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INTRODUCTION

Collisions of energetic ions with the atoms of a solid surface can result in scattering of the primary ions and recoiling of the surface atoms. These scattered and recoiled ions and atoms have discrete kinetic energies that are determined by the nature of the collision. Analysis of these energies and their angular distributions can provide direct information on the identity of the surface atoms and their structural arrangement in the surface.

1.1. ION SCATTERING SPECTROMETRY

Ion scattering spectrometry consists of using a monoenergetic, mass-selected, collimated beam of ions in the low keV energy range to irradiate a surface. As a result of the interaction of these ions with an atom or several atoms of the target, some of the primary ions are reflected from the surface, and some of the target atoms can be recoiled in such a direction that they also leave the surface. Both the scattered primary and recoiled surface particles are atoms that may be in neutral, positive, or negative charge states due to electronic charge exchange processes with the surface itself. These scattered and recoiled atoms have discrete kinetic energies in the low keV range as a result of quasi-single collisions from the impinging ions. The ions and atoms that are scattered or recoiled at a well-defined scattering–recoiling angle are analyzed for their kinetic energies using an electrostatic or magnetic energy analyzer or for their velocities using time-of-flight techniques (TOF). The atoms and ions are detected by an electron multiplier detector with a small acceptance solid angle. The detector signal is plotted as a function of the analyzer pass energy or the TOF. When a large-area, gated, position-sensitive microchannel plate detector is used, time-resolved spatial distribution images of the scattered and recoiled atoms are obtained. Since the scattering process is mass-dispersive, the energies or TOFs of the scattered and recoiled atoms provide a mass spectrum of the constituent atoms in the surface.

The energy and TOF spectra and the images contain information about the elemental composition of the surface and the surface atomic structure, thereby making ion scattering spectrometry a surface compositional and structural analysis technique. This analysis is straightforward because the kinematics of energetic atomic collisions is accurately described by classical mechanics. Such scattering occurs as a result of the mutual coulomb repulsion between the colliding atomic cores, that is, the nucleus plus core electrons. The scattered atom loses some of its energy to the target atom. The latter, in turn, recoils into a forward direction. The final energies of the scattered and recoiled atoms and the directions of their trajectories are determined by the masses of the pair of atoms involved and the closeness of the collision. By analysis of these final energies and angular distributions of the scattered and recoiled atoms, the elemental composition and structure of the surface can be deciphered.

Atomic collisions in the keV energy range can result in transfer of energy to both translational and internal degrees of freedom of the target atoms. If the collision involves only transfer of translational energy, it is known as an *elastic collision*. This is sometimes called a *hard sphere* or *billiard ball* collision. If the collision involves transfer of both translational and internal energy, it is known as an *inelastic collision*. Transfer of energy to internal degrees of freedom results in electronic excitation of the target and/or the projectile atom. This can produce a variety of phenomena, such as secondary electron, Auger electron, and photon emission. The physics of the mechanism of electronic excitation in atomic collisions is currently an active area of investigation. Since these inelastic energy losses are typically less than 5% of the beam energy for atomic collisions in the low keV energy range, they can be ignored for most elemental and structural analyses.

1.2. IMPORTANCE OF SURFACES

When we observe the world around us, we see predominantly the surfaces of objects. Interactions of these objects with their surroundings are largely through their surfaces. A detailed understanding of the surface and its properties is of utmost importance for understanding its interactions with the environment and for developing materials with specific properties. Since the surface forms the boundary between materials and gases or liquids, it is the surface that reacts with the environment. Adsorbed species on surfaces occupy specific chemically active sites, and atoms of the surface itself often arrange themselves so as to have different symmetry or different interlayer spacings from that of the bulk; the former is known as *reconstruction* and the latter as *relaxation*. Knowledge of surface composition and atomic positions is important for many applications: (a) understanding the oxidation of metals resulting in rusting and tarnishing; (b) the reactive sites in catalysis; (c) the chemical conversion of gaseous molecules by a catalyst; (d) friction; (e) adhesion of paint and glue to surfaces; (f) defining atomic templates for epitaxial film growth; and (g) fabricating well-defined interfaces between different materials. From a heuristic viewpoint, we are interested in knowing if atomic sites and bond lengths in surfaces are as well defined as those of the bulk and if there are important new phenomena to be derived therein. Although the many significant advances in surface science over the past three decades have greatly increased our understanding of surface phenomena, the incessantly decreasing size of microelectronic devices and their requisite atomic-scale surface analysis drive the development of surface science techniques. The study of surfaces is therefore interesting from both a scientific and a practical point of view.

