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Invited

Use of Synchrotron Radiation for Solid-State Devices and Materials Study

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Major applications of synchrotron radiation are reviewed to encourage its use for study of electronic materials and devices. It is important to identify the impurity atom and crystallographic defect as origins of electronic structure of materials. From this point of view, main techniques for bulk and surface characterization utilizing the advantage of synchrotron radiation are described. Possibilities of its industrial use in the future are also referred.

§1. Introduction

In the past decade, research with synchrotron radiation (SR) has grwon dramatically in various fields such as physics, chemistry, mineralogy, biology, and medical science. Its industrial use has now begun. Let us first look at activities at the synchrotron facility "Photon Factory" in Tsukuba; 117 experiments were proposed from universities and national research laboratories in the first half of 1985, and only 6 of them were subjects related to electronics. Experiments for electronic materials and devices were carried out mainly by investigators from industry. In 1984, a beam time of 1125 hours was allotted to 36 experiments proposed from industry (with charge); 2 of them were for lithography, 2 for fundamental experiments for photochemical vapor deposition, 5 for observations of dislsocation motion in semiconductor crystals, 6 for trace impurity analysis, 13 for EXAFS (Extended X-ray Absorption Fine Structure) for amorphous and catalisis materials. Now three beam lines from the electron storage ring were under construction by three industrial companies. Applications of SR are expected to begin in earnest. The purpose of this paper is to encourage use of SR by reviewing its major applications.

§2. Properties of Synchrotron Radiation

When the path of a very fast ultrarelativistic electron is bent by a strong magnetic field, it emits radiation.[1] This phenomenon was first discovered with a 70 MeV synchrotron in 1947, and since then the radiation is called synchrotron radiation (SR). It has outstanding properties: (1) Continuum from the infrared to the x-ray region, (2) High intensities with high degree of collimation (~1 mrad to 0.1 mrad), (3) Polarization in the plane of orbit, and (4) Pulse structure (fwhm: a

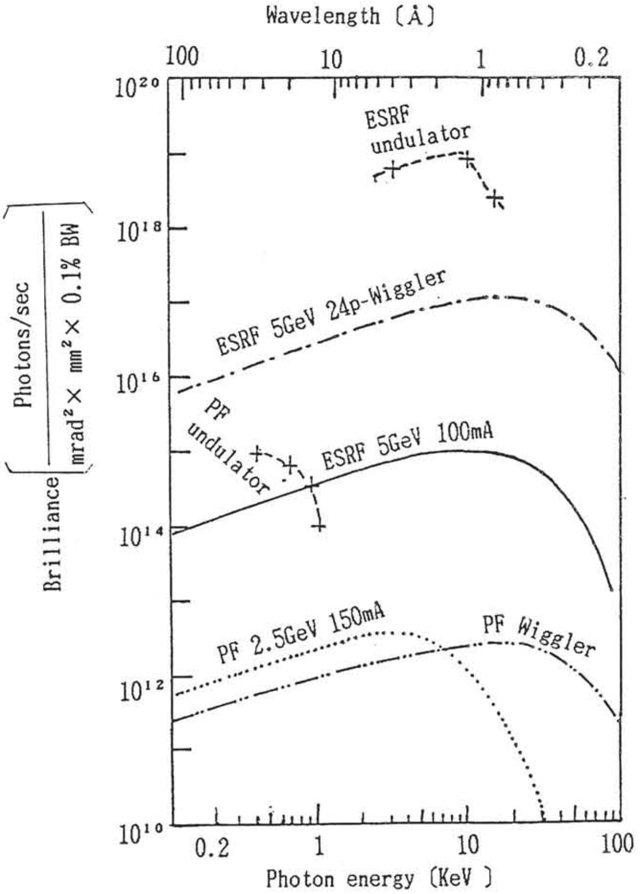

Fig. 1. Spectral distribution of brilliance for the Photon Factory (2.5 GeV) bending magnet, vertical wiggler, and undulator. For comparison, the future plan of the Europian Synchrotron Radiation Facility (ESRF) as a project of thr European Economic Community is shown by the calculated brilliance for the bending magnet, 24-pole wiggler, and undulator on the newly designed 5-GeV storage ring.

few ps to several 100 ps). These properties enable measurements with high resolution in time, space, momentum, and/or energy. Both stroboscopic measurement employing the pulsed nature and continuous observation have been carried out to investigate change in property and structure of matter[2]. Spatial variations in property were also measured with a very finely focused spot. SR provides an ideal source not only for spectroscopic study of matter but also for microscopy and diffraction experiments.

The future trend in SR facilities involves the construction of new electron storage rings (5 GeV) designed to maximize the brightness of radiation from insertion devices, undulators and multipole wigglers.[3] Such rings offer brightness increases by factors of from 50 to more than 100 over the best SR sources available today, as seen from Fig. 1. Such facilities will enable new types of experiments as well as great improvement in resolution of measurements.

§3. Characterization of materials

Electronic structures of various semiconductor crystals have been investigated extensively. However, it is very important but not easy to identify the impurity atom and/or crystallographic defect as their origins. For such purposes, x-ray fluorescence analysis and extended x-ray absorption fine structure measurement are now useful by use of SR.

Trace impurities often change mechanical, electical, and optical properties of semiconductor crystals, as seen from some examples such as nitrogen and oxygen in Si. These impurities even with trace amount also acts as nucleation centers for clustering of point defects in Si. Compound semiconductor crystals such as GaAs are behind silicon crystals and are expected to contain trace impurities. Using SR, non-distructive analysis of impurity in ppb levels is now possible by the x-ray flourescence method with effective exitation of wavelengths near the absorption edge selected by a band-pass filter.[4] It is possible to analyse an area as small as 1 um^2. The detection limit is 10^{-12} g.

