4 Electrochemically-prepared 2D and 3D photonic crystals

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4.1 Introduction

In the last ten years, photonic crystals have gained considerable interest due to their possibility to mold the flow of light [1]. Photonic crystals are physically based on Bragg reflections of electromagnetic waves. In simple terms, a 1D photonic crystal is a periodic stack of thin dielectric films with two different refractive indices n_1 and n_2 . The two important geometrical parameters determining the wavelength of the photonic bandgap, are the lattice constant $a = d_1(n_1) + d_2(n_2)$ and the ratio of d_1 to a, where $d_{1,2}$ is the thickness of the layer with refractive index $n_{1,2}$. For a simple quarter-wavelength stack, the center wavelength λ of the 1D photonic stop band would be $\lambda = 2n_1d_1 + 2n_2d_2$. In the case of 2D photonic crystals, the concept is extended to either air holes in a dielectric medium or dielectric rods in air. Therefore, ordered porous dielectric materials like porous silicon or porous alumina are intrinsically 2D photonic crystals.

Electrochemically grown pores in metals and semiconductors have been studied for about 50 years [2, 3]. However, only in the last ten years intense research efforts have enabled the preparation of ordered pore arrays, with pore diameters in the range of a few nanometers to some tens of micrometers. The most studied materials are porous alumina and macroporous silicon and very recently porous III–V compounds. Porous alumina has been known for more than a century, but not before 1994 ordered arrays of porous alumina have been achieved [4]. This ordering was initially given by self–organization and the ordered domains were in the micron range. However, electron–beam lithography [5] and a new related technique of nano–indentation [6] allowed to prepare monodomain porous alumina structures with domain sizes limited only by the prepatterned area (some mm²) and structure sizes in the nm–range.

Macroporous silicon has been pioneered in the early 1990s by V. Lehmann and H. Föll [7, 8]. Very regular pore arrays (pore size d: microns, domain size: up to wafer size) have been obtained by photolithographic prepatterning. These pores were called macropores² in contrast to microporous silicon, which is a sponge–like nanostructured material with photoluminescence properties that were intensively studied in the early 1990s [9]. Moreover, very

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²All pores are classified according to the IUPAC (Internat. Union for Pure and Applied Chemistry) – conventions unless otherwise indicated: microporous (equivalent to the often used term nanoporous): pore diameter d < 5 nm, mesoporous: d = 5 - 50 nm, macroporous: $d \ge 50 nm$

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recently, a few other semiconductors like InP, GaAs and GaP have been shown to exhibit micron– and nm–sized pores [10, 11]. Whereas standard nanostructuring techniques are limited to small pore aspect ratios h/d < 40 (ratio between pore/rod length to pore/rod diameter) and resolutions limited by the lithographic tools, electrochemically prepared pores exhibit high aspect ratios of 100 to 10000 and inherent short–range order. In the following, macroporous silicon, porous alumina, and porous III–V semiconductors will be discussed in detail. Due to the regular pore arrangements, these materials are extremely well suited as photonic crystals.

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4.2.1 Porous silicon

p-type porous silicon

Porous silicon formed by anodization of p-type silicon in hydrofluoric acid has been studied by numerous groups. State-of-the-art summaries are given by Allongue [12], Lehmann [13], Zhang [14] and Föll et al. [15]. Three different pore formation regimes as a function of the dopant concentration have been observed experimentally. For degenerately doped p-type silicon, a special type of mesopores has been observed experimentally and attributed to tunneling of holes through the space–charge region [16, 17]. Their size is typically in the range of 5 to 50 nm. For moderately doped p-type silicon, micropore formation is observed with pores in the range of 2 nm - 5 nm [9]. For highly resistive crystalline and amorphous p-type silicon (the resistivity is typically larger than 10 Ω cm), macropore formation (0.4 μ m to 10 μ m diameter) is observed below a thin layer of micropores [18]. Previously, macropore formation in lowdoped Si had only been reported in anhydrous electrolyte [19, 20]. In the macropore regime, the wall thickness is about two times the space charge region, whereas the pore diameter is governed by the properties of the silicon-electrolyte interface, the resistivities of the silicon wafer and the properties of the electrolyte [21]. Depending on the current density and HF concentration, these macropores can either grow in the current-limited regime (low-currents) or in the crystallographic regime (high currents). These two regimes can easily be distinguished from the form of the pores. If the pores have a pyramidal pore tip and no micropores in the macropores, they are grown in the crystallographic regime. Electropolishing occurs at the pore bottom. If the pores are round and filled with micropores, the pores are grown in the current-limited regime. However, the exact growth mechanisms remain controversial in the literature [22, 23]. To obtain ordered arrangements of pores, being a prerequisite for photonic crystals, the crystallographic regime is typically used [24]. A p-type silicon wafer with $\langle 100 \rangle$ orientation is first prepatterned by standard photo-lithography. Subsequent alkaline etching produces inverted pyramids acting as initial pores. Etching starts selectively at these etch pitches when self-ordering conditions and lithography match [21, 22, 24].

Pore growth directions are mainly governed by passivation kinetics during the etching process, i.e. surfaces which are passivated fast and effectively with hydrogen are etched less. As (100) surfaces are passivated the worst and slowest, pores on (100) wafers proceed in $\langle 100 \rangle$ directions perpendicular to the wafer surface. On (111) wafers, on the other hand, $\langle 100 \rangle$ pores would grow under an angle of 54° to the normal. In this configuration, the second slowest

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passivated direction ($\langle 113 \rangle$ with an angle of 34°) governs the pore growth [25]. At the nucleation points on the surface, tripods consisting of three equal $\langle 113 \rangle$ -directions begin to grow. They form a criss-cross network of pores. If pores are grown with lithographically defined nucleation spots, a Yablonovite-like structure [26] results. However, up to now, lithographically prestructured samples have not yet reached optical quality. Application of pore etching requires homogeneous and reproducible etching of large areas, e.g. standard size Si wafers. This is not easy, but possible as demonstrated in [27–29] and by the Kiel group (cf. Fig. 4.1b).