There are three basic questions that we would like to answer about surfaces: (1) What is the elemental composition of the surface? (2) What is the structural arrangement of the surface atoms? (3) What are the electronic properties of the surface? A battery of surface analysis techniques has been developed over the past 30 years to answer these questions. These techniques are based on the interaction of particles (i.e., photons, electrons, atoms, molecules, or ions), with a surface, followed by detection of the scattered primary particle or the emitted secondary particles (i.e., electrons, photons, ions, atoms, molecules, or fragments). The experimental conditions are chosen so that the incident particles and/or the secondary particles interact primarily with the outermost atomic layers of the solid; therefore, the measured signals originate from the surface or subsurface regions.

1.3. SURVEY OF ION-SURFACE INTERACTIONS

Since this book is concerned with deriving composition and structural information about surfaces from ion scattering techniques, it is informative to survey the range of interactions accessible when using ion beams on surfaces. Ion beams provide a method of delivering unique atomic and molecular species to surfaces while controlling the interaction parameters by means of the ion kinetic energy. Consider the various phenomena that can occur when ions impinge on surfaces as illustrated[1] in Figure 1.1.

1. Electronic interactions—The incoming ions can be neutralized by electron capture from the surface. In the reverse process, electrons from incoming ions or atoms can be captured by the surface. Either process can result in excited electronic states. These processes depend on the relative energies of the filled and unfilled energy levels of the atoms and the surface.
2. Photon and electron emission—As a result of electron exchange and energy level crossings in the close collision encounters between atoms, electrons can be promoted to highly excited states that can relax by either photon or electron emission.
3. Scattering and recoiling—Ions can be scattered from the surface and atoms of the surface itself can be recoiled either into or out of the surface in positive, neutral, or negative charge states.

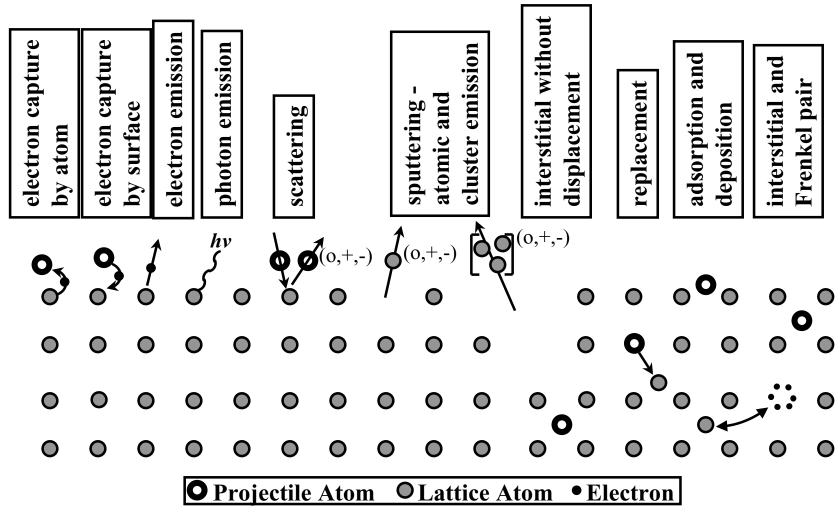

FIGURE 1.1. Schematic diagram of various phenomena involved in ion surface collisions (From Rabalais, 2001, with permission.)

4. Sputtering—The momentum imparted to surface atoms by impinging ions can cause collision cascades in the material, resulting in “sputtering” of low-energy atoms, molecules, fragments, and clusters in various charge states.
5. Adsorption, desorption, and chemical reactions—The impinging ions can be adsorbed on the surface, they can cause desorption of atoms and molecules from the surface, and chemical reactions can occur between the constituents.
6. Interstitials, displacements, and replacements—The ions can be inserted into the lattice as interstitial atoms without displacement of host atoms or they can displace host atoms, thereby creating Frenkel pairs. This can result in radiation damage.