At photon energies above the absorption edges of atoms constituting specimens, the extended x-ray absorption fine structure (EXAFS) is observed by interference effects in the scattering of the ejected core electron and gives information concerning the local geometry of the absorbing atom:[5] The distance between the neighboring atoms can be determined in an accuracy of 0.1 to 0.01 A from the periodic variation in absorption. This technique can be applied for amorphous, liquid, and gas states as well as crystalline states.

EXAFS was applied to investigation of atomic configuration in III-V semiconductor mixed crystal systems. The atomic distances for Ga-AS and In-As in a $Ga_{1-x}In_xAs$ system were found to be greatly different from the average distance based on the virtual crystal approximation (Vegard's law), i.e., Ga and In atoms are distributed in bimodal distribution.[6] Similar results were obtained for a GaP_xAs_{1-x}[7] and $In_xGa_{1-x}As_yP_{1-y}$ system[8]. The EXAFS profile observed for the latter system indicates that anions around In atoms are disordered.[8] Such disorder has been assumed to interpret the broad DLTS profiles observed for the $In_xGa_{1-x}P$ system.[9] This is a good example to demonstrate the capability of EXAFS with SR for identifying origin of electronic system.

X-ray topography with SR makes dynamic observation of crystal imperfections such as dislocations with high resolution easy. An x-ray sensing TV camera employing an amorphous photoconductive layer was developed for this purpose, and with a resolution of 6 um was achieved, as seen from Fig. 2. This camera has been used for observation of phase transition of quartz and magnetite, melting processes of GaAs and Sn, and motion of magnetic domains in Fe-3%Si crystals.[10]

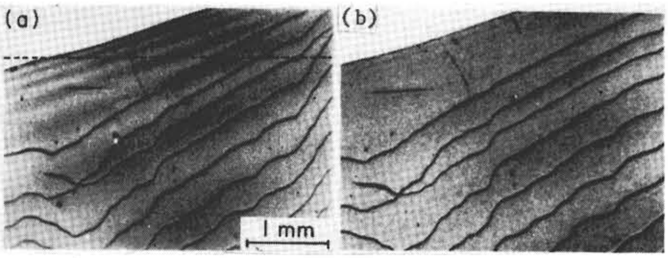

Fig. 2. X-ray diffraction topographs of a Si wafer. (a) image by the high-resolution TV camera tube having the amorphous Se-As photoconductive layer. (b) Topograph recorded with a nuclear plate by the conventional fine-focus X-ray generator.

§4. Characterization of surfaces

Characteristics of electronic devices strongly depends upon the nature of semiconductor surfaces, and we need techniques which can identify the crystallographic structure, chemical composition, and electronic structure of surface layers. To study surface structure, LEED (low energy electron diffraction) has been widely used. However, interpretation of its diffraction patterns is complicated because of the strong multiple scattering of electrons. Recently surface structure has been studied successfully by x-ray diffraction in a grazing incidence geometry[11]; the data obtained can be interpreted easily by kinematical treatment. Using SR, structure of reconstructed surface monolayers has been determined.[12] It was pointed out that this x-ray method will be capable for investigating interface structure such as silicide layers-silicon, metal-insulator-semiconductor, and superlattices by penetrating power of x-rays.

To investigate the chemical composition of surface layers, Auger electron spectroscopy and x-ray photoelectron spectroscopy have been used extensively.[13] By employing a SR source and spectrometer, photoemission spectroscopy offers a tunable surface sensitivity and has been applied to characterization of interfaces such as MES.

Electronic band structure of semiconductors is now measured by angle resolved UV photoelectron spectroscopy (ARUPS) using SR sources as a standard method. This technique may be applied to study on electronic structure of films such as superlattices.

Using SR, x-ray fluorescence, photoelectron diffraction, and surface EXAFS have also become powerful tools to investigate adsorbed atoms on semiconductors.

EXAFS Profiles can be obtained by measuring the total amounts of fluorescent x rays, secondary electrons, Auger electrons, or dissociated ions from the specimen surface excited by absorbed x rays. The spectra give geometrical information on the location of the species in the surface layer, depending upon the escape depth of the electrons or x rays. This technique has been referred to as "surface EXAFS".[5] In particular, it can be applied to disordered surfaces and has been used to probe gases such as Cl_2 and O_2 adsorbed on silicon surfaces.

In-situ characterization of surfaces in crystal growth such as molecular beam epitaxy may be possible by these techniques.

§5. Industrial use

Lithography with SR was first made in 1976.[14,15] Patterns of 0.1 um lines and spaces has been obtained easily by soft-x-rays with high degree of collimation from a SR source.[16] For practical use of this technique in future VLSI, high precision of mask alignment must be obtained. As mentioned previously, x-ray fluorescence analysis with SR has so high sensitivities that impurity in a small area can be detected. This technique may be promissing in achieving precision of mask alignment required.

Applications of photo-chemical reaction to VLSI processing such as photo-CVD and photo etching have been investigated extensively.[17] For this purpose, photon energies around 10 eV are required, and discharge lamps (Ar, H_2) and excimer lasers were used. However, strong effects on chemical reaction have been observed when electrons in inner shells of the atoms were excited by soft x-rays with energies of 0.1 to 1 keV. To examine the possiblity of SR, preliminary work is under way.

As seen from the above examples, we may expect the possibility that SR will be used for industrial production lines as well as characterization of materials and devices. To use SR in factories, a compact synchrotron accelerator (COSY) has been developed using superconducting magnets.

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