An iterative method for retrieval of structural parameters of surfaces with two relaxed overlayers

1999 J. Phys.: Condens. Matter 11 3443

(http://iopscience.iop.org/0953-8984/11/17/303)

J. Phys.: Condens. Matter **11** (1999) 3443–3448. Printed in the UK PII: S0953-8984(99)01371-5

An iterative method for retrieval of structural parameters of surfaces with two relaxed overlayers

S Mukhopadhyay and T K Ballabh

Condensed Matter Physics Research Centre, Department of Physics, Jadavpur University, Calcutta-700 032, India

Received 27 January 1999

Abstract. In this work we have proposed an iterative method for direct determination of relaxation parameters from low-energy electron diffraction (LEED) intensity patterns. The algorithm is based on the layer-doubling method. It is shown that, with some realistic constraints, the relaxation parameter for a single relaxed structure can be obtained, and this solution can be utilized to determine the two-layer relaxed structure iteratively. With simulated intensity patterns for a one-dimensional model, the method is found to work well.

1. Introduction

To date, the majority of surface structures have been determined through low-energy electron diffraction (LEED) experiments [1]. The large scattering cross-sections for low-energy electrons make LEED an ideal surface-sensitive probe but, due to this large scattering cross-section, multiple scattering dominates and LEED pattern analysis becomes a really difficult task.

In the conventional method of LEED pattern analysis, the structure is determined from the optimal match of the experimental and computed intensity patterns among a large number of plausible structures. This process of finding surface structures requires for complex systems an enormous amount of computer time for calculation of the intensity patterns for many points of the probable parameter space and for comparing with experimental intensities through calculation of R-factors.

Various attempts have been made to reduce the computational time required to generate I–V curves for a given structure through perturbative approaches. These approaches—e.g. the renormalized forward-scattering (RFS) [2], reverse-scattering perturbation (RSP) [3], beam set neglect (BSN) [4] and tensor LEED [5] methods—have been applied to different systems with certain required characteristics with varying degrees of success. In particular, a drastic reduction of computer time in the calculation of I–V curves in the TLEED method made it possible to determine the structures of a large number of complex structures which are almost impossible to obtain from conventional full dynamical calculations [6]. Cerda *et al* [7] developed a fast algorithm based on the combination of the first-order perturbation in RFS and a search in parameter space with simulated annealing to determine the relaxation of up to eight layers.

These trial-and-search techniques have had a tremendous impact on the determination of surface structures for a large number of materials. In spite of all of the successes, however, a structure determined by a trial-and-search method can never be claimed to be definitely the

0953-8984/99/173443+06$19.50

actual structure, but it may be the most probable one. A direct method for determination of surface structure based on TLEED was put forward by Pendry *et al* [8] and shown to work for many surfaces if the initial reference structure is very close to the real one.

Also, there is holographic LEED which records the intensity as well as the phases of the diffraction patterns. Inversion of these data complemented by TLEED for fine tuning determined the complex structure of SiC very accurately. But the applicability of this elegant method is still limited to systems with large enough unit cells and one prominent atom acting as a beam splitter [9].

In this work, we attempt to determine surface structural parameters directly from the LEED intensity patterns for a class of possible structures, on the basis of the formalism of the layer-doubling method. The motivation of this work came from the success of conventional techniques of LEED pattern analysis, including that for multiple scattering. In the method, a crystal surface is considered to be the result of a stacking of parallel atomic planes. We show here that in the one-dimensional case the relaxation parameter for a single-relaxed-overlayer structure can be determined from intensity patterns alone. For the two-relaxed-overlayer structure, which includes an intermediate relaxed layer in between the top layer and the periodic substrate, an iterative method can be adopted to retrieve the surface structural parameters correctly.

In the next section we describe the basic framework and the strategies for retrieving the relaxation parameters. In section 3 we present the outcome of this algorithm as applied to some simulated experimental parameters. In the final section we discuss the significance of the results and the formalism.

2. Theory

A surface structure is considered to consist of a stack of atomic layers parallel to the surface. In standard LEED intensity calculations, firstly intralayer multiple scattering is taken into account in calculating the reflection and transmission coefficients for each layer, and thereafter interlayer scattering is considered. The two-dimensional periodicity of each layer results in a set of reflected and transmitted beams and gives rise to energy-dependent reflection and transmission coefficients for them. We consider here single-beam complex reflection and transmission coefficients for the layer, r and t respectively, for simplicity, so it is effectively a one-dimensional model.

