Chapter 1

Introduction

This thesis deals with time integrated and time resolved high energy x-ray diffraction on ultrasound excited crystals. Time resolved investigation of condensed matter gives the opportunity to understand the dynamics in solids and fluids. In particular, time resolved x-ray diffraction enables one to observe time dependent structural changes on the atomic scale. With modern third generation synchrotron sources like the European Synchrotron Radiation Facility (ESRF) short-pulsed x-radiation sources with a pulse duration of 100 ps are available. In principle all time dependent phenomena in condensed matter can be investigated which show a time dependence on the picosecond or slower time scales. Thereby periodically repetitive events can be the subject of matter as well as single but reversible perturbations. Non-reversible sample changes are more difficult to investigate since the single shot intensity of an x-ray pulse may not be sufficient. Sacrificing time resolution in taking longer x-ray pulses make non-reversible changes still possible to investigate. In the present work the time evolution of rocking curve intensity profiles of ultrasound excited silicon single crystals was investigated by stroboscopic x-ray diffraction, in which the generation of the ultrasonic waves is synchronized with x-ray pulses emitted from the storage ring.

Since the influence of acoustic excitation in crystals on the x-ray diffracted intensity was discovered for the first time [Fox 31], this field of research found a growing interest. The demand of the semiconductor industry in the 1960's to grow perfect crystals was accompanied by several experimental verifications of the dynamical diffraction theory, which was developed at the beginning of the 20th century [Dar 14a, Dar 14b, Ewa 16a, Ewa 16b, Ewa 17, Lau 31]. Ultrasound excitation as a periodic and controllable perturbation triggered investigations of x-ray-acoustic interactions to study the dispersion surface and to experimentally confirm the diffraction theory of perturbed crystals. This lead only very recently to interesting applications: The optimization of x-ray flux and bandwidth via acoustic excitation in synchrotron x-ray monochromators is one example

[Pol 94, Rev 95, Pol 99a, Pol 99b], the acoustic control of x-ray beams in space and time another one [Ros 92, Pol 98]. The high sensitivity of acoustically induced diffraction effects to small intrinsic strains lead to propositions of methods to characterize the structural quality of semiconductors [Zol 93]. The dynamical focusing of x-rays through crystals subjected to ultrasound was investigated in [Nos 94a, Nos 94b]. Furthermore ultrasound excited crystals were proposed as x-ray beam choppers [Tuc 98] and fast x-ray switches with switching times between 50 and 100 ps [Iol 95b]. The study of diffraction phenomena in complex dynamic deformation fields is therefore a challenging task. Through all the years difficulties related to the interpretation of experimental data accompanied the research field due to the complexity of dynamical diffraction phenomena, not at least because the effects had to be manifested experimentally by measuring the integrated intensity due to missing angular resolution capabilities (comments in [LeR 75], [Zol 95a]). The goal of the present work is to resolve acoustically induced satellite reflections in space and time and to measure and explain their dependence on the ultrasound parameters frequency and amplitude and the x-ray parameters energy and choice of reflection. The interpretation of measured data is thereby based on simulations of the interaction of dynamical x-ray diffraction with a periodic and dynamic (i.e. time dependent) elastic perturbation in the crystal. This work will contribute to further understand the effects of vibrating disturbances to the diffraction process.

Chapter two reviews the mathematical and physical concepts of kinematical and dynamical diffraction theory. The geometrical concept of the dispersion surface as well as expressions like the atomic susceptibility, the extinction length and the pendulum solution are introduced. Rocking curve intensity distributions of diffracted x-rays in the framework of dynamical theory of perfect crystals are presented along with a discussion of the absorption aspect and the Borrmann anomalous transmission through thick perfect crystals. The definitions of thick and thin crystals are given together with the range of application of these approximations and the connection to the kinematical diffraction theory will be shown.

