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Quantitative Determination of the Order Parameter in Ordered III-V Semiconductors by TEM and TED

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We have developed a method to obtain quantitative information from transmission electron diffraction patterns. This method has been used to measure the order parameter in CuPt-ordered GaInP. We find the order parameter to be lower than the one extracted from optical measurements. This difference is expected, since the optical measurements are sensitive to the maximum order parameter (lowest band gap) while electron diffraction measures the average order parameter of the area probed by the electron beam. We have also begun to analyze TEM high resolution images and find a signal correlated to the order in the material.

Ternary III-V semiconductors like GaInP often crystallize in an ordered phase, if grown under appropriate conditions by MBE or OMVPE. Various forms of ordering have been found in different semiconductor systems. Here, we concentrate on the so-called 'CuPt' ordering in OMVPE grown GaInP. This type of ordering has profound consequences for the band structure of the material. The ordering leads to a reduced band gap due to zone folding and a repulsive interaction of the folded bands with the unfolded ones. While this can have a significant impact on devices made from these materials, the exact correlation between order parameter and band gap reduction is not known experimentally. This is due to the fact that up to now no technique was available, which could measure the order parameter directly and quantitatively.

Attempts have been made to obtain a quantitative measure of the order parameter by measuring the intensity of dark field images in TEM experiments [1], and applying kinematical theory to obtain the order parameter. This method has recently been extended to incorporate some dynamical aspects of electron diffraction,[2] but the calculated values are very large and it is likely that a full dynamical treatment will result in significantly different order parameters.

Transmission electron diffraction has been used in many studies to obtain a *qualitative* measure of the order parameter, i.e., 'strong' or 'weak'. While this has helped tremendously to establish the optimum growth parameters for ordering to occur, it is not sufficient to establish a firm basis for comparison with theoretical values. CuPt ordering leads to very distinct extra spots in the diffraction patterns at 1/2{111} positions. Quantitative determination of the order parameter through analysis of the spot intensity, however, has not been attempted so far due to the complicated dynamic nature of electron diffraction.

We have developed and implemented a method for the quantitative measurement of diffraction intensities, the simulation of diffraction intensities using a Bloch wave approach, and a fitting procedure for the calculated and experimental diffraction intensities. These approaches will be detailed below:

a) Quantitative measurement of diffraction intensities

Historically, the medium for recording transmission electron microscopy (TEM) data has been the use of silver halogenide films. Quantitative extraction of data from films, however, is difficult, because these films usually have a strongly non-linear response function. We have therefore replaced the film in our microscope with a 1024x1024 pixels charge coupled device (CCD) camera, which is exposed via a fiber optic to a phosphorus

screen in the TEM. Tests showed that the camera is linear over its whole dynamic range (12 bit), and that we can measure the diffraction intensities quantitatively. The fiber optic introduces a weak gaussian blur, which can easily be extracted from the diffraction patterns. We fit the peaks in the diffraction patterns with 2-dimensional, symmetrical gaussians, and thus obtain the amplitude and width for every peak in the pattern. These numbers are then used for the fitting procedure.

b) Calculation of diffraction intensities

The interaction of electrons with matter is about 10,000 times stronger than the interaction of x-rays with the material. In contrast to x-ray models, electron diffraction therefore has to take into account multiple scattering in the crystal as well as incoherent scattering (absorption). Various techniques exist to calculate the propagation of fast electrons through the periodic potential of a crystal. Here we have adopted the 'Bloch wave' approach[3], which is based on solving the Schrödinger equation for fast electrons in the presence of a periodic potential. The periodic potential can be used to construct a matrix A, whose eigenvectors and eigenvalues represent the bloch waves in the material. By way of linear combination of the bloch waves, the total wave function at the exit surface of the crystal of thickness z can be calculated. This wave function then contains information about the intensity of the diffracted beams. Absorption in the crystal leads to additional imaginary terms in the periodic potential. Apart from a more complex calculation of the eigenvectors and eigenvalues this requires the knowledge of these imaginary potentials. These numbers are generally not well known, which may impose a limitation on the sample thickness, whose diffraction patterns is to be calculated. We have extracted the parameters from the literature [4]. Since no data were available for GaInP, we used the data for crystalline Ge instead. This is a source of error, but we believe the actual errors are small, since Ge has the same crystal structure, and the density of the material is very similar. We have checked our calculations against the results from commercially available high resolution image simulation packages, and found identical results for "Pendellosungs oscillations".

c) Fitting procedure for diffraction patterns

The intensity of diffracted electron beams shows an extremely complicated oscillatory behavior on sample thickness and sample tilt with respect to the electron beam. We have therefore incorporated the bloch wave program into a least squares algorithm to fit the calculated to the experimental diffraction patterns. Fit parameters are: tilt (x and y), sample geometry (minimum and maximum thickness, assuming a wedge shaped sample and a circular aperture), and 2 order parameters for two order variants separately. While the fit for the sample thicknesses can be performed without recalculating the bloch waves, this has to be done for each change in one of the other paramerters. Depending on the size of the matrix A, this is the most time consuming step (A is typically 200x200 in size). We have therefore structured the program so that a complete fit for the thickness is performed before one of the other parameters is changed.

