CALCULATIONS OF OPTICAL FUNCTIONS OF Cd$_{3-x}$Zn$_x$As$_2$ SOLID SOLUTIONS

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ABSTRACT

The number of fundamental optical functions parallel and perpendicular to the $c$ axis of single crystals Cd$_{3-x}$Zn$_x$As$_2$ is determined at room and liquid nitrogen temperature from 1 to 5 eV by Kramers-Kronig analysis of reflectivity data. Weak anisotropy is observed. The character of dependence of interband energies on molar composition is established.

INTRODUCTION

Cadmium arsenide and zinc arsenide belong to $A_2^2B_2^5$ group of semiconductors. Cd$_3$As$_2$ has five polymorphic modifications (four tetragonal and one cubic) just when Zn$_3$As$_2$ has two tetragonal and one cubic modifications. Lattice parameters are cited in [1-3]. The crystal structure of their solid solutions is reported in [4]. The elemental cell contains from 10 to 160 atoms. The methods of growing are described in [5-7].

The laws of dispersion and rules of selection are described for body-centered lattice ($C_{4v}$) and for primitive tetragonal lattice ($D_{4h}$) in articles [8-9]. The band structure of Cd$_3$As$_2$ and Zn$_3$As$_2$ was calculated with the pseudopotential method in [9-10]. In the first case the hypothetical crystal structure of fluorite was used. In the second case the calculations were performed for real crystal structure with employment of well-known pseudopotential of Cd (Zn) and As.

The optical properties of solid solutions (magnetoabsorption, thermoreflection) were studied in [11-13]. Wagner et al. [11] suggested existence of inverted band structure in Cd$_3$As$_2$. This conclusion is confirmed in [12]. Authors of [13] observed that dependencies of arrangement of experimental peaks from “x” are unmonotonical. Far-infrared reflectivity spectra of Cd$_{3-x}$Zn$_x$As$_2$ monocrystals were measured at room temperature within the range of 50-700 cm$^{-1}$ [14]. The compositions of the samples investigated were ($x$=2.55, 2.25, 1.8, 1.2).

The reflectivity spectra of Cd$_3$As$_2$ and Zn$_3$As$_2$ at 77 and 293 K were studied in [15]. The spectra $R$ of Cd$_3$As$_2$ at room temperature were measured with polarized light in [16-17]. The samples in this case were subject to mechanical and chemical processing. All these spectra are characterized with sharp drop of reflectivity in near ultraviolet. More reliable spectra $R$ of single crystals Cd$_3$As$_2$ and Zn$_3$As$_2$ are reported in [18]. The features of the reflectivity spectra of solid solutions Cd$_{3-x}$Zn$_x$As$_2$ are published in [19]. The calculations of optical functions are carried out for Zn$_3$As$_2$ at 300 K in the range 1-5 eV [20] and for Cd$_3$As$_2$ at 300 K in the range 0-20 eV [21]. However only $n$, $k$, $\varepsilon_2$, $\varepsilon_1$, $n_{ef}$ were calculated in [21] and $\varepsilon_2$, $\varepsilon_1$ were calculated in [20]. Significantly more optical functions for both compounds were received in [22] for 293 and 80 K.

In this communication we present for the first time the results of calculations of the optical functions of single crystals Cd$_{3-x}$Zn$_x$As$_2$ in the range 1-5 eV in polarized light ($E \perp c$, $E \parallel c$) at 80 K and at 293 K. The calculations were made using the Kramers-Kronig relations [23-24] and our reflectivity data. The description of experimental equipment is cited in [25]. It is necessary to mark that Philipp-Taft method requires a large measurement range and the SKK method requires a high accuracy of the reflection coefficient measurements. The data in the range 0-1 eV and 5-20 eV were taken from articles [14,21].
RESULTS AND DISCUSSION

The vapour grown single crystals of solid solutions \( \text{Cd}_{3-x}\text{Zn}_x\text{As}_2 \) usually represent the needles or long mirror-likes plates. Some samples have axis \( c \) in the surface and this allowed the reflectivity to be measured in two polarizations. The composition and modification of the obtained crystals have been determined by means of the X-ray analysis.

The crystals with \( \alpha \) modification and \( x = 0, 0.6, 0.9, 3.0 \) are examined. At 80 K the reflectivity structure at 1.6 eV (\( E_{\perp c} \)), doublet at 1.75-1.90eV (\( E_{\perp c}, E_{\parallel c} \)), broad structures at 3.08 (\( E_{\parallel c} \)) and 3.20eV (\( E_{\perp c} \)), sharp peaks at 3.93eV (\( E_{\perp c} \)) and weak structure at 4.01 eV have been observed in case of \( \text{Cd}_3\text{As}_2 \).

The same structures in \( \text{Zn}_3\text{As}_2 \) are observed at 1.7eV, 2.25-2.47 eV, 2.95-2.98 eV and 4.15-4.05 eV. With increase of temperature to 293 K all reflectivity structures were broadened and shifted with the mean of negative temperature coefficient \(-1 \) to \(-3 \times 10^{-4} \text{eV K}^{-1}\).

