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Semiconductor Surface Characterization by Total Reflection X-Ray Fluorescence Analysis

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Surface sensitive X-ray fluorescence analysis has been developed using synchrotron radiation. The angular dependence of the fluorescent X-rays from impurity atoms was analyzed both qualitatively and quantitatively. It is shown that the profile of the angular dependence of the fluorescence X-rays near the critical angle reflects the concentrational distribution along the depth. It is also shown that careful analysis is needed for the determination of the trace element concentration.

1. Introduction

The development of analytical methods sensitive to the surface of the material is vital as a result of recent advances both in technology and material science. X-ray fluorescence (XRF) analysis is widely used for the non-destructive elemental determination, but the depth analyzed spreads over the escape depth of the fluorescent X-rays, typically from um to mm.

Recently the external X-ray reflection or the grazing incidence condition is widely used for the surface characterization in various research fields. For XRF analysis, two types of experiments have been done to develop surface sensitive XRF using X-ray total reflection phenomenon: One was the determination of trace elements in solution by energy dispersive X-ray fluorescence in which an X-ray mirror was used as a sample support[1,2]. This method was also applied to analysis of trace impurities at the surface of the silicon wafer[3]. Another application of the external X-ray total reflection is the depth profiling. The analysis of the air-liquid interface of the dissolved polymer was done by Bloch et al.[4]. Applications to the semiconductor materials were also made[5,6,7].

In this presentation, typical examples of angular dependences of the XRF intensities from semiconductor materials are compared in detail and the procedure for qualitative and quantitative analysis is discussed.

2. Experimental

The experiments were carried out using synchrotron radiation at the Photon Factory. Fig.1 shows the side view of the typical experimental arrangement. Synchrotron X-rays were monochromatized by the silicon (111)

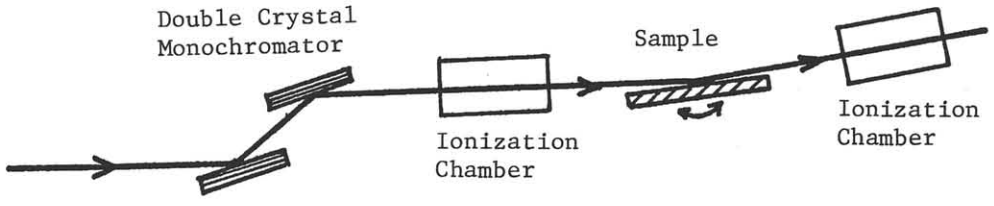

Fig.1 Experimental arrangement for the total reflection X-ray fluorescence analysis using synchrotron radiation.

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crystal. The energy of the X-ray beam was fixed at the energy which is high enough to excite the analyte elements. The sample was mounted on a diffractometer. The X-ray intensities of the incident and the reflected beams were monitored by two ionization chambers. The XRF intensities were measured by a Si(Li) detector as a function of the glancing angle. The detail of the experimental procedure was described elsewhere.

The three samples used were mirror polished semiconductor wafers: 1) The Ga diffused Si wafer after deposition process. The Ga precipitation was formed at the surface. 2) The InP wafer in which Ga and As contamination layer is formed at the surface during the liquid phase epitaxy process. 3) The As ion implanted Si wafer where the projection range of implanted atoms is about 500 A. These samples have different impurity distribution along depth and were chosen so as to demonstrate the difference in the angular dependence of the XRF intensity. The details of the process condition of each sample were described elsewhere[5)6)].

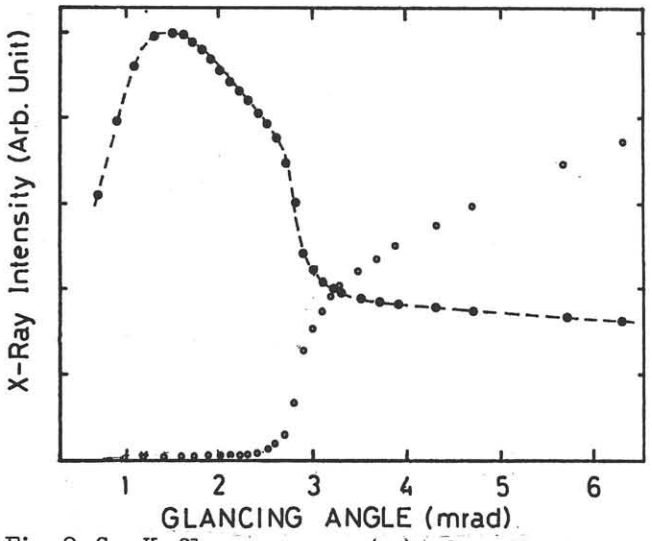

Fig.2 Ga K fluorescence (●)and reflected X-ray (○) intensities from Ga diffused Si as a function of the glancing angle. The excitation energy was 11 keV.

