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INTERPRETATION OF THE PIEZOELECTRIC PHOTOTHERMAL SPECTRA OF *p*-TYPE SILICON SAMPLES

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This paper presents both experimental and theoretical amplitude and phase piezoelectric photothermal spectra (PPTS) of *p*-type silicon samples. Two dominant peaks at 1.07 eV and 1.18 eV were observed in PPT spectra at room temperature. The relative intensities of these peaks change by a surface treatment. Numerical analysis is performed by supposing that an inactive layer exists at the sample surface. The characteristic structure observed in the piezoelectric amplitude spectra of *p*-Si samples is well explained by the model proposed for a multilayer structure. We found that the proposed inactive layer model is quite helpful in investigating the surface properties of a semiconductor material.

1. Introduction

Piezoelectric Photothermal (PPT) spectroscopy of solid state samples is a tool that enables the detection of nonradiative relaxation transitions in solid state materials. Since such a nonradiative transition is usually studied by a difference between, say, absorption and photoluminescence spectra, it is treated as a direct method of measurement in this sense.

However, it is an indirect method as the PPT spectra are functions of a number of material and experimental parameters. The complexity of the physical processes involved in the generation of a piezoelectric signal makes the numerical analysis of the spectra difficult.

The piezoelectric voltage signal generated in the piezoelectric transducer is a result of periodical heating of a sample by the intensity-modulated beam of incident light. The light absorbed in the sample generates thermal waves that propagate, reflect and interfere

resulting in a periodical temperature field inside the sample. The periodical temperature field causes a periodical thermal expansion (TE) and thermoelastic bending (TEB) resulting in changes of the thickness and shape of the sample. These changes are next converted into a periodical voltage signal V in the piezoelectric transducer attached to the sample.

The theory of the piezoelectric effect was developed by JACKSON & AMER [1] and next by BLONSKIJ *et.al.* [2]. In their papers the theory of the piezoelectric effect in single layer samples was described. That was, however, an ideal case. Real samples exhibit a more complex structure called in general a multi-layer structure. The surface oxide layer affects the physical explanation for the investigation of the observed spectra. The experimental piezoelectric spectra of silicon samples met in literature show a complex structure. The spectra show a strong dependence on the technological treatment such as annealing and the ion implantation processes [3–5] and on the carrier concentration [6, 7]. Furthermore, it is also influenced by the surface properties of the semiconductor sample [8]. The large number of experimental data of piezoelectric amplitude and phase spectra met in the literature brought about the necessity of developing numerical methods of analysis of the spectra in order to make the interpretation of the spectra a quantitative one and clear up the physical nature of the characteristic structure observed in the experiment.

The aim of this paper is to present an approach to the numerical analysis of amplitude and phase piezoelectric spectra comprising both the thermal and optical aspects and also the physical structure of the sample. A possible explanation of the nature of the piezoelectric photothermal amplitude spectra observed in experiments is presented. The detailed analysis of both the amplitude and phase PPT spectra indicated that the measured samples exhibit a two-layer character that can be very well described by an inactive layer model.

2. Theoretical calculation of the PPT signal generation mechanism

For the computations of the piezoelectric amplitude and phase spectra the temperature distribution is formulated as [9].

$$T(x) = T(x, f, l, \alpha, \beta, R). \tag{1}$$

This temperature distribution is a function of several material and experimental parameters: x is the spatial coordinate, f is the frequency of modulation, l is the thickness of the sample, α is the thermal diffusivity, β is the optical absorption coefficient, and R the thermal reflection coefficient between the sample and the backing material.

