Current Applied Physics 16 (2016) 8–11

Contents lists available at ScienceDirect

Current Applied Physics

journal homepage: www.elsevier.com/locate/cap

# Influence of the temperature on the dispersion of the surface polaritons in $Zn_3P_2$ – Material for the photovoltaic applications

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ARTICLE INFO

*Article history:*
Received 14 August 2015
Received in revised form
17 September 2015
Accepted 2 October 2015
Available online 14 October 2015

*Keywords:*
Zinc diphosphides
Single crystal
Photovoltaics
Surface polaritons
Reflectance
ATR
Low temperatures

ABSTRACT

Zinc diphosphide $Zn_3P_2$ is promising material for photovoltaic applications due to its physical properties. In this study dispersion of the surface polaritons $\nu_s(k)$ in $Zn_3P_2$ has been investigated at 10 and 300 K. Surface polaritons were excited using method of attenuated total reflection (ATR) spectroscopy. Influence of the temperature on the dispersion of the surface polaritons $\nu_s(k)$ in $Zn_3P_2$ is analyzed and discussed.


## 1. Introduction

Producing of clean energy and increasing of the efficiency of photovoltaic technologies became one of the principal challenges raised by the XXI century. Another relevant challenge is reducing costs and toxicity of the mass deployment of solar cells. Therefore, new materials are required to reach these goals. $Zn_3P_2$ is a semiconductor material of p-type with a direct band gap of 1.5 eV [1] of $A^{II}B^{V}$ group, which has a potential for various optoelectronic applications as working elements of optical, electronic and thermal detectors. In [2] possible use of diphosphides for infrared converter systems has been discussed. Besides, it has been shown that the set of the material parameters of binary diphosphides allows more effectively use the converter for the transformation of infrared radiation into the electricity for the operating temperature range (1000–2500 K) of the heat source, in addition replacing CdTe by $Zn_3P_2$ in thin film solar cells will lead to simplify their mass deployment [3]. That is why it is important also from the industrial point of view to know how IR light interacts with the surface of $Zn_3P_2$ at different temperatures. Therefore, all these facts attract our attention to perform this study.

In the previous paper [4], we have reported on the surface polaritons in $Zn_3P_2$ which have been detected by ATR spectroscopy. It has been shown in [5–8] that the temperature has an effect on the reflectance spectra of diphosphides in the IR and therefore the point to note is lack of information about the influence of low temperature on the dispersion of the surface polaritons in $Zn_3P_2$. In current work, we present comprehensive account of our reflectance and ATR measurements of $Zn_3P_2$ used to study properties of the surface polaritons in $Zn_3P_2$ at different temperatures.

## 2. Experimental details

$Zn_3P_2$ crystallizes in tetragonal crystal structure described by $P4_2/nmc$ ($D_{4h}^{15}$) space symmetry group, the unit cell of $Zn_3P_2$ consists of 40 atoms [9]. In our experiments we used a set of samples of single crystals of $Zn_3P_2$ cut into plates of size $4 \times 4 \times 1$ mm.

Reflectance measurements of $Zn_3P_2$ were performed at 300 K in the 25–600 $cm^{-1}$ range, using a Bruker IFS 66v/s spectrometer with Hg lamp as source of non polarized radiation with a resolution of 0.5 $cm^{-1}$, 256 scans per 20 s were collected in each experiment. We used a 300 nm thick layer of gold deposited on glass (reflectance index of 0.99 in the FIR) as a reference for reflectance

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http://dx.doi.org/10.1016/j.cap.2015.10.001
1567-1739/

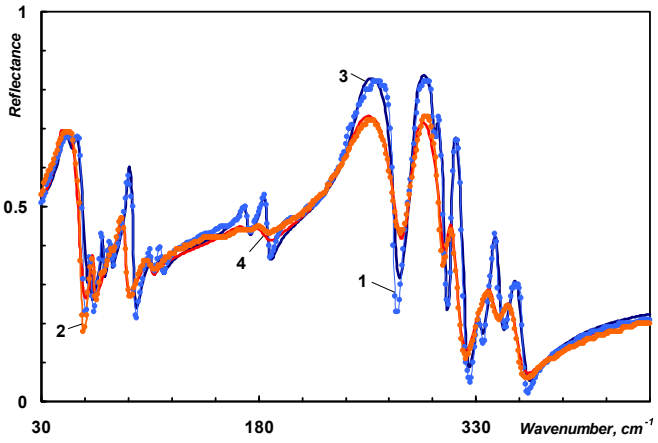


**Fig. 1.** IR reflectance spectra of $Zn_3P_2$. experimental: 1–10 K [5], 2–300 K; calculated: 3–10 K, 2–300 K.

measurements. The angle of incidence of radiation was less than 10°.

Furthermore, the ATR-spectra of the surface polaritons were recorded in the usual manner (Otto geometry) in the 200–500 $cm^{-1}$ frequency range. In our experiments we used p-polarized radiation and spectrometer KSDI-82 equipped with attachment NPVO-1. CsI semicylinder served as ATR element. We recorded ATR spectra with several angles of the incidence of the radiation of 44°, 48°, 50°, 52°, 55° and 57°. The polystyrene spacers were used to make an air gap between the investigated sample and the semicylinder, it varied from 6 to 8μ.

