1

Introduction

Reflection high-energy electron diffraction (RHEED or R-HEED) is a technique for surface structural analysis that is remarkably simple to implement, requiring at the minimum only an electron gun, a phosphor screen, and a clean surface. Its interpretation, however, is complicated by an unusually asymmetric scattering geometry and by the necessity of accounting for multiple scattering processes. First performed by Nishikawa and Kikuchi (1928a, b) at nearly the same time as the discovery of electron diffraction by Davison and Germer (1927a, b), RHEED has assumed modern importance because of its compatibility with the methods of vapor deposition used for the epitaxial growth of thin films. We take RHEED to encompass the energy range from about 8 to 20 keV, though it can be employed at electron energies as high as 50 to 100 keV.

Because of its small penetration depth, owing to the interaction between incident electrons and atoms, RHEED is primarily sensitive to the atomic structure of the first few planes of a crystal lattice. Diffraction from a structure periodic in only two dimensions therefore underlies the observed pattern, and the positions of the elastically scattered beams can be computed from single-scattering expressions. Nonetheless, because the elastic scattering is comparable to the inelastic scattering, multiple scattering processes are also crucial, and these must be included to obtain the correct intensity. The RHEED geometry – an incident beam directed at a low angle to the surface – has a very strong effect on both the diffraction and its interpretation. For example, atomic steps can produce large changes in both the measured intensity and the shape of the diffracted beams when the important atomic separations are parallel to the incident beam direction; in contrast, the role of atomic structure in the diffracted intensity is primarily determined by the atomic separations perpendicular to the beam direction. Both of these phenomena result from the low glancing angle of incidence. The extent of these sensitivities, the importance of multiple scattering, the shape of the diffraction pattern, and the salient features of calculation are all determined by the combination of a small glancing incident angle and the conservation of parallel momentum. This book is an exploration of the consequences of the combination of these two main features in the presence of multiple scattering.

RHEED is very similar to its counterpart, low-energy electron diffraction (LEED), and many of the same geometric constructions and analytical methods are used in its interpretation. But there are important differences. We will see that because of the glancing geometry of RHEED, particular advantage can be gained by selecting a sensitivity to particular atomic features. For example, at incident azimuths away from symmetry directions the interplanar separations normal to the surface dominate the intensity and the diffraction is very kinematic-like. Or, by choosing the incident azimuth appropriately, particular rows of scatterers can be made to dominate the diffracted intensity. In addition, RHEED is particularly sensitive to disorder because of the low angle of incidence and because of the easier electron optics at high energy, which allows highly collimated incident beams. In short the interpretation can be simplified, single-scattering theory serving as a basis with the important multiple scattering artfully included.

Our purpose in this book is to develop RHEED as a practical tool in surface structure determination. Often RHEED is used just as a means to determine whether there is epitaxy and whether the surface is rough or smooth. With somewhat more effort it is more powerful than this, but one must consider the fundamental principles of the technique. In nearly every aspect we will make connections between the dynamical or multiple-scattering treatment and the simpler kinematic analysis. In our minds, the latter serves as a framework upon which the results of dynamical calculation are based. We will look for ways to make the kinematic results more useful. But fundamentally this process, involving strongly scattered beams, is dynamical and dynamical methods must be the final arbiter.

2
Historical survey

2.1 Early experiments

The first RHEED experiment was conducted by Nishikawa and Kikuchi in 1928. Their interest at that time was whether the Kikuchi patterns that had been observed previously in transmission electron diffraction (Kikuchi, 1928a, b) were also observed in reflection. Later they were interested in effects due to the refraction of electrons by a mean inner potential (Kikuchi and Nakagawa, 1934).

At the outset, efforts were made to understand the angles at which the diffracted beams showed intensity maxima. For reflection diffraction, the angular positions of the diffraction maxima do not follow Bragg's law. These shifts were explained to some extent by considering the beam to be refracted by an inner potential (Thomson, 1928).

Owing to refraction, the lowest-order diffracted beams are totally internally reflected and so are not observed. Using this effect, efforts were made to determine the mean inner potentials, the values of which are related to paramagnetic susceptibilities (see Chapter 9). In order to determine the mean inner potentials, the RHEED intensity was measured as a function of incident angle, a measurement that has become known as a rocking curve. From the systematic deviation of the positions of diffraction maxima from Bragg's law, the values of the inner potentials for several materials were determined for the first time by Yamaguti (1930, 1931). The refraction effects of the inner potential are also observed in RHEED patterns as parabolic Kikuchi lines and envelopes (Shinohara, 1935).