Let the complex reflection coefficient of a regular periodic surface be R_S and that of the overall structure be R_L for the single-relaxed-overlayer structure. Then, in the layer-doubling formalism [3]

$$R_L = r + \frac{R_S t^2 \mathrm{e}^{\mathrm{i}k\,2d_{12}}}{1 - r R_S \mathrm{e}^{\mathrm{i}k\,2d_{12}}} \tag{1}$$

where d_{12} is the distance between the top layer and the next and $\boldsymbol{k}$ is the wave vector of the incident electron. R_S can be computed from the known interplanar distance of the bulk using equation (1) repeatedly, by the layer-doubling method.

Equation (1) which gives the complex reflection coefficient is essentially two equations, one for the magnitude $|R_L|$ and another for the argument of R_L. We can recast the equation in the form

$$R_L = \frac{r(1 + r R_S(t^2/r^2 - 1)\mathrm{e}^{\mathrm{i}k\,2d_{12}})}{1 - r R_S \mathrm{e}^{\mathrm{i}k\,2d_{12}}} \tag{2}$$

to calculate the magnitude. Taking absolute values of the two sides of equation (2) and after

some cumbersome algebra, we obtain

$$\cos(2kd_{12} + \phi + \theta) = \frac{|R_L|^2(1 + |R_S|^2|r|^2) - |r|^2(1 + |R_S|^2|r|^2||t^2/r^2 - 1|^2)}{2|R_S||r|A} \tag{3}$$

where

$$A\sin\theta = |t^2 - r^2|\sin\zeta \qquad \phi = \arg(R_S) + \arg(r)$$
$$A\cos\theta = |R_L|^2 + |t^2 - r^2|\cos\zeta \qquad \zeta = \arg(t^2/r^2 - 1).$$

The phases of R_L do not appear in equation (3). We here apply the constraints of intensity matching for the system and the matching of the complex reflection coefficient of the substrate deep inside the bulk. Therefore, from the known information and the value of the intensity, the right-hand side of equation (3) can be evaluated. Hence the value of d_{12} can be determined. For a fixed value of the right-hand side of equation (3), two angles, α and $2\pi - \alpha$, satisfy the equation. With the physical restriction that d_{12} is close to the bulk interplanar distance a, four possible values can be obtained at each energy. Of these four possible distances, two are contractive ($d_{12} < a$) and the other two are expansive ($d_{12} > a$). The common intersection of the sets of four distances at different energies gives a unique value of d_{12}. A value of R_S incompatible with the diffraction intensity may produce a result for the right-hand side outside the range $[-1, +1]$ and thus lead to imaginary values of d_{12}.

Now let us consider the case of a two-relaxed-overlayer structure. Here there is an intermediate layer in between the top layer and the periodic substrate. Let the reflection coefficient of the system with one relaxed layer over the substrate be R_{S1} and that for the same system with two relaxed layers over the substrate be R_L. Then the following equations hold:

$$R_L = r + \frac{R_{S1}t^2 e^{ik\,2d_{12}}}{1 - rR_{S1}e^{ik\,2d_{12}}} \tag{4}$$

$$R_{S1} = r + \frac{R_S t^2 e^{ik\,2d_{23}}}{1 - rR_S e^{ik\,2d_{23}}} \tag{5}$$

where d_{12} is the distance between the top layer and the intermediate layer and d_{23} is the distance between the intermediate layer and the substrate.

For surfaces with the two-relaxed-overlayer structure we try to apply the same principle, that the intensity pattern should match at the top layer and d_{12} and d_{23} should be computed using equation (4) and (5) in such a way that the reflection coefficient R_S for the substrate matches properly. It should be noted that if the phases of R_L had been available, then $|R_{S1}|$ could easily have been calculated from inversion of equation (4):

$$\frac{R_L - r}{t^2 - r^2 + rR_L} = R_{S1}e^{ik\,2d_{12}}. \tag{6}$$

Once $|R_{S1}|$ is known, d_{23} can be computed in the same way as for the single-relaxed-overlayer surface. However, due to the non-availability of the phases of R_L, this is not a workable algorithm.

