Development of multipurpose laboratory XIEES spectrometer and its application to surface XAFS analysis of Al_2O_3 films.

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A new laboratory spectrometer for X-ray Induced Electron Emission Spectroscopy (XIEES) has been developed. This spectrometer is suitable for measurements of X-ray Absorption Fine Structure (XAFS) spectrum in surface sensitive fluorescence and electron emission detection modes as well as in standard transmission mode. It is the advantage of this spectrometer that a wide range of x-ray energy scanning between 0.48 and 41 keV is available. At the Cu K-edge, a energy resolution of about 2 eV has been achieved. The spectrometer has been used to analyze the Al_2O_3 (40 Å and 500 Å)/Si(100) with total electron yield measurement.

Keywords: XIEES, laboratory XAFS, surface analysis

1. Introduction

Progress in the development of semiconductor device technology has to be accomplished by the development of the new characterization methods as well as enhancement of the existing ones, which give information on the local spatial and electronic structure of the devices. One of the perspective methods is XAFS analysis that is quickly developed with appearance of the powerful synchrotron radiation sources (Winick, 1989). However the available x-ray photon energy range at the synchrotron ports and accessibility of the needed port restrict the use of the synchrotron radiation. Moreover there are difficulties if "on the fly" analysis is needed. Therefore many people have made a number of attempts to construct the laboratory device for the EXAFS measurements (Williams, 1983; Thulke et al, 1983; Cohen et al, 1980; Georgopoulos & Knapp, 1981; Song et al, 1997). With the appearance of the high power rotating anode x-ray sources the quality of the EXAFS data obtained with the laboratory spectrometers became comparable, in parts, to the data measured with synchrotron facilities. In this paper the recent progress in development of a multipurpose laboratory device for x-ray induced electron emission spectrometry (XIEES) that allows us employing the XAFS analysis in surface sensitive regime is described. The application of the new spectrometer to surface XAFS analysis of Al_2O_3 films is reported.

2. Design and specification

Figure 1 illustrates an overview of the spectrometer. X-ray white radiation is produced by the rotating anode source (18kW generator). The Johanson focusing optic scheme (600 mm Rowland circle radius) is used to increase the x-ray flux and energy resolution. Monochromated x-ray passes through the receiving slit and irradiates the sample. Two x-ray detectors (gas proportional counters) are used as a monitor detector and a transmitted radiation detector to collect XAFS data. For surface sensitive experiments a channeltron is set in front of the sample to measure the total electron yield (TEY) produced by absorption of x-rays in the near surface region. The whole optical scheme is situated in the vacuum chamber which is directly connected to the vacuum volume of the x-ray generator without Be window. This design provides measurements with soft x-rays. To simplify the transformation from one energy region to another a special multi-crystal exchanger is used. With 6 crystals installed on the exchanger (LiF(422), LiF(200), SiO_2(3140), Ge(111), PET(002), KAP(100) - 10×30 mm^2 size) the whole available energy range is

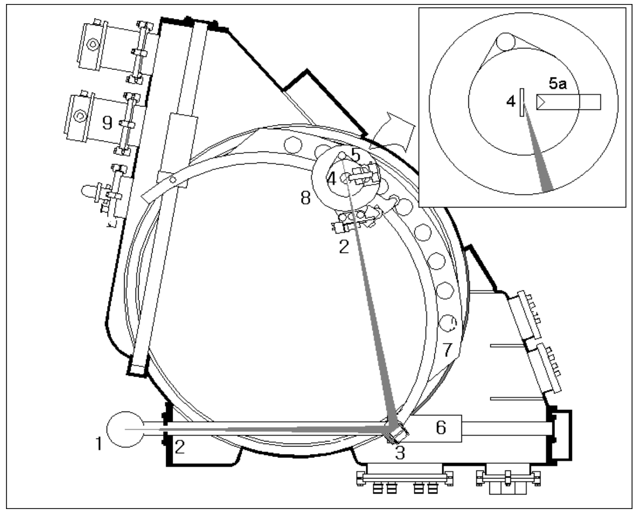

Figure 1
Optical scheme of XIEES: 1. X-ray source; 2. Receiving slits; 3. Crystal- monochromator; 4. sample; 5. Detectors; 5a. Channeltron; 6. Linear drive; 7. Rowland sector; 8. Aiming system; 9. Pumps;

