

Proceedings of the ISSRNS '94, Jaszowiec 1994

X-RAY PHOTOELECTRON SPECTROSCOPY AND OPTICAL REFLECTIVITY STUDIES OF Si SURFACES PREPARED BY CHEMICAL ETCHING

R.J. IWANOWSKI^a, J.W. SOBCZAK^b AND B.J. KOWALSKI^a^a Institute of Physics, Polish Academy of Sciences
Al. Lotników 32/46, 02-668 Warszawa, Poland^b Institute of Physical Chemistry, Polish Academy of Sciences
Kasprzaka 44/52, 01-224 Warszawa, Poland

Complementary X-ray photoelectron spectroscopy and optical reflectivity studies of crystalline Si(111) surfaces prepared by two different wet chemical etching processes were performed. These included aqueous HF solution etch or diluted CP-4 bath. Optical reflectivity spectra of Si surfaces, measured in the range 3.7–11 eV, were found strongly dependent on the applied etching process. Analysis of the core level X-ray photoelectron spectroscopy data has shown similarity of the surface structure, irrespectively of the etching procedure. Finally, comparison of optical reflectivity and valence band X-ray photoelectron spectra revealed a qualitative correlation between them indicating dominant influence of the bulk (here, the subsurface region containing polishing-induced defects) in the case studied. This paper is the first one which presents correlations between optical reflectivity and X-ray photoelectron spectroscopy data for Si and thus illustrates a bulk sensitivity of both techniques considered.

PACS numbers: 78.40.Fy, 79.60.Bm

1. Introduction

Optical reflectance (OR) spectroscopy in the ultraviolet (UV) range is well known as a method for investigating band structure of solids, especially semiconductors (e.g. [1]). Obviously, this technique is very sensitive to a quality of solid surface (roughness, oxidation, contamination, etc.) and lattice perfection of a subsurface region, limited by a penetration depth of the UV photons.

Due to the above factors, for a case of Si the OR technique was also successfully applied for investigating the influence of particle irradiation on a crystalline structure [2–8]. Nevertheless (except for [9]), there is a lack of literature reports concerning the effect of Si surface preparation (specially chemical treatment) on its reflectivity spectrum.

On the other hand, X-ray photoelectron spectroscopy (XPS) is a typical surface analysis technique (see [10]) with effective penetration depth limited by the electron escape depth (e.g. [11]). Numerous papers have been devoted to study different surface effects in Si with the use of XPS (see references in [10]). These included also XPS investigations of silicon surfaces prepared by wet chemical etching [12–14].

The object of our paper was to perform complementary OR and XPS studies of chemically treated (111) surface of crystalline silicon (c-Si), taking into account the following aspects:

— the influence of particular process of chemical etching on the reflectivity spectrum, $R(E)$;

— determination, from the XPS measurements, of the prevailing factor (surface or bulk) which contributes to the effect of chemical treatment on the $R(E)$ spectrum.

2. Experiment

We used *n*-type silicon wafers cut from the dislocation-free FZ Si (float zone Si) with resistivity of 800 Ω cm, produced by the Institute of Electronic Materials Technology (Warsaw, Poland). Their front surfaces were subjected to mechanical and chemical fine polishing provided by the producer.

Optical reflectivity measurements were performed at room temperature in the spectral range 3.7–11 eV. The experimental setup consisted of a vacuum UV monochromator (based on the Seya–Namioka scheme) with a hydrogen discharge lamp and a detecting system [15]. During measurement the sample was maintained in hydrogen atmosphere, under a constant pressure of 4×10^{-1} torr. The incident and reflected beams were detected by intensity modulation spectroscopy, using sodium salicylate powder as luminophor, photomultipliers with quartz windows and UNIPAN 232B lock-in amplifiers.

XPS measurements were performed in a spectrometer Vacuum Generators ESCALAB 210 with use of Mg K_{α} (1253.6 eV) irradiation source. The detector was placed perpendicularly to the wafer surface (take off angle, $\theta = 90^{\circ}$). During experiment the pressure in the spectrometer chamber was about 3×10^{-10} torr.

