Evaluation of the quality of the etching process with the piezoelectric spectroscopy method

M. Maliński¹, J. Zakrzewski², K. Strzałkowski²

¹Department of Electronics and Computer Science Technical University of Koszalin
Śniadeckich St, 75–453 Koszalin, Poland
²Instytut Fizyki, Uniwersytet Mikołaja Kopernika, ul. Grudziądzka 5/7, 87–100 Toruń, Poland

miroslaw.malinski@tu.koszalin.pl

Abstract. This paper is the presentation of photothermal piezoelectric studies of the optical properties performed on a series of AII-BVI mixed crystals. This approach enables not only determination of the basic optical parameters of mixed crystals such as the energy gap value or Urbach edge parameters but it also turned out to be a useful tool for investigations of the surface quality of the samples.

1. Introduction
Piezoelectric photoacoustic (PP) method of detection has been widely applied for the investigations of different defects in semiconductors and it is recognized as a very helpful tool for the complement of optical methods [1–11]. This method takes advantage of processes that occur in solid-state samples heated by a periodically modulated beam of light. As a result of periodical heating, a spatial and temporal temperature field arises in the sample. This temperature field induces thermal expansion of the sample causing both the so-called piston and drum effects. A piston effect describes a thermal linear expansion of the sample resulting in periodical changes of the thickness of the sample while the drum effect describes the periodical thermoelastic bending of the sample. In piezoelectric experiments the sum or difference of these two effects are observed simultaneously depending on the applied experimental configuration.

ZnSe, ZnBeSe or ZnBeMgSe crystals with different content of Be and Mg were investigated. Two etching solutions were investigated to compare their influence of PP spectra: K₂Cr₂O₇ and NaOH. The paper presents experimental and theoretical amplitude and phase piezoelectric spectra measured after surface treatment. Different etching solutions applied cause creation of different surface states visible in the piezoelectric spectra in the range of photon energies below the energy gap of the crystals.

The piezoelectric method of detection enables the localization of the appropriate surface defects on one of the surfaces of the sample as the phase of the piezoelectric signal brings information about the location of the surface states [8, 9]. This method of detection also enables to distinguish between the surface and volume type defects in the crystal. This is the result of the fact that volume and surface defects create different temperature spatial distributions in the sample and the piezoelectric signal is a function of these temperature distributions.
2. Theoretical piezoelectric spectra

The basis of the piezoelectric detection was developed by Jackson and Amer [12]. This theory modified to include the existence surface states was developed [8] and use for characterization of semiconductors [9]. The theoretical piezoelectric spectra (rear mode) of an ideal crystal with a perfect surface are shown in Fig.1.

![Theoretical amplitude a) and phase b) spectra of a perfect crystal.](image1)

**Fig.1.** Theoretical amplitude a) and phase b) spectra of a perfect crystal.

The influence of the surface defects on the piezoelectric spectra is presented in Fig.2. Surface states are visible as the sub band in the amplitude spectrum and appropriate change of the phase spectrum.

![Theoretical amplitude a) and phase b) spectra of a crystal exhibiting surface defects.](image2)

**Fig.2.** Theoretical amplitude a) and phase b) spectra of a crystal exhibiting surface defects.

3. Experimental piezoelectric spectra

Mixed crystals were grown from the high-purity powder using the high-pressure Bridgman method. The crystal rod was cut into about 1 mm thick samples which were first ground using grinding powder (10 µm diameter), then polished with diamond paste (1µm), and finally chemically etched. A solution of H₂SO₄ (96%), K₂Cr₂O₇, and water was used for etching the samples or the samples were rinsed in distilled water and then immersed for a few seconds in boiling NaOH. Then the samples were rinsed again in cold water, next in boiling distilled water, and finally in ethyl alcohol.
The theoretical and experimental spectra of Zn$_{0.81}$Be$_{0.04}$Mg$_{0.15}$Se mixed crystal are shown in Figs.3 and 4.

![Fig.3](image1.png)

**Fig.3.** Theoretical and experimental spectra of ZnBeMgSe crystal etched in $\text{K}_2\text{Cr}_2\text{O}_7$ and water exhibiting surface defects. $E_g=2.9$ eV.

![Fig.4](image2.png)

**Fig.4.** Theoretical and experimental spectra of ZnBeMgSe crystal etched in NaOH and water solution exhibiting surface defects. $E_g=2.9$ eV.

Surface states are visible as the sub bands in the energy range from 2.2 eV to 2.8 eV. The energy gap is 2.9 eV.

The piezoelectric spectra of different ZnSe samples cut in the plane [1 1 1] and etched in HCl water solution exhibit a destroyed surface with the maximum of the surface absorption band at 2.3 - 2.6 eV. The surface states are visible as the sub band in the energy range from 2.0 eV to 2.6 eV. The energy gap is at 2.7 eV. The amplitude of the piezoelectric signal, for energies above the energy gap, indicates a strong surface destruction of the samples. Comparison of the spectra presented in Figs.5 and 6 shows that etching in a HCl water solution does not decrease density of surface states visible on the surface of the samples i.e. does not improve the surface quality.

4. Conclusions
Analyzing preliminary results of investigations presented in this paper one can conclude that the applied piezoelectric method of detection is a sensitive tool for investigations of the surface states of semiconductors. It could help to find the best etching solvent for surface treatment of A2B6 mixed crystals.
Fig. 5. Piezoelectric spectra of two ZnSe samples etched in HCl water solution. $E_g = 2.7$ eV. Piezoelectric spectra of a ground ZnSe sample cut (111) plane are shown in Fig. 6.

Fig. 6. Piezoelectric amplitude a) and phase b) spectra of ZnSe (111) sample.

References
[1] K. Yoshino, H. Mikami, K. Imai, M. Yoneta, T. Ikari, Physica B, 320, 299 (2001)
[2] P. Wang, T. Nakagawa, A. Fukuyama, K. Maeda, Y. Iwasa, M. Ozeki, Y. Akashi, T. Ikari, Mat. Sci. and Engineering C 26, 826 (2006)
[3] A. Fukuyama, S. Sakamoto, S. Sonoda, P. Wang, K. Sakai, T. Ikari, Thin Solid Films 112, 511 (2006)
[4] K. Sakai, T. Kakeno, T. Ikari, S. Shirakata, T. Sakemi, K. Awai, T. Yamamoto, J. App. Phys. 99, 043508 (2006)
[5] K. Yoshino, H. Komaki, T. Kakeno, Y. Akaki, T. Ikari, J. Phys. and Chem. of Solids, 64, 1839 (2003)
[6] S. Sato, A. Memon, A. Fukoyama, S. Tanaka, T. Ikari, Rev. Sci. Instruments 74, 340 (2003)
[7] A. Memon, A. Fukuyama, S. Sato, T. Ikari, Mat. Sci. and Engineering B 102, 12 (2003)
[8] M. Maliński Phys. Stat.Sol. (a), 198, 169 (2003)
[9] M. Maliński Archives of Acoustics 28, 43 (2003)
[10] M. Maliński, J. Zakrzewski, EPJ ST 154, 354 (2008)
[11] M. Maliński, J. Zakrzewski, K. Strzałkowski, Intern. J. of Thermophysics 28, 299 (2007)
[12] W. Jackson, N. M. Amer, J.Appl.Phys. 51, 3343 (1980)