## 3. Results and discussion

Surface polaritons can be excited at the interface between two media, one having a negative dielectric permittivity and the other a positive one. Surface polaritons propagate along the interface and decay exponentially for directions normal to the interface. To study dispersion of the surface polaritons in $Zn_3P_2$ spectral ranges of their existence should be determined. Therefore we performed reflectance measurements of $Zn_3P_2$. Experimental reflectance spectrum of $Zn_3P_2$ measured at 300 K is displayed in Fig. 1 (curve 2). We observed 13 peaks in the measured range, which are placed in two spectral regions. In the first region at low wavenumbers there are six peaks visible. In the second, at high wavenumbers, seven peaks

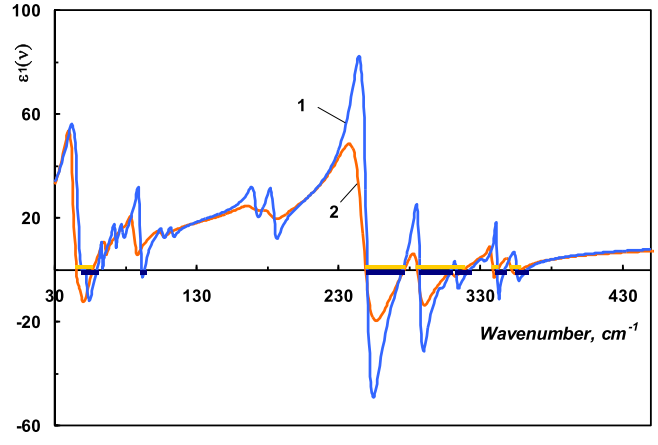


**Fig. 2.** Dispersion of the real part of the dielectric function of $Zn_3P_2$ in the IR. 1 10 K, 2–300 K.

are observed. In between these regions there is a relatively flat reflectance plot. These data correlate with data from our previous study [4] (curve 1). In the same figure we also plot experimental reflectance spectrum of $Zn_3P_2$ measured at 10 K from [5], where the Urey–Bradley force field model and potential energy distribution were applied in the phonon calculations. Theoretical concepts of the temperature dependence of the phonon self-energy are discussed in [6]. As one can notice from Fig. 1, phonon peaks of $Zn_3P_2$ at low temperature follow behavior of other diphosphides described in [7–9]: phonon peaks become more pronounced and shift to the higher wavenumbers. These phenomena motivate us to examine the temperature dependence of the reststrahlen $Zn_3P_2$. Furthermore, the dielectric function of the $Zn_3P_2$ can be estimated from the Drude and Lorentz oscillators [10]:

$$\varepsilon(\nu) = \varepsilon_1(\nu) + i\varepsilon_2(\nu) = \varepsilon_\infty\left(1 - \frac{\nu_p^2}{\nu(\nu + i\gamma_p)}\right) + \sum_{j=1}^{N} \frac{S_j}{\nu_j^2 - \nu^2 - i\gamma_j\nu}. \quad (1)$$

where $\varepsilon_\infty$ is the high-frequency permittivity; $S_i$ is the $i$-th oscillator strength; $\nu_{Ti}$ and $\gamma_{Ti}$ ($\nu_p$ and $\gamma_p$) are the frequency and the damping coefficient of the $i$-th transverse optical phonon (plasmon). The summation is made for the multi-phonon vibration system of the $Zn_3P_2$ crystal lattice. Both experimental spectra were fitted using equation (1) by variation of its parameters minimizing least square deviation.

Corresponding dispersion of the real part of the dielectric permittivity of the $Zn_3P_2$ obtained from the fit of reflectance spectra are shown in Fig. 2. Several spectral ranges where $\varepsilon_1$ has negative values (reststrahlen bands) are marked with bold blue and yellow lines. Table 1 indicates spectral ranges of the possible excitation of the surface polaritons in $Zn_3P_2$. As one can notice, these spectral ranges are strongly temperature dependent: there are 6 ranges detected at 300 K and 7 ones at 10 K, widths of all ranges depend on the temperature.

In order to evaluate the dispersion of surface polaritons, the method of ATR was used for excitation of the surface waves. The general principles of the excitation of surface waves by ATR has been proposed and described by Otto in [11] for the surface plasma waves on metals. Six experimental spectra we present as an ATR surface $R(\nu, \alpha)$ (Fig. 3), which is a three-dimensional presentation of the system transmission that depends on the radiation frequency ν and angle α. In the presence of the SP damping and dissipation of the electromagnetic wave energy the surface $R(\nu, \alpha) = I(\nu, \alpha)/I_0(\nu, \alpha)$ has 5 "canyons" connected with a "pass". $I(\nu, \alpha)$ is the intensity of radiation passing through the "ATR semicylinder–gap–sample" system; $I_0(\nu, \alpha)$ is the intensity of incident radiation onto the ATR unit. The depth of the "canyon" depends on the following system parameters: gap $d$ between the ATR semicylinder and sample, radiation frequency $\nu$, complex permittivity $\varepsilon(\nu, k)$ of the sample, refractive indexes of the ATR unit and gap. The surface polariton

**Table 1**
Temperature dependence of the width of reststrahlen of $Zn_3P_2$.

| | 300 K | | | 10 K | | |
|---|---|---|---|---|---|---|
| | $\nu_1$, $cm^{-1}$ | $\nu_2$, $cm^{-1}$ | Δν, $cm^{-1}$ | $\nu_1$, $cm^{-1}$ | $\nu_2$, $cm^{-1}$ | Δν, $cm^{-1}$ |
| 1 | 46 | 56 | 10 | 52 | 59 | 7 |
| 2 | – | – | – | 92 | 93 | 1 |
| 3 | 250 | 276 | 26 | 251 | 275 | 24 |
| 4 | 286 | 310 | 24 | 288 | 309 | 21 |
| 5 | 310 | 318 | 8 | 313 | 322 | 9 |
| 6 | 339 | 342 | 3 | 343 | 346 | 3 |
| 7 | 352 | 358 | 6 | 358 | 360 | 2 |