Before every OR or XPS measurement the samples were subjected to one of the following wet chemical etching processes:

A — etching in aqueous HF (10%) solution;

B — double-step etching: aqueous HF (10%) rinse followed by the diluted CP-4 bath.

Typically, an air exposure of the treated samples, prior to insertion into spectrometer chamber, lasted about 4 min.

3. Results and conclusions

Figure 1 gives typical reflectivity spectra for the Si(111) surface subjected to different chemical treatment.

It can be seen that OR spectrum of Si significantly depends on the applied wet chemical etching process.

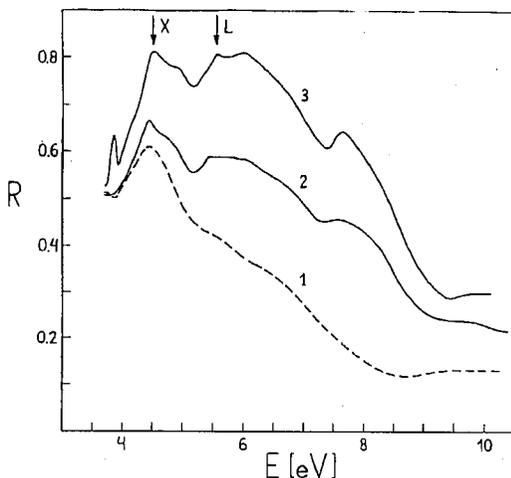


Fig. 1. Reflectivity spectra (normal incidence mode) of Si(111) surface after being exposed to the following wet chemical etching processes: 1 — aqueous HF etch (process A); 2 — 2 min double-step etch (process B); 3 — 4 min double-step etch (process B).

In particular, simple etching in HF solution (process A), which leads to deoxidation of silicon surface, results in low intensity reflectivity spectrum (curve 1 — Fig. 1). On the other hand, use of the B treatment procedure with CP-4 solution, which removes Si surface layer (in our case, up to $\approx 2 \mu\text{m}$), provided highest intensity $R(E)$ dependence (curve 3 — Fig. 1) typical of single crystalline Si (e.g. [1, 2]). The latter spectrum (denoted by 3) includes two characteristic peaks at $E_1 = 4.51 \text{ eV}$ and $E_2 = 5.55 \text{ eV}$ (denoted by X and L, respectively — Fig. 1). The first one refers to the threshold energy for direct interband transitions in the X point of the Brillouin zone ($X_4 - X_1$) and was found earlier to be specially sensitive to the lattice disorder [2-4]. The E_2 peak corresponds to the $L'_3 - L_3$ transitions [1, 5].

The above effect of chemical treatment on the $R(E)$ spectrum of c-Si resembles damping of a reflectivity coefficient due to radiation damage of a subsurface region produced by ion implantation [2-7].

Since optical reflectance is both surface- and bulk-sensitive research technique (effective penetration depth of UV photons in Si in the energy range studied, $\lambda \approx 50\text{--}100 \text{ \AA}$ [5]) it became logical to perform complementary XPS measurements that could enable us to indicate which factor dominates in the effect observed here.

The core level XPS data obtained for Si(111) surfaces studied are partially represented in Fig. 2, which gives the Si 2p (2a) and O 1s (2b) core level spectra. These refer to the surface subjected to B-type treatment, although identical spectra were recorded after aqueous HF etching.

Monitoring of the Si 2p core level by XPS provides specially useful information since it shows a distinct (up to 4 eV) chemical shift toward higher binding energies when silicon is in the form of suboxide or SiO_2 [13, 16, 17]. Similar shift appears when formation of SiF_x ($x = 1, 2, 3$) on the crystalline Si surface occurs [18].

