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Vacuum-ultraviolet reflectance difference spectroscopy for characterizing dielectrics–semiconductor interfaces

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ABSTRACT

Reflectance difference spectroscopy (RDS) was applied to the characterization of SiO_2/Si, GeO_2/Ge, and high-k/III–V interface structures. We extended the spectral range of RDS to 8.4 eV in order to explore the optical transitions at the dielectrics–semiconductor interfaces as well as to have a high sensitivity to the interface anisotropy. Si surfaces with (110), (113), (331) and (120) orientations showed oxidation-induced RD changes in the vacuum-ultraviolet (VUV) range which were dependent on the surface orientation, oxidation method (dry or wet), and oxidation temperature. The Ge(110) surface also showed characteristic oxidation-induced changes in the VUV range, whereas Al_2O_3 deposition on GaAs(001) and InP(001) surfaces induced only the RD amplitude changes.

1. Introduction

Complementary metal-oxide-semiconductor (CMOS) devices for large-scale integrated circuits (LSIs) have been scaled down to the nanometer dimensions. In order to improve the device performances further, new structures and materials have been proposed for implementation into the CMOS devices [1]. One example is the Si nanowire channel structure. The MOS interfaces on the nanowire surface involve the high-index planes such as (11*n*) and (1*n*0) [2] for which the structures and properties of the SiO_2/Si interfaces are not understood well. Other examples are the high-mobility channel materials such as Ge and III–V compound semiconductors [3]. Various dielectric materials (oxides, nitrides, high-k, *etc.*) are under investigation in an effort to realize high-quality MOS interfaces on these non-classical channel materials. Since there are such an increasing variety of the MOS gate-stack structures, versatile probes for characterizing the dielectrics/semiconductor interfaces are strongly needed.

Reflectance difference spectroscopy (RDS) measures the anisotropy in the normal-incidence reflectance of linearly polarized light [4]. For the bulk-isotropic materials, RDS sensitively detects the surface- and interface-induced anisotropies, making itself a complimentary technique to spectroscopic ellipsometry. Past studies by the experimental [5–7] and theoretical [8–11] approaches showed that the RD spectra for the SiO_2/Si system *indirectly* reflect the interface structure, in that the Si bulk states perturbed by the presence of the interfaces, rather than the states associated with the interface Si–O bonds, are the origin of the observed optical anisotropy. We expect that the RD signals that *directly* reflect the interface structure appear in the vacuum-ultraviolet (VUV) range. This is because the chemical bonds at the dielectrics/semiconductor interfaces should have relatively large energy separation between their bonding and antibonding states (typically >5 eV) which determines the threshold energy of the optical transitions associated with these states. It is also expected that VUV-RDS has high sensitivity to anisotropic interface morphology due to the short wavelength of the probing light [12].

This paper reports a newly developed VUV-RDS apparatus and its application to characterization of the dielectrics–semiconductor interfaces that are of interest for the development of the future CMOS devices: SiO_2/Si interfaces on the high-index surfaces, GeO_2/Ge (110) and high-k/III–V interfaces.

2. Optical setup for VUV-RDS

The optical setup for VUV-RDS is illustrated in Fig. 1. Details and basic performances of this measurement system were reported previously [13]. The light source was a 30 W D_2 lamp which was enclosed in an N_2-purged VUV monochromator of 200 mm focal length. The exit slit of the monochromator acted as a virtual point source of light for the rest of the optical system which was placed in a N_2-purged glove box (820 mm × 400 mm × 280 mm). The flow rate of N_2 was typically 30 L/min. Arrangements of the polarizer and analyzer prisms, photoelastic modulator (PEM) and mirrors followed the visible-UV setup reported by Aspnes et al. [14]. The Rochon prisms and PEM were made of MgF_2. The setup as described above covered a

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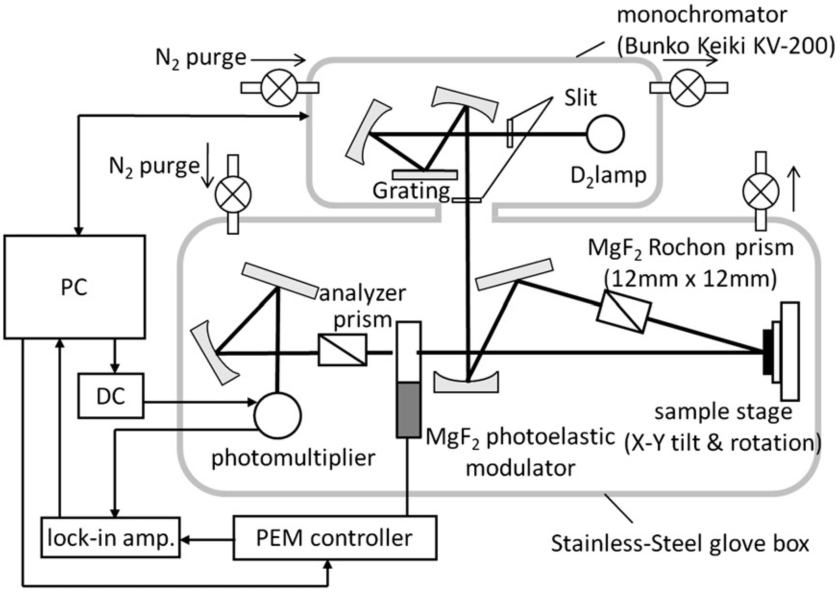

Fig. 1. Experimental setup for the VUV-RDS measurements.

spectral range of 4.2–8.4 eV. The samples were loaded into (or unloaded out of) the glove box by opening the top rid of the box. When multiple samples were loaded, the sample exchange and alignment was performed via plastic gloves.