Therefore we adopt an iterative scheme which does not require the phases of R_L. Initially we chose $d_{23} = a$, the bulk interlayer distance, and calculated R_{S1} from equation (5). So initially, $R_{S1} = R_S$. With this R_{S1} and the experimental values of $|R_L|$, we get a value of d_{12} using equation (3). It should be noted here that for this value of R_{S1} the computation may not be successful for all energies. The computation will certainly be successful if the computed value of R_{S1} is very close to the actual value, i.e. if d_{23} is chosen correctly and R_{S1} is computed from equation (5). But here the assumption that $R_{S1} = R_S$, which initially means that $d_{23} = a$, gives, from equation (5),

$$\frac{\delta R_{S1}}{R_{S1}}\frac{t^2 R_{S1}}{r(R_{S1} - r)(R_{S1} - r + t^2/r)} = 2ik\delta d_{23}. \tag{7}$$

In most situations, $|t^2/r| \gg |R_{S1} - r|$, and thus

$$\frac{\delta R_{S1}}{R_{S1}} \simeq 2\mathrm{i}k(1 - r/R_{S1})\delta d_{23}. \tag{8}$$

Therefore the value of $|\delta R_{S1}/R_{S1}|$ is large when $|R_{S1}|$ is very small for the same values of δd_{23}. Therefore it is expected that computation failures will occur mainly in between Bragg peaks. Also, equation (8) suggests that the possibility of computation failure at large energy is comparatively large. The algorithm initially ignores the failures and computes a value of d_{12} from the successful calculations.

Once a value of d_{12} is obtained, R_{S1} is recalculated back. For the energy values at which computations have failed, the value of R_{S1} is interpolated from those from successful computations at neighbouring energies. These values of R_{S1} together with the computed value of R_S give similarly a value for d_{23}. With this d_{23}, the iteration is repeated until d_{12} and d_{23} converge to a limit with prescribed precision.

The iterative algorithm essentially attempts to compute the reflection coefficients R_{S1} and d_{12} from the intensity pattern and an assumed function R_{S1}. Then this R_{S1} together with R_S provides a value for d_{23}. Therefore, in this algorithm, the diffraction pattern intensity is taken as input and real-valued relaxation parameters are iteratively set such that the complex reflection coefficient R_S for the substrate matches with that computed from the known bulk lattice constant.

3. Results

We have tested our algorithm for four surfaces. The energy-dependent complex reflection and transmission coefficients, r and t, for each layer were taken as those of the (00) beam for Al(111), Cu(111), Pd(100) and Rh(111) surfaces. These r- and t-values are computed from the inputs of the standard phase shift and the two-dimensional bulk lattice constants for the respective surfaces using modified versions of standard dynamical codes [3].

The intensity patterns for the above-mentioned surfaces with one and two relaxed overlayers were computed for a good number of expansive, contractive and mixed relaxations. These simulated intensities are considered as pseudo-experimental data. These intensity patterns, energy-dependent complex reflection and transmission coefficients, bulk lattice constants and bulk interplanar distances are taken as inputs.

The retrieval of a relaxation parameter for a single relaxed structure using equation (3) is a non-iterative process. It is found that the relaxation parameter can be correctly determined for relaxation to up to 20% variation from the bulk interplanar distance.

In table 1 we show the parameters of the surfaces used to simulate the intensity patterns, which are considered as pseudo-experimental data for double-relaxed-layer structures. The relaxation for typical real systems is always less than the values shown here [10].

Table 1. Typical values of parameters of surfaces for simulating intensity patterns.

		Simulated parameter values (Å)	
Surfaces	Bulk interplanar distance, a (Å)	d_{12}	d_{23}
Al(111)	2.338	2.216	2.402
Cu(111)	2.087	2.146	2.103
Rh(111)	2.192	2.146	2.178
Pd(100)	1.945	2.056	2.012

Table 2. Retrieved parameter values and Pendry R-factors obtained as the iteration proceeds.

