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The Influence of the Silicon Surface Treatment on the Reflectivity Spectra in the 0.2µm – 0.6µm Wavelength Range

The reflectivity spectra from the surface of monocrystalline Si plates, processed by different methods have been studied. The measurements were carried out at 300 K in the 0.2 µm–0.6 µm wavelength range. The three singular points observed in the reflection spectrum and corresponding energies 3.39 eV, 4.52 eV and 5.4 eV were attributed to the transitions in silicon band structure. The influence of surface processing methods on the reflection spectra has been stated and probable reasons of this effect have been discussed.

1. Introduction

The state of the surface of semiconductor materials as determined by its smoothness, flatness and purity as well as structural perfection of the near-surface layer is a decisive factor of parameters and reliability of many modern electronic devices (see e.g. [1]). During typical technological processes (like slicing, grinding and polishing) the crystal lattice of the near-surface layer suffers from a considerable deformation (in extreme cases an amorphic layer is produced), a deformation in the band structure occurs which is associated with creation of surface states.

The state of the surface affects essentially the whole set of properties, like the MIS structures, metal-semiconductor contacts and semiconductor heterojunctions. Thus the processing and control of the semiconductor surface are the most important stages in the technology of the semiconductor devices.

There exist a number of methods by which the state of surface after each technological operation can be examined e.g. such which employ the measurements of: carrier life-time, photoconductivity, and surface conductivity as well as of electron and X-ray diffraction. Optical methods are also very often used, and elipsometric measurements [2,3] light reflection measurements [4, 5], Auger's spectroscopy, photoemissive spectroscopy in the U.V. wavelength range [6], in particular. An extensive survey of the optical methods used in surface state examination may be found in [7] and [8]. The purpose of this paper is to analyze the reflection spectrum of the monochromatic light reflected from the silicon surface as well as to evaluate influence of the method of semiconductor surface processing on the reflection spectrum, i.e. to estimate the applicability of the reflection spectra for determining the quality of the semiconductor surface after processing.

2. Experimental part

2.1. Preparation of the silicon plates

An original material to be examined consisted of silicon plates of 250 µm in thickness, cut out from a monocrystal along the [111] plane. The measurements of reflectivity were performed with respect to the plates where surfaces were subjected to the final processing operations described below.

1. The silicon plates of n-type of about 5 Ω cm resistivity were polished with the diamond paste of 1 µm grain size, under the pressure of 200 G/cm². In the course of 9HR polishing a layer of 70 µm thickness was removed from the surface. The examinations carried out earlier showed that the surfaces obtained in this way were very smooth, but the near--surface layer of the material had a completely destroyed crystalline structure [9].

2. The silicon plates of n-type of resistivity amounting to about 10 Ω cm and about 40 cm, respectively, were polished with a mechanic--chemical method by using a solution con-

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taining copper nitrate and amonium fluoride. In the course of 30 min polishing on a soft substrate under the load of 150 G/cm² a layer of 40 μm was removed. The surface obtained in this way possesses a satisfactory smoothness and the near-surface layer does not exhibit any perturbations of the crystal lattice (see also [9]).

3. In order to remove from the surface processed by method (2), that external layer which might be damaged or polluted in the course of machining it, the surfaces have been subjected to anodice oxidation and the SiO_2 layer produced in this way was diluted in the hydrofluoric acid. The procedure repeated three times, resulted in removing a 0.2 μm layer from the silicon surface. This way of removing the near-surface allows to preserve the original smoothness of the plate.

4. The plates of n-type silicon polished with a LUSTROX polishing suspension under production condition were the next subject of examination. The surface is satisfactorily smooth and the depth of damage does not exceed 50 nm.

5. The reflection spectra from the silicon plates polished and etched chemically and next exposed to the action of atmosphere for 8 years have been measured for comparative reasons.