Kikuchi and Nakagawa (1933) found an intensity anomaly at certain diffraction conditions. McRae and Jennings (1969) explained that the effect is the same as that found later in low-energy electron diffraction (LEED) experiments and called a "surface wave resonance."

Several RHEED experiments were carried out for polished metal surfaces and on thin metallic films evaporated on metal substrates (Kirchner, 1932). In these experiments, many kinds of RHEED patterns were observed. The origin of these patterns, especially the streaks and transmission patterns, were explained in detail by using kinematic diffraction theory (Kirchner and Raether, 1932; Raether, 1932). The patterns were explained in a very elegant way, according to which RHEED streaks arise from small domains on the surface, as shown in Fig. 2.1 (see the detailed explanations in Chapters 6 and 8).

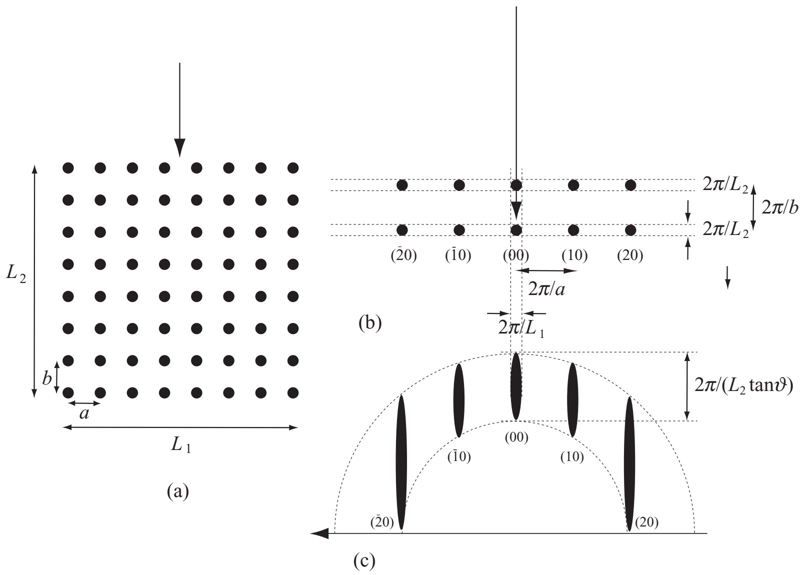

Figure 2.1 Explanation of the origin of RHEED streaks. (a) Arrangement of the two-dimensional array of lattice points. The finite sizes, L_1 and L_2, of the lattice are perpendicular and parallel to the incident direction, respectively. The incident direction is indicated by the arrow. (b) Reciprocal lattice for the arrangement in (a). (c) RHEED construction for (b); the lengths of the streaks depend on the glancing angle of incidence, ϑ.

From the late 1930s to early 1940s, many experiments relating to processes such as surface oxidation and epitaxial growth were carried out with RHEED. Miyake (1938) studied RHEED patterns from faceted islands formed by the oxidation of Sn surfaces. The first *in situ* experiment on epitaxial growth was performed by Uyeda *et al.* (1941). By analyzing RHEED patterns from epitaxial silver films on NaCl, ZnS and MoS_2 surfaces and measuring the total amount of silver deposited, Uyeda found that the silver films grew with an island growth mode (Uyeda, 1942). This was the first observation of the island growth mode in epitaxy.

2.2 Molecular beam epitaxy

Arthur and LePore (Arthur and LePore, 1969; Arthur, 1972) incorporated a RHEED measurement into an apparatus developed by Arthur for the molecular beam epitaxial (MBE) growth of GaAs. Arthur's study of the reconstructions of GaAs(111)B showed the power of the technique. This was reinforced by a single image that Cho (1970) published in a key review paper on MBE. This image, shown on the left in Fig. 2.2c, influenced the design of most commercial machines. RHEED was a particularly essential tool in the growth of GaAs by MBE since the diffraction pattern told the grower first whether the the native GaAs was desorbed, then whether the conditions were Ga rich or As rich, and finally whether

