Surface Resonance Scattering of High Energy Electrons

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A solution of equations of resonance scattering of high energy electrons is found which is alternative to that given by McRae [Rev. Mod. Phys. **51**, 541 (1979)] and which does not assume the existence of a surface state. It is shown that the angular dependence of the reflectivity does not follow the Breit-Wigner law, and this conclusion agrees well with the result of numerical computation.

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Reflection high energy electron diffraction (RHEED) techniques are widely used now for *in situ* monitoring of molecular-beam epitaxial growth of semiconductor crystals [1–3] and visualization of crystal defects [4,5]. Several successful attempts have been made to determine surface structure existing under the conditions of dynamic equilibrium in an MBE chamber [6]. Theoretical consideration of the observed angular and energy distributions of scattered electrons requires a knowledge of the wave function of the diffraction problem as a fundamental feature, and in some cases this wave function can be found numerically. However, it has recently been admitted [7] that realistic computations are very time consuming and the possibility of carrying out such an analysis is remote. On the other hand, analytical results are almost unknown in the theory of RHEED. This stems from the fact that it is often more convenient experimentally to perform observations along orientations, where the influence of many-beam effects is strong, and also from the fact that the surface reflectivity falls off very rapidly with increasing glancing angle, making a weak coupling approximation impracticable [7]. This distinguishes RHEED from the transmission high energy electron diffraction case (THEED), where there exists an analytical two-beam solution which is found to be useful for many applications, and constitutes a starting point for any consideration of the diffraction contrast [8,9].

The aim of this paper is to show that an analytical solution of the equations of RHEED is also possible, and that this solution describes one of the most interesting phenomena known in RHEED, namely, the resonance scattering of high energy electrons. This phenomenon was discovered experimentally more than 60 years ago by Kikuchi and Nakagawa [10] as a large increase in the intensity of the specular beam reflected from a surface at some particular conditions of grazing incidence of the electron beam on a crystal. This increase makes the resonance condition very convenient for practical applications, and utilization of this condition has become a routine technique of reflection electron microscope observation of surface defects and dynamical processes on a surface [4,5,11].

However, the interpretation of the origin of the phenomenon remains controversial. Following the ideas developed in the theory of low energy electron diffraction [12,13], some authors have attributed RHEED resonance scattering to trapping of electrons by surface states [5,7,14]. Results obtained by other authors [15–19] suggest that bulk states are involved. However, it is difficult to make a distinction between these two models numerically. Indeed, the wave function of a shallow surface state can extend deeply into the crystal bulk, while a tightly bound orbital belonging to a narrow band of bulk Bloch states can be localized near the surface, and simple examination of the wave function calculated numerically cannot be interpreted unambigiously as being for or against the two aforementioned models. The only analytical solution of the equations of the resonance scattering which has been given so far is that of McRae [12]. His result is based on the concept of the existence of a nondegenerate surface state, which is supposed to be well separated in energy from all other states. In our paper we demonstrate for the first time that there exists an alternative solution of the equations of resonance diffraction [i.e., Eqs. (25a) and (25b) from Ref. [12]], and that this solution can be obtained without using the concept of a surface state.

We consider a model in which the resonance scattering involves a band of bulk states tightly bound in the potentials of adjacent planes parallel to the surface of the crystal. All the parameters characterizing this band follow from the first-principles solution of the Schrödinger equation for the bulk crystal. For this model we prove the formal equivalence of the equations of resonance scattering to a problem of scattering of an electron by a one-dimensional set of non-Hermitian δ-function potentials. For the latter an exact analytical treatment is available, and therefore, by analogy, so is a solution for the equations of resonance diffraction, as we now proceed to show.

