Nuclear Instruments and Methods 208 (1983) 605–608
North-Holland Publishing Company

INTERFEROMETRIC INVESTIGATION OF THE Si–SiO_2 INTERREGION AT WAVELENGTHS OF 110–130 Å

W. BLAU
Technical University, Dresden, GDR

E.S. GLUSKIN, A.P. LYSSENKO and G.N. KULIPANOV
Institute of Nuclear Physics, Novosibirsk, USSR

K. HÜBNER
Wilhem Pieck University, Rostock, GDR

The energy and angular dependence of the reflectivity in the soft X-ray region contains valuable information concerning the microstructure of thin films and interfaces. Because of its high quantum effectivity, the method is less destructive compared with other ones. Reflectivities from $R \approx 1$ down to $R \approx 10^{-5}$ have been measured. In the theoretical model, as well as the optical constants and the thicknesses, the roughness of all interfaces must be taken into account.

1. Introduction

Investigations on optical X-ray reflectivity, especially its angular dependence, are not frequently met in the literature. Very accurate measurements in the short wavelength region were performed by Martens [1]. Our aim was to check the applicability of reflectivity measurements to the investigation of the microstructure of SiO_2 films on Si substrates. Particularily the structure of the SiO_x interregion at the Si/SiO_2 interface, which determines the properties of MOS microelectronic circuits, has not been fully understood so far [2]. Measuring techniques utilizing hard radiation and possessing low quantum effectivity (SIMS, ESMA, REM, AES) destroy the metastable interregion. XPS [3] does not distinguish oxides with higher oxygen content ($x > 1.25$). The same holds for the spectroscopical ellipsometry [4], the most non-destructive method. SiO_2 and $SiO_{x>1.25}$ show differences in their optical properties only in the region of the SiO_2 conduction-band edge [5], where ellipsometry is not possible because of strong absorption in the SiO_2 film and in the apparatus itself.

However, the main optical features and differences of Si and its oxides occur again in the soft X-ray region near 100 eV (transitions $Si_{2p} \rightarrow$ conduction band). Absorption does not cause as much disturbance as in the VUV, and the short wave length enables more interferences in the reflectivity. Because of the higher quantum effectivity, X-ray reflection should be less destructive than some other methods.

2. Experimental

The measurements were performed at the storage ring VEPP-2M of the Institute of Nuclear Physics of the Sibirian Division of the Academy of Science of the USSR (Novosibirsk). Energy and current varied between 300 and 700 MeV, 1 and 15 mA, respectively ("parasitic" regime).

Regarding the optical system see fig. 1. The mirror block (S_1, M_1, M_2) [6] deminishes the high energy background. The optical components of the grazing incidence spectrometer RSM-500 are the focusing mirror M_3, the entrance slit S_2 (2–10 μm), the grating G (600 lines/mm, Au-coated) the divergence slit S_3 (100 μm) and the exit slit S_4 (15 μm). The reflectometer possesses a (ϑ, 2ϑ)-gearing, which allows the sample Sp to be positioned with an accuracy of 0.05° between zero and $\vartheta = 56°$. The detector consists of a CsI photocathode (Fk) and a VEU-6 type channeltron (Ch).

Control of the instrument and data acquisition were carried out by a computer, M-6000. The intensities were normalized to the current in the storage ring. To get reflectivities the spectra were normalized to the wavelength dependent intensity of the primary beam. For this purpose the reflectometer was positioned at $\vartheta = 0$ and the sample moved out of the primary beam.

The energy calibration of the present results is better than 0.5 eV.

0167-5087/83/0000–0000/$03.00

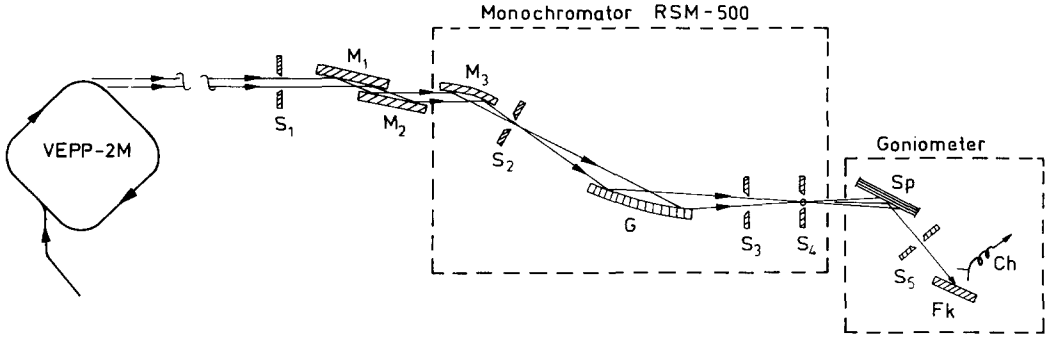

Fig. 1. Grazing incidence spectrometer and reflectometer at the storage ring VEPP-2M (for symbols see text).