A variety of ions with kinetic energies in the range 10^{-2}–10^{7} eV can be used to probe surfaces and interfaces. Various phenomena are dominant or emphasized in different energy regions and thereby, the chemical and physical processes that are induced by the ion impacts are also controlled by this energy. The terminology that has evolved to define approximate energy ranges is as follows: <1 eV, thermal; 1–500 eV, hyperthermal; 0.5–10 keV, low energy; 10–500 keV, medium energy; and >0.5 MeV, high energy.

A schematic diagram of the various phenomena involved, along with an energy scale, is shown in Figure 1.2.[1] The equivalent translational temperature range and the common terminology for describing the various energy ranges are indicated on the lower abscissa. Particle beams in the range of 10 meV–10 eV probe the long-range atomic potentials and exhibit quantum mechanical and diffraction effects. As energy increases, the de Broglie wavelength of the particles becomes significantly

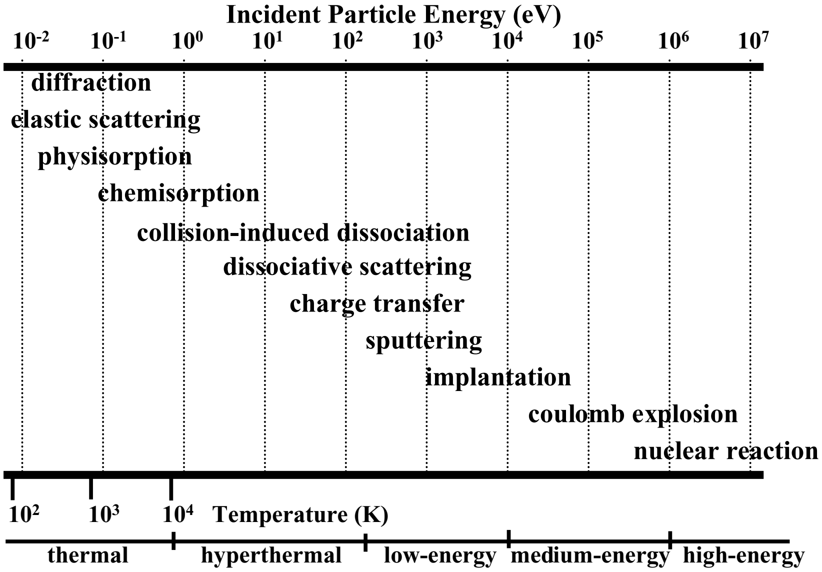

FIGURE 1.2. Selected particle–surface processes as a function of ion kinetic energy (From Rabalais, 2001, with permission).

smaller than the interatomic distances in the crystal lattice (∼5 Å), and the scattering process can be treated by classical mechanics. At energies above ∼10 eV, the repulsive potential begins to dominate the interaction and the surface potential becomes highly corrugated. In the range of ∼10–100 eV, it is difficult to make ion beams of sufficiently high intensity for ion scattering due to space charge limitations. In the low-energy regime between 0.5–10 keV, the space charge limitation decreases, and the ions interact with the atomic cores of the lattice atoms. Hence, the surface appears more open and penetration can occur. Various interactions, such as sputtering, implantation, surface reactions, and atom deposition can accompany the scattering process. Ions that penetrate are efficiently neutralized. In the medium energy range of 10–500 keV, most particles penetrate into the lattice and are implanted. Energies above 0.5 MeV are used for doping of semiconductors, and energies above 1 MeV can result in nuclear fusion and fission.