In chapter three the previous work in the field of x-ray diffraction on ultrasound excited crystals will be reviewed as required for understanding the present work. Due to the large

amount of available publications it was necessary to clearly distinguish between investigations on volume acoustic waves, surface acoustic waves, diffraction topography studies and optically excited phonons. The discussion is thereby focused on the investigation of x-ray diffraction on volume acoustic waves, even though hints for the explanation of a part of newly discovered effects could be found in the literature of the entire field. A further separation in the subfield of x-ray diffraction on volume acoustic waves with respect to the ultrasound frequency was undertaken. In fact, it has to be distinguished between low frequency ultrasound (LFVAW), where the acoustic wavelength is larger than the extinction length of the x-rays, the x-ray acoustic resonance (XAR), where it has the same value (taking into account the geometry), and high frequency ultrasound (HFVAW), with an acoustic wavelength being much smaller than the value of the extinction length. The appearance of satellite reflections in the diffraction pattern due to ultrasound excited superstructures is closely connected to the frequency range above the x-ray acoustic resonance condition. During the course of this thesis ultrasound excited satellite reflections of volume acoustic waves have been resolved for the first time.

Chapter four treats simulations of x-ray diffraction on ultrasound excited silicon crystals with the main emphasis on the high ultrasound frequency regime. After the presentation of the computer code SIMSAT, which was developed in this work to calculate rocking curve intensity distributions of x-rays diffracted by ultrasound excited crystals, simulations for different reflections, x-ray energies, ultrasound frequencies and amplitudes are discussed. Due to differences in the theoretical approach it is of great importance to distinguish between the small and the large ultrasound amplitude regime. The distinction is based on the relation of the applied ultrasound amplitude with respect to the absolute value of the diffraction vector, i.e., the lattice spacing. If the ratio of the ultrasound amplitudes are considered as small. If the ratio is exceeding unity, one is talking about large amplitudes. In order to evaluate the chances to resolve diffraction satellites with the given mechanical resolution of the diffractometer of 0.01 arcsec, the full width at half maximum (FWHM) of satellite reflections are calculated. Theoretical approaches dealing with the time resolved

evolution of the intensity distribution of satellite reflections are rarely investigated [Pol 98]. To our knowledge no treatment is available for large ultrasound amplitudes.

Chapter five describes the experimental conditions for the investigation of ultrasound excited crystals with high energy x-ray diffraction. It starts with a brief presentation of the high energy beamline ID 15 of the European Synchrotron Radiation Facility (ESRF), where the experiments were carried out within the framework of an ongoing collaboration with the Institut für Kristallographie und Strukturphysik of the Friedrich-Alexander Universität Erlangen-Nürnberg. The advantages of high energy x-ray diffraction with respect to penetration depth and high angular resolution are explained along with a description of the high resolution triple axis diffractometer. The scanning procedures as well as the instrumental resolution function are shown. The mechanisms to excite ultrasonic waves in the silicon samples, a more general description of the propagation of elastic waves in crystals and the scattering geometry are described. Finally, the time-resolving electronics to obtain x-ray diffraction measurements with 200 ps resolution is presented.

In chapter six the experimental results are analyzed and the comparison to simulated data is discussed. Apart from the measurement of angular and time resolved diffraction patterns of ultrasound excited satellite reflections it was possible to measure and understand rocking curves at different x-ray energies and ultrasound amplitudes. The oscillation of satellite intensities as a function of the x-ray energy is explained by a dynamical diffraction behavior of the satellite reflections. The extinction lengths of the satellite reflections are discussed together with the determination of the absolute value of the superlattice structure factor. Reciprocal space maps were most helpful to determine the unexpected propagation direction of the sound waves.

Chapter seven concludes this thesis, summarizes the obtained results and will give an outlook to possible future research directions.

Chapter 2

Basic Dynamical Diffraction Theory

2.1. Equations of the kinematical diffraction theory

After the discovery of x-rays by W.C. Röntgen in 1895 and the proposition of Laue in 1912 that crystals could serve as natural diffraction gratings for x-rays, both the electromagnetic wave nature of x-rays and the periodic structure of crystals were proofed. A main contribution to the rapid development of the field of x-ray diffraction on crystals represents the improvement of the experimental technique due to W.H. and W.L. Bragg. Since the wavelength λ of x-radiation is of the same order of magnitude or smaller than the interatomic distances of the smallest lattice periods in crystals ($\approx 10^{-10}$ m), interference maxima of the diffracted waves can be measured at conveniently large scattering angles. If $\mathbf{k_i}$ and $\mathbf{k_f}$ are the incident and diffracted (final) wave vectors, the Laue vector equation (2.1) describes the direction of the diffraction maxima, whereas the scattering vector \mathbf{G} has to be a vector of the reciprocal lattice given in equation 2.2.