Figure 4.1: Large area etching of p-type silicon: (a) Scanning electron microscope (SEM) cross section of an ordered pore array with a pore diameter $d = 5 \ \mu$ m and an interpore distance $a = 8 \ \mu$ m. (b) Photograph of the first homogeneously electrochemically etched 8" wafer worldwide. (To our knowledge; previously unpublished results by the Kiel group.)

n-type porous silicon

A detailed description of macroporous silicon formation in n-type Si can be found in [7,8]. Since holes (necessary for the dissolution reaction) are minority carriers in n-type silicon, they have to be generated by backside illumination. Then, they diffuse to the etch front through the wafer to promote dissolution of silicon, mainly at the pore tips. This technique has high requirements on the minority carrier diffusion length so that normally float-zone (FZ) wafers are used. Due to the fact that in this technique the holes move by diffusion and not by drift as in the p-type case, the strong boundary condition of a fully depleted pore wall is relaxed and thicker walls can be obtained up to 10 times the space-charge region width [8]. It is even possible to change the pore diameter during pore growth, which is hardly possible with p-type silicon in a controlled manner [30, 31]. To obtain ordered arrangements of pores, a ntype silicon wafer with (100) orientation is first prepatterned by standard photo-lithography. Subsequent alkaline etching produces inverted pyramids acting as initial pores. Under anodic bias and backside illumination, the wafer is then etched in hydrofluoric acid. As a result, pores grow straight along the (100) direction with a very high aspect ratio. The arrangement of these pores can be controlled by the lithographic mask and the pore diameter by the illumination intensity. By controlling these parameters, unintentional variations of the pore diameter with depth can be made negligible. Interpore distances in the range of a = 500 nm to a few tens of microns are possible. Figure 4.2 shows a scanning electron microscope (SEM) image of a porous Si sample, which was etched on 0.1 Ω cm n-type FZ silicon substrates, having a photo-lithographically-defined hexagonal pore arrangement. The pores have a center-to-center distance of 500 nm and a depth of 100 μ m. The pore diameter after electrochemical etching is 370 nm. Initially the pores are slightly squared since etching is preferred in the (100) direction, stopping at the [110] planes of the crystal. However, by successive oxidation and etching steps, the pore diameter can be increased and the pores become rounder. It turned out recently, that for very deep pores, the dark current becomes significant. It can contribute up to 25 % to the total etching current. Carrot-shaped pores are obtained since the current contributes less to the pore growth and more to the dark current. This is very pronounced in structures exhibiting a very high surface area, thus typically structures with interpore distances smaller than 1.5 μ m. By increasing the surface potential barrier at the interface HF/Si with an anionic tenside, the Halle group was able to reduce the dark current below 1 % of the etching current.

Like in p-type silicon, also in n-type silicon, $\langle 113 \rangle$ -pore networks can be grown on (111)oriented samples [32] for the production of 3D full photonic bandgap materials. Additionally, the pore diameter can be modulated during the growth which has a tremendous effect on the bandgap [33].



Figure 4.2: (a) Ordered porous n-type silicon (a = 500 nm). (b) Self-ordered mesoporous Si. The pores (d = 500 nm) self-organize in a hexagonal array (Inset: Cross section shows no significant pore wall roughness.) (Unpublished results by the Kiel group.)

Very recently, self-ordered pore arrays have been discovered in Si (Fig. 4.2b). They are something between meso- and macropores, i.e. they grow in a similar manner to mesopores but with dimensions in the macroporous regime. Conventional mesopores are normally only used for 1D – PhCs which are formed by layers of different porosity [34], while their dendritic structure with random side branches makes them unusable for 2D and 3D structures, as described above. However, in the present case, branching could be suppressed yielding extremely smooth pore walls like in InP [35]. The growth sequence is similar to InP (cf. Section 4.3.7): First a layer of crystallographically oriented pores grows which constantly increases the number of pores by branching. When the density of pores reaches a critical value, the growth switches to a current line oriented growth, i.e. follows the flow of the electrical current. This results in pore growth in the otherwise never observed $\langle 111 \rangle$ -direction, e.g. on (111) Si samples. To transport the maximum electrical current through the pore tips, the system tries to close-pack the pores which results in a hexagonal self-ordering of the porous

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ensemble (cf. Fig. 4.2b). With this technique, it was possible to reach diameters as small as 100 nm (not possible with the conventional technique [7,8]). The etching speed could also be increased by a factor of 6 (up to 400 μ m/h compared to typically 60 μ m/h for the conventional technique). Still, optical quality has yet to be demonstrated by optical measurements.