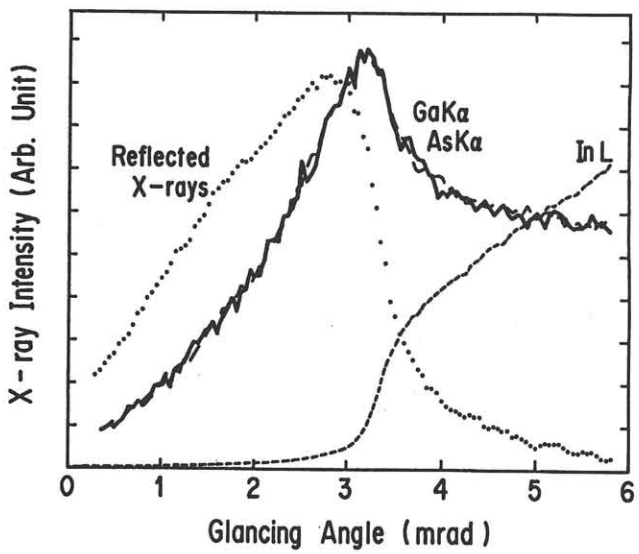

Fig.3 Intensities of reflected X-rays, Ga Ka, As Ka and In La fluorescent X-rays from a processed InP substrate. The excitation energy was12.6 keV.

3. Result

Fig. 2 - 4 show intensities of the reflected X-rays and the XRF from analyte elements and from the major elements of the bulk material as a function of the glancing angle. The glancing angle in each figure is determined by adjusting the rise point of the bulk (major element) fluorescent signal to the calculated critical angle. XRF intensities below the critical angle is stronger than that above the critical angle

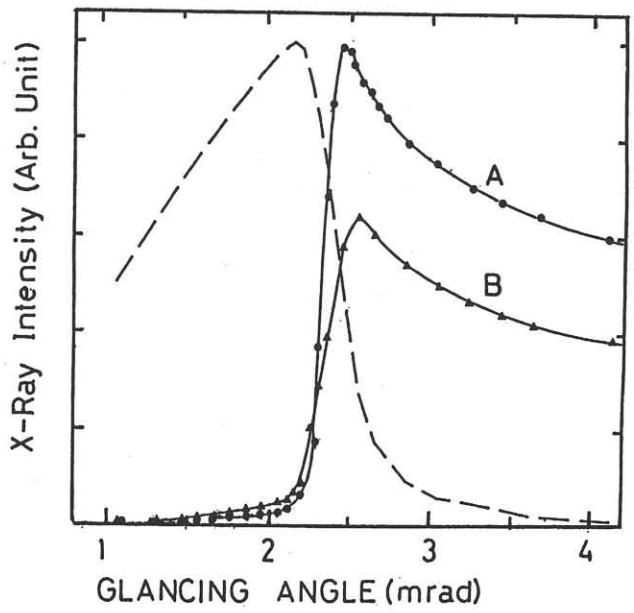

Fig.4 As Ka fluorescence (● and ▲)and reflected (broken line) X-ray intensities for As ion implanted Si wafers before (A) and after (B) annealing.

in Fig. 2, while XRF intensities has maximum at around the critical angle in Fig.3 and 4.

4. Discussion

In order to analyze the angular dependence of the XRF intensity (I), the surface intensity of X-rays (M), the X-ray penetration depth (d), and the reflectivity were calculated for the Si substrate with 13 keV incident X-rays according to the following equation and is shown in Fig. 5.

$$I(\theta) \propto M(\theta) \int \exp(-t/d(\theta)) \cdot f(t) \cdot dt$$

where f(t) is the concentration profile of the analyte element along the depth, and t and θ are the depth from the surface and the glancing angle respectively. The enhancement of the surface X-ray intensity at the critical angle is attributed to the standing wave formed above the surface due to the interference between the incident and the reflected X-rays.