1.4. HISTORICAL DEVELOPMENT OF ION SCATTERING SPECTROMETRY

The origin of scattering experiments has its roots in the development of modern atomic theory in the early 20th century. As a result of both the Rutherford experiment on the scattering of alpha particles by thin metallic foils and the Bohr theory of atomic structure, a consistent model of the atom as a small massive nucleus surrounded by

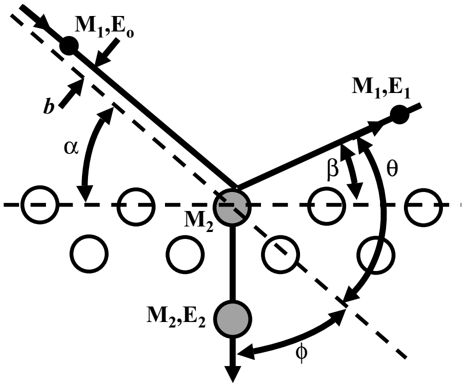

FIGURE 1.3. Atomic collisions illustrating scattering and recoiling from a surface. The angles are: incident (α), exit (β), scattering (θ), and recoiling (ϕ) angles. M_1 and M_2 are the masses of the projectile and target atoms, respectively, E_o is the initial energy of the projectile atom, E_1 is the energy of the projectile atom after scattering, and E_2 is the energy of the recoiled target atom. p is the impact parameter.

a large swarm of light electrons was confirmed. It was then realized that the inverse process, namely analysis of the scattering patterns of ions from crystals, could provide information on composition and structure. This analysis is straightforward for atomic collisions in the keV range because the kinematics of the event are accurately described by classical mechanics. Such scattering occurs as a result of the mutual coulomb repulsion between the colliding atomic cores (i.e., the nucleus plus core electrons). The scattered primary atom loses some of its energy to the target atom which, in turn, recoils into a forward direction as shown in Figure 1.3. Here, M_1, E_o, and E_1 are the mass, initial kinetic energy, and final scattered energy of the projectile atom, M_2 and E_2 are the mass and recoiled energy of the target atom, and p is the impact parameter of the collision. The final energies of the scattered and recoiled atoms and the directions of their trajectories are determined by the masses of the pair of atoms involved and the closeness of the collision.

In the early 1960s it was shown[2,3] that a clear correlation existed between the energy loss of a scattered ion and the type of surface atoms. Low energy (1–10 keV) ion scattering spectrometry had its beginning as a modern surface analysis technique in the late 1960s with the work of Smith[4] and of researchers in the former Soviet Union. The latter work has been thoroughly reviewed in books and review articles.[5–8] In the following 30 years it has been clearly demonstrated, as noted in the extensive reference list of this book, that direct surface compositional and structural information can be obtained from ISS.

Various names and acronyms have been used for ion scattering spectrometry. The terms ion scattering spectrometry (ISS) and low-energy ion scattering spectrometry (LEIS) are general names. More specific names include TOF scattering and recoiling spectrometry (TOF-SARS),[9] scattering and recoiling imaging spectrometry (SARIS),[10] and impact collision ion scattering spectrometry (ICISS).[11]

1.5. OTHER TYPES OF ION SPECTROMETERIES

There are two types of ion spectrometeries that are related to ISS. These are secondary ion mass spectrometry (SIMS) and Rutherford backscattering spectrometry (RBS). SIMS[12] derives its information from the sputtering process. When primary ions penetrate into the solid, they undergo a sequence of collisions. During each of these collisions, target atoms can be put into motion. These recoiling atoms also generate new collisions, and collision cascades develop in the solid. The cascades develop nearly isotropically so that energy and momentum can be transferred back to surface atoms. If this transfer is sufficient, secondary particles (i.e., atoms, molecules, and fragments in neutral, positive, and negative charge states) are emitted; this is the sputtering process.[13] The energy deposited into the electronic system of the target atoms can also contribute to emission of secondary particles.[14] The energy distribution of sputtered secondary particles is broad and peaked at low energy ($\sim$10–30 eV) so that they are in a different energy and TOF range from the scattered and recoiled particles with keV energies.

RBS differs from ISS in that it uses ion beams in the MeV energy range. These high-energy ions penetrate deeply into materials, and the dominant energy loss is by electronic interactions rather than atomic collisions.[15] The ions lose their energy continuously along straight-line trajectories in the material. Since the kinetic energies are so high, only the large repulsive potentials encountered in near direct head-on collisions with target nuclei result in backscattering. This results in small backscattering cross sections of $\sim 10^{-5}$ nm^2 compared to ISS, where scattering cross sections are of the order $\sim 10^{-3}$ nm^2.

