Oxidation Induced Anisotropic Deformation in Perfect Si Crystals. Dynamical X-Ray Diffraction Study

J. Burgeat[1], R. Caciuffo[2], J. Primot[1], and F. Rustichelli[3]

Z. Naturforsch. **37a**, 433—436 (1982); received January 22, 1982

Dedicated to Professor G. Hildebrandt on the occasion of his 60th birthday

Double X-ray diffractometry has been used to investigate perfect Si crystals of different orientations, on which SiO_2 layers of different thickness were grown. For the (111) and (110) orientations no appreciable modification of the theoretical diffraction pattern is observed. An important modification, which depends on the SiO_2 thickness, appears however for the (100) orientation. The observed effect does not change when the SiO_2 is removed and can be interpreted as an enhancement of the lattice parameter.

Oxidation-induced defects in Si crystals are of great importance in the development of electronic devices. The present paper reports a room temperature study of the orientation-dependence of stresses produced in perfect Si crystals by surface oxidation.

The stress present during the SiO_2 growth can be ascribed, according to a recent theoretical model [1], to a lack of free volume due to the difference in the SiO_2 and Si densities. By means of an optical technique EerNisse [2] has shown that these stresses are dependent on the growth temperature; during SiO_2 growth they are sufficiently strong to produce plastic deformation of Si; for growth temperatures greater than 1000 °C, they are of tensile type, whereas for temperatures lower than 950 °C they are of compressive type.

We have investigated by double X-ray diffractometry three series of perfect crystals ($2 \times 5 \times 8$ mm^3) with an external face (cut parallely to (100), (110) and (111) planes respectively) covered by different SiO_2 thicknesses. Before the oxidation, we have checked the quality of the samples by recording the diffraction patterns with the monochromator crystal oriented as the sample. The measured widths of the reflexion curves are in good agreement with the theoretical values calculated in the frame of dynamical diffraction theory.

Every crystal series has been subject to three different oxidation treatments in order to obtain SiO_2 layers of different thickness*:

a) a 2500 Å thick SiO_2 layer has been obtained at 1050 °C after 10 min in dry O_2, 30 min in wet O_2 and finally 20 min in dry O_2;

b) a 5000 Å thick SiO_2 layer has been obtained at 1050 °C after 10 min in dry O_2, 43 min in wet O_2 and 20 min in dry O_2;

c) a 12000 Å thick SiO_2 layer has been obtained at 1150 °C after 20 min in dry O_2, 180 min in wet O_2 and 20 min in dry O_2.

After oxidation the diffraction patterns were recorded with the double X-ray diffractometer. In all the measurements, the monochromator was a perfect Si crystal set in the non-dispersive arrangement.

No effects were detected for crystals with an SiO_2 layer of any thicknes on a (111) or (110) plane. The shape of the diffraction pattern after the treatment does not differ from that recorded before the treatment, except for a slight intensity reduction due to X-ray absorption in the oxide layer. Table I shows the theoretical and experimental values of the full width at half maximum (FWHM), the integrated reflectivity power R_H, and the peak reflectivity

$$r_{\max} = \left(\frac{P_H}{P_0}\right)_{\max}, \tag{1}$$

where P_H and P_0 are the diffracted and incident powers [4], respectively.

Figure 1 shows the results of the (111) oriented crystals after the formation of a 5000 Å thick (1 a)

---

[1] Centre National d'Etudes des Télécommunications, Bagneux, France.
[2] Joint Research Centre of European Communities, Ispra Establishment, Physics Division, Ispra, Italy and Institut Laue-Langevin, Grenoble.
[3] Università di Ancona, Italy.

Reprint requests to F. Rustichelli, ILL 156X, F38042 Grenoble, France.

* For the (111) planes the thickness is slightly lower, due to the smaller SiO_2 growth rate.

0340-4811 / 82 / 0500-0433 $ 01.30/0. — Please order a reprint rather than making your own copy.

Table 1. CuKα_1 diffraction patterns for oxid doted Si crystals.