Following [12], we expand the potential $U(\mathbf{r}) = U'(\mathbf{r}) + iU''(\mathbf{r})$ of the crystal as a two-dimensional Fourier series, and the wave function $\Psi(\mathbf{r})$ of the high energy electron, as a two-dimensional Bloch function, viz.,

$$U(\mathbf{r}) = \sum_{\mathbf{g}'} U_{\mathbf{g}'}(z) \exp(i\mathbf{g}' \cdot \mathbf{R}),$$

$$\Psi(\mathbf{r}) = \sum_{\mathbf{g}'} \Phi_{\mathbf{g}'}(z) \exp[i(\mathbf{k}_{\|} + \mathbf{g}') \cdot \mathbf{R}], \tag{1}$$

where $\mathbf{g}'$ denotes a two-dimensional reciprocal lattice vec-

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tor, $\mathbf{R} = (x, y)$, and $\mathbf{k}_\parallel$ is the projection of the wave vector $\mathbf{k}$ of the incident electron on the (x, y) plane, the surface of the crystal. Near the condition of resonance [20] there exists a particular reciprocal lattice vector $\mathbf{g}$ which satisfies the inequality $|(\mathbf{k}_\parallel+\mathbf{g})^2-\mathbf{k}^2| \ll |(\mathbf{k}_\parallel+\mathbf{g}')^2-\mathbf{k}^2|$ for all $\mathbf{g}' \neq \mathbf{g}$. In this case only two functions need to be retained in the expansion (1), namely [12], $\Phi_0(z)$ and $\Phi_{\mathbf{g}}(z)$. These functions satisfy the system of two coupled equations,

$$\begin{aligned} -\frac{\hbar^2}{2m}\frac{d^2}{dz^2}\Phi_0(z) + U_0(z)\Phi_0(z) + U_{-\mathbf{g}}(z)\Phi_{\mathbf{g}}(z) &= \frac{\hbar^2 K_0^2}{2m}\Phi_0(z), \\ -\frac{\hbar^2}{2m}\frac{d^2}{dz^2}\Phi_{\mathbf{g}}(z) + U_0(z)\Phi_{\mathbf{g}}(z) + U_{\mathbf{g}}(z)\Phi_0(z) &= \frac{\hbar^2 K_{\mathbf{g}}^2}{2m}\Phi_{\mathbf{g}}(z), \end{aligned} \qquad (2)$$

where $K_{\mathbf{g}}^2 = \mathbf{k}^2 - (\mathbf{k}_\parallel + \mathbf{g})^2$. Equations (2) represent a "two-rod" approximation in RHEED theory. In an equivalent transmission diffraction pattern this corresponds to the case where two parallel rows of Bragg reflections are strongly excited [21]. The positive z axis is the inward directed normal to the crystal surface ($z = 0$). The asymptotic behavior of $\Phi_0(z)$ and $\Phi_{\mathbf{g}}(z)$ as $z \to -\infty$ and $U_{\mathbf{g}'}(z) \to 0$ is as follows: $\Phi_0(z) \to \exp(iK_0z) + R_0\exp(-iK_0z)$ and $\Phi_{\mathbf{g}}(z) \to R_{\mathbf{g}}\exp(-iK_{\mathbf{g}}z)$. Our goal is to determine the value of R_0.

Defining the Green's function $G(z, z', E)$ for the potential $U_0(z)$ and energy E, we obtain from (2)

$$\begin{aligned} \Phi_0(z) &= \Phi_{K_0}^{(+)}(z) + \int dz' G\left(z, z', \frac{\hbar^2K_0^2}{2m}\right) U_{-\mathbf{g}}(z')\Phi_{\mathbf{g}}(z'), \\ \Phi_{\mathbf{g}}(z) &= \int dz' G\left(z, z', \frac{\hbar^2K_{\mathbf{g}}^2}{2m}\right) U_{\mathbf{g}}(z')\Phi_0(z'). \end{aligned} \qquad (3)$$