2.2. Measuring system

The block diagram of the used measuring system is presented in Fig. 1. The source of the white light was a halogen lamp of 250 W power. The SPM-2 monochromator used produced by Carl Zeiss Jena firm was equipped with a quartz prism. For modulation of the radiation a mechanical chopper of frequency range adjustable within 10 Hz to 1250 Hz was applied. An evaporated Al layer because of a very great coefficient of reflection, and almost constant value for the wavelengths exceeding 0.2 μm has been used as a standard [10]. In order to avoid greater errors the measurements were always performed on freshly evaporated layers of Al.

Fig. 2 presents a relative error in determining the wavelength depending on the slit width in the monochromator. The measurements were performed within the 0.2–0.6 μm wavelength range. It has been estimated that within this range the error of wavelength determination defined by its energy $h\nu$ amounts to about 0.01 eV [11]. In order to increase the accuracy of the measurement the sample

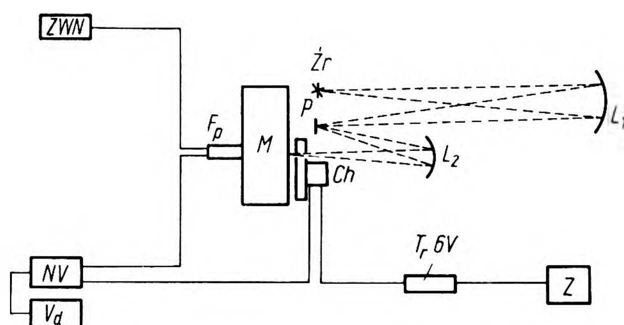

Fig. 1. Set up of the reflection measuring system
Zr – source of radiation, L_1 and L_2 – spherical mirrors, P – sample under test, Ch – chopper, M – monochromator, F_p – photomultiplier, ZWN – high voltage supplier, NV – selective nanovoltmeter, V_d – digital voltmeter, Z and T_r – a supply with a transformer for chopper

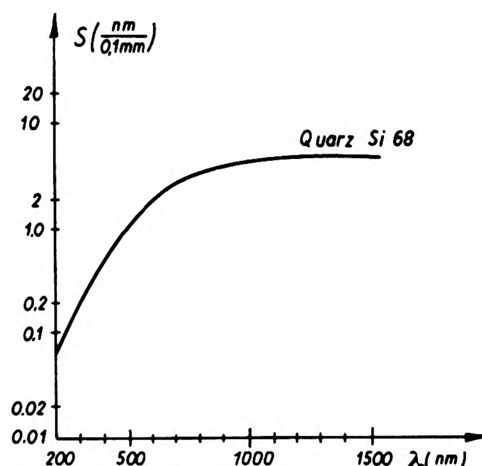

Fig. 2. An error S of the wavelength determination as a function of the wavelength value for the monochromator slit width equal to 0.1 mm

was measured three times at each point and the results presented were calculated as arithmetic means of these measurements. To check the uniformity of polishing process the measurements of reflectivity were made at several points on each plate surface.

3. Discussion of results

Beside the behaviour of the optical constants in the vicinity of the critical points the proper association of the observed maxima of $R(\lambda)$ to the respective transitions in the band structure of semiconductor is of a basic importance for the interpretation of the reflectivity spectrum. The probability of interband transition for a given energy of light may be a sum of probabilities of transitions at several different points of the Brillouin zone [12, 13]. The problem of interpretation of reflectivity spectrum was simplified by the fact that the band structure of silicon is, in principal, well known.

Spectral dependences of the coefficient of reflection from the silicon surfaces processed in the ways described above are shown in Figs. 3a, b, c, d and e. In all these Figures two main reflection maxima of energies 3.39 eV (3.32 eV in Fig. 3c) and 4.52 eV can be distinguished. In Fig. 3c the latter maximum is spread in a way suggesting the existence of two superposed peaks in the reflectivity spectrum. This spread will be discussed further. Beside the two main maxima mentioned above there is also (except for Fig 3e) another remarkably less distinct maximum of energy amounting to 5.4 eV.