4.2.2 Porous alumina

Aluminum is electrochemically oxidized to alumina (Al₂O₃) under positive polarization. For certain electrolytes, which weakly dissolve the alumina, the growth of disordered pore arrangements has been observed and studied for a century now. A unique relationship between the anodization voltage U and interpore distance a was found: $a = d + 2\alpha U$ where d is the diameter of the pores and $\alpha \approx 1.2$ nm/V [3,36]. In 1994, Masuda and Fukuda first discovered that after long anodization times, self-ordered porous alumina films can be obtained at the growth front, which are arranged in a hexagonal close-packed pattern [4]. They have obtained ordered pore arrays with a lattice constant of 60 nm [37], 105 nm [4], and 500 nm [38] depending on the anodization conditions. The size of the pore domains increases with time [39]. The domains can reach micron size and domains touching each other have typically different orientations [39]. Mechanical stress between neighboring pores, due to the volume expansion of alumina with respect to the aluminum substrate, has been proposed as a mechanism for the self-ordering. For example, it is observed that the volume expansion for optimal pore growth is in the range of 1.2 to 1.4, i.e., there is an incorporation yield of 60 - 70 % aluminum in the alumina film. This corresponds to an initial porosity of the porous film of 10 %. We have recently shown that all ordered regimes exhibit an initial porosity of 10 % after etching (10 %-porosity rule) [39]. Since the interpore distance is determined by the potential only, the pore diameter is the key to tuning the range of selfordered pore growth. We have shown experimentally that the pH-value of the electrolyte controls the pore diameter [39]. This is in line with a recent linear stability analysis [40]. Thus, by adjusting the pH-value and the potential, other ordered regimes can also be obtained. To date, it is possible to obtain ordered pore growth with 50, 65, 105, 420 and 500 nm interpore distance.

To obtain monodomain pore arrays, three strategies are possible. First, if one starts with a single crystal seed, i.e., a single pore, one would expect that the other pores arrange themselves hexagonally around it due to repulsive forces. The second one is based on the observation of Li et al. [41]. As the anodization time increases, one should end up with a single domain since it is the total energy minimum of the system. Note that this assumes an aluminum monocrystalline substrate. However, both approaches seem to be quite impractical. Therefore, a third strategy is used. Knowing the optimum potential U and electrolyte for a certain interpore distance a, the aluminum substrate can be lithographically prepatterned. Since the feature sizes are in the range of 50 nm, electron beam or imprint lithography is applied. Figure 4.3 shows a SEM image of a hexagonally-ordered pore array in alumina, prepared from an imprint-lithography prepatterned substrate [6]. The pattern has 500 nm interpore spacing and the anodic voltage was adjusted to 195 V, based on the relationship between a and U. Very recently, Masuda et al. have shown that in addition to the hexagonal lattice, the square and honeycomb lattice can also be obtained by appropriate prepatterning, exhibiting squared or triangular pore shapes [42]. The Halle group has extended this idea and has shown that by nanoimprinting twice under different angles (Moire-pattern) even structures with a 12-fold rotational symmetry can be



Figure 4.3: Ordered porous alumina with a = 500 nm obtained by imprint lithography [6]. By repeated imprint under an angle of 2.2 degrees, a 12–fold symmetry can be obtained [43].

obtained (Fig. 4.3), which have been predicted to exhibit a complete PBG for low-refractive index PhCs [43]. The inset in Fig. 4.3 shows the Fourier transform of the image.

4.2.3 Porous III–V semiconductors

As in Si, anodization of III–V single crystals can lead to uniform dissolution (electropolishing) [44] or selective dissolution, i.e. pore formation [45]. The main factors determining the actual result of anodization are the doping type of the substrate (n– or p–type), the kind of electrolyte used (acidic, basic), voltage, and the current density applied to the sample, temperature etc. It is illuminating to point out major differences to Si pore etching right away: As far as the materials are concerned, they are polar and do not easily form good (anodic) oxides; as far as pores are concerned, no pores of any kind have been found in p–type crystals, and no micropores have been found either. What has been found, are macro– and mesopores in n–type III–Vs [46].

These pores come in two totally different types: crystallographically oriented pores growing in $\langle 111 \rangle B$ directions ("crysto pores" for short) and current line oriented pores ("curro pores") growing in the current flow direction (or, to be more precise, perpendicular to the equipotential surfaces). Crysto pores tend to form at relatively low voltage/current density and have a special crystallographic feature because they grow only in the $\langle 111 \rangle B$ direction, meaning the direction from e.g. As to Ga, but not the other way around. There are thus two $\langle 111 \rangle B$ directions pointing into a (100)-oriented substrate with an angle of 109° between them (see Fig. 4.4a). Crysto pores tend to have a triangular shape and a high tendency for branching. Taking into account that two $\langle 111 \rangle B$ directions are pointing up towards the surface of the sample, branches of crysto pores may also grow upwards, an unusual behavior at first sight, never seen in Si. Moreover, crysto pores may easily intersect each other [47] which is not a common observation in pore growth. These features allow us to produce defined 3D structures of criss-crossing crysto pores. Crysto pores grow relatively slowly, about $1 \,\mu$ m/min similar to macropores in Si. They have been observed in GaAs, InP, GaP (and recently also in Ge [48]). Curro pores have been found in InP and GaP. Their growth rates are rather large compared to the crysto pores, can reach 30 μ m/min and depend strongly on the efficiency of electrolyte flow, to the tips of the curro pores. Similar results have only recently been found in



Figure 4.4: a) Crystallographically oriented pores (crysto pores) in (100)–oriented n–GaAs; b) The switch from curro to crysto pores in (100) InP by switching the current density from high to low values.

Si (cf. Sec. 4.2.1). The reason for the remarkably large growth rates are the "bad" and unstable III–V oxides (formed as a result of anodization at the tips of the pores) in acid electrolytes.

The assumption "*crysto* = *low*" and "*curro* = *high current densities*" has been verified by changing the value of the current density from high to low during the etching of a single sample. By doing so, it is possible to switch between the two morphologies (cf. Figure 4.4b): The first layer consists of curro pores (high current densities) whereas the second layer is made of crysto pores (low current densities).

