Investigation of analyzing depth of N-K absorption spectra measured using TEY and TFY methods

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Abstract. In order to investigate the analyzing depth of N-K absorption spectra measured using the TEY and TFY methods, the spectra of Si$_3$N$_4$ crystals covered with Cr thin films were measured. The thicknesses of Cr films were 1 – 100 nm. The N-K absorption intensity of Si$_3$N$_4$ measured using the TEY method was observed at Cr thickness of less than 3 nm, while that measured with the TFY method was observed for more than 100 nm. The decrease in the TFY peak intensity was explained by the transmittance of Cr film. The results were applied to estimate the damage depth of plasma-etched GaN crystal. The deformation of the crystal structure in n-GaN etched by Ar plasma was restricted in a shallow region of less than 3 nm from the surface.

1. Introduction

In near edge X-ray absorption fine structure (NEXAFS) spectroscopy at soft X-ray region, the total electron yield (TEY) method with the sample current mode is widely used because it can be obtained using relatively simple equipment. The partial electron yield (PEY) method is also often used to examine photoelectron yields with a simple energy discrimination detector. However, because the escape depth of an electron in solids is about a few to a few tens angstrom [1], information obtained by TEY or PEY is restricted in a sample surface. To obtain information from sample bulk, the total fluorescence yield (TFY) method is employed with detection of fluorescent X-rays that can penetrate from deeper region of the sample.

Although, the energy dependence of the typical mean free path of an electron [2] or the X-ray penetration depth [3] in solids has been already reported, such data are rather distributed, and, therefore, precise information of analyzing depth for individual energy and material is insufficient. In this paper, we propose a convenient method to investigate the analyzing depth of the TEY and TFY methods for individual photon energy. Absorption intensity at the N-K edge (~400 eV) of Si$_3$N$_4$ crystals covered with Cr thin film was obtained by the TEY and TFY methods. A photodiode was used as a fluorescence X-ray detector for the TFY measurement; this detector had wide energy range of sensitivity, including visible lights, but was very simple to use. The analyzing depth at the N-K edge for both methods was evaluated. The results of the depth investigation were applied to estimate an etching damage depth of n-GaN crystal treated by Ar plasma.

2. Experiments

The sample used to investigate the analyzing depth was Si$_3$N$_4$ crystal grown on a Si wafer with thickness of 200 nm (NTT-AT Co.). A part of the Si$_3$N$_4$ sample was covered with Cr thin films of
thickness ranging from 1 to 100 nm, which was deposited by magnetron sputtering. Cr was not coated on the entire surface because, to compensate for an absorption intensity difference arising from the surface state difference of the individual samples (about 5%), the N-K absorption intensity was normalized with the intensity of the non–coated area. Cr is a suitable material for uniformly covering the Si$_3$N$_4$ surface because Cr film is less likely to island-grow [4]. The thicknesses of Cr films were controlled with the deposition time because the deposition rate of the sputtering system was very stable.

As the samples for applying the results of depth investigation, n-GaN crystals were etched with Ar plasma using a capacitively coupled RF plasma reactor with asymmetry electrodes and a constant self-bias of -200 V [5]. The etching was carried out with gas pressure of 10 – 200 mTorr [6].

NEXAFS spectroscopy at the N-K edge was carried out at the end station of the beamline BL9A in the NewSUBARU SR facility at the University of Hyogo [7]. The measurements were carried out using the TEY and TFY methods. The TEY measurement was conducted with monochromated soft X-rays incident on the Cr thin film, and the amount of secondary electrons emitted from the Si$_3$N$_4$ layer underneath was detected by means of the sample current mode.

The TFY measurement was conducted by detecting the fluorescence emitted from the Si$_3$N$_4$ layer underneath the Cr thin film. The X-ray detector used for TFY method was a photodiode (AXUV-100, IRD), which was placed at the angle of 30° from the sample normal and a distance of 3 cm. To prevent the inflow of secondary electrons from a sample into the electrodes, the surrounding of electrode leads were covered with Al plate, as shown in Fig.1. Because electrons flow into the acceptance surface of the photodiode run down to the earth through a cathode lead, they are not detected by a pico-ammeter inserted in the anode lead. For GaN samples, the yellow band secondary emission [8] disturbed soft X-ray fluorescence measurement. The photodiode, whose acceptance surface was coated with Al thin film of 40 nm thickness, was used to prevent the influence of secondary emission of visible light.

