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# Photoemission Study of Gate Dielectrics and Stack Interfaces

Seiichi Miyazaki and Akio Ohta
Nagoya Univ.
Furo-cho, Chikusa-ku
Nagoya 464-8603, Japan
Phone: +81-52-789-3588, E-mail: miyazaki@nuee.nagoya-u.ac.jp

**Abstract**

**We have demonstrated how to measure dielectric function, interfacial dipoles and defect states in gate dielectrics and/or their stack interfaces from the analyses of photoelectron energy loss signals, cut-off energy of secondary photoelectrons and total photo-electron yield spectra, respectively.**

## 1. Introduction

In the development of Metal-Insulator-Semiconductor (MIS) devices, gate dielectric technology is of great importance and includes major scientific and technological issues to be solved for required device performance and reliability [1]. In particular, characterization of electronic defects in dielectrics and at their interfaces with semiconductor substrates as well as energy band profiles has been imperative to gain a better understanding of physics of dielectric/semiconductor heterostructures [2, 3].

In this work, we have reviewed our recent achievements on the characterization of gate dielectrics and their stacked interfaces by means of photoemission techniques. First, we have demonstrated how useful the analysis of energy loss signals (ELS) of core-level photoelectrons [4] is not only to determine energy bandgap values of dielectrics but also to characterize dielectric functions of dielectrics. Then, we have shown how valuable the cut-off energy of photoelectrons is to measure directly the potential change due to electrical dipoles at the interface in stacked dielectrics [5] and how powerful total photoelectron electron yield spectroscopy (PYS) [6, 7] is to quantify the energy distribution of electronic defect states in gate dielectrics at the dielectric/semiconductor interfaces.

## 2. Determination of Complex Dielectric Function

In general, photoexcited electrons passing through dielectrics can suffer inelastic losses due to electronic excitations such as plasmons and band-to-band transitions. Since ELS near the primary core line peak are mainly attributable to excitations from the valence band to the conduction band, energy band gap values of practically thin, various gate dielectrics have often been measured from the onset energy of the ELS. Since the ELS typically within 50eV is attributable mainly to interaction between photoexcited electrons and valence electrons in the materials, they provide information about the electronic structure and can be converted into the complex dielectric function concerning optical response of the materials of interest.

Figure 1 shows an example of conversion from the ELS of Si2p3/2 core line to the complex dielectric function of 50nm-thick $SiO_2$ grown at 1000 ºC in dry $O_2$ [8]. As shown in Fig. 1(a), $Si2p_{3/2}$ ELS was elaborately measured at different photoelectron take-off angles (TA) and then, the surface component of the ELS was crudely estimated by subtracting the ELS taken at TA=30º from the ELS at TA=15º to extract a pure bulk component from the ELS at TA=90º. Also, providing the so-extracted ELS for photoelectrons is proportional to the negative imaginary part of inverse dielectric function, the real part of inverse dielectric function can be calculated by Kramers-Kronig transformation. And, using both the real and imaginary parts, the complex dielectric function ($\varepsilon_1$, $\varepsilon_2$) was derived as shown in Fig. 1(b). Almost the same results were obtained from the ELS analysis of O 1s photoelectrons and the result is very consistent with the dielectric function calculated from reported optical constants of $SiO_2$ glass [9] although the spectral width of primary photoelectrons reflects in spectral broadening in the dielectric function. Notice that obtained dielectric function enables us to confirm the validity of the energy band gap value determined simply from the onset energy of ELS.

## 3. Direct Measurement of Interfacial Dipoles

The inner potential changes in dielectric stacks reflect in changes in the cut-off energy of secondary photoelectrons (SEs) measured in high-resolution x-ray photoelectron spectroscopy (XPS) [5]. After calibration of the kinetic energy of core-line signals from the underlying layer, an abrupt potential change due to electrical dipoles at the interface between dielectrics, resultant abrupt potential change can be measured as a change in the cut-off energy of SEs. The observation of cut-off energy provides us an advantage in simple and precise evaluation of the potential change due to electrical dipoles as compared to a discussion on dipole formation based on the energy shift of core-line signals which reflects not only the potential change due to dipoles but also the chemical shift, that is, change in the chemical bonding features. Figure 2 (a) shows the photoemission spectra near the lowest limit in kinetic energy to which SEs contribute mainly for the samples before and after the formation of various high-k dielectrics on thermally-grown thick $SiO_2$. With the formation of either ultrathin $Al_2O_3$ or $HfO_2$ or $TiO_2$ on $SiO_2$, the cut-off energy of SEs was shifted toward the higher kinetic energy side, respectively. On the other hands, with the Y-silicate formation, a slight opposite energy shift was detected. As shown in Fig. 2 (b), the analyses of the core line signals confirm that there is a linear correlation between the observed potential changes and the ratios in the oxygen anion density at the interfaces between $SiO_2$ and high-k dialectics as suggested in Ref. [10].