Let the effect of systematic Bragg reflection of electrons from the potential $U_0(z)$ be relatively weak (experimentally, this condition corresponds to the angle of incidence where the specular reflection lies between a pair of horizontal Kikuchi lines). In this case, neglecting to the first approximation the difference of the transmission coefficient from unity [otherwise we would arrive at some additional terms of the order of $O(|R_0^{(\mathrm{pot})}|^2)$],

$$\Phi_{K_0}^{(+)}(z) = \begin{cases} \exp(i\kappa z), & \text{for } z \to -\infty, \\ \exp(iK_0z) + R_0^{(\mathrm{pot})}\exp(-iK_0z), & \text{for } z \to \infty, \end{cases}$$

$$G(z, z', \hbar^2K_0^2/2m) = -\{im/\hbar^2\kappa\}\exp(i\kappa|z-z'|) \quad \text{as } z \to \infty,$$

where $\hbar\kappa$ is the quasimomentum of the electron moving in the one-dimensional potential field $U_0(z)$. Here we follow the standard terminology and refer to $R_0^{(\mathrm{pot})}$ as the "potential" (i.e., nonresonance) contribution to the reflectivity ($|R_0^{(\mathrm{pot})}| \ll 1$). A sketch of the potential $U_0(z)$ for Pt(111) planes is shown in Fig. 1, where the behavior of this quantity in the crystal bulk and near the surface is depicted. For elements of high atomic number this potential leads to the existence of a narrow band of tightly bound states, and the wave functions of these states (which we have determined numerically as eigenstates of an electron in the periodic potential of the bulk crystal) are highly localized near the centers of the potential wells separated by the interplanar distance d. For Pt(111) planes this band of tightly bound states has a dispersion relation of the form $\epsilon(\kappa) = \epsilon_0 - \Delta\cos(\kappa d)$, where the position of the center of the band ϵ_0 and the band half-width Δ are $\epsilon_0 = -65.7$ eV and $\Delta = 0.037$ eV. In the vicinity of ϵ_0 the Green's function has the following form:

$$G(z, z', E) = \sum_n \frac{\phi_n(z)\phi_n^*(z')}{E - \epsilon_0 + i\frac{\Gamma}{2}} + G_0(z, z', E) + O\left(E - \epsilon_0 + i\frac{\Gamma}{2}\right), \qquad (4)$$

where $\phi_n(z)$ is the wave function of a state confined by the nth well, and Γ ($\gg \Delta$) determines the rate of decay of each of these states due to inelastic transitions [Γ is defined as the diagonal matrix element of the imaginary part of the crystal potential $U''(\mathbf{r})$ over any one of these states]. Numerical analysis shows that inelastic bandwidth Γ for tightly bound states is many times greater than the contribution resulting from elastic scattering. The quantity $G_0(z, z', E)$ in (4) is an analytic function of E in the vicinity of ϵ_0, and in what follows it may be safely neglected. Substituting (4) into (3), the function $\Phi_{\mathbf{g}}(z)$ acquires the form of a linear combination of

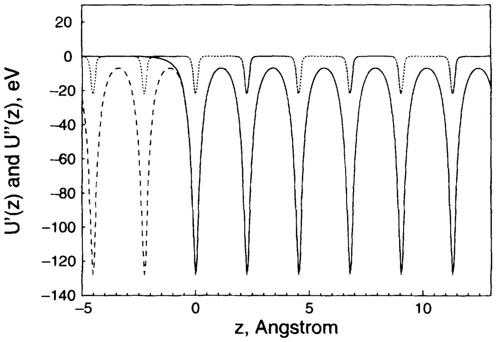

FIG. 1. Profile of the laterally averaged potential of Pt(111) atomic planes for $T = 293$ K. Solid curve: the real part of the potential $U'(z)$ evaluated as a sum of five Doyle-Turner terms. Dashed curve: the real part of the potential $U'(z)$ as calculated by summation of 31 Fourier components in the crystal bulk. Dotted curves: the imaginary part of the potential $U''(z)$ arising from thermal motion of atoms.