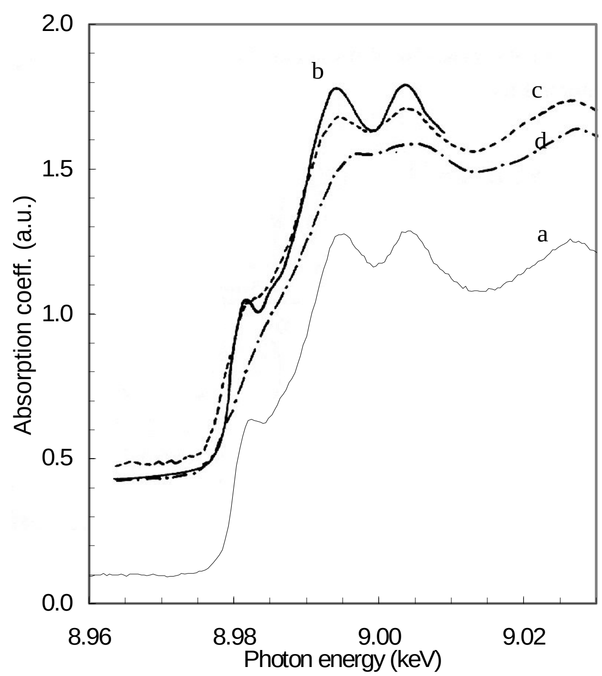

Figure 2
XAFS of Cu K-edge in transmission mode. (a) XIEES data and literature data (Koningsberg, 1988): (b) 2eV resolution, (c) 5eV resolution, (d) 9eV resolution.

0.48-41 keV. Setting of linear drive position, Rowland sector position and aiming system angle provides the scanning over entire x-ray measurement ranges. For these purposes 3 stepping motors controlled by computer are used. Another 7 stepping motors provide a control over exit slit width, sample irradiation angle and detector take off angle. The pumping system consists of one rotary pump, two turbo-molecular pumps and vacuum gauge controlled by the computer. The working pressure of 5×10^{-5} torr is reached in 40 minutes. A controller designed specially for this system provides the commands and data flow exchange between the spectrometer and computer.

Figure 2 gives an example of utilization of the XIEES spectrometer for the measurement of Cu K-edge XAFS in transmission mode. A comparison of our data with the data measured with the synchrotron radiation source and other laboratory devices gives the estimation of the real energy resolution of this spectrometer: at Cu K-edge XANES region the resolution is about 2 eV.

3. XANES of Al_2O_3 films in TEY detection mode

The unified vacuum volume of the XIEES device allows us to carry out the experiments with utilization of soft x-ray radiation. The preparation of the samples for EXAFS experiments in transmission mode at soft x-ray region is more complicated task than at hard x-ray region (especially for laboratory XAFS experiments where the x-ray flux is smaller than for synchrotron facilities). When the properties of the thin surface films are investigated, the total electron yield (TEY) mode becomes particularly useful because of the high surface sensitivity. The XANES spectrum of Al K-edge in Al_2O_3 crystalline film (40 Å) measured with XIEES is shown in Fig.3.

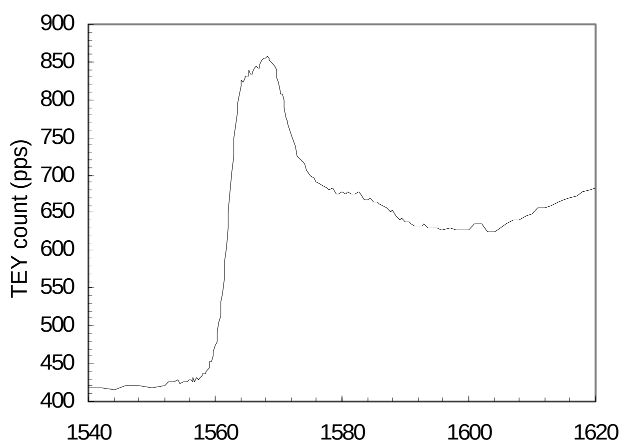

Figure 3
XAFS spectrum of Al K-edge in Al_2O_3 crystalline 40Å film.