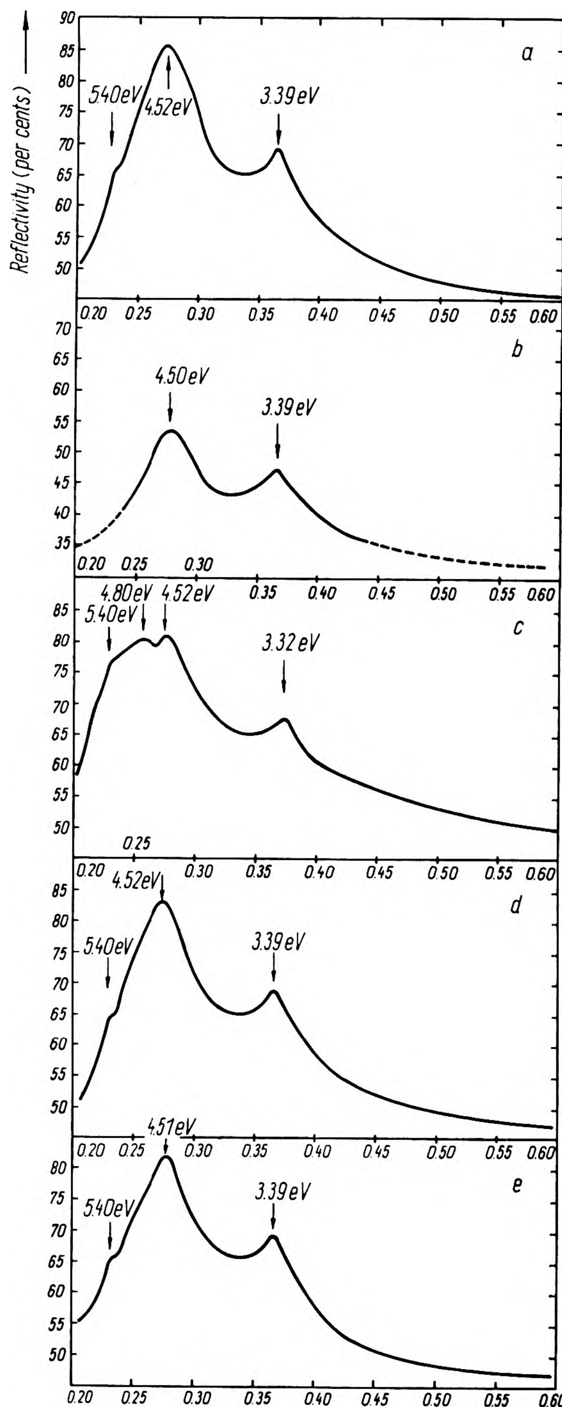

Fig. 3. The reflectivity spectrum from the Si surface processed by the following methods:

a) Method No. 2 $N_D = 5\times 10^{14}\ \mathrm{cm}^{-3}$
b) Method No. 3 $N_D = 5\times 10^{14}\ \mathrm{cm}^{-3}$
c) Method No. 1 $N_D = 10^{15}\ \mathrm{cm}^{-3}$
d) Method No. 4 $N_D = 5\times 10^{14}\ \mathrm{cm}^{-3}$
e) Method No. 5 $N_D = 5\times 10^{15}\ \mathrm{cm}^{-3}$

These points characteristic of the spectrum $R(\lambda)$ may be associated with the transitions in the band structure of silicon. Fig. 4 shows a schematic picture of the band structure calculated with the help of $\hat{kp}$ method [14] for the point Γ and in the directions [111] and [100]. Table presents a list of calculated energy transitions

