NEAR-SURFACE ANALYSIS OF SEMICONDUCTOR USING GRAZING INCIDENCE X-RAY FLUORESCENCE

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ABSTRACT

The X-ray external total reflection was used for the x-ray fluorescence analysis of the near surface layer of a GaAs wafer and a GaAlAs epilayer. Synchrotron radiation was used as an excitation source. The intensity ratio between the Ga K and As K fluorescence signals was measured as a function of the glancing angle. The reduction of As atoms near the surface of less than a hundred Å was observed for the high temperature annealed GaAlAs epilayer.

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. Though X-ray fluorescence analysis is a surface technique in the sense that the X-rays being measured are emitted from the finite thickness of the surface, it is usually used for bulk analysis. Since the depth analyzed by X-ray fluorescence spreads over the escape depth of the fluorescent X-rays, typically from μm to mm, the applications of the X-ray fluorescence analysis to surface problems are limited except for the determination of composition and mass-thickness of the thin film[1].

Recently the external X-ray reflection or the grazing-incidence condition is widely used in various fields. For X-ray fluorescence analysis, two types of experiments were done, utilizing the total reflection phenomenon. One was the determination of trace elements in solution by energy dispersive X-ray fluorescence using an X-ray mirror as a sample support[2,3]. This method was also adapted to analysis of trace impurities on the silicon wafer[4]. The improvement in the signal-to-background ratio leads to minimum detection limits of the order of ppb.

Another notable application of the external X-ray total reflection is the study of depth profile near the surface. Depth profiling of As

ions in the silicon wafer was investigated quantitatively and was in good agreement with analysis by secondary-ion mass spectrometry[5]. The analysis of the air-liquid interface of the dissolved polymer was done by Bloch et al.[6]. Qualitative analysis of Hg in SiO_2 grown by photo-assisted chemical-vapor deposition was also made[7]. In these experiments the determination of trace elements was successfully realized using synchrotron radiation as an excitation source.

X-ray fluorescence analysis is also useful for the determination of major and minor elements with precision. In this report, surface compositions of a GaAs wafer and a $Ga_{1-x}Al_xAs$ epilayer were studied using the grazing incidence X-ray fluorescence excited by synchrotron X-rays. In the next section, the principle of grazing X-ray fluorescence analysis for depth profiling is briefly reviewed.