The temperature distribution formula enables the computations of the instantaneous temperature distribution $T(x, t)$ as

$$T(x, t) = Re\left[T(x, f, l, \alpha, \beta, R) \cdot \exp(i \cdot \omega \cdot t)\right] \tag{2}$$

where $\omega = 2 \cdot \pi \cdot f$ is the angular modulation frequency. Furthermore, the expected

piezoelectric voltage response of the transducer in the front experimental configuration, i.e. beam of light-sample – piezoelectric transducer, is calculated by [1]

$$V \approx -\varepsilon \cdot S \cdot k \cdot \gamma \cdot \left(\frac{1}{l} \cdot \int_0^l T(x) \cdot dx - \frac{6}{l^2} \cdot \int_0^l \left(\frac{l}{2} - x \right) \cdot T(x) \cdot dx \right) \tag{3}$$

where ε is the force-voltage conversion factor of the piezoelectric transducer, S is the surface cross section of the sample, k is the longitudinal modulus of elasticity (Young's modulus), γ is the coefficient of thermal expansion, l is the thickness of the sample, and $T(x)$ is temperature distribution in the sample given by equation (1).

Equation (3) can be rewritten in the following simplified form:

$$V \approx \mathrm{TE} - \mathrm{TEB} \tag{4}$$

where TE denotes the contribution of the thermal expansion of the sample in the x direction and TEB denotes the thermoelastic bending contribution to the total piezoelectric signal.

Apart from the computations of the total PPT spectra, equation (3) makes it possible to determine the relative ratio of the thermal expansion (TE) and thermoelastic bending (TEB) contributions to the piezoelectric signal as a function of the optical absorption coefficient or the photon energy of the exciting light.

Next, the influence of an inactive layer on the amplitude and phase piezoelectric spectra of silicon samples is taken into account. In general, a semiconductor sample exhibits to some extent a multilayer character [10–11]. This results from the fact that the surface layer of a semiconductor is exposed to mechanical, thermal and chemical treatments. The following assumption was made for the model of the inactive layer. The sample has a surface layer of thickness Δ that has thermal parameters different than those of the rest of the crystal, hereafter refered as the proper crystal, but the optical parameters of this layer remain unchanged. When the thermal effusivity of the inactive layer is lower than that of the proper crystal, the thermal waves generated in this layer do not transmit to the proper crystal region. The thermal reflection coefficient between this layer and the crystal R, becomes -1. These thermal waves do not contribute to the piezoelectric signal except in the case of a very high absorption region where the thermal expansion contribution from the inactive layer *TE* to the total piezoelectric signal is observed. From the mathematical point of view, the formula (1) should be replaced in this case by

$$\left(1 - \int_0^{\Delta} \exp(-\beta(h\nu) \cdot x) \cdot \beta(h\nu)\, dx \right) \cdot T(x, f, l, \alpha, \beta, R). \tag{5}$$

The first part of the formula in brackets describes the loss of the energy absorbed in the inactive layer. The formulae (5) and (3) enable the calculation of the amplitude and phase of the piezoelectric photothermal spectra for different thicknesses Δ of the inactive layer.

3. Experimental

P-type <100> oriented silicon samples were used for the measurements. The samples were boron doped and exhibited a resistivity of about 1.82 ± 0.02 Ω-cm. Single side polish wafers of 0.0739 cm thickness were cut to a 1×1 cm^2 size for the PPTS measurements. Initial cleaning was done by treating the samples with organic solutions. After that the native oxide on the sample surface was etched away by rinsing in a $NH_4F : HF$ aqueous solution. Before each step of cleaning, the samples were rinsed in de-ionized water. The PPTS measurements were performed using a disk-shaped lead zicrotitanate ceramic piezoelectric transducer attached to the rear side of the sample by a silver conducting paste. The beam of the exciting light was mechanically chopped at a frequency of 200 Hz and the signal was detected by a lock-in amplifier. All the measurements were performed at room temperature.

Detailed experimental and technological procedures have already been reported [8].

4. Experimental results and discussions

Figure 1 shows PPT signal amplitude spectra for *p*-Si samples with different surface treatments. All the amplitude PPT spectra presented and discussed in this paper exhibit a characteristic structure with local maxima at: 1.07 eV and 1.19 eV and dip at 1.12 eV. No distinctive signal was observed below 1.02 eV. Figure 2 shows PPT phase spectra. The phase decreases from 90 deg around 1.07 eV that corresponds to the first peak.