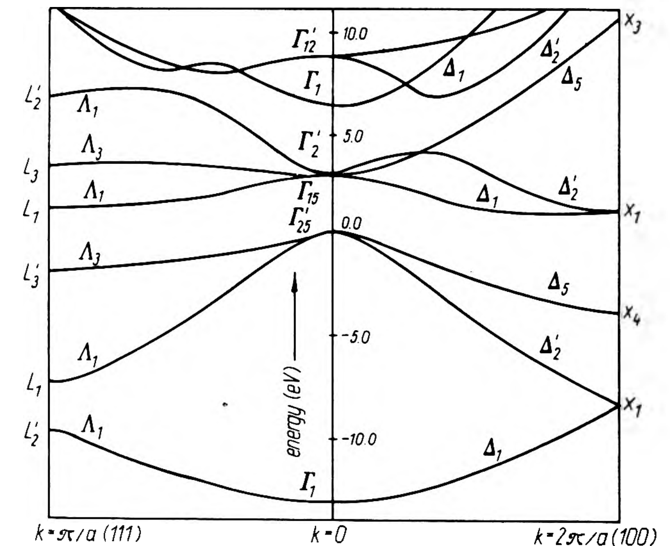

Fig. 4. A schematic Si band structure calculated with the $\hat{kp}$ method [14]: Notation used being in accordance with [14]

The values of transition at some characteristic points of Si band structure

Type of transition after [14]	Energy gap values (eV)		
	calculation by $\hat{kp}$ method	experimental data	
		from references	obtained in present work
$L'_3 \to L_1$ $\left(k = \frac{\pi}{a}\right)$	3.2	3.2 [17]	—
$\Gamma'_{25} \to \Gamma_{15}$ $(k = 0)$	3.4	3.4 [5, 15, 18]	3.39 ± 0.02
$\Gamma'_{25} \to \Gamma_2$ $(k = 0)$	3.6	3.8 [16]	—
$X_4 \to X_1$ $\left(k = \frac{2\pi}{a}\right)$	4.4	4.1 [17] 4.55 [5] 4.56 [15]	4.52 ± 0.03
$L'_3 \to L_3$ $\left(k = \frac{\pi}{a}\right)$	5.55	5.3 [17] 5.3 [5, 15]	5.40 ± 0.05

at the characteristic points of the silicon band structure together with some published experimental data, and the results of this work. In this table the maximal error of determining the energy peaks of $R(\lambda)$ estimated as a sum of the errors presented in Fig. 2 and the maximal error of the estimation of the maximum position in the graph $R(\lambda)$ is also presented. In view of a relatively great half-width of the observed peaks caused, among others, by a high temperature of the measurements the agreement of the results of this work with the earlier results may be considered to be satisfactory.

In the examined Si samples the concentration ranged between 10^{20} m^{-3} and 5×10^{24} m^{-3}. While applying the same methods of surface preparation to the samples of various concentrations no influence of the change in carrier concentration upon the spectrum of $R(\lambda)$ was stated.

The influence of the processing method of Si surface on the reflectivity spectrum may be seen in Figures 3a–e. In particular, when comparing Fig. 3c with the remaining ones two main differences can be noticed:

1. A $\Gamma'_{25}\to\Gamma_{15}$ peak shift from the position of energy 3.39 eV to the position of energy 3.32 eV; and

2. A spread of the peak $X_4\to X_1$.

The first effect seems to be attributed to great stresses in the near-surface layer, developed during the mechanical treatment of the surface. A similar effect was observed in Ge by DONOVAN [4] for the peak 2.1 eV. The hypothesis of influence of stress is consistent with the suggestions of paper [9], that high temperatures which developed during the mechanical treatment of the surface cause the local fusion of the machined material and a formation of a thin polycrystalline layer of 1 μm thickness on the surface. In this layer as well as at its boundary with the monocrystalline substrate relatively high mechanical stresses will ocurr after solidification and crystallization.

