

ELECTRON CURRENT IMAGE DIFFRACTION FROM CRYSTAL SURFACES AT LOW ENERGIES

Low-energy electron diffraction patterns in current images of crystal surfaces were recently discovered and explained as being due to elastic scattering. Features in these patterns have been attributed to channeling of the incident electron beam into specific directions within the crystal caused by elastic scattering from planes of atoms near the surface. Because current image diffraction is surface sensitive, it can become a major new technique for surface analysis.

INTRODUCTION

It has long been recognized that single crystals behave as diffraction gratings to electron beams. Indeed, it was this discovery in the 1920's by Davisson and Germer¹ of Bell Laboratories that established the wave-particle duality of the electron and confirmed de Broglie's relation for material particles. This was one of the revolutionary experiments of that time and resulted in a Nobel prize for Davisson.

The reason crystals behave in this manner is that their atoms are arranged in periodic structures with interatomic separations of the order of the electronic wavelength $\lambda = h/(2mE)^{1/2}$, where h is Planck's constant and m and E are the mass and energy of the electron. It was also realized early that crystallographic information could be obtained from these electron scattering experiments. However, during the early days and for a number of reasons, interest diminished in the method as a tool to probe crystals. Not the least of those reasons was that multiple scattering effects complicate the spectra, making analysis difficult. The stringent requirements of high vacuum and clean crystal surfaces also made experiments very difficult with the technology then available. X rays proved to be a more convenient source for crystal analysis because they penetrate more deeply into the crystal and hence are sensitive to its bulk properties. Also, X rays are only weakly scattered by atoms so that there are no complications from multiple scattering.

LOW-ENERGY ELECTRON SCATTERING

Low-energy electron diffraction (LEED) was revived in the 1960's as a method for surface analysis primarily as a result of the advent of ultra-high vacuum technology and such modern surface-preparation techniques as ion bombardment to clean the surfaces. This, coupled with the theoretical advances of the 1970's dealing with the complications of multiple scattering, has firmly established LEED as a major method for surface investigations. At low ener-

gies (0 to 1000 electronvolts), electrons penetrate only into the surface region or the first few atomic layers and hence probe properties at the surface. The structural information derived from experiments of this nature is essential for understanding the details of processes that occur at surfaces, such as chemical reactions and catalytic activity. The interested reader is referred to Table 1 of Ref. 2 for a comparison of some of the methods of surface analysis and the kinds of information that can be obtained from them.

In a conventional LEED experiment, an electron beam is directed at the surface of a crystal from an electron gun that is placed in the center of a hemispherical fluorescent screen (Fig. 1). The elastic back-scattered electrons, which are only a small percentage (1 to 2%) of the total secondary electron current emitted from the surface, collide with the screen and produce a symmetrical arrangement of spots that directly exhibit the symmetry of the positions of the atoms on the crystal surface. The effect of the secondary electron current due to inelastic processes is minimized by retarding grids. Intensity measurements of the spots, using a Faraday cup or photometer and correlated with theoretical computations, provide information on the size and composition of the surface unit cell, the basic structural unit of the crystal surface.

In 1981, a novel low-energy electron diffraction phenomenon on single crystal surfaces was discovered in APL's Milton S. Eisenhower Research Center.³ An electron beam is rastered across the surface of a crystal sample, and images are obtained from the leakage current absorbed in the specimen from the beam (Fig. 2). The surface is imaged by a scanning electron beam that strikes the specimen at constantly varying azimuthal and polar angles. The specimen current is measured at every position where the beam strikes the surface and is displayed synchronously on a cathode ray tube. Diffraction patterns appear in these current images of the crystal surface as changes in contrast caused by variations of total reflectivity of the crystal surface with incident angle of the elec-