4.3 Application to photonic crystals

4.3.1 Introduction

From the beginning of research on photonic crystals, a major area of investigation concerned two-dimensional (2D) photonic crystals [1]. This was mainly caused by experimental reasons as the fabrication of 3D photonic crystals appeared to be more difficult and cumbersome than that of 2D photonic crystals. Additionally, the calculation of band structures for 2D photonic crystals is less time consuming and a lot of interesting phenomena (e.g. light localization – at least in a plane) can already be studied in 2D photonic crystals. However, an ideal 2D photonic crystal consists of a periodic array of infinitely long pores or rods, so that a structure which approximates this theoretical model has to exhibit very high aspect ratios. Using conventional dry etching techniques, only structures with aspect ratios up to 10 - 30 are possible. To avoid scattering of light out of the plane of periodicity and to reduce the corresponding loss, the socalled slab structures were developed and thoroughly investigated [49,50]. In such low-aspect structures, one relies on guiding of light by total internal reflection in the third dimension and, consequently, deals with a full 3D problem. On the other hand, Lehmann and Grüning [51,52], as well as Lau and Parker [30] proposed macroporous silicon as a model system for 2D photonic crystals. Typically, high-quality photonic crystals with lattice constants of a = 500 nm to 8000 nm can be produced with this process. These structures exhibit photonic bandgaps from the near infrared to the far infrared (Fig. 4.5). Since then, new electrochemically nanostructured materials like III-V compounds or aluminum oxide with photonic properties have



Figure 4.5: Summary of experimentally measured bandgap–center wavelengths for porous alumina (TE gap) and porous silicon (complete gap) as a function of the lattice constant (From references [a]=[51], [b]=[52], [c]=[29], [d]=[65], [e]=[31], [f]=[71], [g]=[72]). Picture taken from [68].

4.3.2 2D photonic crystals made of macroporous silicon

Bulk photonic crystals

The dispersion relation for light propagation inside a photonic crystal is calculated using the plane wave method. Due to the 2D periodicity and the uniformity along the third dimension, the light propagating in a 2D photonic crystal splits into E-polarized (E-field parallel to the pore axis) and H-polarized (H-field parallel to the pore-axis) waves. The band structures for these polarizations differ from each other and so do the bandgaps in width and spectral position. This originates in the different field distributions: Typically, the electric field of the H-polarized waves is located in the veins of the structures whereas the electric field of the E-polarized waves concentrates in the connection points of the veins. Figure 4.6 shows an example of a band structure for our system, calculated for wavevectors in the first Brillouinzone along the path $\Gamma - M - K - \Gamma$. The assumed porosity or air filling factor is p = 0.73which corresponds to r/a = 0.45 (r =pore radius, a =lattice constant) and the refractive index of silicon in the infrared is n = 3.4. For a triangular array of pores, a refractive index contrast exceeding 2.7 [53] and for suitable r/a ratios, the bandgaps for E- and H-polarization overlap and a complete 2D photonic bandgap exists. As the refractive index contrast for air pores in silicon amounts to $n_{\rm Si}/n_{\rm Air}$ = 3.4 in the infrared (IR), these requirements are fulfilled in our system. The band structure shown in Fig. 4.6 thus exhibits such a complete bandgap, indicated by a grey bar.

In addition to the band structure, the density of (photonic) states (DOS) is computed as well and presented in Fig. 4.6b [54]. In the spectral region of the complete photonic bandgap, the DOS is zero such that propagation of light in the plane of periodicity with these frequencies is completely forbidden in the photonic crystal. To verify these theoretical calculations, a triangular lattice was fabricated with a pitch $a = 0.7 \ \mu m$ and r/a-ratio of 0.365. To check the spectral position of the first order bandgap, reflection measurements were performed using an IR microscope connected to a FTIR-spectrometer. The reflection for H- and E-polarized light incident in the Γ -M direction was measured separately. A gold mirror was used as a reference. Figure 4.7 shows a comparison of the measured reflection spectra with the band



Figure 4.6: 2D band structure of a trigonal macroporous silicon photonic crystal (r/a = 0.45) and density of photonic states (DOS), inset: 2D hexagonal Brillouin–zone and appropriately oriented trigonal pore lattice in real space. The grey bar indicates the 2D complete bandgap. In this spectral range neither *H*–polarized nor *E*–polarized photonic states exist (DOS = 0). (Courtesy of K. Busch.)

structure. The shaded spectral ranges represent the theoretically expected regions of high reflectivity stemming from the bandgaps. They correspond very well to the experimental results. Although the reflected light contained contributions from beams with an incidence angle of up to 30° (due to the focusing conditions of the microscope) this off–normal incidence has only a negligible effect. The incident light is bent by refraction towards the normal, propagating with a much smaller angular deviation inside the photonic crystal. Additionally, the width and position of this first order bandgap is not very sensitive for small angular deviations [55]. Please note that the very steep band edges reflect the very high quality of these structures which were obtained by a recently developed, improved etching method. Reflectivities originating from higher order bandgaps, antisymmetric modes or modes with a low group velocity can also be observed and are in very good agreement with the theory (cf. Chapter 1 by Busch et al.).