The effect of $\Gamma'_{25}\to\Gamma_{15}$ peak shift in Si appearing due to a uni-axial stress was examined by GERHARDT [19]. For the preassures of both compressive and tensile type of 9×10^3 atm magnitude a shift of this peak by about 0.04 eV was observed. If it is assumed that in this work uni-axial stresses are also responsible for the $\Gamma'_{25}\to\Gamma_{15}$ peak shifting, then the magnitude of shift shown in Fig. 5 (on average about 0.07 eV) would indicate the existence of slightly higher stresses. A quantitative analysis does not seem to be recommended at this moment, because of

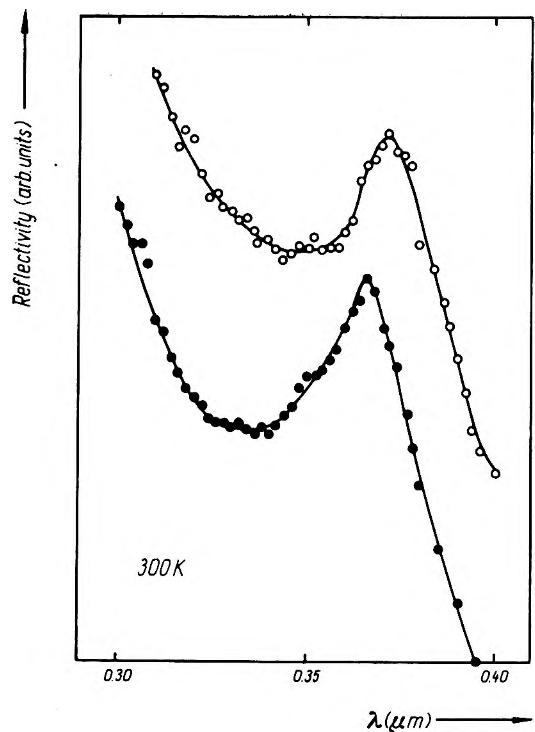

Fig. 5. A shift of the $\Gamma'_{25}\to\Gamma_{15}$ peak for the Si surface processed by using the method No. 4

too small measurement accuracy, and of the unknown nature of the stress (uni-axial or hydrostatic one), although – on the other hand – the information about similar investigations carried out in other laboratories indicate the presence of uni-axial stresses as evoked by the surface treatment [20].

The existence of high stress may be also attributed to the $X_4\to X_1$ peak spreading effect. This peak (see Fig. 4) corresponds to the transitions of the excited electrons from the X_4 valence band to the doubly degenerated conduction band X_1. With so high stresses a splitting of the energy bands at the point X_1 is probable. A possibility of independent transitions from the X_4 band to both the split X_1 bands will then appear. Thus, the result of the reflectivity measurement will correspond to the sum of probabilities of both the transitions, i.e. the shape of the dependence $R(\lambda)$ will be an envelope of two hypothetic peaks corresponding to both the transitions as it is shown in Fig. 6. This effect occurred in the same way at various points of the sample surfaces, polished with a diamond paste (treatment No. 1).

A spread of the peak $X_4\to X_1$ was observed also in the samples processed with other methods mentioned above, this effect however proved considerably weaker. It is also characteristic, that this effect did not occur

allover the surface of these samples, but only at certain points located usually in the vicinity of the plate centre, and for this reason it has not been shown in Fig. 3. By assuming that

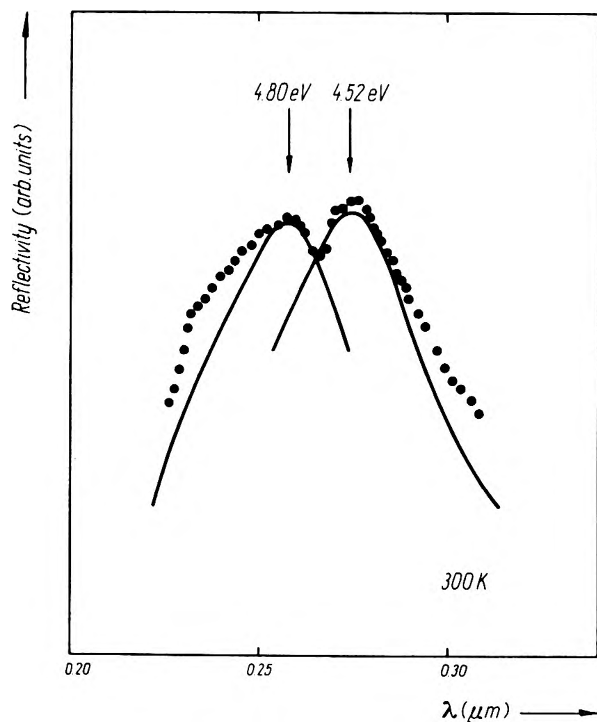

Fig. 6. The splitting of the $X_4 \rightarrow X_1$ peak for the Si surface by using the method No. 1