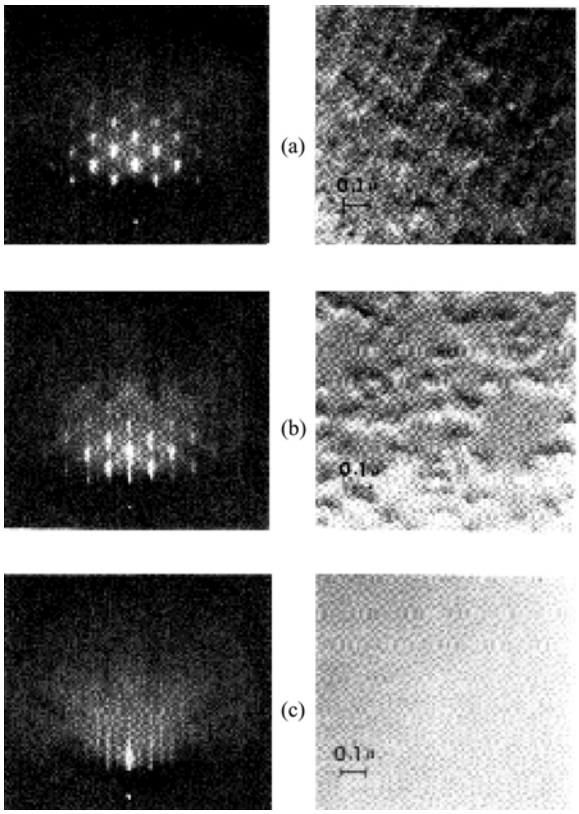

Figure 2.2 On the left, the RHEED pattern (40 keV, ⟨0$\bar{1}$1⟩ direction) for a particular surface and on the right the corresponding photomicrograph (38 400×) of a Pt-C replica of the same surface, for the following cases: (a) a Br_2-methanol polish-etched (001) GaAs substrate heated in vacuum to 855 K for 5 minutes; (b) a deposition of an average thickness of 150 Å of GaAs; (c) a deposition of 1 μm of GaAs (Cho, 1971). The power of RHEED to distinguish qualitatively between rough and smooth surfaces is evident.

two-dimensional growth was proceeding as planned. Later, when Harris *et al.* (1981), Wood (1981), Neave *et al.* (1984), Van Hove *et al.* (1983b) and Sakamoto *et al.* (1986) saw intensity oscillations, RHEED became essential for measuring growth rate.

At this time it was not well understood why the patterns were streaks (there could be no mosaic on these surfaces) and there was confusion as to what the role of surface disorder was in the diffraction. Part of this confusion was perhaps due to the presence of the patterns seen in Fig. 2.2. This led to work on whether the streaks could be due to thermal diffuse diffraction (Holloway and Beeby, 1978). This spurred work to determine the nature of the key surface disorder. Cohen's group showed the importance of surface steps for the diffraction, that they caused splitting and broadening depending upon their distribution. They extended the work of Henzler (1977) and applied it to understand the shape of the diffraction and the RHEED intensity oscillations (Van Hove *et al.*, 1983c). Lent and Cohen (1984a, b) clarified the theory of the role of disorder and showed that the shape of a RHEED streak could be decomposed into a central spike coming from the long-range order and a broad part coming from steps. They developed a sensitive means of measuring: surface misorientations (Pukite *et al.*, 1984a, b); lattice parameter (Whaley and Cohen, 1988, 1990a, b); the transition to Stranski–Krastanov growth and the formation of structures that later became used as quantum dots; sublimation (Van Hove and Cohen, 1985; Van Hove *et al.*, 1985a; Kojima *et al.*, 1985). Furthermore, their work clarified the detailed behavior of the RHEED intensity oscillations. Fuchs *et al.* (1985) showed that the formation of single- and double-layer steps could be determined with RHEED in the growth of Fe on Fe(100). Pukite *et al.* (1985) developed statistical methods for the analysis of general surface-step distributions. Petrich *et al.* (1989) developed rate-equation models that described the intensity oscillations on low-index and vicinal (layered) surfaces. On the latter, a steady state was reached in which the envelope was not a constant. Rather, the maxima and minima forming the envelope decayed to a common intermediate value.

Joyce's groups at Phillips and at Imperial College pioneered developments in the use of RHEED intensity oscillations. They have been a strong proponent of the role of step density as the dominant mechanism for the intensity oscillations, using comparisons with Vvedensky's kinetic Monte Carlo calculation (Shitara *et al.*, 1992b). Using such a comparison for vicinal surfaces they measured the surface diffusion of Ga on GaAs(100) surfaces. Early on they showed that the times after the initiation of growth at which the intensity oscillations reached a maximum depended strongly on the scattering angle. This made it difficult to associate the oscillation maxima with layer completions.