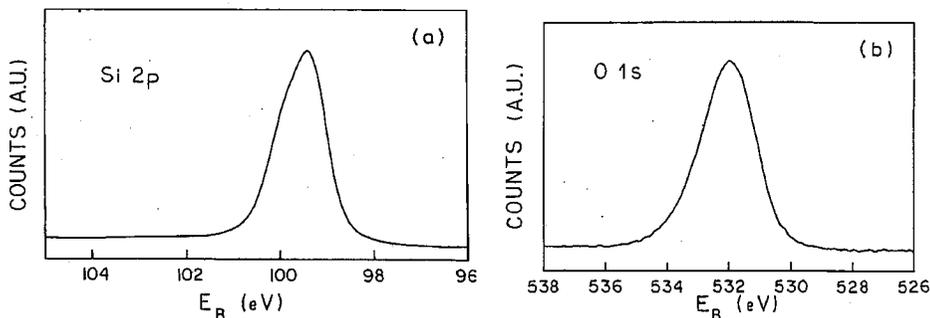


Fig. 2. Typical core level XPS spectra: (a) Si 2*p* and (b) O 1*s* obtained for chemically etched Si(111) surfaces, irrespectively of the chosen process (*A* or *B*).

It should be emphasized that in both cases considered the Si 2*p* core level spectrum did not exhibit any additional structure typical of surface oxide layer or SiF_x overlayer, which could influence the magnitude of reflectivity coefficient.

Lack of evident binding energy (E_B) shift for Si 2*p* core level does not exclude existence of adsorbed oxygen on Si surface (see e.g. [19]). This is the case of Si(111) surfaces studied, where identical line shapes, binding energies as well as comparable intensities of the O 1*s* photoemission peak were observed (irrespectively of applied etching process — see Fig. 2b). The value of E_B (O 1*s*) of the oxygen adsorbed on crystalline Si surface strongly depends on the oxide thickness [16]. Comparison of E_B (O 1*s*) observed here with adequate literature data [16, 19, 20] indicates that the concentration of adsorbed oxygen has reached the order of 1 ML. Possibly, this oxygen can be associated to bridging O atoms in the first layers (see [20]) — the effect characteristic of an early stage of oxide formation.

On the other hand, only trace fluorine concentration ($[F] \approx 0.01 [O]$) was detected on the surfaces studied.

Earlier report of Himpsel et al. [21], who have determined for Si the energy distance between the top of valence band and E_B (Si 2*p*_{3/2}), enabled us to estimate the value of surface Fermi level, E_F^s . In both cases considered, it was found pinned at the midgap position and remained in good agreement with the data given in [21].

In general, the analysis of core level XPS data indicated similarity of Si(111) surface structure, irrespectively of the used etching procedure (*A* or *B*).

On the contrary, the XPS valence band spectra of these surfaces showed remarkable dependence on the applied wet chemical etching (see Fig. 3).

Comparison of the OR with valence band XPS spectra (Figs. 1 and 3) revealed a qualitative correlation between them, thus indicating dominant influence of the bulk, namely (in this case) the subsurface region with residual defects induced by polishing. These defects provide (similarly as radiation defects) perturbation of long-range order of the crystalline lattice and hence a modification of valence and conduction bands.

Evidence of this effect in valence band XPS is specially interesting, since its penetration depth in a crystal volume is smaller than that of OR technique. In

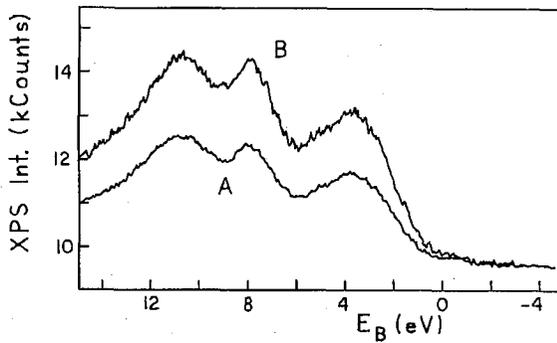


Fig. 3. Valence band XPS spectra of the Si(111) surfaces studied. The spectra denoted by A and B correspond to the $R(E)$ dependences from Fig. 1, numbered by 1 and 3, respectively.

the case of Si the effective electron escape depth, determined experimentally [22], remains smaller than 50 Å.