In the case of solid solution with \( x = 0.6 \) we observed triplet at 1.67, 1.79 and 1.89 eV, the stripes at 1.2-1.3 and 3.3-3.3 eV and the second triplet at 3.83 eV (\( E_{\parallel c} \)), 3.89, 4.04 eV (\( E_{\perp c} \)). For crystal with \( x = 0.9 \) the states of components of triplets are 1.80, 1.89, 2.02 eV and 3.89, 3.95, 4.08 eV. All reflectivity structures of solid solutions are broadening. The value of reflection coefficient falls in the whole energy interval (1-5 eV) as compared with the spectra of binary compounds.

In Figs 1-3 we present spectra of reflectivity \( R \), refractive index \( n \), the real part of dielectric function \( \varepsilon_1 \), absorption coefficient \( \mu \), absorption index \( k \), the imaginary part of dielectric function \( \varepsilon_2 \), effective number of valence electrons \( n_{ef} \), effective dielectric constant \( \varepsilon_{ef} \) and the function of surface plasmons \(-\text{Im} (\varepsilon) \) \text{^{-1}}. The calculations were carried out for compound \( \text{Cd}_{2.1}\text{Zn}_{0.9}\text{As}_2 \) at 80 K and light polarizations \( E_{\perp c}, E_{\parallel c} \) using SCC method.

As distinct from cadmium diphosphide [26] optical functions of cadmium arsenide-zinc arsenide don’t show noticeable anisotropy in its forms and values. Only the components of the first triplet display variously in spectra \( R, n, \varepsilon_\parallel \), at \( E_{\parallel c}, E_{\perp c} \) (Fig.1). The spectra \( n, \varepsilon_\parallel \) are similar to those of \( R \) in region of 2 eV, however at energies \( h\nu > 2.5 \text{ eV} \) the curves \( n, \varepsilon_\parallel \) fall off steeply against of \( R \).

Fig.1. Experimental spectrum (1) \( R \) and calculated spectra (2) \( n \) and (3) \( \varepsilon_1 \) of cadmium arsenide - zinc arsenide at 80 K and light polarization \( E_{\parallel c} \) (left) and \( E_{\perp c} \) (right).
The spectra of $k, \varepsilon_2$ are quite similar to spectrum $R$ (see Fig.2). At 5 eV the absorption reaches the value about $0.9 \times 10^6$ cm$^{-1}$. The functions $n_{ef}, \varepsilon_{ef}$ increase monotonically, but don’t attain saturation at 5 eV. The spectrum of bulk and surface plasmons contains only one noticeable structure near 2 eV (see Fig.3).

The spectra of $\varepsilon_2(h\nu)^2$ are practically identical in region 1-5 eV for both polarizations. The electrooptic function $\alpha$ decrease monotonically with one strong structure at 2.3 eV. The differential function $\beta$ is similar to $R$ at energies 1-3.5 eV, but the structure near 4.0 eV is asymmetric to $R$. The reflected light phase $\theta$ increases monotonically from 0 to 0.6.

Fig.2. Calculated spectra (1) $\mu$, (2) $k$ and (3) $\varepsilon_2$ of cadmium arsenide - zinc arsenide at 80 K and light polarization $E||c$ (left) and $E\perp c$ (right).

Fig.3. Calculated spectra (1) $n_{ef}$, (2) $\varepsilon_{ef}$ and (3) $-\text{Im} (\varepsilon)^{-1}$ of cadmium arsenide - zinc arsenide at 80 K and light polarization $E||c$ (left) and $E\perp c$ (right).
So, for the first time calculations of optical functions of solid solutions \( \text{Cd}_{3-x}\text{Zn}_x\text{As}_2 \) at 293 K and 80 K for \( E_{||}c \) and \( E_{\perp}c \) are executed and the weak anisotropy of spectra obtained is discovered. The functions \( R, n, \varepsilon_1, \varepsilon_2, k, \mu \) are distinguished by distribution of intensities at \( E_{||}c \), \( E_{\perp}c \), otherwise the functions \( n_{ef}, \varepsilon_{ef}, \alpha, \beta, \theta \) have almost the same form and values.

Thus, the main particularities of band structure of system \( \text{Cd}_3\text{As}_2-\text{Zn}_3\text{As}_2 \) are examined. The doublet “\( E_1 \)”, caused by spin-orbit interaction is displaced by 0.5 eV under transition from \( \text{Cd}_3\text{As}_2 \) to \( \text{Zn}_3\text{As}_2 \). This is twice as much than the values of \( E_g \) change. The structure “\( E_2 \)” near 4 eV changes its arrangement only by \( \approx 0.1 \) eV. The value of \( E_g \) of solid solutions \( \text{Cd}_{3-x}\text{Zn}_x\text{As}_2 \) changes in a linear fashion by data of many authors. Our investigations show the nonlinear dependencies of triplet components of crystals studied on \( x \). So, the complication of the band structure in this case is possible.

REFERENCES