In the following description the XANES analysis with the XIEES device was applied to study the crystallization state of Al_2O_3 oxides. Four samples were obtained by vacuum deposition of 500Å Al_2O_3 film on the Si(100) substrate followed by annealing at different temperatures (500, 700, 800 °C). Under the TEY mode the probing depth for this samples is (approximately) equal to that for the 40Å sample. By selecting the proper condition of x-ray generator (20kV, 200 mA, 0.5×10 mm^2 line focus), optic parameters and using the focusing PET(002) monochromator the XIEES was configured for the optimal x-ray flux and photon energy resolution. No special precautions were made to eliminate the x-ray higher harmonics. The 100 V accelerating voltage was applied to the aperture of the channeltron to accumulate the maximum number of the slow electrons from the sample. Al K-edge (1.56 keV) XAFS spectra for all samples were measured. About 1,000~3,000 cps were counted after the Al K-edge. In order to accumulate 300,000 counts for each energy channel the accumulation time of c.a. 300 sec. was necessary.

The normalized results of the measurements are shown in the Fig.4. Simulated absorption spectra (FEFF7 program developed by Zabinsky et al, 1995) for Al_2O_3 were shown in Fig.5. To model the amorphous sample response a small cluster (R=2.7Å, space group of R3-C) is used in calculation. By increasing the size of cluster (R=3.4 and 7.0Å) a higher crystalline content in material could be simulated. The simulated XAFS spectra show the rising of the absorption at the middle energy (around 1580 eV) with increasing the cluster size. We regard this trend is a result of the increase in the crystalline content. The same trend is observed in the experimental spectra shown in Fig.4. Therefore, we may conclude that Al_2O_3 thin films annealed below 700°C are amorphous, while the Al_2O_3 annealed at 700°C and higher contain crystalline phase.

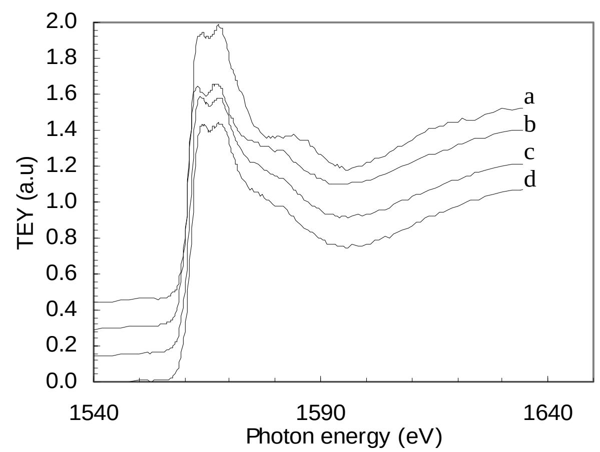

Figure 4
Al K-edge XAFS spectra of Al_2O_3 film (500Å). After the deposition samples were annealed under the different temperature, (a) T=800°C, (b) 700 °C, (c) 500 °C and (d) as deposited.

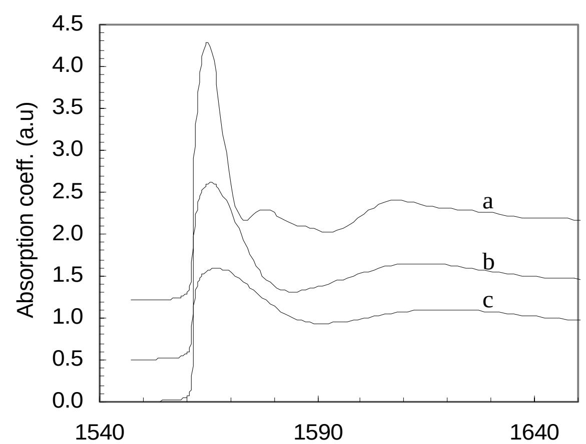

Figure 5
Al K-edge XAFS spectra of Al_2O_3 simulated by FEFF program. The different cluster size R was used to simulate different amorphous content: (a) R = 7.0 Å, (b) 3.5 Å, (c) 2.7 Å.