Orr (1993) and Stroscio *et al.* (1993) followed the path of Cho (1970) but using scanning tunneling microscopy (STM) rather than SEM to compare the microscopic surface structure with RHEED measurements. They showed the evolution of islands as measured by RHEED and STM. In particular, Orr's group (Sudijono *et al.*, 1992) looked at quenched GaAs surfaces with STM at the beginning of growth and at long times, after the intensity oscillations had decayed away. At the initial stages they were able to see the cyclic nature of the surface morphology. Further, they showed that on GaAs relatively few layers comprised the growth front even after many layers had been deposited. Most recently, quantitative measurements by Bell *et al*. (2000) using STM on quenched surfaces showed that step densities and layer coverages behaved similarly.

Braun and his coworkers have analyzed RHEED patterns and intensities during the growth of compound semiconductors in detail (Braun, 1999). They revealed several types of phase shifts of RHEED intensity oscillations and found reconstruction-induced phase-shift phenomena in the growth of AlAs on GaAs (Braun *et al.*, 1998a, b). Knowledge of the effects of inelastically scattered electrons on the RHEED intensity oscillations is also important in studying the growth processes using these oscillations. Braun *et al.* observed energy-filtered RHEED oscillations for several energy losses and concluded that inelastic scattering does not have a significant effect on the oscillations (Braun *et al.*, 1998c).

In the growth of less perfect materials, such as GaN, RHEED has been used to examine the termination of the surface under various growth conditions. For example, by following the decrease and recovery of the RHEED intensity during the addition of Ga to the surface, Crawford *et al.* (1996) and Held *et al.* (1997) were able to monitor the deposition of extra Ga layers on GaN(0001). Adelmann *et al.* (2002) were able to correlate the variation of the RHEED intensity during vacuum desorption and the behavior of RHEED intensity oscillations with different growth modes during the growth of GaN by plasma-assisted MBE. Steinke and Cohen (2003) were able to observe the deposition of individual Ga layers and related growth modes during the metalorganic MBE of GaN. Nonetheless, RHEED rocking curves have not been measured for these surfaces and their atomic structures have been determined by first-principle calculations and X-ray diffraction (Munkholm *et al.*, 1999).

2.3 Surface studies

The technology for the preparation of very clean surfaces was not available for the early RHEED experiments – for example, Germer's studies on galena were on surfaces cleaned with a camel's hair brush (Germer, 1936). More modern RHEED experiments became possible with the advent of the ultrahigh vacuum (Siegel and Menadue, 1967). Menadue (1972) performed early quantitative measurements of RHEED intensities for the Si(111)7×7 surface. Beautiful 7×7 patterns of RHEED were obtained in these experiments. An intensity rocking curve at off-azimuthal angles (later called the one-beam condition) was also measured as well as azimuthal plots, in which the specular intensity was measured as a function of azimuth from a certain direction of incidence. Dynamical theories for interpretation of the rocking curves and the azimuthal plots were developed by Collela (1972) and Moon (1972). The Si(111)7×7 surface structure was, however, too complicated to be determined from these data only. This structure has been solved by STM observation (Binnig *et al.*, 1983) and by the analysis of transmission electron diffraction data (Takayanagi *et al.*, 1985). Ino and his collaborators observed several surfaces with various adsorption species (Ino, 1977, 1980, 1987), exploiting RHEED as a powerful tool for surface studies.

Reflection electron microscopy (REM) in UHV was developed by Honjo and Yagi's group in addition to their continued development of RHEED (for example Yagi *et al.*, 1982). They observed the phase transition from 7 × 7 to 1 × 1 on Si(111) surface at high temperatures by REM (Osakabe *et al.*, 1981) and found that the transition begins from the upper edges of steps. Ichikawa and Hayakawa (1982) developed scanning micro-beam RHEED (μ-RHEED) in UHV. REM and μ-RHEED are very powerful tools for *in situ* observations of dynamic processes on surfaces, such as epitaxial growth, electromigration, step bunching and so on. Yagi's group and that of Aseev and Stenin used mainly REM for investigations of surface-step dynamics (Kahata and Yagi, 1989a, b, c; Latyshev *et al.*, 1989). Using μ-RHEED, Ichikawa and Doi (1987) studied homoepitaxial growth processes on Si(111) surfaces and found the existence of denuded zones at step edges. By this time, there were huge numbers of studies of crystal surfaces and epitaxy by RHEED and related methods.

