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Characterization of Semiconducting Materials

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Since scanning probe microscopy (SPM) enables characterizations of surface structures, dynamical processes, and electronic states of semiconductor crystals in atomic scale, SPM is now widely used not only for academic research but also for applications to device fabrication. However, SPM has some weak points as a characterization tool for semiconductors. First, SPM is quite surface-sensitive, which means, reversely, that it is difficult to obtain the information of interior of semiconductor crystals. Even several atomic layers below the surface are hardly detected by SPM in many cases. Second, since the tips/cantilevers are scanned mechanically over the sample surface, time resolution in imaging is insufficient in some cases. Third, although SPM has very high spatial resolution, it is not suited to analysis of large areas such as the whole area of a wafer. Fourth, in spite of the atomic resolution, SPM basically cannot identify the species of individual atoms. Despite of these faults, however, SPM is widely utilized for semiconductor characterization in various ways as shown in Fig. 18.1. This is wholly owing to the atomic resolution of SPM and some new methods developed to partially avoid the faults mentioned earlier. Further improvements in mechanical parts as well as electrical aspects of SPM will be possible and necessary for specific purposes as described later.

18.1 Characterization of Semiconductor Surfaces

It is now routinely possible by SPM to directly image the surface reconstructions, domain structures, atomic steps, surface roughness, atomic vacancies, and adsorbed atoms and molecules, etc. at atomic resolution. And, “in vivo SPM” is also developed, in which dynamical changes of atomic structures during crystal growths, nanostructures formation, and chemical reactions are in situ observed [1]. By using scanning tunneling spectroscopy (STS) and conductance imaging method (so-called $\mathrm{d}I/\mathrm{d}V$ imaging), furthermore, analysis of electronic structures is also routinely possible with atomic spatial resolution. The SPM has been recently utilized to directly image electric current paths in

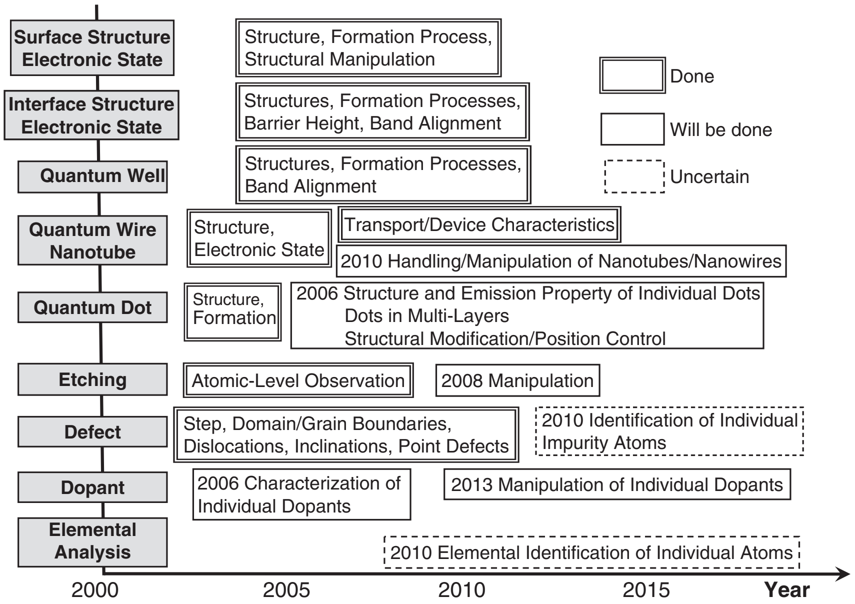

Fig. 18.1. Present status and future prospect about semiconductor characterization by SPM

mesoscopic scales [2] and electron wavefunction [3]. Thus, the SPM can now satisfy almost all requirements of structure analyzes of static and stationary states. However, for lack of time resolution in SPM observations, the SPM does not suite for dynamical analyzes of temporally fluctuating structures and electronic states; the images should be interpreted with aid of theory and assumptions in some cases [4]. To overcome the limit of time resolution in SPM imaging, however, a method is developed in which structural fluctuations are detected in real time as variations in tunneling current by fixing the tip at a specified point, without scanning for imaging [5]. Another method, so-called "atom tracking method," is also developed to trace the diffusion of a targeted atom on a surface at real time, in which the scanning area is limited only near the targeted atom [6]. Both methods, however, can reveal the dynamical phenomena only partially in limited ways and sometimes irritatingly beside the point. On the other hand, high-speed SPM is also developed in which a frame of image is taken on the order of ms, the details of which are described in Chap. 14.

In addition to the imaging of atomic and electronic structures, the SPM is utilized to measure the electrical characteristics of semiconductors. Some examples have been demonstrated; electrical conductivity measurements by four-tip scanning tunneling microscope (STM) (see Chap. 12), by point contact method [7], and by scanning potentiometry by a single-tip STM [8], band bending measurement by using photovoltage phenomenon with light shining during STM observation [9], and so on. These methods can reveal the electrical properties of semiconductor surfaces with high spatial resolution, but we should say that the results are not yet fully utilized for improvements in performance of semiconductor devices as well as for exploring new physics in nanometer scale. In order to break the frontiers of nanoscience, we need to find suitable sample structures as well as to improve the SPM capabilities.