Generally, this paper is the first one which presents complementary investigations of crystalline Si surface (prepared by chemical treatment) with the use of optical reflectance and X-ray photoelectron spectroscopy, indicating correlations between their results and thus illustrating also a bulk sensitivity of both techniques considered.

Acknowledgment

The first author (R.J.I.) would like to express his gratitude to Prof. A. Jabłoński (Institute of Physical Chemistry P.A.S.) and Prof. B.A. Orłowski (Institute of Physics P.A.S.) for enabling him to perform the above experiment in their laboratories.

References

- [1] H.R. Philipp, H. Ehrenreich, *Phys. Rev.* **129**, 1550 (1963).
- [2] T.C. McGill, S.L. Kurtin, G.A. Shifrin, *J. Appl. Phys.* **41**, 246 (1970).
- [3] E.T. Yen, B.T. Masters, R. Kastl, in: *Proc. 4th Int. Conf. Ion Implantation in Semiconductors and Other Materials*, Osaka (Japan) 1974, Ed. S. Namba, Plenum Press, New York 1974, p. 501.
- [4] M. Miyao, T. Miyazaki, T. Tokuyama, *Jpn. J. Appl. Phys.* **17**, 955 (1978).
- [5] R.E. Hummel, Wei Xi, P.H. Holloway, K.A. Jones, *J. Appl. Phys.* **63**, 2591 (1988).
- [6] E. Czarnicka-Such, A. Kisiel, *Surf. Sci.* **193**, 221 (1988).
- [7] P.L. Swart, B.L. Lacquet, H. Aharoni, *IEEE Trans. Nucl. Sci.* **39**, 464 (1992).
- [8] R.J. Iwanowski, B.J. Kowalski, B.A. Orłowski, J. Bąk-Misiuk, in: *Proc. 17th Int. Conf. on Defects in Semiconductors ICDS-17*, Gmunden (Austria) 1993, Ed. K. Lischka, Materials Science Forum, Vol. 143-147, Trans Tech Publ., Switzerland 1993, p. 183.

- [9] Ch. Kleint, M. Merkel, *Surf. Sci.* **213**, 657 (1989).
- [10] J.J. Pireaux, R. Sporken, in: *Analysis of Microelectronic Materials and Devices*, Ed. M. Grasserbauer, H.W. Werner, Wiley, New York 1991, p. 111.
- [11] S. Tanuma, C.J. Powell, D.R. Penn, *Surf. Interface Anal.* **17**, 911 (1991).
- [12] B.R. Weinberger, G.G. Peterson, T.C. Eschrich, H.A. Krasinski, *J. Appl. Phys.* **60**, 3232 (1986).
- [13] J.M.C. Thornton, R.H. Williams, *Phys. Scr.* **41**, 1047 (1990).
- [14] E.T.P. Benny, J. Majdi, *J. Electron Spectrosc. Relat. Phenom.* **58**, 261 (1992).
- [15] B.J. Kowalski, Ph.D. Thesis, Institute of Physics, Polish Academy of Sciences, 1988.
- [16] J. Finster, D. Schultze, F. Bechstedt, A. Meisel, *Surf. Sci.* **152/153**, 1063 (1985).
- [17] F.J. Himpsel, F.R. McFeely, A. Taleb-Ibrahimi, J.A. Yarnoff, G. Hollinger, *Phys. Rev. B* **38**, 6084 (1988).
- [18] F.J. Himpsel, J.F. Morar, J.A. Yarnoff, *J. Electrochem. Soc.* **135**, 2844 (1988).
- [19] G. Margaritondo, J.E. Rowe, S.B. Christman, *Nuovo Cimento B* **39**, 781 (1977).
- [20] G. Hollinger, J.F. Morar, F.J. Himpsel, G. Hughes, J.L. Jordan, *Surf. Sci.* **168**, 609 (1986).
- [21] F.J. Himpsel, G. Hollinger, R.A. Pollack, *Phys. Rev. B* **28**, 7014 (1983).
- [22] M. Klasson, A. Berndtsson, J. Hedman, R. Nilsson, R. Nyholm, C. Nordling, *J. Electron Spectrosc. Relat. Phenom.* **3**, 427 (1974).