As described in the previous section, RHEED is good for monitoring epitaxial growth: RHEED intensity oscillations give much information about this. Following the kinematic diffraction analysis of the oscillations by Cohen *et al.* (1986a), efforts were made to understand the mechanisms of RHEED intensity oscillations during epitaxial growth using dynamical RHEED calculations. Kawamura *et al.* (1984) first tried to explain the oscillations by dynamical calculations for a large-surface unit-cell model. In many observations of RHEED intensity oscillations, phase shifts of RHEED oscillations occurred with a change in incident angle, and double oscillation maxima, called oscillation doubling, were seen by several groups (Van Hove and Cohen, 1982; Zhang *et al.* 1987). Mechanisms of the phase shifts and oscillation doublings were explained by Peng and Whelan (1990) and Mitura and his coworkers (Mitura and Daniluk, 1992; Mitura *et al.*, 1992) as dynamical diffraction effects. Later, these effects were understood as due to the interference of waves reflected at the topmost growing surface and waves reflected in the growing layers, which acquire phase shifts from the potential in these layers (Horio and Ichimiya, 1993).

Tompsett and Grigson (1965) began the work with energy-filtered RHEED, followed by Dove *et al.*, (1973) and Britze and Meyer-Ehmsen (1978). However, these Faraday cup systems were difficult to use. More recently Horio and coworkers (Horio *et al.*, 1995; Horio, 1996; Horio *et al.*, 1996; Horio *et al.*, 1998) used a grid filter to examine the role of inelastic scattering in the Kikuchi pattern. Braun *et al.* (1998d, 1999) also developed an energy-filtered RHEED and observed RHEED intensity oscillations for the GaAs system.

For the purpose of surface-structure analysis, beam-rocking RHEED systems were developed by Meyer-Ehmsen's group (Britze and Meyer-Ehmsen, 1978) and Ichimiya's group (Ichimiya and Takeuchi, 1983). The former group's system was equipped with a beam-rocking device using magnetic deflectors and an energy filter. The latter was equipped with a precise mechanical beam-rocking device that permitted the simultaneous measurement of Auger signals and RHEED intensities. Using this system, RHEED rocking curves and rocking curves of Auger intensities from MgO(001) and Si(111) surfaces were observed (Ichimiya and Takeuchi, 1983; Horio and Ichimiya, 1983a). Anomalous enhancements of the Auger intensities at surface-wave resonance conditions were found for both surfaces and were explained by a strong concentration of the electron wave field near the surface (Ichimiya and Tamaoki, 1986). Marten and Meyer-Ehmsen (1985) studied resonance effects in the RHEED patterns from Pt(111) surfaces in detail.

The first actual determination of a surface structure was carried out by Maksym (1985) for a rocking curve from a cleaved MgO(001) surface measured by Ichimiya and Takeuchi (1983). The MgO(001) surface has a simple 1×1 structure. Tests were made for two possible structures using dynamical calculations. Figure 2.3 shows calculated and experimental rocking curves for the specular beam intensity for MgO(001) surface with a $\langle 100\rangle$ incidence. In this diagram, the peak intensities and the peak positions indicated by the arrows may be compared with the calculated ones. For the simple structure of the MgO(001) surface, the peak intensity is very sensitive to even a 1% change in the topmost layer spacing. The

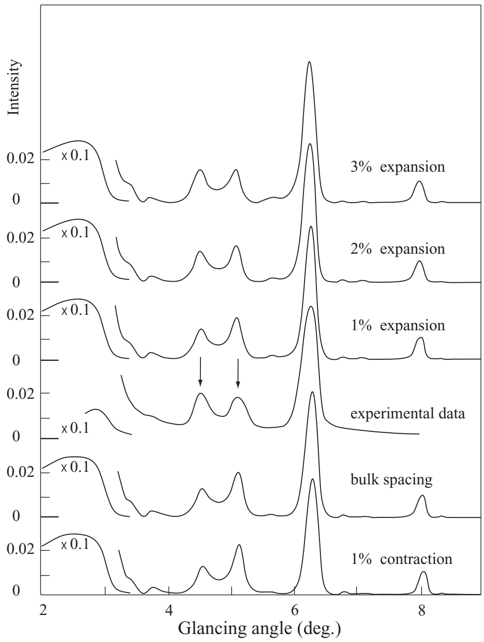

Figure 2.3 Calculated and experimental rocking curves of the (00) reciprocal-lattice rod from MgO(001) surface. The experimental peaks are indicated by the arrows (Maksym, 1985).

calculations for small expansions in the first surface layer correspond very well with the experimental curves. From these (00) beam data one can then distinguish models in which the normal displacements differ by as little as 0.1 Å.