Substratum plane and reflexion	Surface condition	Full width at half maximum	Peak reflectivity $r_{\max}$	Integrated reflecting power R_H
Si (111), (111)	perfect crystal	9.48″ (theor.)	0.704 (theor.)	3.908×10^{-5} (theor.)
Si (111), (111)	5.000 Å SiO_2	10″	0.602	3.49×10^{-5}
Si (111), (111)	12.000 Å SiO_2	9.70″	0.55	3.39×10^{-5}
Si (110), (220)	perfect crystal	6.314″ (theor.)	0.708 (theor.)	2.708×10^{-5} (theor.)
Si (110), (220)	2.500 Å SiO_2	6.6″	0.59	2.41×10^{-5}
Si (110), (220)	5.000 Å SiO_2	6.5″	0.63	2.58×10^{-5}
Si (110), (220)	12.000 Å SiO_2	7″	0.57	2.43×10^{-5}
Si (100), (400)	perfect crystal	4.24″ (theor.)	0.674 (theor.)	1.703×10^{-5} (theor.)
Si (100), (400)	perfect crystal	4.85″	0.635	1.692×10^{-5}
Si (100), (400)	2.500 Å SiO_2	6.70″	0.448	2.453×10^{-5}
Si (100), (400)	2.500 Å SiO_2 removed	6.93″	0.450	2.471×10^{-5}
Si (100), (400)	5.000 Å SiO_2	9.24″	0.388	3.05×10^{-5}
Si (100), (400)	5.000 Å SiO_2 removed	8.09″	0.395	3.06×10^{-5}
Si (100), (400)	12.000 Å SiO_2 removed	16.74″	0.32	3.06×10^{-5}

and of a 12000 Å thick (1 b) SiO_2 layer. The measured FWHM and the integrated reflecting power coincide with the values predicted by the dynamical diffraction theory for a perfect crystal. This is the case also for the (110) oriented samples; the results are shown in Fig. 2 for different values of oxide thickness.

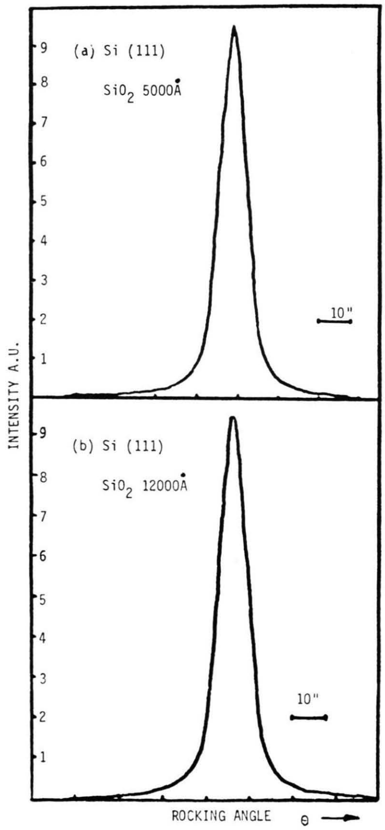

Fig. 1. CuKα_1 X-ray double diffraction patterns for a Si(111) crystal covered with a 5000 Å (a) and a 12000 Å (b) thick SiO_2 layer.

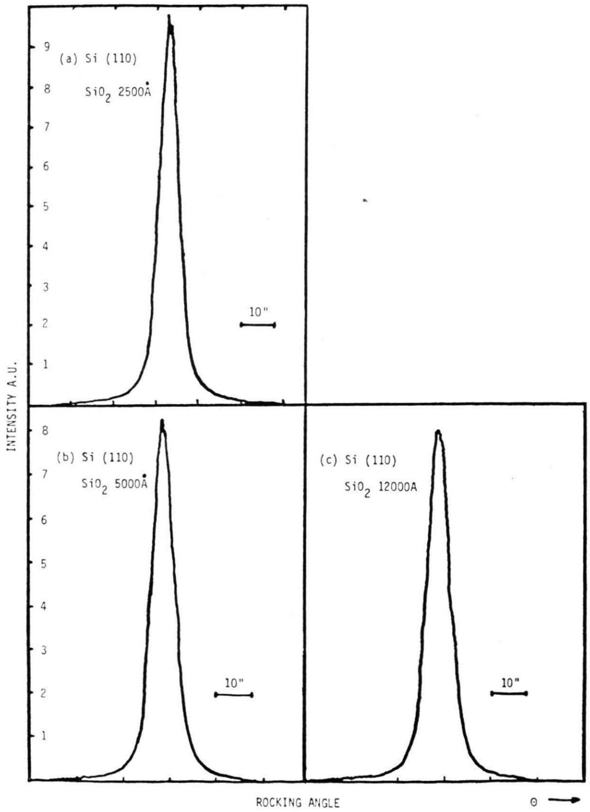

Fig. 2. Si(220) reflexion. Double diffraction pattern for a Si(110) crystal covered with a 2500 Å (a) 5000 Å (b) and 12000 Å (c) thick SiO_2 layer.

