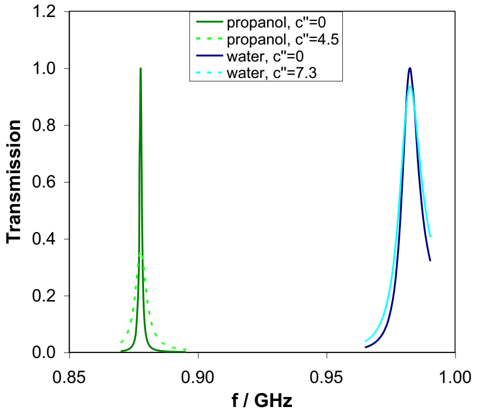

Fig. 1. Transmission peak frequency for a 1 GHz phononic crystal slit cavity sensor calculated with a reduced model. The blue curves at 0.98 GHz show the response when the slit cavity is filled with water, the green curves at 0.88 GHz when filled with 1-propanol. The dark curves represent the case neglecting attenuation due to bulk viscosity, the light dotted curves when considering viscous attenuation.

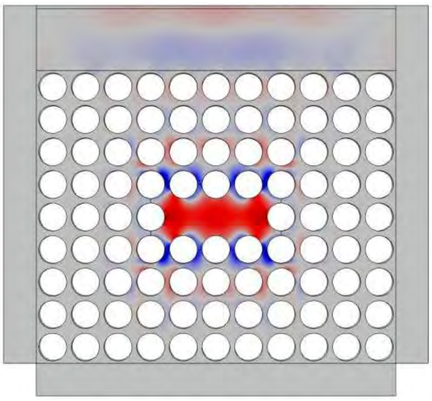

Fig. 2. Mode shape of the phononic crystal slab sensor with solid defect at one selected cavity resonance @ 5.83 GHz. The colors illustrate positive (red) and negative (blue) out-of-plane displacement. A plane longitudinal wave is injected at the upper edge of the phononic crystal.

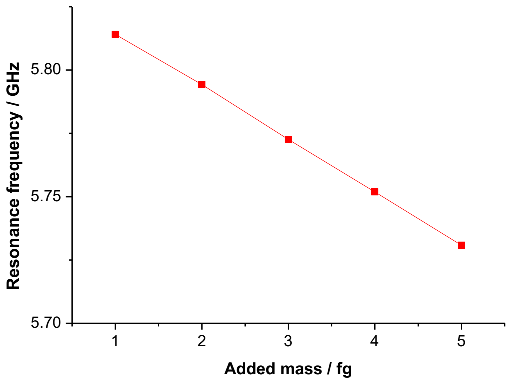

Fig. 3. Change in frequency of maximum transmission of the defect mode shown in Fig. 2 due to mass added to the cavity surface. The mass may represent a sensitive film immobilized at the cavity surface.

1220 m s^{-1}. The decrease in density (997 kg m^{-3} to 804 kg m^{-3}) has much less significance. The sensitivity following (2) is about 390 MHz/m s^{-1} and almost 6 orders of magnitude higher than the sensitivity reported in [8] for the 1 MHz device. The half band width is about 1 MHz for the lower frequency peak and 8 MHz for the higher frequency peak (compared to 4 kHz in [8]). A conservative estimate of the resolution in speed of sound would be 2.5 mm s^{-1}. The increase in frequency enhances the sensitivity as expected. Bulk viscosity defines an upper limit. As one can see in Fig. 1 the lower frequency peak is reduced by 60% when considering viscosity applying (5) in terms of an imaginary part of speed of sound, c'' (see legend), the half band with increases to 7 MHz. This reduction is much less pronounced for the peak at higher frequencies although c'' is larger. The reason for this finding is that the *Q*-factor of this resonance is much lower. It demonstrates the importance of a proper design of the phononic crystal. Whereas the lower peak lies within the band gap of the (regular) phononic crystal, the high frequency peak overlaps with the upper band gap edge at about 1 GHz and the cavity mode couples with the first allowed mode in the following transmission band.