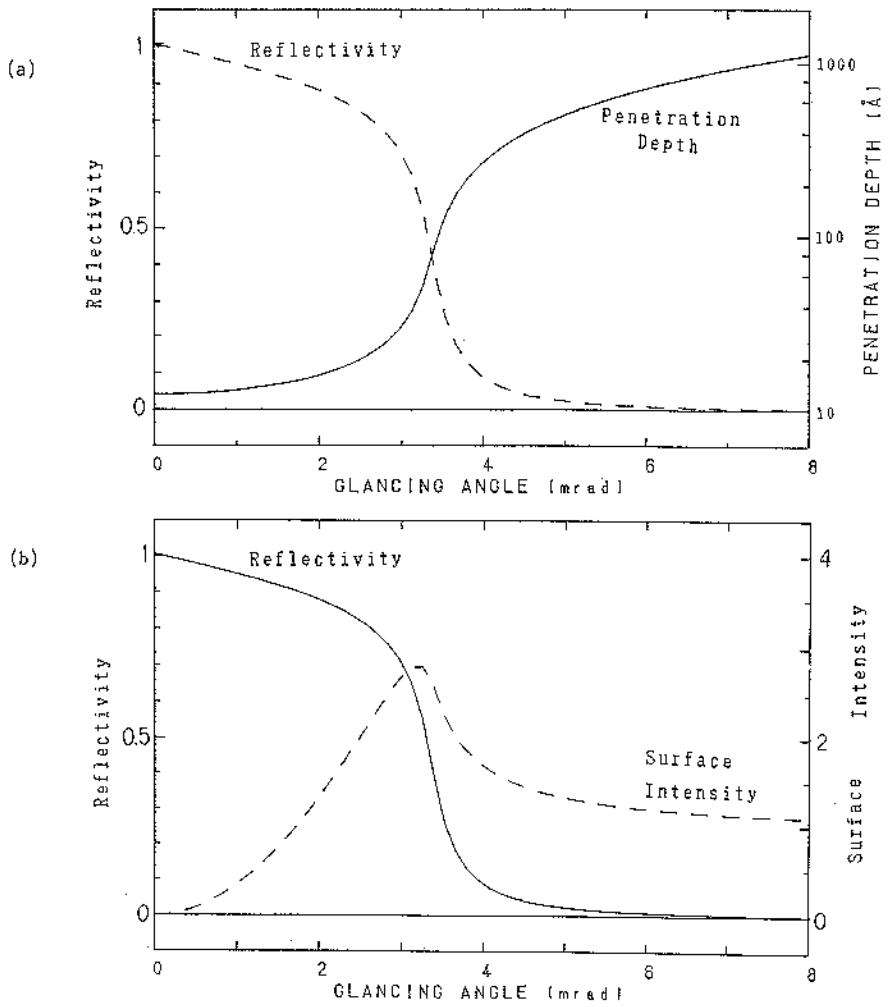

Fig. 1 The calculated angular dependence of the reflectivity and the penetration depth (a), and the surface intensity (b). The GaAs wafer with 13 keV incident X-rays is assumed.

PRINCIPLE OF DEPTH PROFILING

External X-ray total reflection occurs when the collimated beam impinges on a smooth and flat surface of the material with a glancing angle of less than a critical angle, typically a few mrad. Figure 1(a) shows the angular dependence of the reflectivity and the penetration depth for the GaAs substrate with 13 keV incident X-rays. The reflectivity is nearly 1 and incident X-rays are totally reflected below the critical angle of 3.35 mrad. Above the critical angle, the penetration depth is calculated from the absorption coefficient and decreases with decreasing glancing angle. At the critical angle, the penetration depth suddenly decreases, and below the critical angle, it is less than a few tens of Å.

The X-ray fluorescence intensity (I) under the grazing incidence condition is given by the following equations,

$$I(\theta) = I_0 \cdot M(\theta) \cdot \int_0^\infty F(t) \cdot \exp(-\mu(\theta) \cdot t) \cdot dt$$

$$M(\theta) = \frac{4\theta^2}{(\theta + \mathrm{Re}\ (f))^2 + \mathrm{Im}\ (f)^2}$$

$$u(\theta) = 4\pi\ \mathrm{Im}\ (f)/\lambda$$

$$f = (\theta - 2\delta - 2\,i\,\beta)^{1/2}$$

where θ is the glancing angle, I_0 is the intensity of the incident X-rays of wavelength λ, $M(\theta)$ is the X-ray intensity at the surface, $F(t)$ is the variation in the concentration of the analyte element along the depth t, $\mu(\theta)$ is the effective absorption coefficient, and the refractive index of the material is given by $1-\delta-i\beta$. Since the standing wave due to the interference between the incident and reflected X-rays is formed above the surface, the surface X-ray intensity $M(\theta)$ is modulated as shown in Figure 1(b).

EXPERIMENTAL

The experiments were carried out at Beam Line 4A of the Photon Factory (PF). Figure 2 shows the side view of the experimental arrangement. The synchrotron X-ray beam was monochromated by a silicon (111) channel-cut crystal. The energy of the X-ray beam was fixed at 13 keV which is high enough to excite Ga K and As K lines (absorption edges of Ga K and As K are 10.37 keV and 11.86 keV respectively). The dimension of the X-ray beam was made to be 0.1 mm high and 4 mm wide by a slit placed before the sample. The angular divergence in the horizontal direction of the beam passing through this slit was estimated to be about 0.05 mrad. The sample was mounted on a diffractometer with a horizontal rotation axis. The intensities of the incident and reflected beams were monitored by two ionization chambers.

The X-ray fluorescence intensities were measured by a Si(Li) solid state detector as a function of the glancing angle. An inset in Figure 2 shows the arrangement of the Si(Li) detector, which was set at right angle to the incident beam, with a slight inclination to the horizontal plane. A slit was placed between the sample and the detector to avoid the signal from the edge of the sample.

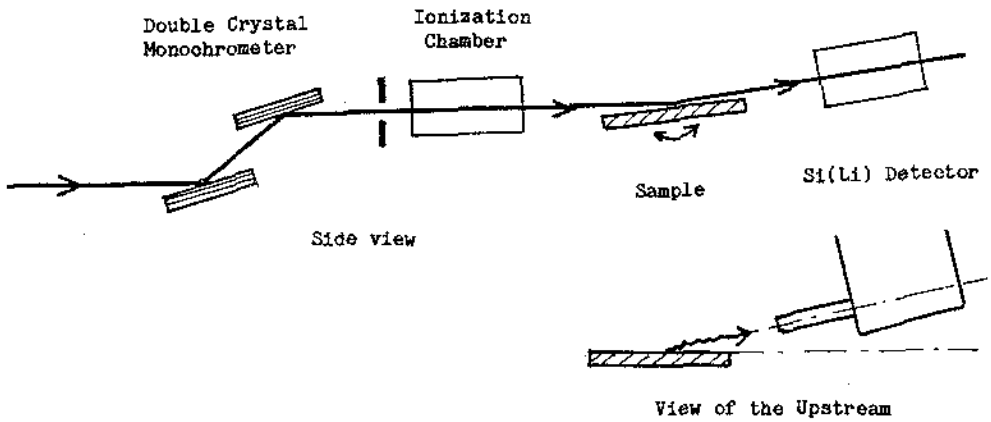

Fig. 2 Experimental arrangement.

