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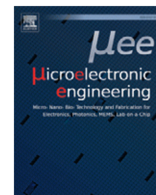

Evaluation of energy distribution of filled defects of Si oxide thin films from total photoelectron yield spectroscopy

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ABSTRACT

We have demonstrated the how powerful total photoelectron yield spectroscopy (PYS) is to evaluate the energy distribution of filled defect states for dielectrics such as Si oxide prepared by thermal oxidation and electron beam evaporation. PYS system with wide measurement energy range from 3 to 10 eV have been developed by the combination of the two light sources with Xe-arc and high brightness D_2 lamps in addition to the control of ambience in optical path. The filled electronic states density in Si oxide were converted from the measured PYS spectra in the consideration of the measured density of states of valence electron from in-situ XPS measurements.

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1. Introduction

Suppression and control of electrically active defects in dielectric layer and at their interface with metal electrodes are of great importance for the improvement in the performance of electronic devices with MOS and MIM structures [1,2]. In addition, the characterization technique of electronic defects in dielectrics is also required to gain a better understanding of physics of the defect generation because the energy distribution of defects can give us the information of physical origins of the defects.

So far, we have reported a novel approach to the study of energy distribution of gap states at chemically cleaned Si surface and at SiO_2/Si interface in the energy range from 4 eV to 6 eV by using total photoelectron yield spectroscopy (PYS) and demonstrated that the PYS technique enables us to evaluate the filled defect density as low as 10^9 cm^{-2} eV^{-1} without gate electrode fabrication [3]. In addition, the depth profile of the defect states in dielectric layer such as SiO_2 on 4H-SiC and $HfSiO_xN_y$ on Si have been also evaluated from the change in the PYS intensity with dielectric thinning [4–6].

Recently, resistive random access memories (ReRAMs) with Si oxide switching layer has attracted much our particular interest because of good compatibility of current *Si*-ULSI technology, and we have reported the repeatable resistive switching properties of Si oxide [7,8]. To evaluate the energy distribution of occupied states in the energy region of entire bandgap of SiO_2, ultraviolet at an energy over 10 eV is needed taking into account of the reported energy level of valence band maximum from the vacuum level [9,10].

The purpose of this work is to enlarge the measurements energy range of PYS system in order to evaluate the occupied gap states of Si oxide in the energy range of entire bandgap of Si oxide. And then, PYS has been applied to evaluate the energy distribution of electronic defect states for the Si oxide layer formed by the thermal oxidation and the electron beam (EB) evaporation.

2. Sample preparation

Two kinds of Si oxide layer with a thickness of around 40 nm were formed on Si substrate as follows process. After wet-chemical cleaning of p-type Si(100) substrates with the resistivity of ~10 Ω·cm, the Si surface was terminated with hydrogen by dipping in 4.5% HF solution and pure-water rinse. Then, a SiO_2 layer was grown by the thermal oxidation at 1000 °C. In some samples, Si oxide layer was also formed by the EB evaporation using SiO_2 target at base pressure of 3×10^{-6} Torr.

3. PYS system

PYS system used in this work was schematically illustrated in the Fig. 1. One of the advantage of this system is that we can do the in-situ XPS measurements, because PYS system has been connected to the commercial XPS chamber (KRATOS: AXIS-HSi). Monochromatized ultraviolet was made by the monochrometer (Bunkokeiki: VUV-200 OS) using the two light sources of Xe-Arc and D_2 lamps. These light sources

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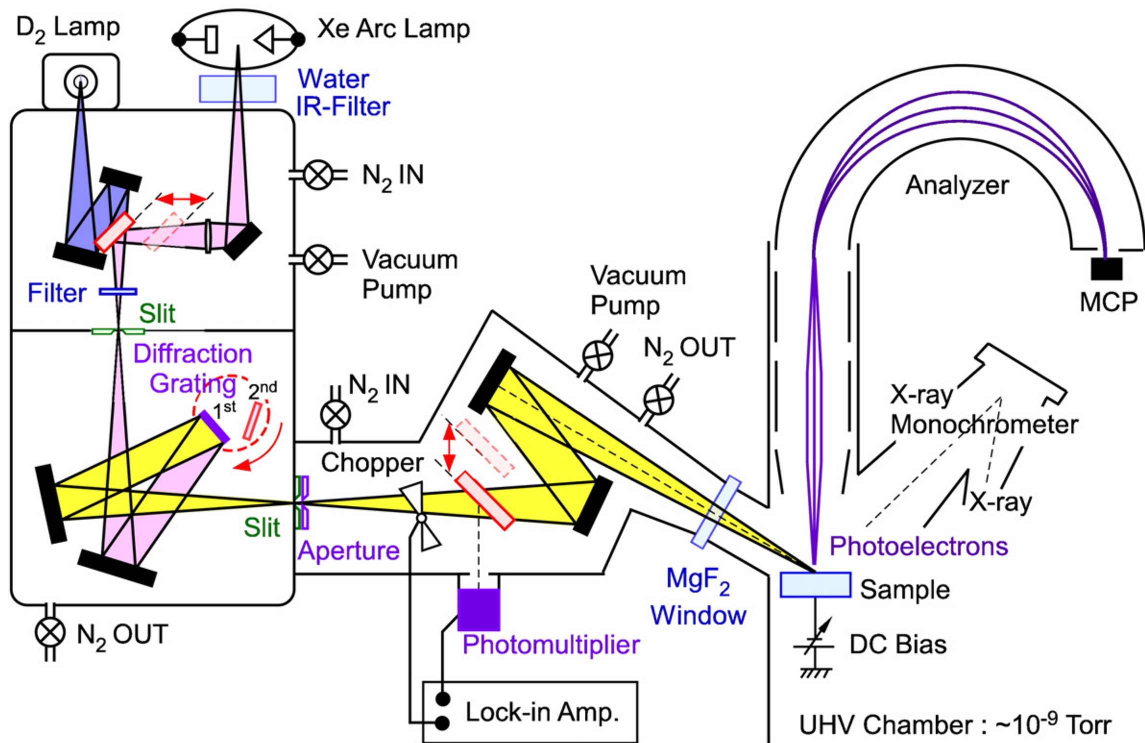