$$\vec{k}_s - \vec{k}_i = \vec{G} \tag{2.1}$$

$$\vec{G} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$$
(2.2)

The indices h,k,l are the Miller indices of a family of lattice planes and the **b**'s are the base vectors of the reciprocal lattice. The reciprocal lattice vector **G** stands perpendicular to the associated set of lattice planes with an absolute value reciprocal to the lattice spacing d_{hkl} (equation 2.3).

$$|\vec{G}| = \frac{1}{d_{hkl}}$$
(2.3)

The equation of the lattice spacing for a cubic crystal with the lattice parameter $a_0 = 5.43$ Å for silicon is given by equation 2.4 [War 69].

$$d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}}$$
(2.4)

For elastic scattering ($k_i = k_f = 1/\lambda$) at an angle θ between the incident wave vector and the set of lattice planes with spacing d_{hkl} the well-known Bragg equation follows from equation 2.1 and 2.3. The scattering angle is 2θ and θ is called the Bragg angle (equation 2.5). The x-ray wavelength is denoted by λ .

$$\lambda = 2d_{hkl}\sin\theta \tag{2.5}$$

A simple geometrical construction in the reciprocal lattice of diffraction vectors associated with a given incident direction and wavelength is most useful for the discussion of the various experimental methods to bring reciprocal lattice points on the so-called Ewald sphere of reflection and thus to observe diffraction maxima (figure 2.1). Therefor the incident beam ends at the origin of the reciprocal lattice. The sphere around the origin of the incident beam is the Ewald sphere. Constructive interference occurs if a reciprocal lattice point (hkl) lies on the Ewald sphere. Then the diffracted beam forms together with the incident beam and the reciprocal lattice vector **G** a closed triangle. The experimental methods to bring reciprocal lattice points on the Ewald sphere are described in several textbooks on solid state physics and x-ray diffraction (for example [Ash 76] and [War 69]). In this work the angle of incidence θ is varied by rotating the sample crystal in order to bring reciprocal lattice points onto the Ewald sphere.

The geometrical part of the diffraction problem concerns only the directions of the diffraction maxima. The detailed intensity distribution of scattered x-rays requires more theoretical investigations. The intensity distribution due to the kinematical theory is included in the dynamical diffraction theory in the limit of thin crystals. The basics of the dynamical diffraction theory are described in the following paragraphs.

2.2. Fundamental equation of the dynamical diffraction theory

A brief presentation of the dynamical theory of x-ray diffraction for perfect crystals is given now. The common approach in dynamical diffraction theory is to treat the propagation of the x-ray wave-field inside and outside the crystal by Maxwell's equations (i.e. classical electrodynamics) and the interaction of the field with the electrons of the crystal by quantum mechanics. This interaction comes into consideration in the description of the electric susceptibility χ [Pin 78]. Neglecting weak magnetic interactions and assuming the electrical conductivity to be zero, the wave equation 2.6 can be derived from Maxwell's equations [Bru 76].

$$\operatorname{curlcurl}\mathbf{E} = 4\pi k^2 (1+\chi) \mathbf{E}$$
(2.6)

Here the relation $k = 1/\lambda$ with the vacuum x-ray wavelength λ was used. The electric field waves **E** are assumed to be of the Bloch wave type,

$$\mathbf{E} = \sum_{hkl} \mathbf{E}_{hkl} \exp 2\pi i \left(\mathbf{k}_{hkl} \mathbf{r} \cdot \mathbf{v} t \right)$$
(2.7)

where v is the x-ray frequency and **r** the propagation vector. Since the crystal lattice is periodic, the electric susceptibility χ can be expanded as a

Fourier series.

$$\chi = \sum_{hkl} \chi_{hkl} \exp\left(2\pi i \mathbf{G}_{hkl} \mathbf{r}\right)$$
(2.8)

Substitution of equation 2.7 and 2.8 in the wave equation 2.6 leads to the fundamental equation of the dynamical diffraction theory [Hae 01],

$$\left(k^{2}-\boldsymbol{k}_{m}^{2}\right)\boldsymbol{E}_{m}+k^{2}\sum_{n}\chi_{m-n}\boldsymbol{E}_{n}=0$$
(2.9)