A $Ga_{1-x}Al_xAs$ epilayer (x=0.298) was used for the sample. The epitaxial layer 3.5 μm thick was grown on the GaAs wafer by liquid-phase epitaxy using the sliding boat technique[8]. The GaAs substrate is placed on the graphite slider boat in contact with the growth solution of Ga containing Al and As. The growth temperature was about 800°C, and the epitaxial wafer was cooled down to about 200°C after the growth process. A mirror-polished GaAs wafer was also used as a reference material.

RESULTS AND DISCUSSION

Figure 3 shows the reflectivity and the intensities of the X-ray fluorescence signals from the GaAs wafer as a function of glancing angle. The absolute glancing angle is determined by adjusting the rise point of the fluorescence signal to the critical angle, because the penetration depth increases abruptly at the critical angle. The calculation predicts that the reflectivity equals 1 at angles less than the critical angle; the reduced reflectivity observed in the lower angle region is ascribed to the reduction of the effective cross section of the sample at extremely small glancing angles. Since the energy resolution of the Si(Li) detector is poor, Ga Kβ and As Kα lines overlap each other. The three fluorescence

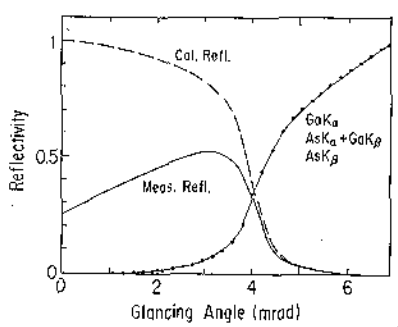

Fig. 3 The reflectivity and the X-ray fluorescence intensities obtained from the GaAs wafer as a function of the glancing angle.

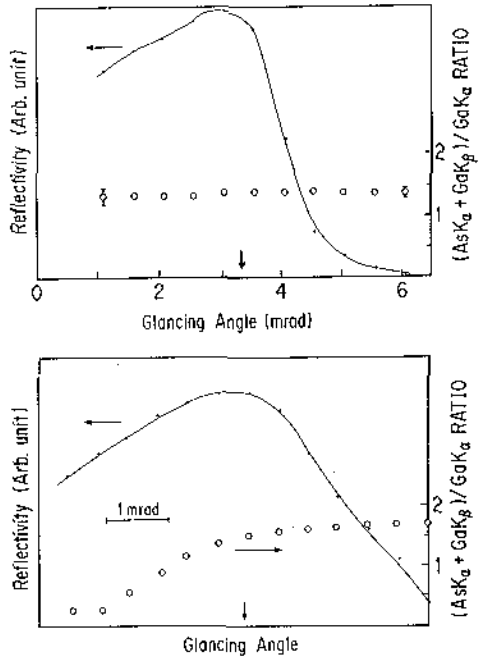

Fig. 4 The angular dependence of the ratio of the X-ray fluorescence intensities and the reflectivity from the GaAs wafer (a) and GaAlAs epilayer (b).

intensities of Ga Kα, As Kα plus Ga Kβ, and As Kβ were measured. All X-ray fluorescence intensities show the same dependence on the glancing angle.

To investigate the angular dependence of the X-ray fluorescence intensities in detail, the ratios of (as Kα + Ga Kβ)/Ga Kα and As Kβ/Ga Kα were plotted in Figure 4. Since the surface of the epitaxial wafer shows the "waves" pattern[8], the reflection curve of Figure 4(b) is rather broad compared to that obtained from the GaAs wafer. From the separation of the direct and reflected beams recorded on the X-ray film, the critical angle was determined and is shown in the figure by an arrow. While the intensity ratio obtained from the GaAs wafer in Figure 4(a) is constant and shows no angular dependence, that in Figure 4(b) decreases at the lower angles. The comparison of the observed Ga K and As K intensities showed that the variation in the ratio in Figure 4(b) was not due to the enhancement of the Ga concentration but was mainly due to the reduction of the As concentration. Since the penetration depth of the incident X-rays is less than a hundred Å in this angular range, the concentration of As atoms is reduced near the surface.