Fig. 1. Schematic illustration of PYS system developed in this work. PYS system was connected to the XPS chamber.

can be selected by the position of the movable mirror at the front of the optical filter. Intensity of the monochromatized ultraviolet ($I_{ultraviolet}$) was monitored by the photomultipliers (Hamamatsu Photonics: R1527 for the Xe-Arc lamp and R6836 for the D_2 lamp) in consideration of the radiant sensitivity and the photon energy ($h\nu$). To suppress the decrease in $I_{ultraviolet}$ by the optical absorption in the energy over 7 eV mainly due to the O_2, O_3, and CO_2 in the atmospheric air [11], the ambience in the monochrometer and the optical path was filled with pure-N_2 gas (purity: 99.999%) after the vacuuming by dry-pump (as shown in Fig. 2). In some cases, a quartz disk was set as the energy filter to avoid the stray light. The optical slit width in the monochrometer was also adjusted in order to make the energy resolution of monochromatized ultraviolet less than 50 meV. During the PYS measurements, the monochromatized ultraviolet was irradiated to the sample in the XPS chamber at vacuum pressure below ~1×10^{-9} Torr through the MgF_2 window with the thickness of 4 mm. Emitted photoelectrons from the sample by the monochromatized ultraviolet irradiation were collected with the hemispherical analyzer for XPS system, where negative bias at -60 V was applied to the sample to detect the photoelectron intensity with high sensitivity. Photoelectron yield intensity (Y) was calculated from the count of photoelectrons ($C_{photoelectron}$) emitted from the sample and the intensity of monochromatized ultraviolet with taking into account of the transmittance of MgF_2 window (T_{MgF2}), as follows equation.

$$Y = C_{photoelectron} / (I_{ultraviolet} \times T_{MgF2}) \quad (1)$$

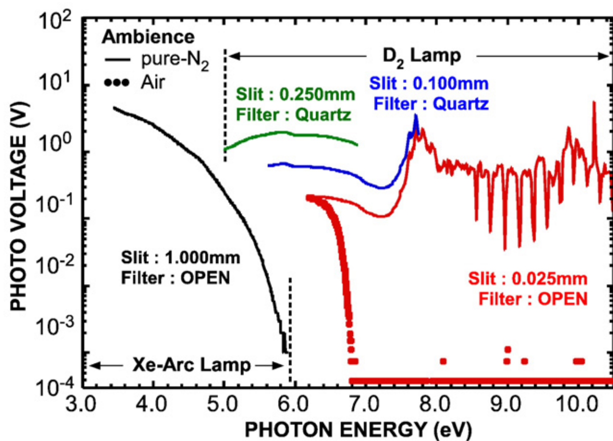

Fig. 2. Intensity of monochromatized ultraviolet using the Xe-Arc and D_2 lamps measured under the air and pure-N_2 at atmospheric pressure. Photo-voltage was monitored by the photomultiplier.

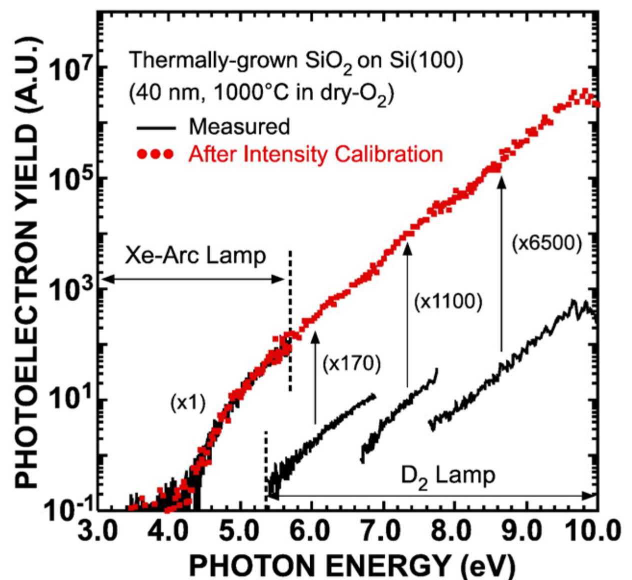

Fig. 3. PYS spectra for a 40 nm-thick thermally-grown SiO_2 calculated from the Eq. (1) before and after the photoelectron intensity normalization.

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