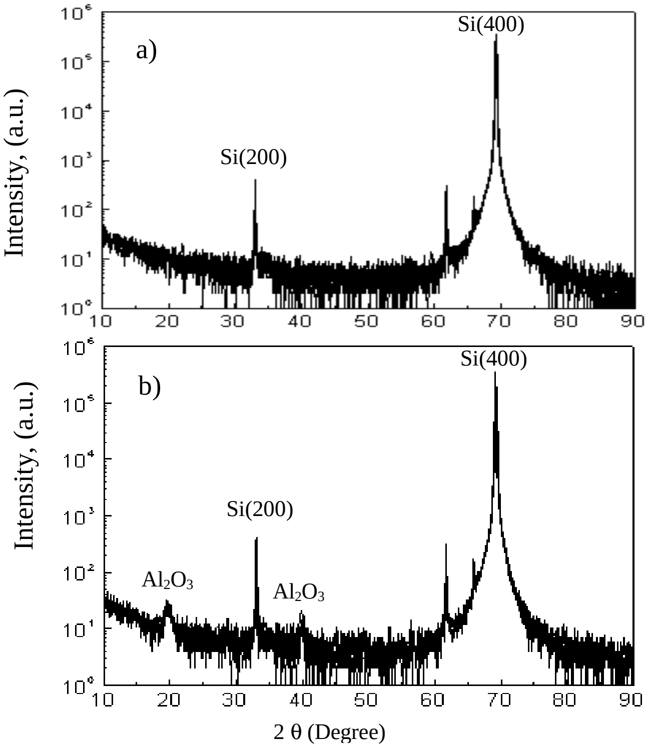

Figure 6
The XRD θ-2θ scan patterns for: a) as deposited 500Å Al_2O_3 film; b) 500Å Al_2O_3 film annealed at 800°C.

The XRD θ-2θ scan pattern has shown the presence of crystalline phase in the Al_2O_3 film annealed at 800°C, which supported our XANES measurement and conclusion (Fig.6).

4. Conclusion

The design and main characteristics of the new laboratory XAFS spectrometer are presented. The possibility to measure the XAFS with resolution about 2 eV over photon energy has been shown on the Cu foil. The reliability of the XIEES spectrometer is demonstrated by comparing the measured data with the literature data obtained at a synchrotron radiation facility and other laboratory spectrometers shown on the Cu foil. The reliability of the XIEES spectrometer is demonstrated by comparing the measured data with the literature data obtained at a synchrotron radiation facility and other laboratory spectrometers.

The possibility to make the surface sensitive XAFS experiments with the XIEES is demonstrated in the experiments of the Al_2O_3 thin films. The real surface sensitivity achieved in TEY mode on the Al_2O_3 samples is shown to be near 40Å. Both amorphous and crystalline samples were examined. The interpretation of XANES spectra revealed that crystallization process in Al_2O_3 thin films started after annealing at 700°C. It is found that XAFS technique in the TEY mode is a sensitive tool for determination of the amorphous content in the sample and may be used together with XRD, which gives complementary data.

References

Cohen, G.G., Fisher, D.A., Colbert, J. & Shevchik, N.J (1980).. *Rev.Sci.Instr.*, **51**, 273-277.

Georgopoulos, P. & Knapp, G. S. (1981). *J. Appl. Cryst.* **14**, 3-7.

Koningsberg, D.C. (1988). in “X-Ray Absorption”, *D.C.Koningsberg and R.Prins (Eds.), John Wiley & Sons*, 163-210.

Song, S. A., Kim, J. H., Lee, J. C., Choi, J. H., Pogrebitsky, K. Ju., Bakaleikov, L. A., Yuryev, Y. & Usov, O. A. (1997). *The Electron, Proceedings of the international centennial symposium on the electron*, 557-565.

Thulke, W., Haenset, R. & Rabe, P. (1983). *Rev.Sci.Instr.*, **54**, 277-283.

Williams, A. (1983). *Rev.Sci.Instr.*, **54**, 193-197.

Winick, H. (1989). *AIP Conf.Proc.*, **184**, 2138-2182.

Zabinsky, S.I., Rehr, J.J., Ankudinov, A., Albers, R.C. & Eller, M.J. (1995). *Phys.Rev.* **B52**, 2995-3009.

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