The epitaxial wafer grown by the sliding boat technique is exposed to high temperature during the cooling process after the growth; therefore sublimation of As atoms from the surface and out-diffusion of As atoms may occur.

Before going into quantitative analysis of the surface composition, the effect of the secondary excitation of Ga atoms by the As K lines is

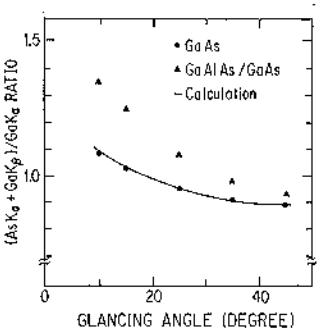

Fig. 5 The fluorescence intensity ratio with a fixed scattering angle of 90 degrees as a function of the glancing angle.

briefly discussed. Figure 5 shows the angular dependence of the fluorescence intensity ratio with a fixed scattering angle of 90 degrees. The solid line shows the calculated intensity ratio[10] and is in good agreement with the experiment for the GaAs wafer. In this angular range, the primary to the secondary fluorescence ratio of the Ga K line is more than 20%. For the extremely shallow penetration of incident X-rays, i.e. the grazing incidence experiment, the contribution from secondary fluorescence is decided by the excitation within a penetration depth and also by the spread of the primary fluorescence from As atoms. Since the effective penetration of the incident X-rays is less than 0.1 μm under the grazing-incidence condition, the variation in the contribution from secondary fluorescence is less than a few % as regards the angular dependence. The Ga secondary fluorescence intensity depends almost linearly on the As concentration. In the following calculation, it is assumed that the contribution from the secondary fluorescence is constant for angular dependence, and depends only on the As concentration.

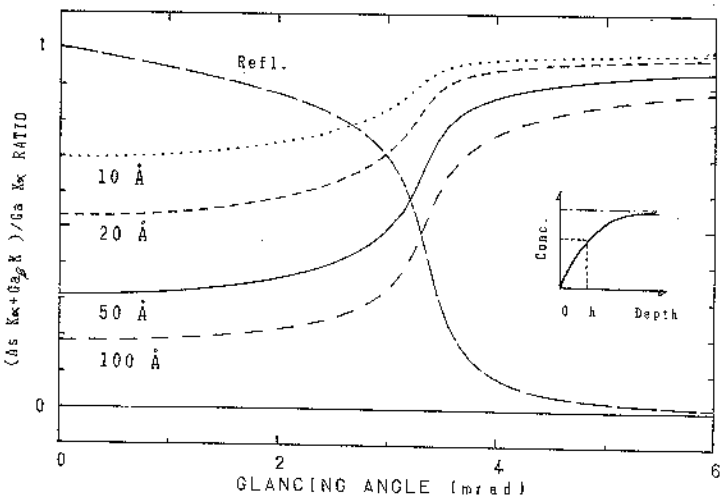

Fig. 6 The X-ray fluorescence intensity ratios are calculated for various exhausted lengths h as defined in an inset.

The calculation was made to evaluate the depth where As atoms are reduced. The model of the As concentration near the surface is shown in an inset of Figure 6, and is the complimentary error function, namely As atoms are totally exhausted at the surface and gradually increase to the bulk concentration. Curves shown in Figure 6 are calculated for the typical width of the exhausted region. Compared to the experimental result in Figure 4(b), the exhausted region is about 100 Å.

Though sublimation of As atoms from the surface during the cooling process is probably the origin of the reduction of As atoms near the surface, the effect of surface oxidation must be also taken into account, especially for the GaAlAs epilayer. If an oxidation layer (mainly aluminum oxide) is assumed at the surface, the exhausted region has different physical meaning other than a simple out-diffusion region. Samples more systematically prepared are needed to determine the surface structure of compound semiconductors. The variation in stoichiometry at the surface of compound semiconductors has been studied mainly by ion channeling and secondary ion mas spectrometry[9], but the present method offers the possibility of nondestructive quantitative analysis of surface stoichiometry.

In summary, grazing-incidence X-ray fluorescence was applied to GaAs and $Ga_{1-x}Al_xAs$ surface analysis. The deviation from the designed composition near the surface was observed. It is suitable to use synchrotron radiation as an excitation source for grazing incidence experiments for the following reasons: (1) Natural collimation of the synchrotron radiation is suitable for experiments with extremely small glancing angle. (2) The energy tunability is suitable for adjusting the incident energy above the absorption edge of the analyte element. (3) The high intensity, of course, is suitable for trace element analysis.

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