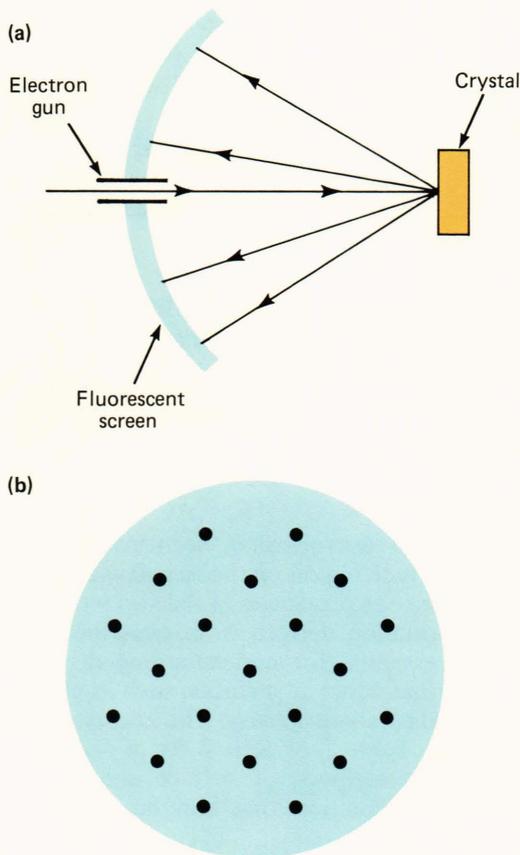


Figure 1 — A schematic diagram of (a) a low-energy electron diffraction (LEED) apparatus and (b) a LEED pattern on a fluorescent screen.

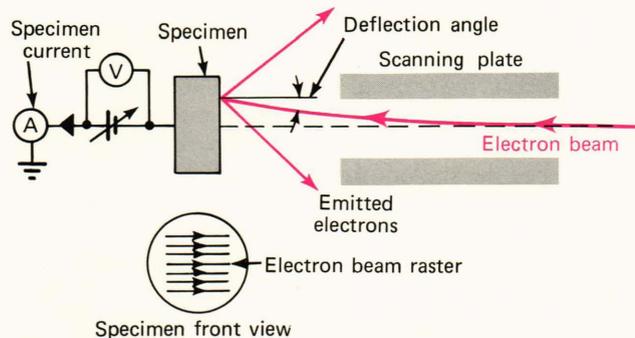


Figure 2 — Schematic diagram of the experimental apparatus for low-energy electron current image diffraction (CID).

tron beam. By conservation of charge, the sum of the specimen current and the current emitted from the crystal equals the beam current. As the beam is scanned across a surface, contrast in such images arises from intensity variations in the emitted current, which includes elastic and inelastic backscattered electrons.

Current image diffraction (CID) is closely related to LEED. Both methods use low-energy electrons to

probe the surface region and both are diffraction phenomena that give information about crystal structure; that is, the distances between the periodic structural units that make up the crystal can be obtained from both LEED and CID experiments. Quantitative information on disposition of the contents of these structural units, i.e., the relative positions of the atoms or molecules within them, can be obtained only by correlating the experimental measurements with a very complex theoretical analysis of electron scattering by the atomic cores (the nuclei and closed shell electrons excluding the delocalized conduction electrons) of the atoms or molecules that make up the crystal. If there are changes in the basic structural unit near the surface compared with the bulk crystals that are brought about by the different environment experienced by the atoms near the surface, they would be manifested by intensity variations in the LEED spots on the fluorescent screen. Also, the CID pattern would exhibit variations. Furthermore, both the CID and LEED methods give structural information on adsorption processes of foreign atoms or molecules on crystal surfaces.

The intensities of LEED spots are usually measured as a function of primary beam energy and exhibit a series of maxima and minima that contain the structural information. A CID pattern, on the other hand, is obtained at a single primary beam energy. It is formed by varying the azimuthal and polar angles of the primary beam in such a way that the beam scans the crystal surface and exhibits intensity variations that also contain structural information. The disadvantage of the CID method is that inelastic scattering of electrons contributes to the images, although its contribution to contrast variations is usually minimal at low energies. This makes quantitative calculations of the surface electron reflectivity, necessary for comparison with experiment, more difficult than calculating the LEED spot intensities. A major advantage of the CID technique is that certain features that appear in some of the images can only be caused by single scattering events; this simplifies the analysis enormously.