3. Results and discussion

3.1. Energy dependent reflectivity

Between 99 eV and 104 eV the spectra of fig. 2 show details known from earlier published reflectivity and absorption data of pure Si [7,8]. Moreover, the spectra exhibit structures which are known from absorption measurements on films of SiO_2 [9,10] and photo-yield measurements [11]. The sharpness of the low lying states ($L_{2,3}$-doublet at 106 eV, resonant maximum at 109 eV) is caused by the long lifetime of the Si-photoelectrons inside the negatively charged potential wall of oxygen ions (SiO_4-tetrahedra). On the other hand, the smearing out of these quasi-Rydberg states in fig. 2(b, c) (Compare the resolved fine doublets from the Si substrate) should be a hint, that the SiO_4-tetrahedra are not perfect in these oxide films. The defects in the 8-nm film may possibly be caused by OH-ions from the wet chemical process [3]. The structures from the very thin oxide layer (~ 0.7 nM) grown between the stripping of the thermally grown oxide and the measurement are shifted by 2 eV to lower energies [fig. 2(a)]. This is in accordance with the XPS-shift [3] and the VUV-properties [5] of SiO.

3.2. Angular dependent reflectivity

Fig. 3 shows reflectivity curves typical for Si and SiO_2. By a least-squares fit of the experimental data the complex refractive index $n = 1 - \delta + i\beta$ was determined at six energies (see table 1). As energy independent parameters, the model contains the polarisation of the primary beam, surface roughness and two background parameters. Whereas the optical constants of SiO_2 are stable against variation of the background model and the surface roughness value, the constants of Si are very sensitive to these. Only the energy dependent trend of the constants is significant; the absolute values may be shifted.

At higher angles the intensity is modulated by interferences between the beams reflected from the vacuum/oxide and the oxide/silicon interfaces (figs. 4

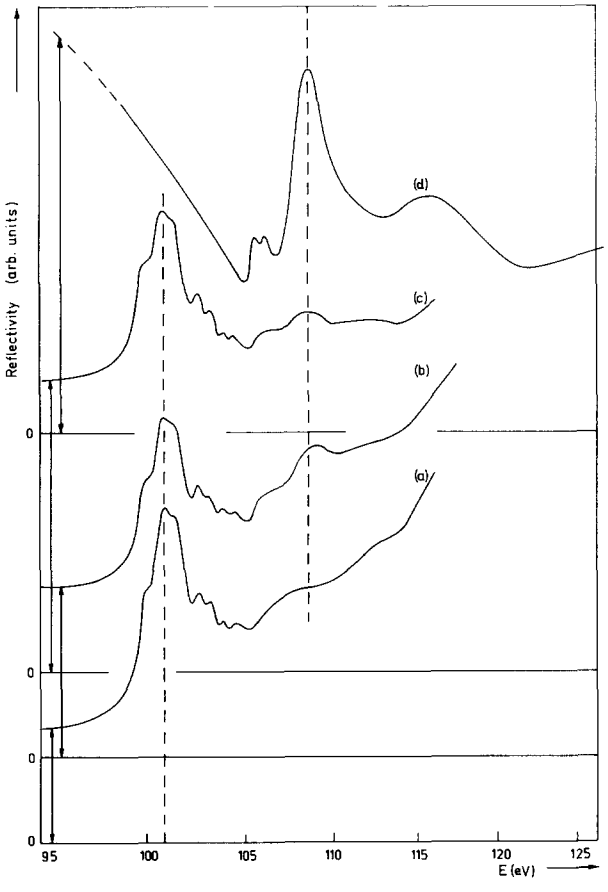

Fig. 2. Energy dependence of the reflectivity at 12° incidence; (a) Si, oxide freshly stripped; (b) silicon with 2.5 nm naturally grown oxide; (c) silicon with 8 nm thermally grown oxide, partially stipped; (d) silicon with 49 nm thermally grown oxide, partially stripped.