A graphic representation of the relationship between gap frequencies and filling ratio is known as a gap map, which for our structure, has been calculated before [54]. To verify this gap map experimentally, transmission measurements for 17 different samples spanning a wide range of r/a-ratios were carried out. The band edges were determined from these measurements and are compared with the theoretical predictions in Fig. 4.7. The overall correspondence is very good. For lower r/a-ratios, only a bandgap for the H-polarization exists. A complete bandgap only appears for r/a > 0.4 since an E-bandgap then appears which overlaps with the H-bandgap. With increasing r/a-ratios, the E-bandgap widens while the H-bandgap shrinks for very high filling ratios. A maximum, complete bandgap of $\Delta \omega / \omega = 16\%$ for r/a = 0.48 can be deduced. This relatively large complete bandgap is a



Figure 4.7: Left: Reflectivity along Γ -M for a 2D trigonal macroporous silicon photonic crystal with a lattice constant of 0.7 μ m for H-polarization (TE). Left: Measured reflectivity of a semi-infinite photonic crystal. Right: Comparison with band structure. Symmetric bands contribute to transmission while for asymmetric bands, the incident plane waves cannot couple. Beside the bandgaps, they also cause total reflection. The shaded range shows the fundamental bandgap for H-Pol from 2 to 3.2 μ m (courtesy from S. Richter and C. Jamois). Right: Position of the bandgaps for H-polarized light (dotted) and E-polarized light (solid) for a 2D trigonal macroporous silicon photonic crystal depending on the r/a-ratio (gap map). A complete bandgap appears as an overlap of the gaps for both polarizations and attains its maximum size for an r/a-ratio of 0.48 [54].

consequence of the strong refractive index contrast between the silicon (pore walls) and air (inside the pores) as well as the synergetic interplay of Mie resonance and Bragg scattering resonance. A summary of experimentally–measured bandgap center wavelengths for porous alumina (TE-gap) and porous silicon (complete gap) as a function of the lattice constant is shown in Fig. 4.5.

Finite photonic crystals

Strictly speaking, the band structure calculations can only be performed assuming an infinitely extended photonic crystal. Therefore, also the bandgap (zero DOS) causing perfect total reflection only appears for infinite bulk photonic crystals. For a very thin bar of the photonic crystal, the incident light of a frequency within the bulk bandgap is no longer totally reflected. A certain amount can penetrate the thin photonic crystal. To investigate this effect, 4 samples containing 1, 2, 3 and 4 crystal rows with a r/a-ratio of 0.453 were fabricated (Fig. 4.8). Transmission measurements for H-polarized light of different wavelengths along $\Gamma - K$ were performed (see Fig. 4.8) [56]. A tunable laser setup was used which covered the spectral range between $3 < \lambda < 5 \,\mu$ m, corresponding to the range of the H-bandgap ($3.1 < \lambda < 5.5 \,\mu$ m) of the corresponding bulk photonic crystal. The experimental results were compared with transmission calculations applying the already mentioned Sakoda method and showed a very good agreement (Fig. 4.8). Plotting the transmittance versus the penetrated crystal thickness, an exponential decay is observed. This corresponds to the expectation that for frequencies within the bandgap, the light penetrating into the bulk photonic crystal is exponentially damped. The slope of the line in the logarithmic plot corresponds to a decay constant of 10 dB per crystal row for light with a wavelength near the center of the bandgap. Even for a bar containing only 1 pore row, the bandgap is already perceptible. This originates in the strong scattering of the single pores due to the large refractive index contrast between air pores and silicon walls.



Figure 4.8: a) SEM image of the macroporous silicon bars with varying width. The inset shows an enlarged view of the center square. b) Measured and calculated transmission for wavelengths within the H-bandgap. Solid lines: calculations for transmission through 1, 2, 3 and 4 crystal rows. Points: Measurements for 0.89 ± 0.04 (\blacksquare), $1.8 \pm 0.1(\bullet)$, 2.9 ± 0.1 (\blacktriangle) and 4.2 ± 0.2 (\blacktriangledown) crystal rows (determined statistically). c) Measured transmission as a function of bar thickness for 2 wavelengths within the bandgap [56].

4.3.3 Photonic defects in electrochemically–prepared 2D photonic crystals

Introduction

Since the beginning of the study of photonic crystals, special attention has been paid to intentionally incorporated defects in these crystals. Point or line defects can be introduced into macroporous 2D-silicon photonic crystals by omitting the growth of a single pore or a line of pores. This can be achieved by designing a suitable mask for the lithography (the pattern defining process). Introduction of defects into porous alumina photonic crystals is more difficult, since intentionally introduced defect anneal out during electrochemical etching. However, for thin slab structures, line or point defects having a slightly smaller pore diameter, might be realizable.

Waveguides

To demonstrate waveguiding through a linear defect, a 27 μ m long line defect (W1 – one missing row) was incorporated along the $\Gamma - K$ direction into a triangular 2D photonic crystal with a r/a- ratio of 0.43 ($r = 0.64 \mu$ m) [60]. However, due to the photo-electrochemical fabrication process, the diameter of the pores in the rows adjacent to the waveguide is increased.

The transmission through the line defect was measured using a pulsed laser source which was tunable over the whole width of the H-stopband in the $\Gamma - K$ direction (3.1 < λ < 5.5 μm). To couple light into the narrow waveguide (with a subwavelength width) with reasonable efficiency, a spatially coherent source of mid-IR light was used. A parametric source was used to produce a beam tunable from 3 to 6 μm , containing 200–fs pulses at a repetition rate of 250 kHz and a typical bandwidth of approximately 200 nm. The H-polarized beam was focused onto the sample by a 19–mm focal–length ZnSe lens, to a spot size of approximately 25 μm . Because the waveguide width was 1.1 μm , this spot size provided a theoretical coupling efficiency of approximately 4.8 %. The transmitted light was passed through a monochromator, chopped, and detected with a pyroelectric detector and a lock–in amplifier. The transmission is defined as the ratio of the transmitted power to the total power incident upon the sample and is about 2 %. The transmission deficit compared to 4.8 % is attributed to the clipping of the beam by the substrate and possible diffraction losses.

The measured spectrum (Fig. 4.9) exhibits pronounced Fabry–Perot–resonances over a large spectral range, which are caused by multiple reflections at the waveguide facets. Comparing the spectrum with an FDTD–transmission calculation, reveals very good agreement and the comparable finesse of the measured and calculated resonances indicate small losses inside the sample.