Almost all of us are aware of such crystals as diamonds and quartz that are formed by repetitive building blocks of atomic structural units of the same size and shape, building blocks that are responsible for the crystals' natural geometrical structures and many of their physical properties. Because metals usually are encountered in polycrystalline form, it is not so well known that large single crystals of metals can also be grown. Crystalline solids can be grouped into seven crystal systems, of which the cubic and hexagonal structures are of interest here (Fig. 3). The basic structural units of aluminum and copper are face-centered cubic with an atom at the eight corners of a cube and the six face centers. Silicon, on the other hand, is also face-centered but has two atoms associated with each corner and face center. (In fact, silicon has the same crystalline structure as diamond.) The other crystalline structure of interest in

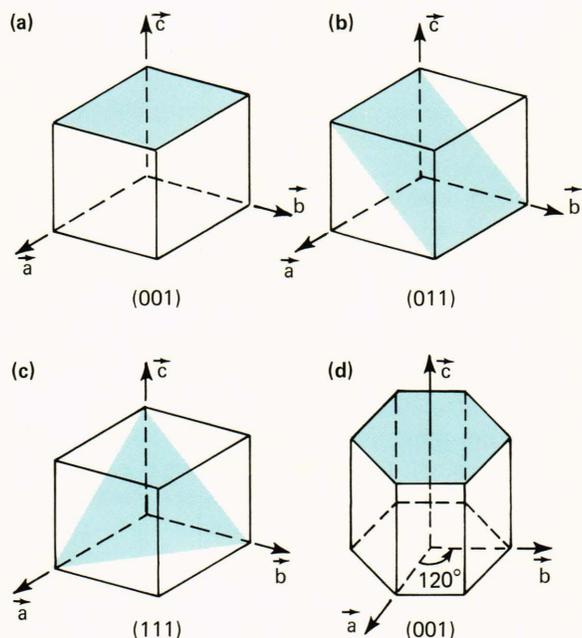


Figure 3 — Crystal lattices for the cubic and hexagonal systems. Planes parallel to the surfaces discussed in the text are shaded, and their Miller indices (hk1) are indicated.

this article is that of titanium, which is called hexagonal-close packed and has two atoms associated with each of the six vertices of the two horizontal faces (Fig. 3d). It is the size and shape of these structural units that are readily extracted by LEED and CID ex-

periments, and, because of the surface specificity of the two methods, such geometrical information is obtained for regions near the crystal surface.

Single crystals can be cut along various crystallographic directions to form surfaces consisting of planes of atoms that exhibit symmetries characteristic of the particular planes. For example, the various surfaces of the cubic and hexagonal systems discussed in this article appear shaded in Fig. 3, and each surface has its own symmetry. Planes of atoms of various orientations and directions can be designated for single crystals, and they are indexed by a set of three integers called Miller indices (hk1). The Miller indices of the shaded planes indicated in Fig. 3 are the planes parallel to the surfaces discussed below.

CURRENT IMAGE DIFFRACTION PATTERNS

CID patterns taken at a primary beam energy of 21 electronvolts appear in Figs. 4a to 4c for the (001), (011), and (111) surfaces of aluminum. Referring to Figs. 3a through 3c, it is apparent that the fourfold symmetry of the (001) surface, the twofold symmetry of the (011) surface, and the trigonal symmetry of the (111) surface appear in the CID patterns. Moreover, the crystal orientations as verified by LEED are also indicated in these images.