Once the optical absorption coefficient is determined, the instantaneous temperature distributions as functions of the distance from the surface are calculated by equations (1) and (2). The results are shown in Fig. 3 (a) and (b) for the typical values of 20 and 200 cm^{-1} respectively. The time intervals of $t = 0$, $T_0/4$, $T_0/2$, and $3 \cdot T_0/4$ are used for the calculations, where $T_0 = 2 \cdot \pi / \omega$ is the period of modulation. These values correspond to the photon energies of characteristic points, i.e. to two dominant peaks at 1.07 eV and 1.19 eV.

The temperature distributions in the sample for the smaller absorption coefficient (Fig. 3 (a)) show a small gradient and in this case the TE contribution dominates among the total piezoelectric signals. However, Fig. 3 (b) shows considerable temperature gradients and the TEB contribution dominates in the total signal in this case. These relative changes of the TE and TEB contributions, resulting from different spatial temperature distributions, are responsible for the characteristics of the PPT amplitude spectra observed in the experiments.

Since Si is an indirect transition semiconductor, it is reasonable to assume that the optical absorption coefficient obeys the following usual equation.

$$\beta(h \cdot \nu) = A_0 \cdot [h \cdot \nu - E_{thr}]^2 \tag{6}$$

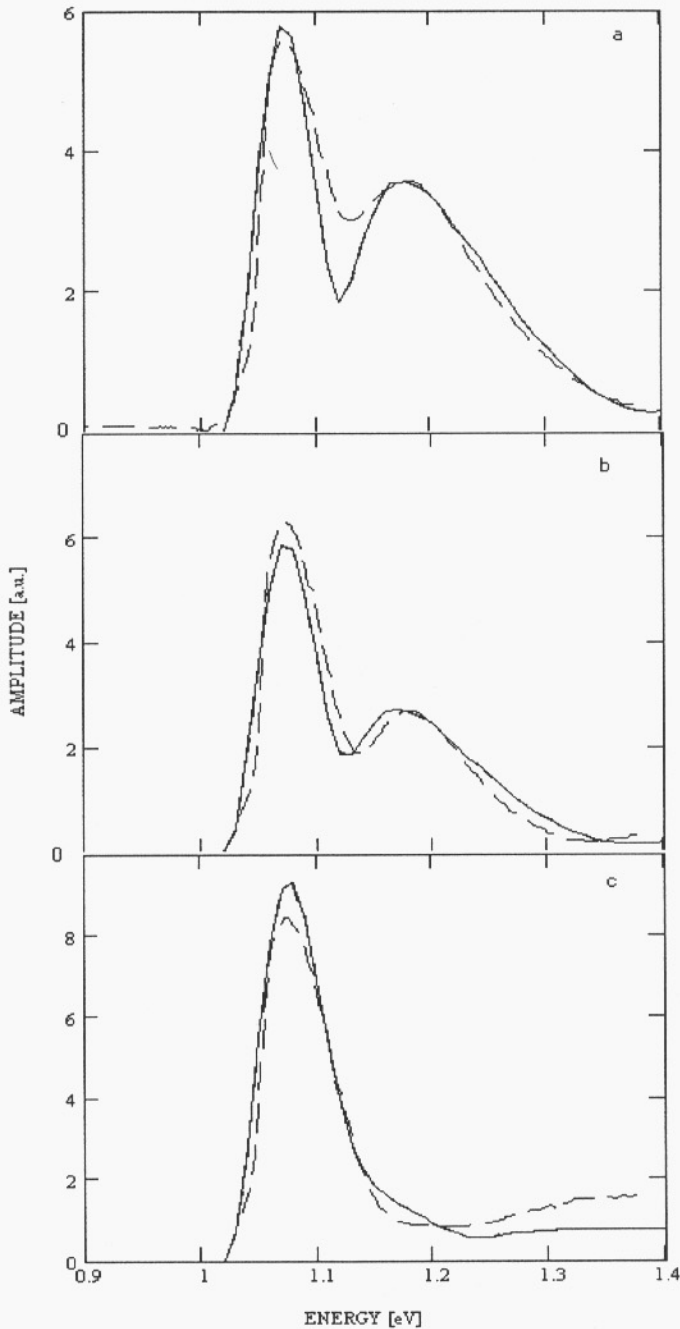

Fig. 1. Experimental amplitude PPT spectra of p-Si (dash lines) for different surface treatments. The thickness of the inactive layers are $\Delta = 0.0037$ cm (a), 0.0050 cm (b) and 0.0100 cm (c), respectively. Thermal diffusivity is $\alpha = 0.1$ cm^{2}s^{-1}. Theoretical results are show by solid curves.

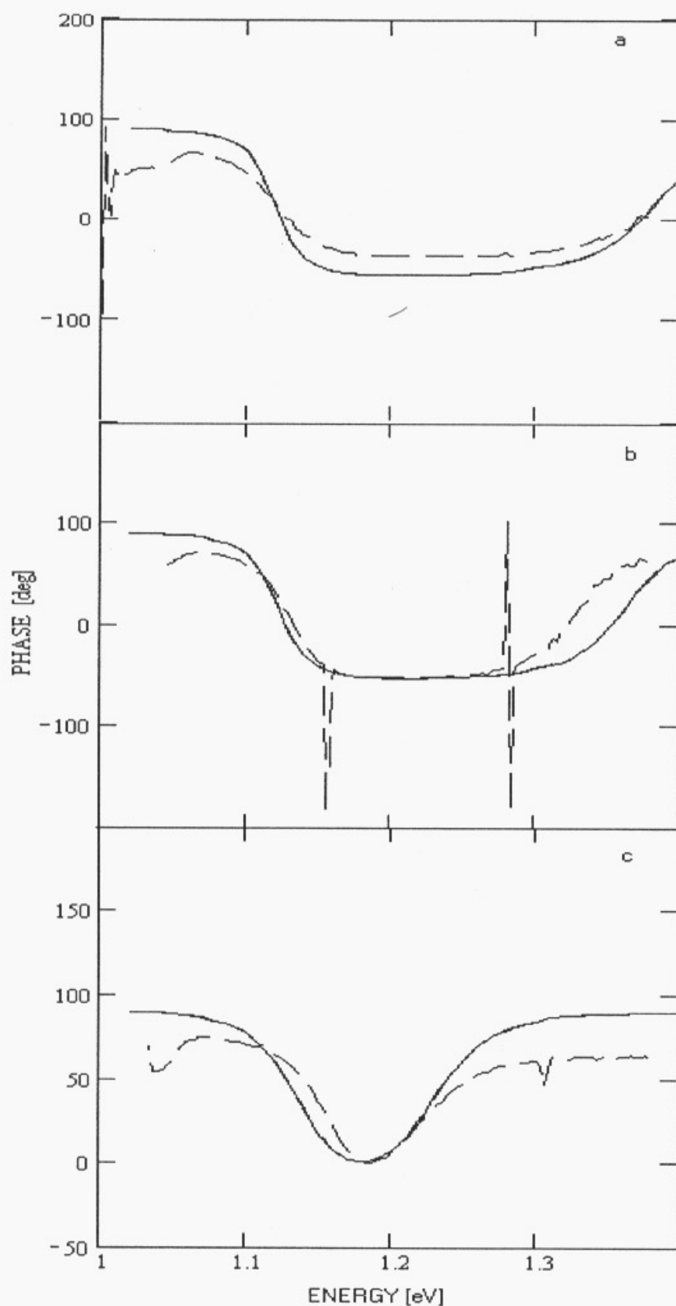

Fig. 2. Experimental phase PPT spectra of p-Si (dash lines) for different surface treatments. The thickness of the inactive layers are $\Delta = 0.0037$ cm (a), 0.0050 cm (b) and 0.0100 cm (c), respectively. Thermal diffusivity is $\alpha = 0.1$ cm^2s^{-1}. Theoretical results are show by solid curves.