localized orbitals,

$$\Phi_{\mathbf{g}}(z) = \sum_n \alpha_n \phi_n(z), \tag{5}$$

where the coefficients α_n satisfy the system of algebraic equations,

$$\alpha_n = \Lambda \left[\frac{\hbar^2 K_{\mathbf{g}}^2}{2m} - \epsilon_0 - M - i\frac{m}{\hbar^2 \kappa}\Lambda^2 + i\frac{\Gamma}{2} \right]^{-1} \left[\exp(i\kappa n d) - i\frac{m}{\hbar^2 \kappa}\Lambda \sum_{l=0}^{\infty} \exp(i\kappa d|n-l|)\alpha_l \right], \tag{6}$$

where

$$\Lambda = \int dz' \phi_n^*(z') U_{\mathbf{g}}(z') \exp(i\kappa[z' - nd])$$

and

$$M = -i\frac{m}{\hbar^2 \kappa} \int\int dz' dz'' \phi_n^*(z') U_{\mathbf{g}}(z') \exp(i\kappa|z' - z''|) U_{-\mathbf{g}}(z'') \phi_n(z'').$$

The magnitude of Λ is proportional to the probability amplitude of capture of an electron from the propagating wave $\exp(i\kappa z)$ into the localized state $\phi_n(z)$, while M is the probability amplitude of release of an electron from state $\phi_n(z)$ with its subsequent capture by the same state via the intermediate propagating state $\exp(i\kappa|z' - z''|)$. The scale of attenuation of the kernel of this equation [i.e., the term $\exp(i\kappa d|n - l|)$] is inversely proportional to the imaginary part of the wave vector, which is assumed to satisfy the condition $(\mathrm{Im}\kappa)^{-1} \gg d$.

To solve (6) we notice that there exists a purely formal similarity between (6) and the one-dimensional Schrödinger equation of the form

$$-\frac{\hbar^2}{2m}\frac{d^2}{dz^2}\Psi(z) + U\sum_{n=0}^{\infty}\delta(z - nd)\Psi(z) = \frac{\hbar^2\kappa^2}{2m}\Psi(z). \tag{7}$$

To illustrate this, we transform (7) into the integral representation,

$$\Psi(z) = J\exp(i\kappa z) - i\frac{m}{\hbar^2\kappa}U\int dz' \exp(i\kappa|z - z'|)\sum_{n=0}^{\infty}\delta(z' - nd)\Psi(z'),$$

where J denotes the amplitude of the incoming wave. For $z = nd$ this equation by the choice of parameters $J = U/\Lambda$ and

$$U = \Lambda^2 \left[\frac{\hbar^2 K_{\mathbf{g}}^2}{2m} - \epsilon_0 - M - i\frac{m}{\hbar^2\kappa}\Lambda^2 + i\frac{\Gamma}{2} \right]^{-1} \tag{8}$$

becomes identical with (6). The solution of Eq. (7) itself can be found by application of the transfer-matrix technique [22]. Defining

$$r = -\frac{i\frac{m}{\hbar^2\kappa}U}{1 + i\frac{m}{\hbar^2\kappa}U} = -\frac{i\frac{m}{\hbar^2\kappa}\Lambda^2}{\frac{\hbar^2K_{\mathbf{g}}^2}{2m} - \epsilon_0 - M + i\frac{\Gamma}{2}}, \tag{9}$$

and $t = 1 + r$ (r and t are the reflection and transmission coefficients of a single δ-function potential), we obtain the resonance part of the coefficient of reflection of high energy electrons from a surface of the crystal as

$$R_0^{(\mathrm{res})} = \exp(-i\kappa d)\frac{\{[r + \exp(-i\kappa d)]^2 - t^2\}^{1/2} - \{[r - \exp(-i\kappa d)]^2 - t^2\}^{1/2}}{\{[r + \exp(-i\kappa d)]^2 - t^2\}^{1/2} + \{[r - \exp(-i\kappa d)]^2 - t^2\}^{1/2}}. \tag{10}$$

The coefficients α_n are as follows:

$$\alpha_n = \Lambda \left[\frac{\hbar^2 K_{\mathbf{g}}^2}{2m} - \epsilon_0 - M - i\frac{m}{\hbar^2\kappa}\Lambda^2 + i\frac{\Gamma}{2} \right]^{-1} \left[1 + R_0^{(\mathrm{res})}\right] \frac{1}{t^n} \left(1 - \frac{r}{R_0^{(\mathrm{res})}}\right)^n \exp(-i\kappa d n). \tag{11}$$