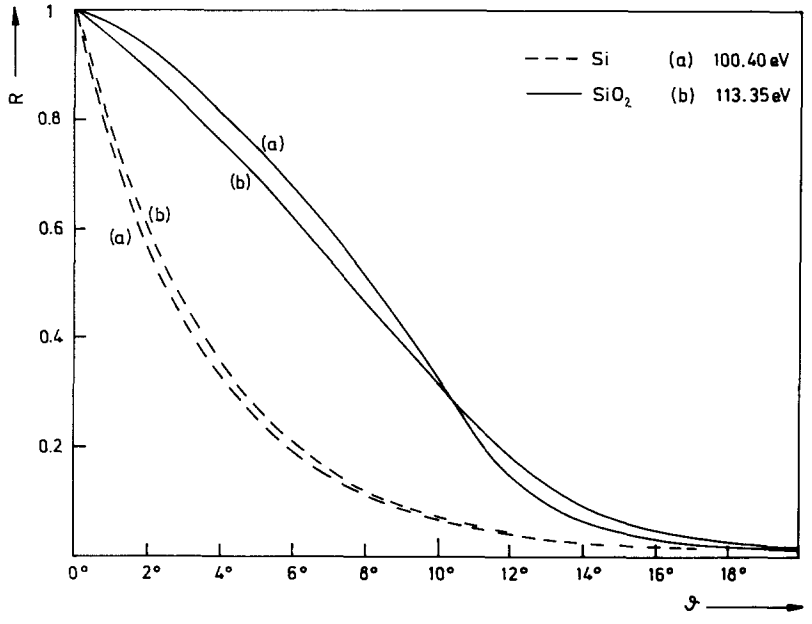

Fig. 3. Angular dependence of the reflectivity of Si and SiO_2 (91.3 nm) at low angles of incidence.

Table 1
Optical constants $n = 1 - \delta + i\beta$ of Si and SiO_2.

E [eV]	Si		SiO_2	
	δ	β	δ	β
93.1	−0.0166	0.0033	0.0239	0.0113
100.4	−0.0281	0.0153	0.0184	0.0086
105.4	−0.0137	0.0209	0.0108	0.0097
106.9	−0.0142	0.0233	0.0118	0.0119
109.4	−0.0105	0.0245	0.0212	0.0140
113.6	−0.0095	0.0265	0.0150	0.0119

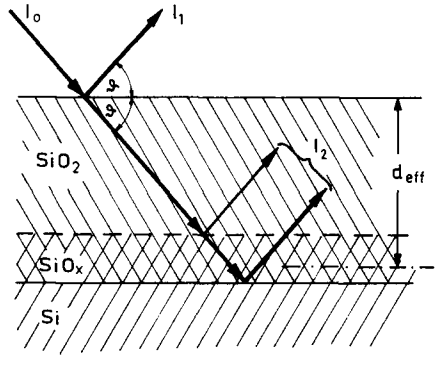

Fig. 4. One layer model for the description of interferences in the reflectivity of SiO_2/SiO_x-films on Si.

and 5). The theoretical multilayer interference model is similar to the one described by Martens [1]. On the contrary, it takes into account not only the surface roughness, but also the roughness of all interfaces. Because the intensity from the surface dominates all the others, the introduction of individual, uncorrelated Debye factors for each interface is a good approximation. This roughness explains the differences between theory and experiment firstly observed by martens, which was overcome by a formal introduction of a physically not explainable "volume-roughness".

Taking into account the optical constants of Si and SiO_2 (table 1) as fixed parameters, from the interferences the effective film thickness and the interface roughness inclusive thickness inhomogeneity was determined. The difference between experiment and model lies within the experimental error. For fig. 5 for instance, the error amounts to $\Delta R/R = 0.002/\sqrt{R} + 0.03$ (counting statistics, primary intensity instability, angular position error). An oxide thickness of 91.3 ± 0.2 nm was derived; 90.7 nm were measured ellipsometrically. The interface roughness amounts to ± 0.7 nm, which is comparable to values determined by electron microscopy [12].

The dependence of the effective oxide thickness on energy (fig. 6) proves, that there is no sharp interface between SiO_2 and the substrate. When the optical constants of the hypothetical SiO_x-interregion are like those of SiO_2, the main part of reflected intensity comes from the deeper SiO_x/Si-interface and vice versa. Therefore,