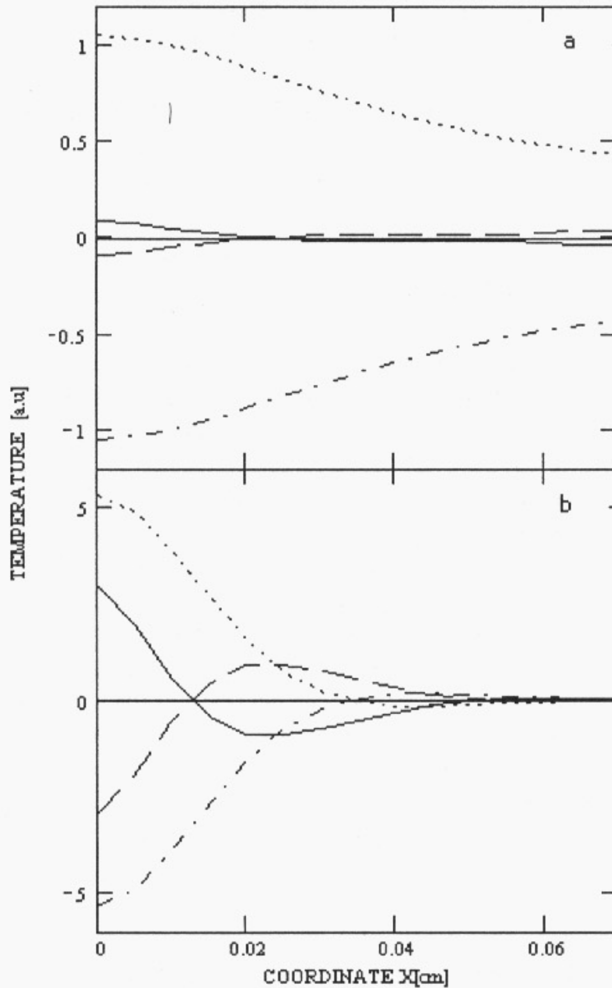

Fig. 3. Spatial distribution of the instantaneous temperature of the sample for $\beta = 20$ (a) and 200 cm^{-1} (b). $\alpha = 0.1$ cm^2s^{-1}, $l = 0.0739$ cm, $f = 200$ Hz were used for the calculation. The time intervals $t = 0$, $T_0/4$, $T_0/2$ and $3 \cdot T_0/4$ were used for the calculations, where $T_0 = 2 \cdot \pi/\omega$ is the period of modulation. Solid, dots, dash-dot and dash lines, respectively.

where $h \cdot \nu$ is the incident photon energy and E_{thr} is the threshold energy. The temperature distributions $T(x)$ and the expected PPT amplitude and phase spectra in the sample are now calculated using equations (6), (3) and (5). The inactive layer in the Si samples is taken into account in these equations. This is because a single layer model could not explain the appearance of the second peak at 1.19 eV. The best fitted curves for the observed experimental results are shown in Figs. 1 and 2 by the solid curve. Very good fittings are observed for all the PPT spectra and the two dominant peaks are well interpreted by the

present model. It is shown that the peak height of the second peak at 1.19 eV decreases with increasing thickness of the inactive layer Δ. However, the best fitted parameters for Δ are 37, 50, and 100 μm.

In the inactive layer model, the amplitude of the piezoelectric signal can be written as:

$$V \approx |\mathrm{TE} - \mathrm{TEB} + \mathrm{TE}\Delta - \mathrm{TEB}\Delta| \tag{7}$$

where TEΔ and TEBΔ are the thermal expansion and thermoelastic bending contributions of the inactive layer, respectively. However in the investigated silicon samples, the thermoelastic bending of the inactive layer was not observed.