Figure 2 displays the result of transmission analysis of a phononic crystal sensor with a solid defect having same lattice constant and hole diameter. It is a perforated plate with the cavity in the middle realized by omitting three holes and four surrounding rows of holes. Additional elements on the sides of the phononic structure are used to condition appropriately acoustic impedances on the boundaries according to contemplated sensor designs including supporting frame (left and right), the feeding (top) and receiving (bottom) waveguides. The upper and lower surfaces of the plate are set to be free. Out-of-plane displacement is illustrated in colors (positive-red, negative-blue). Acoustic energy is highly confined in the cavity which results in a high *Q*-factor of the resonance. Note further, that the node line (white) does not coincide with the geometry of the cavity. To demonstrate mass sensitivity 1 to 5 fg are evenly applied to the defect of the sample, equivalent e.g. to about 1..5 nm polymer film having a density of 1000 kg m^{-3}. The resulting shift of the respective frequency of maximum transmission moves to lower frequencies proportional to the applied mass as shown in Fig. 3. The mass sensitivity is about 20 MHz/fg. The corresponding minimum mass load is 0.8 pg mm^{-2} and can compete with the best MEMS resonators.

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Experimental Verification

The sensitivity to speed of sound of a binary mixture of water and 1-propanol and the sensitivity to the 1-propanol concentration of the phononic crystal sensor featuring a slit cavity has been already experimentally proven in [8]. It demonstrates the sensitivity to volumetric properties of a liquid confined in a cavity. The experimental verification of (surface) mass sensitivity of a phononic crystal sensor featuring a solid defect has been performed again with a macroscopic device due to the absence of a GHz phonon source. The sample is made of RO 6010.2 (Rogers, Advanced Circuit Materials Division, Chandler, AZ), a PTFE/Ceramic microwave laminate having a flexural modulus of 4364 MPa or 3751 MPa and a density of 3100 kg m^{-3} giving rise to speed of sound of about 1190 m s^{-1} or 1100 m s^{-1}, respectively. The plate size is 128 mm x 128 mm x 2.54 mm. The lattice constant is 4.2 mm, the hole diameter is 3.6 mm. The array has 17x19 holes with three missing holes in the center of the structure acting as defect. Since the respective probing frequency is about 100 kHz only, the mass added to the cavity must be in the mg-range. PZT transducers having a resonant frequency of about 150 kHz have been reversibly connected directly onto the upper main surface of the phononic crystal substrate to excite Lamb waves. The generating transducer has been placed outside the photonic structure whereas the receiving transducer has been mounted directly onto the defect similar to [20]. Due to the size of the transducer the electrical signal corresponds to strain applied to the transducer across the cavity. The problem becomes obvious in Fig. 4 which shows the out-of-plane displacement determined with a scanning laser vibrometer, for experimental details see [21]. The estimated minimum mass load is about 0.8 mg/mm^2. The huge difference to the theoretical sensitivity of the microscopic must be addressed to the much lower probing frequency and the low Q-factor of resonance.

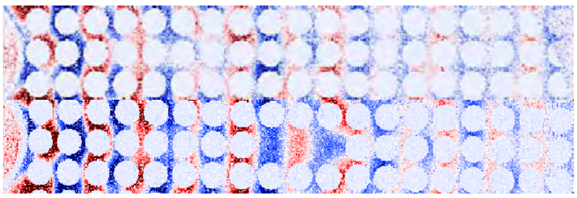

Fig. 4. Out-of-plane displacement of the macroscopic sample of a phononic crystal with solid defect outside the cavity region (top) and along the the cavity (bottom) determined with a scanning laser vibrometer. For excitation, a PZT transducer, partly seen at left, has been placed outside the phononic crystal, respectively.

Fabrication Technology

The challenge is threefold: Devices providing good electromechanical coupling and low insertion loss at MHz frequencies, design of the PnC with appropriate band gaps, technology to realize the structure. Most appropriate for acoustic waves in the mid-MHz range are piezoelectric surface acoustic wave (SAW) devices. It has been shown previously that phononic crystal designs exist featuring a full band gap for SAW [22]. Figure 5 shows the layout of a delay-line device where the acoustic wave propagation path is modified by the phononic crystal. Unfortunately, etching technology is far less developed for piezoelectric materials compared to Si. We have started with AT-quartz wafers although $LiNbO_3$ is the acoustically more attractive material but more challenging in technology [23]. Figure 6 shows an array of etched holes as required for different SAW frequencies. A chromium/gold seed layer is deposited by PVD, lithography is based on AZ 15nXT. An Atotech electroplating process creates a nickel hard mask between the developed photoresist elements. The key dry etching process applies a mixture of SF_6/O_2 etch. During the process a backside cooling of helium was necessary to prevent any modifications of the piezoelectric quartz structure. Finally all process residuals, the nickel hard mask and the chromium/gold layer are removed to release the structures.