As an example of the hexagonal close-packed structure, the CID patterns of the basal (001) plane

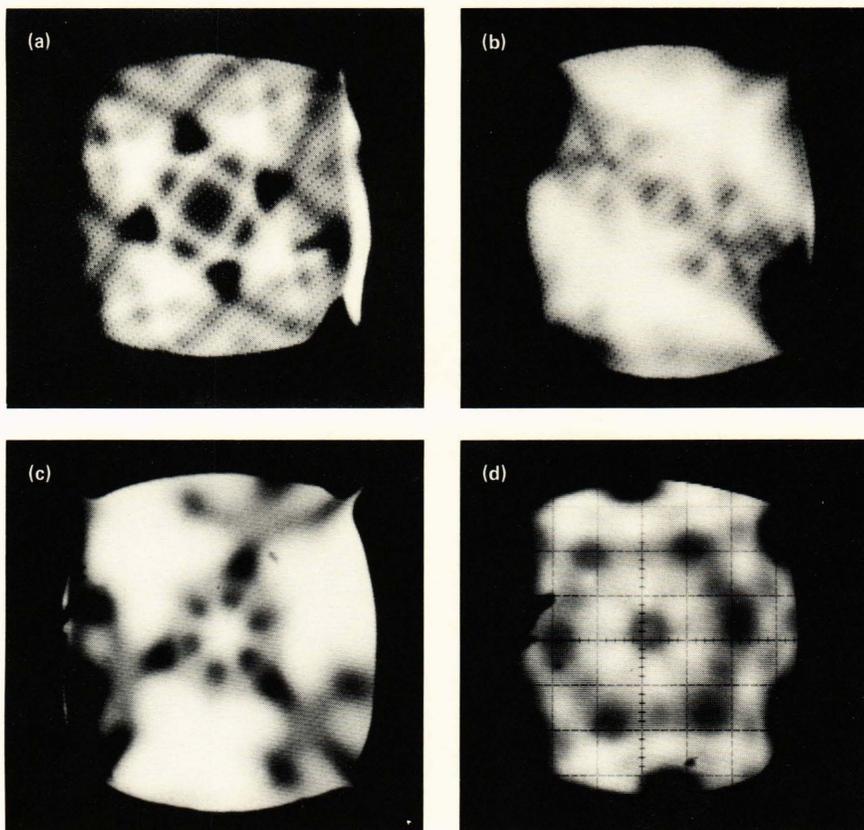


Figure 4 — CID patterns of (a) the (001), (b) the (011), and (c) the (111) surfaces of aluminum taken at a primary beam energy of 21 electronvolts with respect to the vacuum. (d) The CID pattern of the basal plane of titanium at 20 electronvolts with respect to the vacuum.

of titanium is shown in Fig. 4d, taken at a primary beam energy of 20 electronvolts. This image has many of the features of the (111) face of aluminum (Fig. 4c). The basal plane of the hexagonal close-packed structure and the (111) surface of the face-centered cubic lattice are similar. The atomic positions in the first two layers of atoms parallel to the surface of these two crystals are identical. They only differ in the third layer, where the hexagonal lattice repeats the first layer while the face-centered cubic lattice has a third layer where atoms are at different sites than in the first two layers.

In Fig. 4a, there are four bright white lines corresponding to surface regions of relatively large absorbed currents. Calculations indicate that these four symmetrical lines are due to forward scattering into the crystal or electron channeling caused by elastic scattering from four specific sets of planes of atoms that are not parallel to the crystal surface. These planes are equivalent and are related to one another by the fourfold symmetry of the particular surface. An example of electron channeling from planes that are inequivalent appears in Fig. 5. Here the darkened contrast indicates that the electrons are backscattered from three sets of planes of atoms, each of which exhibits the fourfold symmetry of the (001) surface of the face-centered cubic system (Fig. 3a). Theoretical

positions of these channeling lines appear in Fig. 5a, where the calculations were based on simple Bragg theory. It is noted from Fig. 5 that there are regions of relatively large electron reflectivity whenever the channeling lines cross, corresponding to the Bragg condition being satisfied for elastic scattering from two or more planes. (The shading in the theoretical image at these crossing points (Fig. 5a) is arbitrary and was done to facilitate comparison with the experimental image.)