1.6. FEATURES OF ION SCATTERING SPECTRA

An ISS spectrum is a plot of the measured intensities of the scattered and recoiled particles versus their kinetic energies or their flight times from the sample to the detector. An energy spectrum is obtained by scanning the range of kinetic energies and plotting the number of particles exhibiting a given kinetic energy (i.e., counts per unit time versus kinetic energy). A TOF spectrum is obtained by pulsing the primary ion beam and measuring the flight times of scattered and recoiled particles from the sample to the detector. Spectra are normally displayed with the ordinate labeled as *count rate, relative intensity,* or *intensity (arbitrary units)*. The latter two designations are sufficient because the absolute count rate is a facet of many complex experimental variables, usually differing from one instrument to another, and is essentially meaningless for any given sample. However, the relative intensities are meaningful and carry information about the elemental composition and structure of the surface. A mass spectrum of the atoms in the surface can be obtained from these spectra by using the kinematic relations to convert the measured energies or TOFs of the scattered and recoiled atoms into masses.

Since the features observed in an ion scattering experiment are a function of the various angles involved in the measurement, it is necessary to specify all of the angles

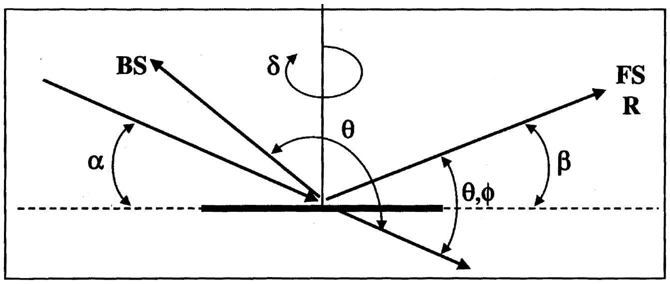

FIGURE 1.4. Definition of the various angles and terms used in ion scattering spectrometry. BS, backscattering; FS, forward scattering; R, recoiling; α, ion beam incidence angle with respect to the surface; β, exit angle; θ, scattering angle; ϕ, recoiling angle; δ, azimuthal angle of the crystal.

involved in the measurement in order to be able to identify the spectral peaks observed. The definitions of the various angles involved in a typical experiment are shown in Figure 1.4. Examples of simulated ion scattering spectra plotted with energy axes and TOF axes are shown in Figures 1.5 and 1.6. The figures exhibit spectra obtained with two different projectile atoms (i.e., He^+ and Ne^+) and two different scattering

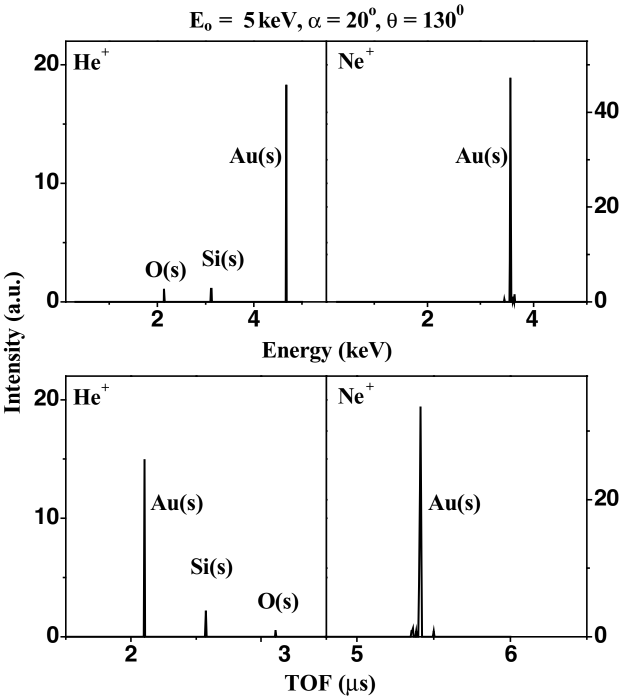

FIGURE 1.5. Examples of simulated ion scattering spectra for 5-keV helium (He^+) and neon (Ne^+) scattering from a surface composed of a random distribution of hydrogen, oxygen, silicon, and gold (H, O, Si, and Au) atoms at a backscattering angle of 130°. The scattering peaks are denoted by (s). TOF, time-of-flight.