All the presented experimental amplitudes and phases of the piezoelectric photothermal (PPT) spectra exhibit three characteristic regions clearly visible in Figs. 1 and 2. The low absorption region from 1.0 eV to 1.12 eV, with a maximum at about 1.07 eV, exhibits an optical absorption coefficient β of the order of 20 cm^{-1}. This is the region where the TE contribution is greater than the TEB one and the modulus of the difference TE-TEB reaches its maximum value at 1.07 eV. The phase of the signal is equal to +90 degs in this low absorption region. This region is followed by the 'dip' at about 1.12 eV. This is the point where the TE and TEB contributions are almost equal and the difference TE-TEB reaches its minimum value. At this point the phase of the signal decreases to zero. For the energies above 1.12 eV the TEB contribution is greater than that of TE and the value of /TE-TEB/ reaches its local maximum at about 1.19 eV. The decrease of the signal in the region above 1.2 eV is caused by the loss of the exciting energy absorbed in the inactive layer. In this sense, the peak observed at 1.19 eV and the optical absorption coefficient around $\beta = 200$ cm^{-1} can be treated as false ones, i.e. they are not connected with any special electron transitions. The phase of the signal tends to – 50 degs. For the photon energies above 1.4 eV all the exciting energy is absorbed in an inactive layer and both TE and TEB contributions tend to zero. The light absorbed entirely in the inactive layer causes its thermal expansion TEΔ. This small TEΔ contribution can be observed as the TE and TEB contributions of the proper crystal are very small in this high absorption region. The phase of the signal tends to +90 degs like in the case of the thermal expansion contributions.

As discussed before, the optical absorption coefficient spectrum is supposed to obey equation (6). The best fitted parameters to explain the observed experimental spectra for E_{thr} is 1.02 eV. Therefore, the equation should be written as follows:

$$\beta(h \cdot \nu) = A_0 \cdot [h \cdot \nu - 1.02]^2. \tag{8}$$

However, this value is different from that of the energy gap of Si at room temperature. Next, we consider the reason for this difference. Since Si is an indirect gap semiconductor, the absorption and emission of phonons are necessary for the electron transition between the energy gap. In this case, the optical absorption coefficient is written as [12, 13]

$$\beta(h \cdot \nu) = \frac{A \cdot [E_{exc} - E_g - E_{ph}]^2}{1 - \exp(- E_{ph}/k \cdot T)} + \frac{A \cdot [E_{exc} - E_g + E_{ph}]^2}{\exp(E_{ph}/k \cdot T) - 1}. \quad (9)$$

Where A is a constant, E_g is the energy gap, E_{ph} is the energy of a phonon involved in the process, k is the Boltzman constant and T is the temperature.

Since the literature values of the parameters for the silicon are as follows: $E_g = 1.12$ eV, $E_{ph} = 0.0508$–0.060 eV, the optical absorption process connected with electron transitions accompanied by emission of phonons may be used to explain equation (8). However, in this case E_{thr} should be around 1.06 eV and this does not agree well with the curve fitting results. The presence of the indirect exciton also does not explain the difference. Although the possibility of the acceptor impurity level with the activation energy of about 0.030 eV may be possible, the functional forms for the absorption coefficient deviate from equation (8). Details are now being discussed. This kind of considerations can be treated, however, as only a tentative explanation of the character of the optical absorption spectrum of *p*-type Si samples extracted from PPT spectra.

5. Conclusions

Both the experimental results of the amplitude and phase PPT spectra observed for the series of Si samples as also the theoretical characteristics, fitted well to the experimental ones, indicated the multilayer structure of real samples. The computations performed by the inactive layer model allowed to draw the conclusion that the uppermost layers of the samples exhibited worse thermal parameters than the rest of the crystal. From the model considerations it was possible to determine both the thickness of the inactive layer Δ and extract the value of the thermal diffusivity ($\alpha = 0.1$ cm^2/s), which was much lower than that expected from the literature data for perfect Si monocrystals ($\alpha = 0.9$ cm^2/s), and also determine the optical absorption coefficient spectrum of the investigated samples. The nature of the characteristic structure observed in the PPT spectra was explained quantitatively too.

The results of the investigations and considerations presented in this paper throw new light on the matter of thermal and optical characterization of semiconductor materials and indicate the significant role of the multilayer structure of the samples in the process of analysis and interpretation of experimental piezoelectric spectroscopy data.

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