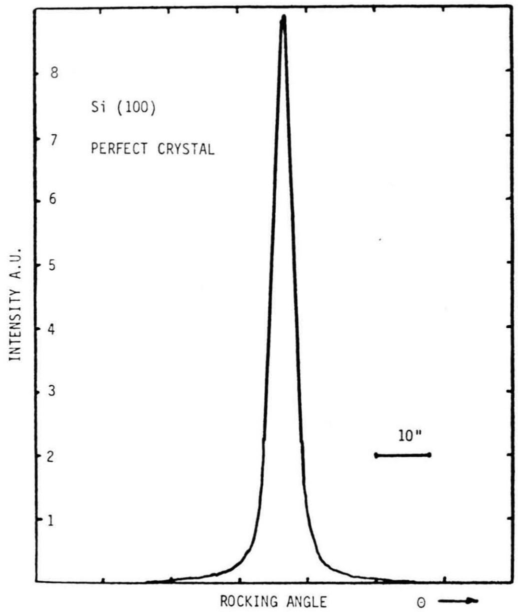

Fig. 3. Si(400) reflexion. Double diffraction pattern for a perfect crystal before the oxidation treatment.

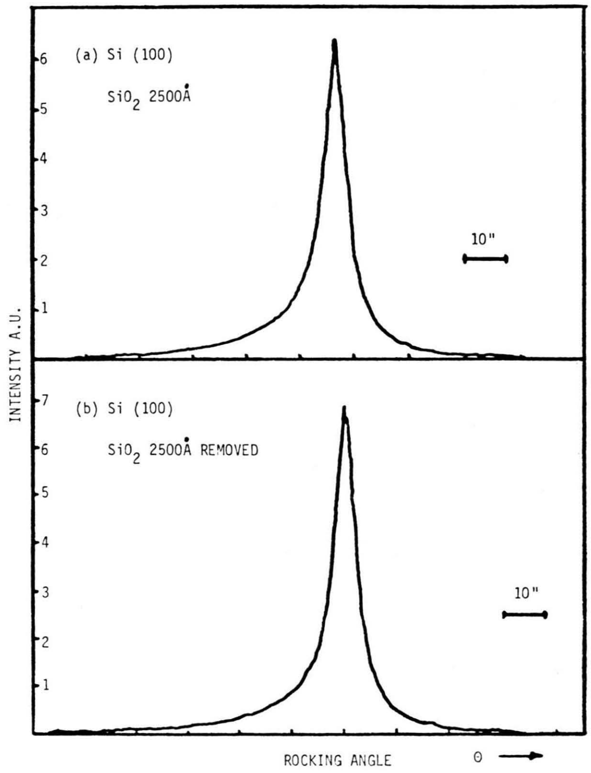

Fig. 4. Si(400) reflexion; (a) crystal with a 2500 Å oxide thickness growth on the (100) face; (b) the same crystal after removal of the SiO_2 layer.

On the contrary, for the (100) oriented samples an important effect due to surface oxidation is observed. The (100) diffraction pattern recorded before oxidation is shown in Fig. 3; it agrees with