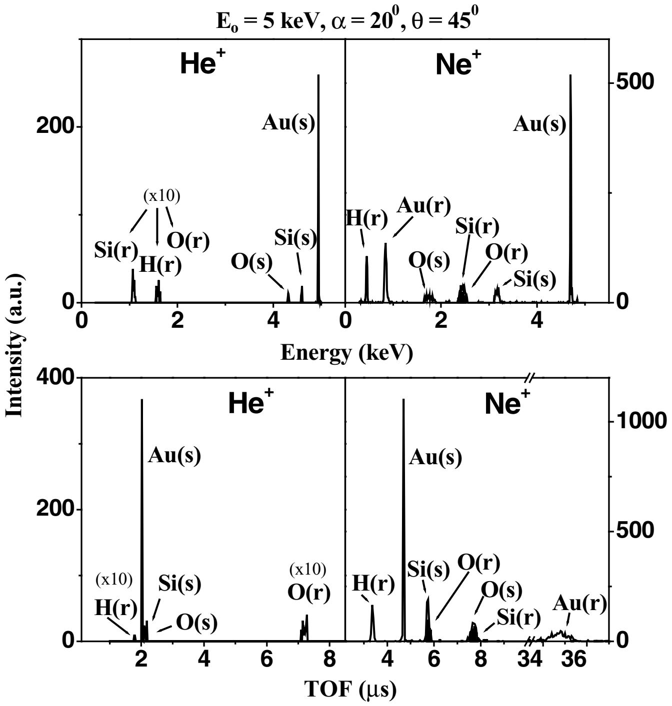

FIGURE 1.6. Examples of simulated ion scattering and recoiling spectra for 5-keV He^+ and Ne^+ scattering from a surface composed of a random distribution of hydrogen, oxygen, silicon, and gold (H, O, Si, and Au) atoms at a forward-scattering angle of 45°. The scattering and recoiling peaks are denoted by (s) and (r), respectively. TOF, time-of-flight.

angles (i.e., 130°, back scattering, and 45° forward scattering), using projectile ion energies of 5 keV. The backscattering spectra exhibit only scattering peaks, while the forward scattering spectra exhibit both scattering and recoiling peaks. The most intense features in all of the spectra are the peaks corresponding to scattering of the primary ion from Au atoms. Heavy atoms such as Au have large scattering cross sections, and light ions such as He^+ and Ne^+ retain a large portion of their kinetic energy upon scattering from such a heavy atom, resulting in energetic scattered atoms. Scattering from the light atoms O and S results in low-intensity peaks due to their low scattering cross sections.

When the yields of scattering or recoiling atoms, such as in Figures 1.5 and 1.6, are plotted as a function of the ion beam incident (α), exit (β), or crystal azimuthal (δ) angles, peaks and valleys are observed. These features are related to the shadowing and blocking features from neighboring atoms. Since these effects can be directly calculated from Newtonian mechanics, these angular anisotropies can be directly related to the relative positions of atoms with respect to each other near the surface. The shadowing and blocking effects have a range of ~1 nm. As a result, ion scattering spectrometry requires only short-range order to obtain structural information.

The number of experimental variables available in an ion scattering experiment is large. These variables are as follows: (1) incident projectile ion (i.e., mass and atomic number); (2) incident projectile ion energy; (3) incident angle (α) of the ion beam with respect to the surface; (4) crystal azimuthal angle (δ_1) that is aligned with the ion beam; (5) scattering angle (θ); (6) exit angle (β) of scattered or recoiled particles; (7) energies of the scattered and recoiled atoms; and (8) crystal azimuthal angle (δ_2) that is aligned with outgoing scattered or recoiled atoms. For most experimentalists, it is not possible to explore all of this multidimensional parameter space due to limitations imposed by the experimental apparatus. A typical experiment usually measures the scattering and/or recoiling intensity as a function of α, β, or δ while the remaining parameters are fixed. However, recent developments[16] in large-area position-sensitive detectors have made it possible to collect the spatial intensity distributions of scattered and recoiled atoms over a large range of angular space. Such data sets allow direct observation of the focusing, shadowing, and blocking patterns, providing a rich data set for structural analysis.

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