The information that is extracted from the comparison of simple Bragg theory and experiment is the distances between atomic planes and the crystal inner potential. The inner potential is the potential felt by an electron upon entering the crystal and is roughly the negative of the Fermi energy (the maximum energy of the conduction electrons relative to the ion cores at a temperature of absolute zero) plus the work function (the magnitude of the energy difference between the vacuum and the Fermi energy or the energy needed to extract an electron from the crystal). The energy difference between the theoretical line positions that were computed for a primary beam energy of 40 electronvolts with respect to the ion cores in Fig. 5a, and the experiment, Fig. 5b, where the beam energy is with respect to the vacuum, gives 10 electronvolts for the inner potential. The energy difference is corroborated at this energy by independent studies such as LEED for copper.

CONCLUSIONS

The CID method is still largely in a state of development. For example, the changes in CID patterns that occur as the result of ordered adsorption of foreign gas atoms have been established,⁴ but quantitative work remains to be done to correlate these observed variations in reflectivity with theory. Because of the problems associated with sample charg-

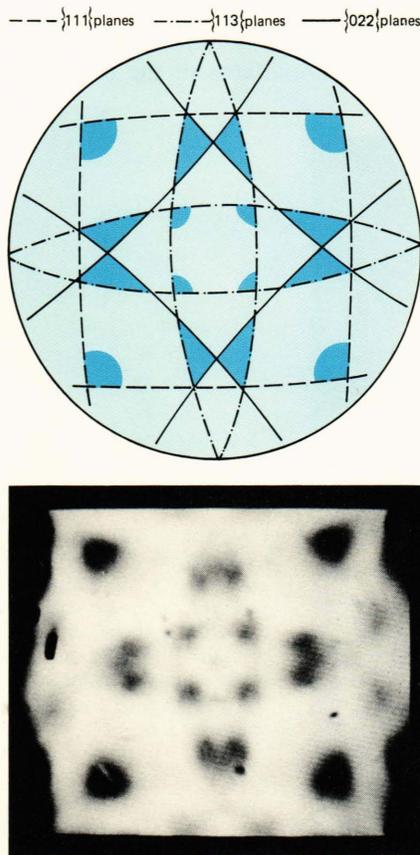


Figure 5 — Comparison of (a) theoretical channeling lines with (b) the experimental CID pattern for copper taken at a primary beam energy of 30 electronvolts with respect to the vacuum.

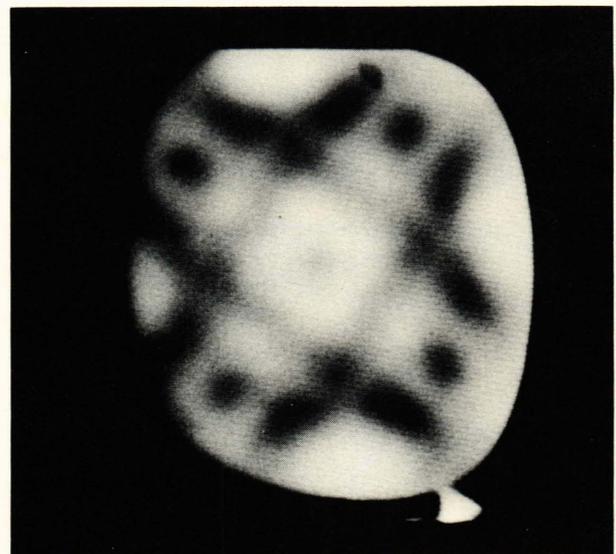


Figure 6 — CID pattern of the (001) surface of silicon taken at 4 electronvolts with respect to the vacuum.