Measurements were also made by using the conventional visible-UV RDS system which covered the spectral range of 1.5–5.5 eV. The VUV-RD spectra were in good agreement with the visible-UV ones in the overlapping energy range of 4.2–5.5 eV [13]. For the samples covered by an oxide layer, the measured spectra were corrected for the amplitude modulation caused by the isotropic oxide overlayer according to Eq. (2) in Ref. [5]. The thickness and dielectric functions of the oxide layers (SiO_2, GeO_2 and Al_2O_3) were evaluated by spectroscopic ellipsometry measurements in the range of 1.2–9 eV. All of the RD spectra shown in this paper are for the real part of the complex reflectance difference, $\Delta r/r$.

3. SiO_2/Si interfaces on the high-index surfaces

The (110) and high-index surfaces of the crystals with the diamond structure (*e.g.* Si and Ge) are suited for RDS characterization, since their low symmetry allows non-zero RD signals without requiring any special sample preparation. The (001) surfaces of these materials were not investigated in this study because they need special surface preparation to form the single-domain structure [15].

SiO_2/Si samples were prepared on p-type Si wafers (1–10 Ω cm) of four different surface orientations: (110), (113), (331), and (120) [13]. The initial H-terminated Si surfaces were finished by cleaning the wafers according to the standard RCA procedure followed by etching in a 1:30 diluted HF solution. Thermal oxidation was carried out by either the dry or wet (H_2:O_2 = 1:1) method. Oxidation temperature was varied from 700 to 950 °C. Oxidation time was adjusted so that the oxide thicknesses were in the ranges of 6–10 nm and 15–30 nm for the dry and wet oxidations, respectively.

Fig. 2 shows the RD spectra for the (110), (120), (113), and (331) surfaces of Si. The VUV and visible-UV data are merged to cover the 1.5–8.4 eV range. In this figure, spectra for the surfaces with H termination and thermal oxide are compared. The (110), (120) and (331) surfaces showed spectral lineshapes that are qualitatively similar to the imaginary part of the dielectric function of Si, whereas the (113) surface showed the derivative-type one. Implication of these spectral features, which appeared near the critical points of Si, had been discussed previously [5,6] and will not be repeated here. As for the (110), (120) and (331) surfaces, the oxidation-induced changes appeared not only near the E_1, E_2 and E_1' transition energies but also above 7 eV. The spectra for the (113) surface showed a large oxidation-induced change above 4 eV.

A new finding supplementing our previous results [13] is that the oxidation-induced RD signals in the UV and VUV ranges were dependent on the thermal oxidation method (dry or wet) and temperature, as shown in Fig. 3. Dependence on the oxidation temperature was remarkable for wet oxidation on the (110) surface but was almost absent for dry oxidation on the same surface. The (331) and (113) surfaces showed moderate dependency on the oxidation conditions, while the RD spectra for the (120) surface were least affected by the oxidation condition. In contrast to these VUV data, the spectra in the visible-UV region (not shown in Fig.3) were

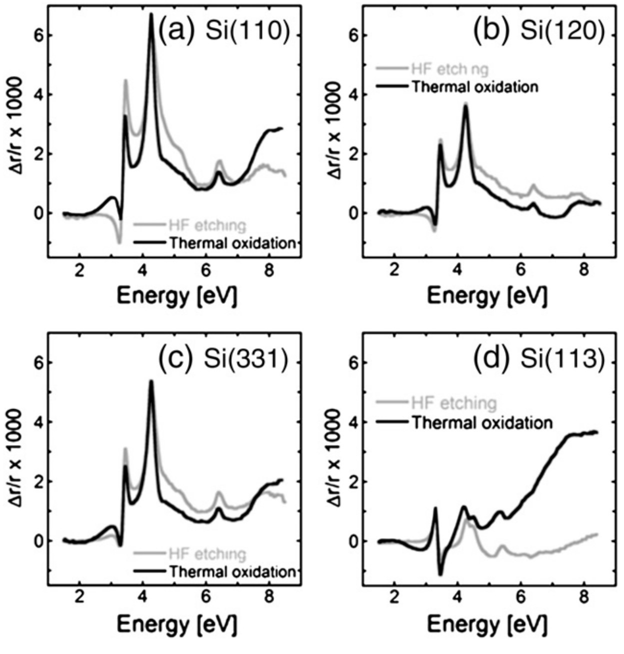

Fig. 2. RD spectra for (110), (120), (113), and (331) surfaces of Si. Spectra for the surfaces with H termination and thermal oxide layer formed at 850 °C (dry oxidation) are shown.