Figure 4.9: (a) Measured and (b) calculated H-polarized transmission spectrum of a 27 μ m long waveguide directed along $\Gamma - K$ covering the spectral range of the H-bandgap of the surrounding perfect photonic crystal (transmission in %). Only the even waveguide modes contribute to the transmission as the incoming plane wave can not couple to the odd waveguide modes. The small stopgap at a frequency of 0.45 c/a is caused by the anticrossing of 2 even waveguide modes [60].

Microcavities

Besides line defects, point defects consisting only of one missing pore, are also of special interest. Such a micro-resonator-type defect also causes photonic states, whose spectral positions lie within the bandgap of the surrounding perfect photonic crystal. The light fields belonging to these defect states are therefore confined to the very small volume of the point defect, resulting in very high energy densities inside the defect volume. As the point defect can be considered as a microcavity surrounded by perfectly reflecting walls, resonance peaks with very high Q-values are expected in the transmission spectra. Since the symmetry is broken in both high-symmetry directions, a band structure cannot be used to describe point defects anymore. To study this experimentally, a sample was fabricated which included a point defect which was placed between two line defects, serving as waveguides for coupling light in and out [61].

Measuring transmission through a waveguide-microresonator-waveguide structure demands an optical source with a very narrow linewidth. Therefore, a continuous wave optical parametric oscillator (OPO) has been used, which is tunable between 3.6 and 4 μ m and delivers a laser beam of 100 kHz line width. For spatially resolved detection, an uncoated, tapered fluoride glass fibre mounted to a SNOM-head was applied and positioned precisely to the exit facet of the outcoupling photonic crystal waveguide (for detailed information on SNOM-measurements on PhC-structures: see Chapter 11 by Sandoghdar et al.). In the transmission spectrum, two point defect resonances at 3.616 μ m and 3.843 μ m could be observed. Their spectral positions are in excellent agreement with the calculated values of 3.625 μ m and 3.834 μ m. These walls were predicted by 2D–FDTD calculations taking into account the slightly widened pores surrounding the point defect. The measured point defect resonances exhibited Q-values of 640 and 190 respectively. The differences to the theoretically predicted values of 1700 and 750 originate from the finite depth not considered in 2D-calculations and the exact pore shape near the cavity. Recent 3D-FDTD calculations show that for high Qvalues, the finite depth as well as the shape of the pores near the cavity, plays an important role in the determination of the Q-value [62]. Therefore, the 2D-limits breakdown for high-Q cavities under realistic conditions. Intuitively, this can be explained as follows. Any out-ofplane component of the incoming light will result in a spreading of the mode with depth and in a reduction of the Q-value. However, the high Q-values reported for this 2D microresonator, might already be sufficient for studying the modification of radiation properties of an emitter placed in such a point defect.

4.3.4 3D photonic crystals made of macroporous silicon

Up to now, the most significant work based on macroporous silicon and photonic crystals concerned 2D photonic crystals. However, recently attempts have been undertaken to use macroporous silicon for 3D photonic crystals. One approach to introduce a refractive index variation in the third dimension is the modulation of the pore diameter with pore depth [63]. As described in the first paragraph of this review, the pore diameter of the macropores can be controlled during the fabrication process by the intensity of the back side illumination of the wafer. Strong illumination leads to high etching currents and, therefore, wide pores while the opposite is valid for low illumination.

The illumination intensity was now varied periodically during the etch process, applying a zig-zag profile. Figure 4.10 shows a SEM-image of a longitudinal section of the sample. The pore diameter modulation can be approximated well by a sinusoidal dependence on the pore depth. The modulation period amounts to 1.69 μ m and the porosity varies from 81 % to 49 % between the planes of wide and narrow pore diameters. The lattice constant a of the 2D pore pattern is again 1.5 μ m. The resulting 3D photonic crystal has a hexagonal lattice and the corresponding Brillouin zone has hexagonal shape, too. Note, that this is the first three-dimensional photonic crystal in the infrared region which perfectly extends over more than 10 lattice periods. To investigate the optical properties of the structure introduced by the pore diameter modulation, reflection measurements were performed along the pore axis which correspond to the $\Gamma - A$ direction. The spectrum is shown in Fig. 4.10 and compared to a 3D band structure calculation using the plane wave method. For comparison with the experiment, the leftmost part of the band structure shows the relevant dispersion relation along $\Gamma - A$. The stop gap in this direction, caused by the periodic pore diameter modulation, is indicated by a grey bar. It coincides well with the range of zero-transmission between 1350 $\rm cm^{-1}$ $(\lambda = 7.41 \ \mu m)$ and 1680 cm⁻¹ $(\lambda = 5.95 \ \mu m)$ measured along the pores.



Figure 4.10: (left) SEM-image showing a longitudinal section of the modulated pore structure. The variation of the pore diameter with depth can be modelled by a sinusoidal modulation $r = r_0 + \Delta r sin(2\pi z/l_z)$ with $r_0 = 0.63\mu$ m, $\Delta r = 0.08\mu$ m and $l_z = 1.69\mu$ m. [63]. (right) Transmission is measured in the $\Gamma - A$ direction (along the pore axis) and comparison with calculated 3D band structure. The grey bar indicates the stopgap for light propagation in this direction causing zero transmission [63].