the hypothesis on the influence of stress on the $X_4 \rightarrow X_1$ peak profile is correct it may be assumed that the above observations give the evidence to the errors in the processing (e.g. nonuniform pressure, nonparallel surface position during the processing, and so on). It is also highly probable, that this fact is connected with the observed stress as being evoked by the changes of the crystallization point position during the Si crystal growth [21] rather than by the surface processing. The final establishment of the stress influence on the $X_4 \rightarrow X_1$ peak profile requires some further examinations.

By comparing Fig. 3b with the other figures a considerable drop in the reflectivity in Fig. 3b may be noticed within the whole wavelength range. This fact and the lack of more essential differences in the run of $R(\lambda)$ function with respect to those presented in the other figures suggests that this effect is evoked by slight matting of the surface due to the technological process used, and to an increase in the diffused light intensity.

4. Final remarks

The reflectivity measurements performed within the 0.2–0.6 μm range for the surfaces processed with five different methods have shown that — independently of the processing method — two main maxima of energies 3.39 eV, (3.32 eV) and 4.52 eV as well as a weaker maximum of energy 5.40 eV are observed. These points characteristic of the $R(\lambda)$ run have been attributed to the transitions in the silicon band structure computed with the $\widehat{kp}$ method.

An influence of the surface processing method on the reflectivity spectrum which has been proved, is displayed in two ways:

1. For the surface polished mechanically with a diamond paste as an increase in the half width spread of the $X_4 \rightarrow X_1$ maximum and a shift of the $\Gamma'_{25} \rightarrow \Gamma_{15}$ maximum by about 0.07 eV on average (treatment No. 1); and
2. For the surfaces processed with the method No. 3 as a distinct lowering of the reflective index.

The first of these processing methods most probably introduces the greatest mechanical stress to the near-surface layer. The third method of processing leaves probably on the processed surface a great number of micro-unevenesses which result in an increase in the radiation intensity diffused at this surface. The other methods of treatment did not change the examined reflectivity spectra in a remarkable way.

Thus the examinations performed have shown that no methods of surface preparation, except for the processing methods No. 1 and No. 3, influence the reflectivity spectrum. In other words, so far as examination of the energy structure in semiconductors by optical methods is concerned, the technology of surface preparation may be to a certain extent chosen arbitrarily (cf. methods No. 2, 4 and 5). Consequently the measurements of the reflection spectra cannot be recommended for the analysis of the state of surface after the technological process, when the method of surface processing has not destroyed the crystal structure down to the thickness comparable with the thickness of radiation penetration.

No influence of the doping concetration on the character of the $R(\lambda)$ function was observed. This result is consistent with the conclusion of the work [5]. For the final solution of the problem the examination should be performed

in a broader region of concentrations, which was impossible within the frame of this work.

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Влияние обработки поверхности кремния на спекторы отражения в области 0,2–0,6 μм

Исследованы спектры отражения от поверхностей монокристаллических пластинок Si, обработанных различными методами. Измерения производились при 300 К, в области длин волн от 0,2 до 0,6 μм. Обнаружены три особенные точки в спектре отражения, соответствующие энергиям 3·39 эВ, 4·52 эВ и 5·4 эВ; они были соотнесены с переходами в полосной структуре кремния. Отмечено влияние некоторых методов обработки поверхности на спектры отражения и обсуждены вероятные причины этого влияния.

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