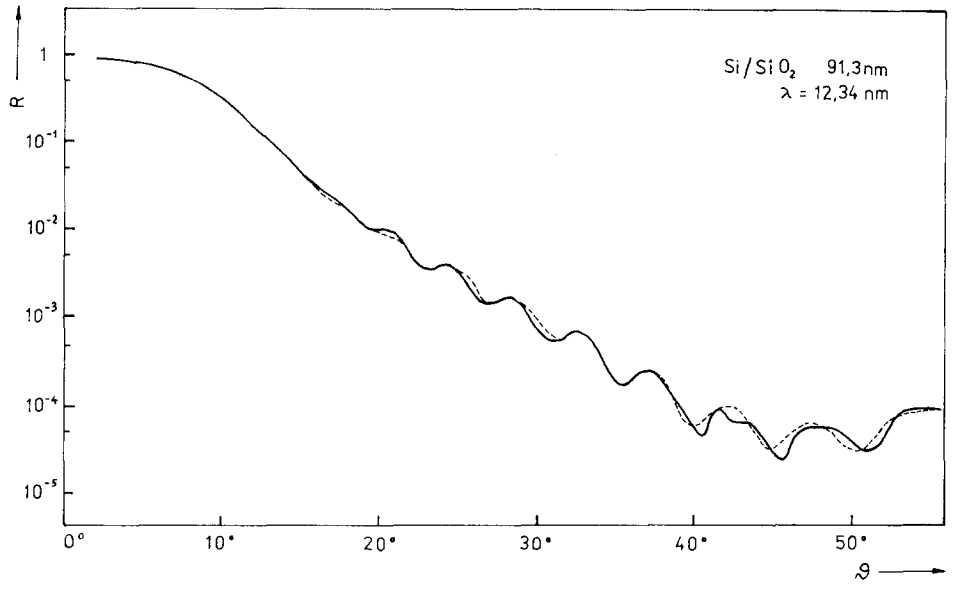

Fig. 5. Angular dependence of the relfectivity of 91.3 nm SiO_2 on Si: solid curve experimental, broken curve least-squares fit.

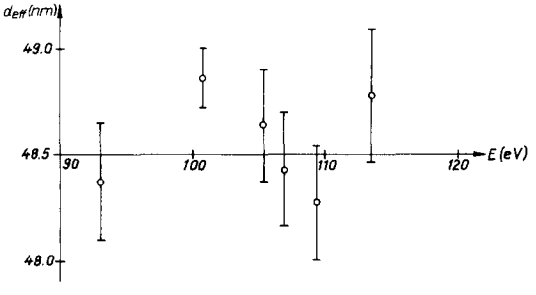

Fig. 6. Energy dependence of the "effective" oxide layer thickness of thermally grown and partially stripped oxide (49 nm).

from fig. 6 conclusions may be drawn regarding the optical constants of the interregion: the conduction band edge should lie between those of Si and SiO_2, for instance.

4. Conclusions

Unfortunately, during the last discussed measured series the SR intensity was very unstable; the oxide film thickness of the partially etched sample was very inhomogeneous (± 3 nm) compared with as-grown films. Therefore, the errors of the measured effective thicknesses are high (± 0.3 nm), and the conclusions are not very significant.

In further experiments at normal conditions and with optimal samples we expect an error of $\leqslant 0.1$ nm. Moreover, the accuracy of the optical constants of pure Si and the point density on the energy axes must be enlarged.

However, we think that these preliminary investigations have proved the high information content of soft X-ray reflectivity regarding thin films and interface problems.

We thank L. Pajasova and O.A. Makarov for stimulating discussions and the staff of the VEPP-2M for support during the experiments. One of us (W.B.) thanks the Academy of Science of the USSR for the opportunity of a post-doctoral fellowship.

References

[1] G. Martens, Doctoral Thesis, university of Kiel (1980).
[2] K. Hübner, Proc. 26. Intern. Wiss. Koll., TH Ilmenau, GDR (1981) pp. 99–103.
[3] J. Finster and D. Schulze, phys. stat. sol. (a) 68 (1981) 505.
[4] D.E. Aspnes and J.B. Theeten, J. Electrochem. Soc.: Sol. State Sc. & Techn. 127 (1980) 1359.
[5] H.R. Philipp, J. Phys. Chem. Solids 32 (1971) 1935.
[6] E.S. Gluskin, E.M. Trachtenberg and A.S. Vinogradov, Nucl. Instr. and Meth. 152 (1978) 133.
[7] H. Fujita and Y. Iguchi, Jpn. J. Appl. Phys. 14 (1975) 220.
[8] F.C. Brown and O.P. Rustgi, Phys. Rev. Lett. 28 (1972) 497.
[9] O.A. Ershov and A.P. Lukirskij, Fiz. tverd. tel 8 (1966) 2137.
[10] E.S. Gluskin, L.N. Mazalov, A.A. Krasnoperova, V.A. Kochubey, A.N. Skrinsky, E.M. Trachtenberg and G.M. Tumaykin, Izv. Akad. Nauk SSSR, ser. fiz. 40 (1976) 226.
[11] I.A. Brytov, Yu.P. Dikov, Yu.N. Romascenko, S.P. Dolin, E.I. Debolskij, Izv. Akad. Nauk SSSR, ser. fiz. 40 (1976) 411.
[12] M. Pasemann and O.P. Pchelyakov, phys. stat. sol., submitted.