There remains a question about the uniqueness of the calculated solution. The highly oscillatory character of the beam intensity as a function of thickness and tilt can lead to local minima in the fitting function, and there is no analytical way to determine if a found minimum is local or global. We have therefore applied a Monte Carlo approach to the problem. Once a minimum is found, the calculation is restarted with a different set of initial conditions. If the final result is identical or sufficiently close to the first result, it is likely a global minimum.

To apply this technique, a sample was grown by OMVPE under conditions favoring ordering, consisting of a 30 nm layer of GaInP, lattice matched to the GaAs substrate. TEM samples were produced by etching away the GaAs substrate without further preparation of the thin GaInP film. Transmission electron diffraction patterns of circular areas 200 nm in diameter were recorded on a CCD camera for the [013] zone axis (fig. 1). The sample showed only one subvariant of the CuPt ordering. 37 diffracted beams were subsequently fitted simultaneously to obtain the order parameters for this subvariant (fig. 2). The fitting procedure yielded an average order parameter of 0.23. Optical investigations measuring the band gap and the crystal field splitting of the valence band resulted in a maximum order parameter of 0.34, assuming a parabolic

dependence of the band gap on the order parameter.

Electron diffraction measures the order parameter averaged over the area of the aperture used. To obtain more localized information on the order parameter, we have applied the recently developed technique of "chemical mapping" [5] to high resolution images of the ordered material. In essence, this technique allows to extract chemical information at the atomic level from appropriate high resolution images (see fig. 3) by means of vector pattern recognition, if the structure of the material is known. Preliminary results (fig. 4) show that the method is indeed sensitive to the order parameter. These results will be presented together with the results of the electron diffraction experiments.

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References

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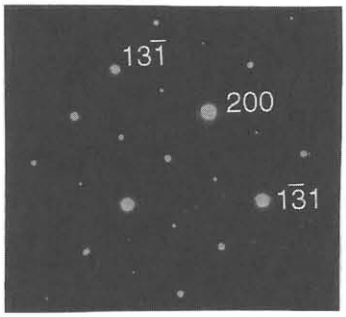

Fig. 1: Experimental [013] zone axis diffraction pattern of CuPt ordered GaInP.

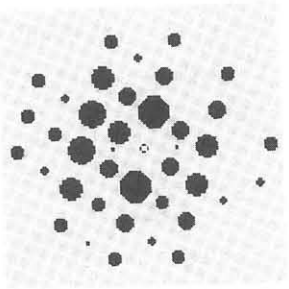

Fig. 2: Simulated diffraction pattern fitted to data in fig. 1.

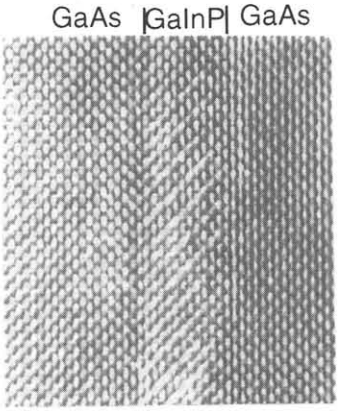

Fig. 3: High resolution TEM image of a thin layer of ordered GaInP between GaAs layers in a superlattice.

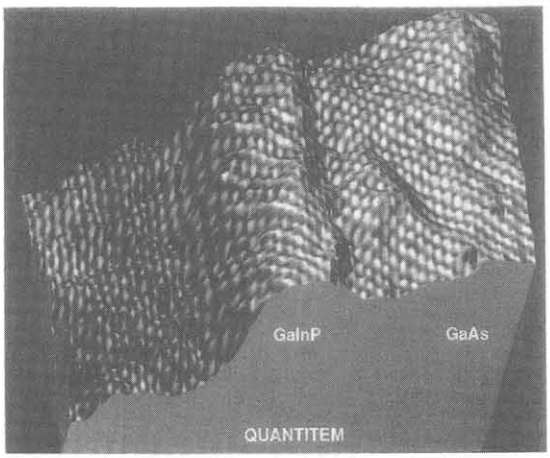

Fig. 4: Analysis of fig. 3 by 'QuantiTEM'. Note the signal due to the ordering.