From above equation, the following qualitative interpretation of the angular dependence of the XRF intensity is made. The XRF intensity below the critical angle reflects the concentration profile less than a hundred angstroms from the surface, while the intensity above the critical angle reflects the concentration more than a few thousand angstroms. When f(t) is constant for all t, I(θ) is proportional to M x d.

When f(t) is non-zero only at the surface, I(θ) is proportional to M, i.e. I(θ) has a sharp maximum at the critical angle.

From above consideration, it is easily concluded that the impurities are localized at the surface for Fig.3 and spread deeper from the surface for Fig.4. For Fig.2, however, XRF profile is different from other profiles. In this case, the sample is considered to be the layered structure and the significant enhancement of the XRF intensity at the surface occurs. For the more complicated layered structure, for instance, the interference effect is dominant over the XRF intensity profile and is shown in Fig.6. This situation is sometimes observed even for the layered semiconductor structure such as Si/SiO_2. Detailed analysis is needed for depth profiling.

The trace element analysis in solution[1)2)] and the surface contamination measurement of the semiconductor wafer[3)] correspond to above examples. The absolute XRF intensity is very sensitive to the distribution of the impurity and the glancing

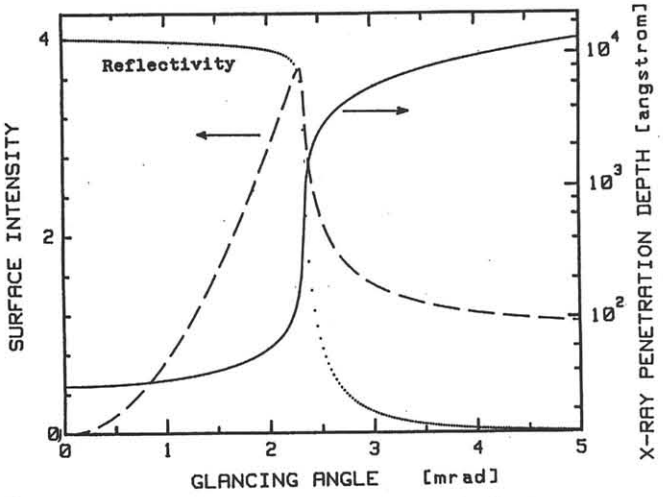

Fig.5 The angular dependence of the X-ray intensity at the surface and the penetration depth of the incident X-rays. The X-ray reflectivity is also shown. Si sample with excitation energy of 13.4 keV is assumed.

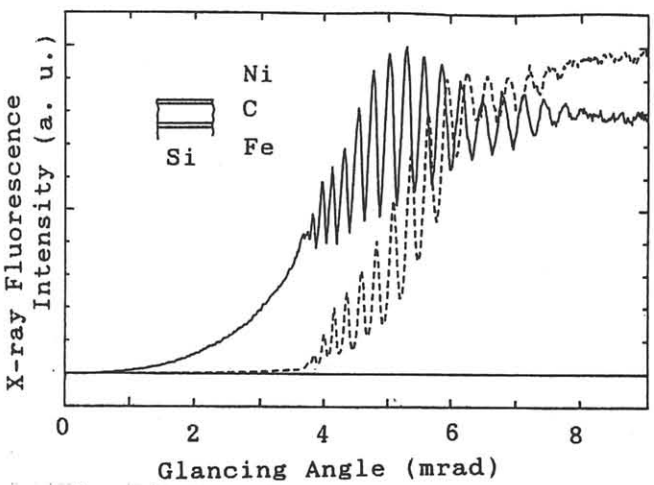

Fig.6 The angular dependence of the Ni K (solid line) and Fe K (broken line) intensities from the Ni(34 A)/C(843 A)/Fe(111 A) film on the Si wafer.

angle, careful analysis is necessary for the determination of the elemental concentration.

To analyze the XRF intensity profile quantitatively, the calculation based on the above equation is needed and fitting procedure is usually adopted. The resolution of the depth profile is mainly limited by the X-ray penetration depth. The resolution is about 10 % except for the region where the X-ray penetration increases abruptly, i.e. from a hundred to a few thousands angstrom.

5. Summary

X-ray external total reflection was used for the impurity depth profiling in the semiconductor. The angular distribution of the X-ray fluorescence intensity were analyzed qualitatively and quantitatively. It is shown that the determination of the depth profile of the trace element in the semiconductor is possible by synchrotron radiation.

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