Horio and Ichimiya (1983b) developed the one-beam rocking curve method and analyzed a Si(111) $(\sqrt{3} \times \sqrt{3})$R30°-Ag surface by kinematic diffraction theory. The surface normal component of the atomic position of Ag was determined, and the result was in very good agreement with X-ray results (Takahashi *et al.*, 1988; Vlieg *et al.*, 1989). Since Maksym's analysis, many articles on the structural analysis of crystal surfaces by RHEED have been published.

A convergent-beam RHEED method (Smith, 1992; Smith *et al.*, 1992; Lordi *et al.*, 1994; Zuo *et al.*, 2000) involving a combination of rocking curves and azimuthal plots. In this method, a cone-like electron beam is used. Although the azimuthal dependence of rocking curves simultaneously (Ichimiya *et al.*, 1980; Smith, 1992; Smith *et al.*, 1992) using convergent-beam RHEED patterns, a few such experiments have been carried out in high-vacuum conditions (for example, Ichimiya *et al.*, 1980; Smith *et al.*, 1992).

One can analyze the intensity distributions of RHEED patterns by dynamical calculations. This method has been successful in establishing the atomic structure of the GaAs(100) 2×4 surface, in combination with scanning tunneling microscopy (STM) (Hashizume *et al.*, 1994, 1995). For this surface, McCoy *et al.* (1998) also determined the structure by dynamical calculations for experimental rocking curves obtained by Larsen *et al.* (1986), and the result was consistent with that above. Ohtake *et al.* (2002) measured rocking curves from the GaAs(100)2 × 4 surface in detail and determined the atomic structures.

For surfaces that have undergone epitaxial growth, the atomic structure has been studied in order to understand the growth mechanisms. Yakovlev *et al.* (1995) studied fluoride growth on Si(111) surfaces by obtaining RHEED rocking curves and analyzing them using dynamical theory. Nakahara and Ichimiya (1991) measured RHEED rocking curves during silicon growth on Si(111)7 × 7 with very slow deposition rates and revealed the mechanism of rearrangement of the atomic structure during the growth. Fukaya *et al.* (2000) developed a high-speed-beam rocking method for RHEED and measured rocking curves during homoepitaxial growth on Si(111).

Mitura and Maksym (1993) developed an analysis method of surface and thin film structures using the azimuthal dependence of the specular-beam intensity in RHEED. Mitura *et al.* (1996) succeeded in determining the thin film structure during the growth of $DySi_{2-x}$.

Hasegawa and Ino (1993) combined X-ray spectrometry and RHEED, and the system is called RHEED-TRAXS (total-reflection-angle X-ray-spectroscopy). They measured the surface conductivity of silicon surfaces as a function of metal coverage using surface-structures monitoring by RHEED.

2.4 Theories of surface-structure determination

In the year following the first electron diffraction experiments (Davison and Germer, 1927a, b; Thomson, 1927a, b), a dynamical theory of electron diffraction was developed by Bethe (1928) using a Bloch-wave scheme for crystals. Bethe's theory is still used for the interpretation of diffraction contrast in electron micrographs and, to some extent, for RHEED dynamical theory. In regard to reflection diffraction, however, this theory is hard to use for the structural analysis of reconstructed surfaces. Harding (1937) first developed a RHEED dynamical theory for distorted surface layers, using Darwin's X-ray dynamical theory (Darwin, 1922) and Bethe's theory with Hill's determinant. After digital computers were developed, many-beam dynamical calculations were used for the accurate determination of crystal structure factors by electron diffraction (for example, Goodman and Lehmpfuhl, 1967). For dynamical calculations, analytical forms of the scattering factors were required. Doyle and Turner (1968) developed such analytical forms using the Hartree–Fock approximation.

Bethe's theory is not efficient for a many-beam calculation for RHEED, because an eigenvalue problem must be solved for a huge matrix, and many equivalent eigenvalues in a Brillouin zone are obtained simultaneously. In order to avoid this inefficiency, Moon (1972) adopted Hill's determinant for RHEED dynamical calculations in the same way as in Harding's theory.

The modern dynamical RHEED theories were developed independently in the 1980s by Maksym and Beeby (1981) and Ichimiya (1983) to overcome the difficulties of the lack of the periodicity, using a two-dimensional Fourier expansion of the crystal potential parallel to the surface (Kambe, 1964). Similar methods were reported by Zhao *et al.* (1988) using