18.2 Characterization of Semiconductor Interfaces

Although the surface phenomena are very important for semiconductor processes such as thin crystal growths and etching, many of the functions of semiconductor devices come from the interface at, e.g., heterojunctions. Therefore, it is quite important to analyze the structures and properties of such buried interfaces. Although, unfortunately, the SPM does not suit well for this purpose, some trials are made. By cleaving semiconductor crystals having quantum well structures and superlattice structures, the SPM is employed to observe the cleaved surface and analyze the band offsets at the heterojunctions [10]. But when the crystal is cleaved and the heterojunctions are exposed to the surface, the band bending can change in some cases. So we need some complementary measurements by other techniques for reliable analysis.

One of the most important features for the semiconductor heterojunctions may be roughness at the interface. The device properties depend on whether the interface is atomically abrupt and smooth. But the SPM is not able to analyze the buried interface roughness at atomic scale in the in-plane direction. Although one of the SPM-derived techniques, ballistic electron emission microscope (BEEM), can reveal the spatial distribution of Schottky barrier at metal–semiconductor interfaces, the interpretation of data is not straightforward in usual cases. Since imaging and analysis of buried interfaces are one of the challenges for the future SPM technology, we may need to combine the SPM with some other techniques such as tomography and magnetic resonance imaging.

18.3 Characterization and Manipulation of Semiconductor Nanostructures

When the size of semiconductor devices is reduced to be on the order of nanometers, comparable to the Fermi wavelength of conduction electrons there, quantum phenomena appear due to the confinement and correlation effects of electrons. We can expect novel functions and properties from such nanostructured semiconductors, and high-speed and low-energy-dissipation devices can be fabricated. For the research along this direction, we need to measure the electrical, magnetic, and optical properties of individual nanostructures, not the averages of assemblies of the nanostructures. For example, it is strongly required to measure band alignment of individual quantum wells, conductivity, and electronic state of individual quantum wires, quantized energy levels and light-emission property and magnetization of individual quantum dots, and so on. Some of them are already done by the SPM techniques. These quantum structures are so small that the SPM can wholly probe the properties. Light emission spectra from individual quantum dots, for example, are directly measured by STM-induced photon emission spectroscopy (see Chap. 8) and near-field optical microscope (NSOM) (see Chap. 4). It has been revealed that the emission property is actually affected by the dot size/shape and interface conditions between the substrate. Atomic structure, chirality, electronic states, and electrical conductivity of individual carbon nanotubes are measured by STM/STS and by two-terminal method using multitip STM [11, 12].

In addition to characterizations of structures and properties of semiconductor nanostructures, the SPM is utilized to manipulate and control the formation processes of nanostructures and also to handle them. Stimulation by tunneling current from an STM tip is utilized to initiate the nucleation of quantum dots at specified positions [13], and also to initiate a chain reaction of polymerization [14].

While, as mentioned so far, great progress has been made in the uses of SPM techniques for characterization and manipulations of semiconductor nanostructures, there remains a lot of issues to be solved. For example, we yet cannot separate semiconducting carbon nanotubes from metallic tubes. We cannot position individual carbon nanotubes at specified positions, either. The SPM may not be suitable for integration of nanostructures as well as mass production of nanostructures. The SPM techniques will be used only for producing a kind of mold which will be used afterward for integration and mass production of semiconductor nanostructures. Thus, it will be important not only to improve the SPM techniques, but also to find the structures and fabrication processes in which the SPM can show the merits.

18.4 Characterization of Defects in Semiconductors

There are a variety of defects on semiconductor surfaces, such as steps, grain/domain boundaries, point defects like vacancies and adatoms, penetrating dislocations, and so on, which are easily observed by SPM. These defects play important roles in oxidation, etching, chemical reactions, and crystal growths. Furthermore, they affect life time and scattering of carriers near the surface, which in turn determine the transport and light emission properties. Although we can know the position, distribution, and density of defects from SPM observations, it is quite rare to demonstrate the influence of defects on the properties by SPM. The SPM must be useful to analyze how much the individual defects shorten the carrier life time and how much electrical resistance the individual defects produce. Four-tip STM has been used to measure the resistance produced by a single monatomic step on an Si crystal surface [15]. Such applications of SPM to measure the properties should be more explored. It will be necessary for this purpose that SPM measurements should be done with changing the environment conditions such as temperature, magnetic/electric fields, light illumination, current flowing through the sample, and under device operation.

The most important defect in semiconductors is impurity dopants. Individual dopant atoms at subsurface region are imaged by STM as standing waves around them [16]. But it is generally impossible to image the dopant atoms in semiconductor crystals. We yet cannot identify the atomic species of individual dopants, either. For this purpose, we need some improvements of STS techniques combined with section imaging techniques.

18.5 Characterization of Semiconductor Processes

Surface reactions such as crystal growths, oxidation, etching, metal film condensation, and silicide formation play main roles in the processes of semiconductor device fabrication. The SPM is used to observe the atomistic phenomena in these processes, and the results are utilized to optimize the conditions in the processes and subsequently improve the device performance. Local chemical reactions such as oxidation and etching can be induced by SPM probes. But the ultimate control of the process like doping of individual dopant atoms in semiconductor crystals with controlled manners is not yet done. The SPM may have potentiality for such atomistic controls.

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