## 4. Quantification of Energy Distribution of Defect States

Since, in the photoelectron yield measurements, the total number of photoelectrons emitting from the sample is counted considering the incident photon flux, the yield spectrum is related to an integral over the occupied density of states existing near the sample surface [6]. The photoelectron yield spectra of 2nm-thick $SiO_2$ formed 500ºC by remote plasma enhanced CVD on n-type GaN(0001) before and after $N_2$ anneal at 800ºC are shown in Fig. 3 (a). Observed high yields in the incident photon energy region over ~8eV are attributable mainly to the emission from the GaN valence band. Obviously, with the $N_2$ anneal at 800ºC, the yield from the defects was reduced. The 1st derivative of the measured yield spectrum with respect to incident photon energy leads us to the energy distribution of occupied defect state densities in consideration of density of states of the GaN valence band, measured photoelectron yield from the GaN VB and photoelectron escape depth (Fig. 3(b)). As a result, occupied states are reduced down to ~$1x10^{11}cm^{-2}eV^{-1}$ at the energy corresponding to the midgap of GaN near the $SiO_2$/GaN interface with the $N_2$ anneal at 800ºC. The defect state density near the conduction band edge, which was crudely estimated in consideration of electron occupation probability based on the Fermi-Dirac distribution, are in good agreements with the result obtained from the capacitance-voltage (C-V) analysis using the Terman method [7].

## 3. Conclusion

The analyses of photoelectron energy loss signals, cut-off energy of secondary photoelectrons and total photo-electron yield spectra are very useful to gain better understanding of electronic characteristics in gate dielectrics and their stack interfaces.


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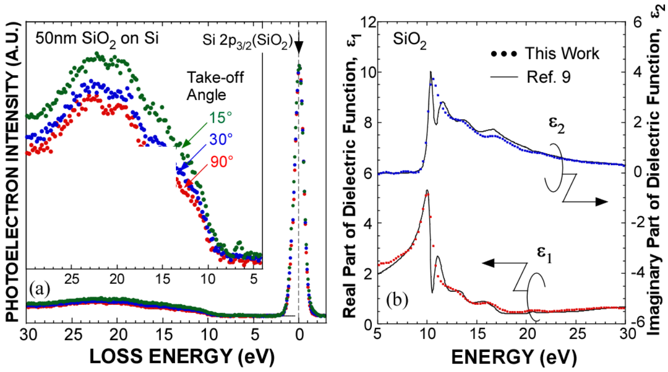


Fig. 1 Energy loss signals (ELS) of $Si2p_{3/2}$ photoelectrons measured for 50nm-thick thermally-grown $SiO_2$ at different photoelectron take-off angles (a), and real and imaginary parts of dielectric function derived from the analysis of measured ELS (b) compared with those reported for the $SiO_2$ glass [9].

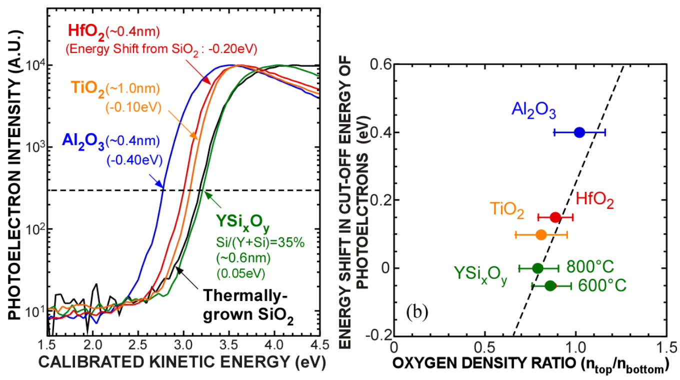


Fig. 2 Photoemission spectra in the low kinetic energy region near the cut-off energies for photoelectrons measured for various high-k dielectrics on thermally-grown $SiO_2$ (a), and measured energy shifts in the cut-off energy for photoemission from the $SiO_2$ value, which correspond to potential changes due to interfacial dipoles, plotted as a function of oxygen density ratio evaluated from the analyses of core-line spectra (b).

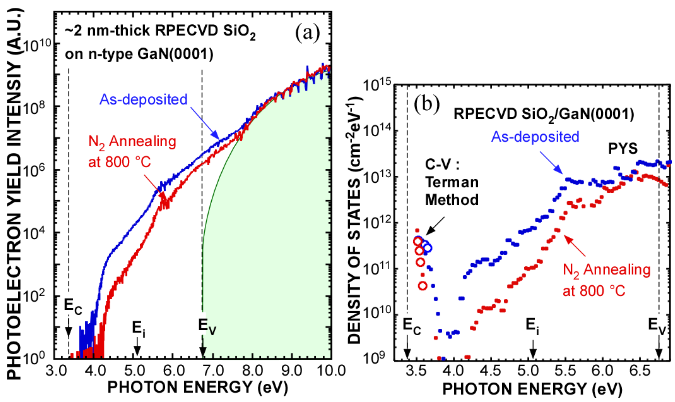


Fig. 3 Total photoelectron yield spectra for 2nm-thick $SiO_2$ deposited on n-GaN(0001) by remote plasma enhanced CVD at 500 °C and after $N_2$ anneal at 800 °C (a) and energy distributions of occupied defect state densities estimated from the 1st energy-derivative of the measured yield spectra (b). In (b), defect state densities of both samples evaluated by C-V analyses are also shown as references.