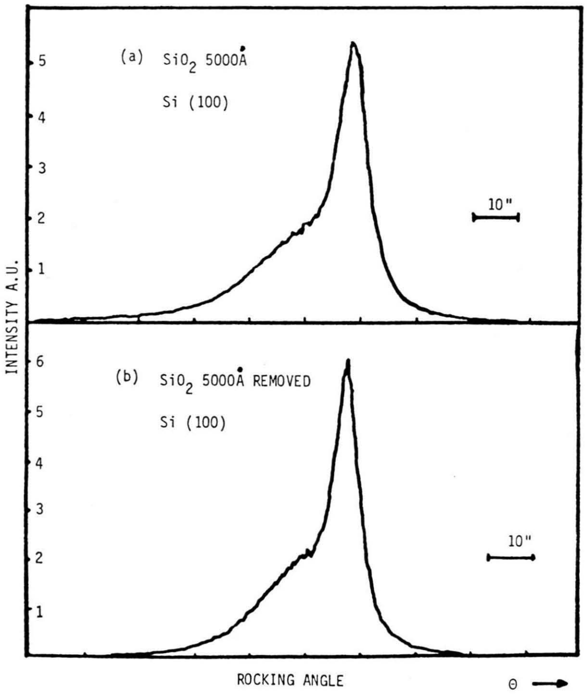

Fig. 5. Si(400) reflexion; (a) crystal with a 5000 Å oxide thickness growth on the (100) face; (b) the same crystal after removal of the SiO_2 layer.

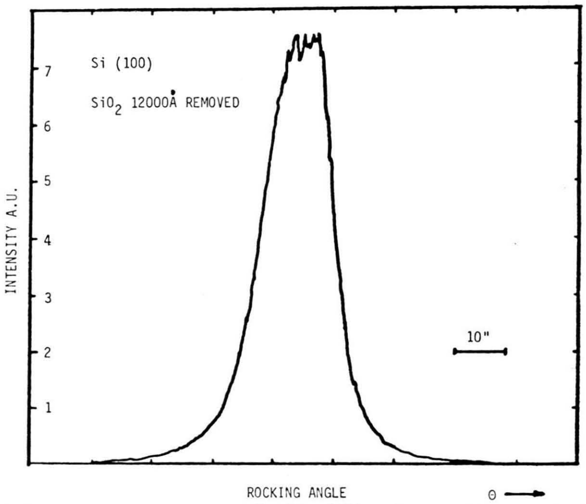

Fig. 6. Si(400) reflexion; double diffraction profile recorded after removal of a 12000 Å SiO_2 thickness grown on a (100) external face.

the theoretical calculation for a perfect crystal reported in Table 1. After oxidation the diffraction curve shows a modification similar to that produced during boron diffusion in perfect Si crystals [5] but, contrary to that case, the side perturbed corresponds to angles smaller than the Bragg angle. The shape of the diffraction patterns indicates the existence of a depth-dependent lattice parameter enhancement.

The results for a 2500 Å and a 5000 Å thick SiO_2 layer are shown in Fig. 4a and Fig. 5a, respectively. One can see that the perturbation increases with increasing thickness and that it persists even after the oxide layer has been removed (Fig. 4b and Figure 5b).

Therefore, the oxidation induced deformation in (100) oriented Si crystals is not elastic; this is in contrast with the results of previous works [6]. Figure 6 reports the diffraction profile recorded after removal of a 12000 Å SiO_2 thickness. The enhancement of the effect is evident.

In conclusion, we have observed a variation of the X-ray diffraction for a perfect Si crystal due to the oxidation of a crystal face cut in parallel to the (100) planes. This variation depends on the SiO_2 thickness and does not change if the oxide layer is removed. This effect is interpreted as a deformation of the crystal lattice which decreases with the depth and corresponds to an enhancement of the lattice parameter. However, no effects are observed when the oxidation face is cut in parallel to (110) or (111) planes. This orientation dependence is perhaps correlated with the well known [7] orientation dependence of SiO_2 growth-rate. Anyhow further work based on different techniques seems suitable.

[1] W. A. Tiller, J. Electrochem. Soc. **127**, 619 (1980).
[2] E. P. EerNisse, Appl. Phys. Lett. **35**, 8 (1979).
[3] J. Burgeat, Thèse de Doctorat, Paris 1969, juin.
[4] W. H. Zachariasen, Theory of X-Ray Diffraction, Dover, New York 1967.
[5] J. Burgeat and D. Taupin, Acta Cryst. A**24**, 99 (1968).
[6] N. Kato and J. R. Patel, J. Appl. Phys. **44**, 965 (1973).
[7] A. G. Revesz and R. J. Evans, J. Phys. Chem. Solids. **30**, 551 (1969).