The quantities (9) and (11), considered as functions of $\hbar^2K_{\mathbf{g}}^2/2m$, exhibit a clear resonance behavior, the resonance width of (9) being equal to $\Gamma_{\mathrm{tot}} = \Gamma + 2\,\mathrm{Im}(-M)$. Virtual transitions result in a shift of the resonance from its initial position at ϵ_0 towards $\hbar^2K_{\mathbf{g}}^2/2m = \epsilon_0 + \mathrm{Re}(M)$. The wave function of resonance diffraction belongs to the continuum of Bloch states and can be characterized by the quasimomentum $\hbar q = -\hbar\kappa - i(\hbar/d)\ln[\{1/t\}(1 - \{r/R_0^{(\mathrm{res})}\})]$. The behavior revealed by the coefficient of reflection of high energy electrons from a surface of the crystal is identical with the behavior of the coefficient of reflection of a particle from an array of non-Hermitian δ-function potentials, the magnitude of each potential being given by expression (8). This magnitude explicitly depends on the orientation of the electron beam via the parameter $\hbar^2K_{\mathbf{g}}^2/2m$, and at the exact resonance position the effective potential U becomes a purely imaginary quantity. This distinguishes the surface resonance diffraction of high energy electrons from ordi-

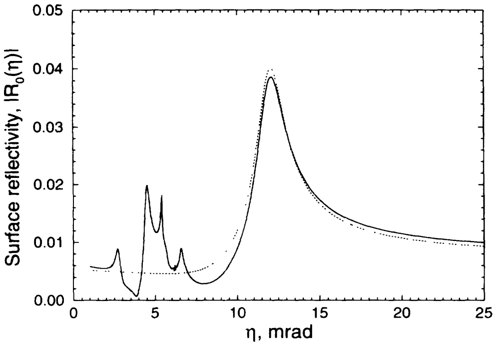

FIG. 2. Absolute value of the surface reflectivity $|R_0|$ plotted as a function of azimuth η for glancing angle $\zeta = 58.6$ mrad and energy of electrons $E = 100$ keV. The solid curve has been obtained by numerical integration of Eqs. (2). The dotted curve has been evaluated using formula (10). $\eta = 0$ corresponds to the $[11\bar{2}]$ azimuth in the (111) surface.

nary Bragg scattering. It is important to emphasize that behavior of the reflectivity (10) does not follow the standard Breit-Wigner law. There exists a rather complicated relation between r from (9), which indeed has the Breit-Wigner form, and the resulting expression for the reflectivity (10). The origin of the violation of the Breit-Wigner resonance law results from the fact that many states having nearly the same energy ϵ_0 participate in the process of scattering, and the standard requirement that the localized state must be well separated in energy space from all other states (as is assumed to be the case for scattering via a surface state [12]) is not satisfied.

To evaluate the accuracy of our approach, we compare our analytical solution with the results of numerical integration of (2). To solve (2) numerically, we used the $\hat{\mathcal{R}}$-matrix method [17], where $\hat{\mathcal{R}}$ is so defined to relate the components of the wave function and their derivatives.

Alternatively, the wave functions of localized states $\phi_n(z)$ as well as their inelastic widths have been determined independently from solving the bulk 31-beam Bloch wave problem (this needs to be performed only once for a particular value of ζ). The "potential" contribution to the reflectivity has been calculated by numerical solution of the one-dimensional diffraction problem [23]. Figure 2 shows the azimuthal dependence of the absolute value of the reflectivity $|R_0(\eta)|$ (full curve) obtained by numerical integration of (2) and the corresponding dependence of $|R_0^{(\mathrm{res})}(\eta)+R_0^{(\mathrm{pot})}|$ (dotted curve) evaluated from expression (10), where η is the angle of azimuth and $\eta = 0$ corresponds to the $[11\bar{2}]$ direction in the (111) surface. The curves in Fig. 2 exhibit a strong increase in reflectivity in the vicinity of the resonance, and in this region there is excellent agreement between the results of the analytical treatment (10) and the exact numerical solution.

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