3. Results and discussion

3.1. N-K absorption spectra of Si$_3$N$_4$ covered with Cr thin film

Figure 2 shows the N-K absorption spectra of Si$_3$N$_4$ crystal covered with Cr thin film of various thicknesses measured using the (a): TEY and (b): TFY methods. In Fig. 2(a), the spectra of the samples covered with Cr thicknesses of 0 – 4 nm are shown. There is no change in spectra for the sample with Cr thickness greater than 4 nm. The peak intensity near 405 eV originated from Si$_3$N$_4$ crystal decreased with increasing Cr thickness and was observed to a Cr thickness of 2 nm. A slight peak was detected for the Cr thickness of 3 nm, and none was detected at 4 nm. Another peak near 400 eV was observed for the samples with Cr thickness greater than 3 nm. Because the peak was observed only at the Cr-deposited part, the 400 eV peak must arise from a native chromium nitride film. From the result above, the N-K absorption spectra obtained by the TEY method reflected the information at a shallow region of less than about 3 nm from the surface. An electron mean free path in solids at 400 eV is about 1 nm as previously reported [1,2]. Therefore, the analysing depth obtained by the TEY method in this study can be almost explained with the electron mean free path.

As shown in Fig. 2(b), the peak intensity near 405 eV measured with the TFY method decreased with increasing Cr thickness. However, it was detected even from the sample with Cr thickness of 100 nm with an intensity of about 30% of that detected at the non-coated Si$_3$N$_4$ surface. From the result above, the N-K absorption spectra obtained by the TFY method was found to reflect the information.
from the sample bulk, and the amount of contribution from a region of a few nm depth from the surface was relatively small. As making a close look at Fig. 2(b), the absorption intensity did not decrease in the order corresponding to the Cr thickness of 1, 5, 10 nm, and decreased extraordinary at 440 eV for 1 and 10 nm samples. Although we did not investigate them in detail, one possible explanation can be an effect of interference between the light waves reflected from Cr surface and Cr-Si$_3$N$_4$ interface, because the wavelength of incident light is comparable to the thickness of the Cr film.

Figure 3 shows the thickness dependence of the peak intensity near 405 eV calculated with the transmission coefficient of Cr film [3] and the peak intensity measured using the TFY method. According to a previous report [9], the N-K fluorescent photon energy of Si$_3$N$_4$ is mainly about 393 eV. Therefore, the transmission coefficient was calculated with incident photon energy of 405 eV and with output photon energy of 393 eV. The angle of output light (30°) was also considered to calculate the light path length. The experimental intensity agrees well with the calculated value for various Cr thickness samples. Therefore, the peak intensity obtained by the TFY method can be explained almost fully by the absorption of the upper Cr layer.

3.2. Application to etching damage analysis of GaN crystal

The N-K absorption spectra of n-GaN samples etched by Ar plasma with various pressures and with treatment time of 200 min are shown in Fig. 4. Figure 4(a) illustrates spectra obtained by the TEY method, and Fig. 4(b) shows those obtained by the TFY method for the same samples. As shown in Fig. 4(a), the peak and shoulder shapes in the N-K absorption spectra near the photon energies of 402, 406, and 408 eV became smooth or blunt with increasing gas pressure. This is because the structure of GaN crystal became disordered at the surface by Ar plasma etching.

On the other hand, as shown in Fig. 4(b), the spectra obtained by the TFY method were almost identical to those of the as-grown sample even in the sample etched under the highest Ar pressure condition of 200 mTorr. The effect of etching damage was not observed in the spectra measured using
the TFY method. According to the PIS (particle model for Plasma behavior and its Interaction with Surface reaction) model calculation [10], the etching damage containing a compositional change is estimated to reach 5 nm from the surface. The TFY spectral results confirm the model-simulated prediction. The amount of disorder could be small in the bulk region deeper than 5 nm, and the GaN crystal structure will be fully maintained. Therefore, the etching damage to the n-GaN sample was found to be restricted in the shallow region of a few nm from the surface.

4. Summary
The combined use of the TEY and TFY methods is effective to investigate material with a different structure in surface and bulk. We proposed a convenient method to estimate the analyzing depth of the TEY and TFY methods for individual photon energy. N-K absorption spectra of Si$_3$N$_4$ crystals covered with Cr thin films with various thicknesses were measured using the TEY and TFY methods to evaluate the analyzing depth. The N-K absorption intensity of Si$_3$N$_4$ was observed at Cr thickness of less than 3 nm, while that measured with the TFY method was observed for more than 100 nm. The decrease in the TFY peak intensity can be explained by the transmittance of the Cr film. The results were successively applied to estimate the damage depth of the Ar plasma-etched n-GaN crystal.

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