Although the structure does not show a complete 3D bandgap, it has another distinct property: As it is not based on building blocks of a fixed shape, e.g. spheres or ellipsoids, the periodicity can be different for all directions. The modulation period along the pore axis (zaxis) can be controlled independently from the periodicity in the x-y-plane. Consequently, the dispersion relation along the pores can be adjusted nearly independently of the dispersion relation perpendicular to them. It turned out recently that the same structure but with an initial 2D cubic lattice does have a complete photonic bandgap. The resulting structure is an inverted simple cubic lattice with a complete bandgap of around 4 % for realistic etching parameters [64]. First realizations can be seen in Fig. 4.11.

Another approach to fabricate 3D photonic crystals on the basis of macroporous silicon, includes a 2–step–process [65]. In the first step, a conventional 2D array of straight pores

4.3 Application to photonic crystals



Figure 4.11: SEM cross section of one of the first modulated pore structure having an inverted simple cubic symmetry. The lattice constant a is $1.5 \ \mu$ m.

is photo–electrochemically etched. Afterwards, additional pores are drilled at oblique angles from the top, using a focused ion beam (FIB). In this way, a set of 3 different pore directions is established which cross each other in the depth. The fabricated structure is very similar to the well–known Yablonovite–structure for the microwave region. However, a complete 3D–bandgap could not yet be shown experimentally, as the angles between the 3 different pore sets have not been properly aligned.

A fabrication technique which should give a very similar result uses the electrochemical etching of macropores on a (111) Si surface [32], where pores grow into $\langle 113 \rangle$ -directions (cf. Sec. 4.2.1). As there are three equivalent $\langle 113 \rangle$ directions available from the (111) surface, 3 pores start to grow from each nucleation point at the surface, leading to a three dimensional interconnected pore grid. The resulting structure is similar to the Yablonovite [26] but slightly distorted, as the pore angle to the normal is not 29.5° but 34°. Band structure calculations for a corresponding structure show that the pores along the three $\langle 113 \rangle$ directions grow at suitable angles, such that the structure should exhibit a complete 3D photonic bandgap of up to 16% [33] (Fig. 4.12).



Figure 4.12: (a) SEM cross section of a $\langle 113 \rangle$ -pore crystal (Kielovite). The quality has still to be improved to allow for optical experiments. (b) Calculated band structure for the Kielovite (modulated pores with r/a = 0.26) [33].

Very recently, different crystal structures with complete bandgaps larger than 20 %, based on macroporous silicon, have been predicted and are under current investigation [66] (Tab. 4.1).

Crystallographic structure Complete bandgap [%] Ref. Common name distorted fcc 8/16ª % [33] Kielovite Modulated hexagonal Inv. sh 0%[31] Modulated cubic Inv. sc 4 % [64] Hallite or SP₂ 25 % tetragonal [66], [67]

Table 4.1: Proposed 3D silicon photonic crystals based on electrochemical pore etching.

^{*a*} for modulated pores

4.3.5 2D photonic crystals made of porous alumina

The possibility to use mono-domain porous alumina as two-dimensional photonic band gap material has been predicted theoretically. Early numerical calculations show that perfectly hexagonally-ordered porous alumina exhibits a photonic band gap for TE polarized light only due to the low refractive index ($n \approx 1.7$ for corundum). For porous alumina, the interpore spacing that can be varied between 50 nm and 500 nm, leading to theoretical photonic bandgaps centered at wavelengths in the range between 100 and 1300 nm, depending on the filling ratio. Note that the bandgap of alumina (corundum) is around 7.5 eV, while porous alumina has a lower bandgap due to its amorphous nature. Experimentally however, absorption for wavelengths above 400 nm is negligible over the size of a photonic crystal. Masuda's group has recently shown transmission measurements through porous alumina photonic crystals with 200 and 500 nm interpore distance, exhibiting photonic bandgaps around 600 nm and 1300 nm (see data point in Fig. 4.5). We have recently extended this work to also obtain the gapmap of porous alumina similar to that of porous silicon (Fig. 4.13). It turned out that porous alumina cannot simply be described by a simple refractive index of n = 1.7. The structure actually consists of at least three layers: An inner high-purity layer of $n \approx 1.7$, a highly an ion-contaminated layer of $n \approx 1.4$ and a rather pure outer layer $n \approx 1.6$. Thus depending on the widening degree, the effective refractive index changes (Fig. 4.13).

4.3.6 1D photonic crystals made of InP

InP exhibits two growth modes: Crystallographically oriented pores ("crysto") for low current densities and current line oriented pores ("curro") for high current densities. Porous layers of crysto and curro pores have different refractive indices due to their different porosities, e.g. the porosity of the curro layer is higher therefore the refractive index is smaller. Switching the current periodically from high to low values, produces multilayers of curro/crysto pores and thus a Bragg mirror, i.e. a 1D photonic crystal. An example of such a structure is presented in Figure 4.14a. This structure could be used, e.g., as a mirror for a Vertical Cavity Surface Emitting Laser (VCSEL). The optimization of such a structure for a defined wavelength can easily be made by adjusting the periodicity of the HIGH/LOW current cycling [70].

4.3 Application to photonic crystals



Figure 4.13: (left): Transmission electron micrograph (TEM) of porous alumina obtained by imprint lithography and subsequent anodization (195 V, 1 wt% H₃PO₄). It reveals that the two oxide layers consisting of inner oxide and outer oxide exist. Thickness of the inner oxide is 50 nm, whereas that of the outer oxide decreases with increasing the pore diameter (initial diameter: 180 nm) by the isotropic etching. (right): Bandgap determined by reflectivity measurements versus theoretical band structure for different r/a-values and both polarizations ($\Delta = TE$, $\bigcirc = TM$) in Γ -M direction [69].