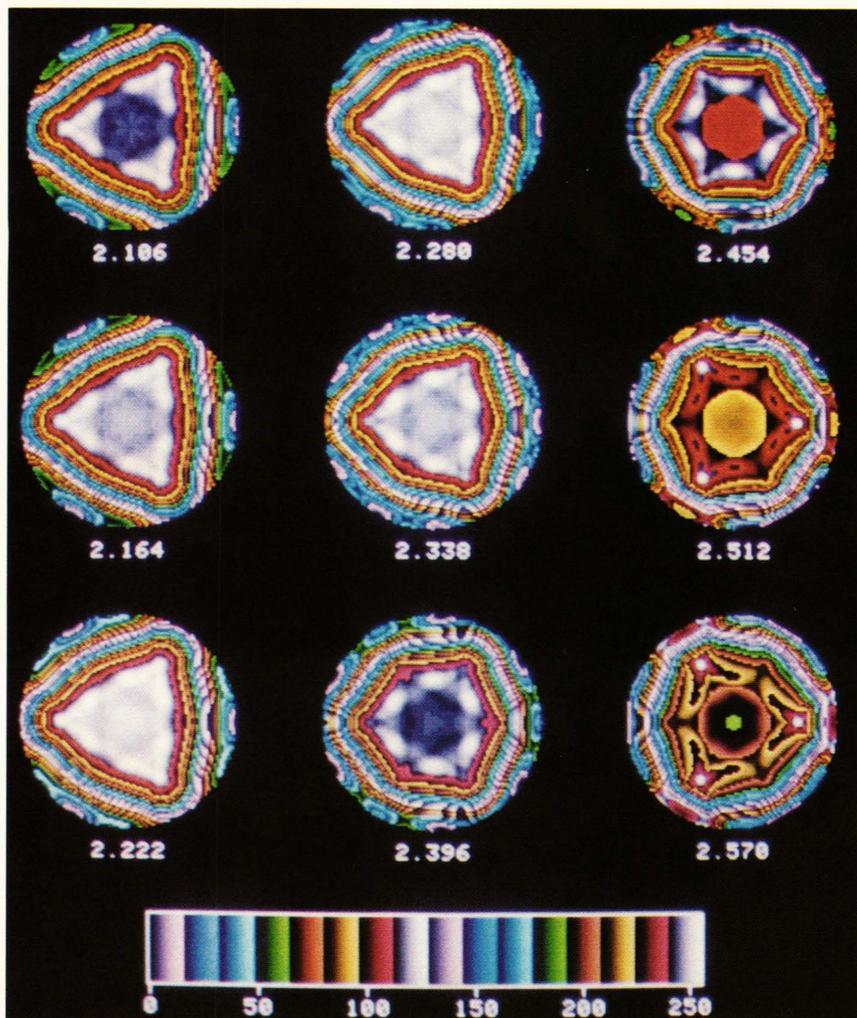


Figure 7 — Theoretical CID patterns of the (111) surface of aluminum calculated for an electron beam energy of 30 eV with respect to the vacuum for the indicated distances (in angstroms) between the surface layer and the second layer of atoms. The layer spacing of the bulk crystal is 2.338 Å. The relative intensity of reflected electrons is indicated by the color table at the bottom of the figure.

ing of nonconductors, investigations to date have concentrated on metals, but CID patterns have been observed recently (unpublished) on the (001) surface of silicon, a material of considerable technological importance (Fig. 6), extending the applicability of the CID method to semiconductors.

Theoretical calculations indicate that the interlayer separation of atomic planes parallel to the crystal surface can be obtained to an unprecedented accuracy with CID.⁵ This would require modifications of the present apparatus to obtain a more monochromatic electron beam, which is within the feasibility of present-day technology. It would also provide the exciting prospect of directly observing the layer oscillations that occur at the surfaces of some metals as indicated by theory, which would manifest itself as a splitting in electron channeling lines. Thus, the prospects for the CID method to emerge as a major new method for surface analysis appear encouraging.

Note Added in Proof

Figure 7 illustrates the results of a very recent theoretical calculation of CID pattern variation due

to changes in distance between the surface layer of atoms and the second layer. These calculations are for the (111) surface of aluminum whose characteristic trigonal symmetry is exhibited by the images. The intensity of features in the CID pattern is clearly sensitive to the surface layer separation.

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