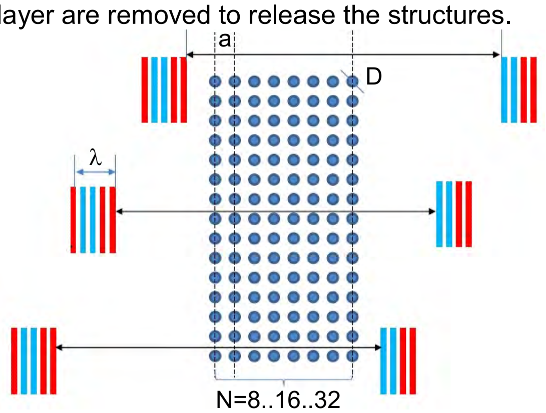

Fig. 5. Basic scheme of a SAW delay line phononic crystal sensor.

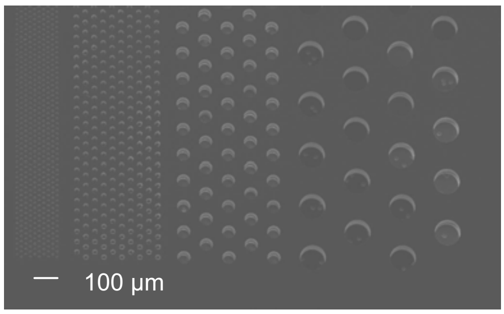

Fig. 6. SEM picture of a set of hole arrays etched into a piezoelectric quartz crystal.

Applications

The phononic sensor can be expected having a large impact in measurement, monitoring or analysis of complex systems. This especially applies to biosensors or medical sensors as well as chemical sensors for microreactors. The sensor exploits an approach to characterize complex molecules like proteins alternative to advanced spectroscopic measurement units. It is known that e.g. antigen-antibody interactions or enzymatic reactions and protein synthesis are associated with changes in molecular conformation accompanied by changes in mechanical properties of the biomolecules. The capability of phononic sensors to determine volumetric properties of the analyte, i.e. to investigate properties of biomolecules in their physiological environment in very small volume without the need of immobilization of DNA, proteins e.t.c. onto a solid surface, can be expected to become the feature with the largest impact. Due to the absence of any electronic component at the place of measurement the sensor offers significant advantages under harsh environmental conditions as well.

To take advantage of this unique feature intensive research is required to reveal the relation between chemical or biochemical signals and acoustic values governing the sensor response. Use of labeling technologies like the introduction of functionalized nanoparticles to the analyte to amplify the biochemical sensor signal and to introduce selectivity is thinkable as well. Whereas optical sensors have a reliable knowledge base, acoustic sensors at ultrasonic and hypersonic frequencies have just opened the gate to information on structure or morphology of biomolecules, supramolecules or aggregates [24].

To cross the "valley of death" between 'proof-of-concept' and successful market adoption of the technological platform and to reach the ambitious long-term goals demands heterogeneous integration of enabling technologies. The key components at technology domain level are tunable phononic sources, broadband phononic detectors, micro- and nanofluidic systems and components meeting the special requirements of devices based on wave propagation, integrated electronics for smart systems and packaging interfacing micro- and macroworld. Furthermore, new approaches in system-level modeling and simulation integrating molecular dynamics, bio-phononics, nanofluidics, structural mechanics and wave propagation beyond current multiphysics packages is required. Special attention should be paid to quantitative structure–activity relationship models to relate the set of sensor data, physico-chemical properties and theoretical molecular descriptors to response variables of the bio- or chemical system to overcome the limitations of the currently practiced empirical approach. Potential impact of high relevance can be expected in prediction or estimation of biological activity, inhibition or amplification of metabolic pathways, bioavailability, ligand efficiency, mutagenesis, or toxicity.

Conclusions

Sensitivity has been theoretically investigated by changes of speed of sound of a liquid confined in a cavity and applying additional mass to the surface of the cavity. The sensor can therefore measure volumetric properties of a measuring object confined in the phononic cavity as well as interfacial properties of a measuring object immobilized at or in close proximity to the phononic cavity. Interchangeable recognition units, either in volume or immobilized at the cavity surface can be integrated, introducing selectivity to the sensor. Viscosity is one of the most prominent limiting factors to drive sensitivity to single molecule detection. This inherent disadvantage can be turned into a specific measure if the phonon cavity resonance can be tuned to correspond with molecule-specific relaxation times.

The experimental measurements of phononic sensors performed with a macroscopic sample have proven the sensor concept. Although the sensitivity of this macroscopic sample must be much lower than that of the microscopic phononic crystal sensor sensitivity to both speed of sound representing properties of a liquid analyte [8] and mass increase representing the adsorption of molecules could be shown.

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