4.3.7 2D photonic crystals made of InP

A particularly interesting feature of the curro pores is their strong tendency for self–organization into a close packed hexagonal lattice like alumina pores (see Section 4.2.2). An example of a self–arranged hexagonal curro pore lattice in n–InP is presented in Fig. 4.14b, c and d. The pores do not branch, have "high quality" pore walls (Fig. 4.14b) and diameters in the sub- μ m range. The diameter of the pores as well as the pore wall thickness are mostly determined by the doping; both can be increased by choosing a lower doped sample, e.g. for $n = 10^{16}$ cm⁻³, 5% HCl, the pore diameters increase up to 1 μ m. The 2D Fourier transform taken from Fig. 2a results in a "diffraction" ring (see the inset), which means that "single crystal" domains are arranged in a structure without long range order. The observed short range ordering is due to pore–pore interaction via space charge regions.

By optimizing the etching conditions, it is possible to obtain long range ordering of these curro pore domains, too (see Fig. 4.14d), and thus finally a single pore crystal: The Fourier transform taken from Fig. 4.14 shows a clear "diffraction pattern" of a hexagonal single crystal. Such single crystalline pore arrays are promising for 2D photonic crystal applications [57], where a highly ordered and high quality array of pores is required.

In order to understand the 2D long range ordering of the curro pores, it is necessary to discuss their nucleation in more detail: Curro pores cannot form without a nucleation layer formed by crysto pores. The thickness of this nucleation layer depends on the etching conditions; it is normally $1 - 2 \mu m$. Its thickness decreases as the currents/voltage increases or the concentration of the HCl electrolyte decreases. As the crysto pores have much smaller diameters than the curro pores and nucleate at larger distances relative to each other; therefore the surface of an anodized sample at high current/voltages still appears mirror–like.



Figure 4.14: (a) 1D-PhC stack of crysto and curro pores. (b) Cross sectional view of the curro pores. (c) Polycrystalline hexagonal arrangement of curro pores. (d) The hexagonal (single crystalline) arrangement of the curro pores; plane view after the nucleation layer was removed.

The density of crysto pores increases rapidly as they grow into the substrate due to repeated upward and downward branching. Thus from one primary nucleation point at the surface, an extended set of new pores is generated, in particular for (100) oriented substrates. The set of all pore tips from one root ancestor (starting point) will form a (square) domain of nuclei for curro pores, which are to some degree aligned along $\langle 011 \rangle$ directions [58]. Consequently, the curro pores, which start from the tips of the crysto pores, will tend to align along this $\langle 011 \rangle$ direction. Thus all domains of curro pores, resulting from just one originally nucleated crysto pore, will tend to have the same global alignment. Thick nucleation layers allow for many branching events, the domains will thus be larger and the alignment tendency stronger. However, the long range order is lost at voltages deviating from some optimal conditions in either direction, because two opposing mechanisms govern the self-ordering: Close packing leads to local order while a sufficiently developed nucleation layer gives global orientation of close packed domains. If one factor is too weak, no strong ordering is possible. If the anodization voltage is lower than the optimum one, the space charge region of the pores is too small, i.e. the interaction between pores decreases and the local closed packed order disappears. This insufficient interaction between pores is also expressed by their tendency to assume triangular shapes at lower voltages. On the other hand, at voltages higher than the optimum, the thickness of the nucleation layer is too small, i.e. the domain size decreases, and as a result global order is lost. The same model can be applied to the (111) oriented samples. However, in this case the domains of crysto pores within the nucleation layer will have a triangular shape.

The quality of the self-organized pore single crystals can be rather high, but is certainly not good enough for PhC purposes. As in the case of porous Al_2O_3 , lithography or nanoimprinting might be used to induce perfect ordering, but this has yet to be shown.

4.4 Summary

4.3.8 3D photonic crystals made of InP and GaAs

The results discussed above were obtained at potentiostatic conditions. At galvanostatic conditions, a new phenomenon is observed which is potentially useful for 3D PhC's: Self-induced voltage and pore diameter oscillations [59]. These (perfectly synchronized) diameter oscillations provide a certain periodicity in the third direction and a first 3D PhC self induced periodic structure was obtained in this way. [35]. A collage of such a structure is presented in Figure 4.15a. Again, the quality of the self-ordered 3D structure is not good enough to produce PhCs with optical quality, but in connection with externally defined nucleation and resonant diameter oscillations, it may be used for 3D PhCs in the future.

3D structures may also be obtained from crysto pores. An example is presented in Fig. 4.15b for GaAs. Only two $\langle 111 \rangle B$ pores nucleate and grow into the substrate from a (100) oriented sample (see the inset in Fig. 4.15b, randomly nucleated pores in this case). First experiments using lithography showed that externally induced order is possible in principle, but more difficult than in n-type Si, since the externally defined pore pitches and the intrinsically preferred length scales must be matched closely.



Figure 4.15: (a) Curro pores combined with self–induced voltage and diameter oscillations could result in a self–induced 3D structure; collage picture; (b) 3D structure on a (100) GaAs sample.

4.4 Summary

In the last ten years, ordered pore arrays with high aspect ratio have been studied extensively. Ordered porous dielectric materials are *intrinsic* 2D photonic crystals. Although there is a large variety of materials exhibiting pores, only silicon, alumina and InP are exhibiting the extremely high pore quality, to date, required in photonic crystal applications. Over the last 5 years, macroporous silicon as an infrared photonic crystal has been described in numerous publications. Porous alumina is a favorable candidate for photonic crystals, operating in the visible and InP for active devices as well as for non–linear optical applications.

Finally, concepts and first realizations of 3D photonic crystals based on macroporous silicon were presented. All these experiments show that electrochemically–prepared photonic crystals are a model system to study the properties of photonic crystals in the visible and infrared regime as well as for possible technological applications operating in this spectral range.

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