Surfaces	Iteration No	Retrieved parameter values (Å) d_{12}	d_{23}	Pendry R-factor
Al(111)	1	2.202	2.342	2.8×10^{-1}
	3	2.216	2.400	7.5×10^{-5}
	10	2.216	2.402	9.2×10^{-6}
Cu(111)	1	2.148	2.087	1.2×10^{-2}
	4	2.146	2.106	2.3×10^{-3}
Rh(111)	1	2.145	2.154	6.1×10^{-4}
	5	2.146	2.162	9.1×10^{-5}
	12	2.146	2.178	2.2×10^{-6}
Pd(100)	1	2.051	1.952	3.1×10^{-1}
	5	2.055	2.016	1.5×10^{-3}
	9	2.056	2.012	5.1×10^{-6}

In table 2 we present the results of the iterations. The initial value of d_{23} was taken as the bulk interplanar distance a. Typically, the iteration converged to an accuracy of three decimal places in four to twelve iterations. The convergence in general depends on the natures of the reflection coefficients r and transmission coefficients t of the layers. The number of iterations increases for systems having coefficients r and t exhibiting large numbers of maxima and minima. Pendry R-factors obtained as the iteration proceeds are shown for some parameter values. It is seen that in most cases the R-factors improve by five orders of magnitude and the retrieved values of the parameters agree well with the actual parameter values.

4. Discussion

In contrast to the trial-and-search method of conventional LEED analysis, our algorithm starts from an experimental intensity pattern in order to determine the relaxation parameters directly, imposing the constraint of matching of the intensity pattern for the whole system and the complex reflection coefficient of the bulk-terminated surface at the same time. Our results for an effectively one-dimensional structure show that the solution is straightforward for a single-relaxed-overlayer structure. This appears to be a multivalued function at each energy, and a unique value is resolved from the energy-dependent intensity spectra. For a two-relaxed-overlayer structure this principle is implemented in an iterative process. The Pendry R-factors in table 2 show the progressive improvements as the iteration proceeds. It may be noted that computation of R-factors is not necessary at any step of the iteration, as convergency is checked through the recalculation of values of the relaxation parameters. There is scope for making a better choice of the initial values of the relaxation parameters to achieve faster convergence. Also, external convergence-acceleration techniques can be applied.

In the three-dimensional model, the equations for the complex reflection coefficients are similar to equation (1), but now in a matrix form. So the same strategy can be applied for the multibeam situation, and a single beam cannot be treated in isolation. The stepping stone of this algorithm is the solution for a single-relaxed-overlayer structure (equation (3)) in the one-dimensional model. In principle, a solution can also be obtained in three dimensions; at worst, the solution may have to be obtained numerically. Work in this direction on direct determination of real surface structure is in progress. Also, the perturbative approach of tensor

LEED may be applied, with this algorithm reducing the computational time.

In conclusion, we have shown that a one-dimensional model LEED intensity pattern together with information on the chemical composition of surfaces and bulk structure can be used effectively to determine the surface relaxation parameters in an iterative method. As this method does not search in parameter space, the solution obtained can be confidently considered to be the actual structure.

Acknowledgments

One of the authors (SM) is grateful to the University Grants Commission (UGC), Government of India, for providing a research fellowship. The authors acknowledge the valuable suggestions of Professor A N Basu, Jadavpur University, Calcutta.

References

[1] Heinz K, Kottcke M, Loffler U and Doll R 1996 *Surf. Sci.* **357–358** 1
[2] Pendry J B 1974 *Low Energy Electron Diffraction* (London: Academic)
[3] Van Hove M A and Tong S Y 1979 *Surface Crystallography by LEED* (Berlin: Springer)
[4] Van Hove M A, Lin R F and Somorjai G A 1983 *Phys. Rev. Lett.* **51** 778
[5] Rous P J, Pendry J B, Saldin D K, Heinz K, Muller K and Bickel N 1986 *Phys. Rev. Lett.* **57** 2951
[6] Heinz K 1995 *Rep. Prog. Phys.* **58** 637
[7] Cerda J, Gallego S and de Andres P L 1996 *Surf. Sci.* **348** 197
[8] Pendry J B, Heinz K and Ode W 1988 *Phys. Rev. Lett.* **61** 2953
[9] Reuter K, Bernhardt J, Wedler H, Schardt J, Starke U and Heinz K 1997 *Phys. Rev. Lett.* **79** 4818
[10] Van Hove M A, Weinberg W H and Chan C M 1986 *Low Energy Electron Diffraction* (Berlin: Springer)