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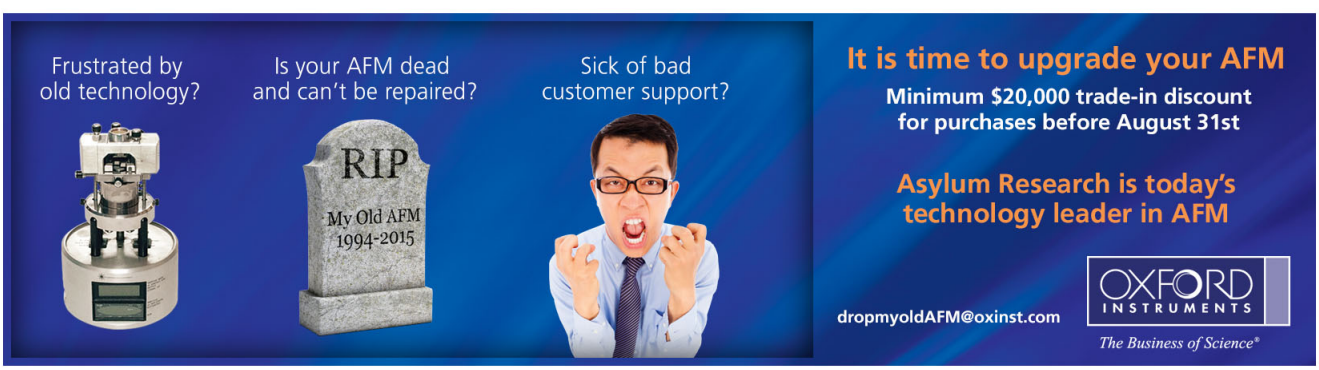

Band gap and refractive index tunability in thallium based layered mixed crystals

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Compositional variation of the band gap energy and refractive index of $TlMeX_2$-type (Me = Ga or In and X = S or Se) layered mixed crystals have been studied by the transmission and reflection measurements in the wavelength range of 400–1100 nm. The analysis of absorption data of $TlGa_{1-x}In_xSe_2$, $TlGa(S_{1-x}Se_x)_2$, $TlGa_{1-x}In_xS_2$, and $TlIn(Se_{1-x}S_x)_2$ mixed crystals revealed the presence of both optical indirect and direct transitions. It was found that the energy band gaps of mixed crystals decrease at the replacing of gallium atoms by indium and of sulfur atoms by selenium ones. Through the similar replacing of atoms (smaller atoms by larger ones) in the studied mixed crystals, the refractive index shows the quite opposite behavior. © *2015 AIP Publishing LLC*.
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I. INTRODUCTION

$TlMeX_2$-type compounds (Me = Ga or In and X = S or Se) crystallize in a monoclinic ($TlGaS_2$, $TlGaSe_2$, and $TlInS_2$) or tetragonal ($TlInSe_2$) cell.[1–3] The lattice of the first three compounds consists of strictly periodic two-dimensional layers arranged parallel to the (001) plane. Each successive layer is rotated by 90° with respect to the previous one. Interlayer bonding is formed between Tl and S(Se) atoms while the bonding between Ga(In) and S(Se) atoms is an intralayer. The fundamental structural unit of a layer is the Me_4X_{10} polyhedron representing a combination of four elementary tetrahedra MeX_4 linked together by bridging X atoms. The Tl atoms are located in trigonal prismatic voids resulting from the combination of the Me_4X_{10} polyhedra into a layer. These atoms form nearly planar chains along the [110] and [1$\bar{1}$0] directions.

In view of their possible applications in optoelectronic devices in the visible range, a great deal of attention has been devoted to the study of the optical and photoelectrical properties of $TlGaS_2$, $TlGaSe_2$, and $TlInS_2$ crystals.[4–12] They are of significant interest because of their highly anisotropic properties, semiconductivity, and photoconductivity. Moreover, they exhibit nonlinear effects in *I–V* characteristics (including a region of negative differential resistance), switching and memory effects. A high photosensitivity in the visible range of spectra in conjunction with a wide transparency range of 0.6–16 μm makes these crystals useful for optoelectronic applications.[13]

The monoclinic $TlGaS_2$ and $TlGaSe_2$, $TlGaS_2$, and $TlInS_2$ form a series of $TlGa(S_{1-x}Se_x)_2$ and $TlGa_{1-x}In_xS_2$ mixed crystals, respectively, with no restrictions on the concentration of the components: $0 \le x \le 1$.[14,15] The tetragonal $TlInSe_2$ and monoclinic $TlInS_2$ compounds form a continuous series of mixed crystals $TlIn(Se_{1-x}S_x)_2$ $(0 \le x \le 1)$.[16,17] The transformation from the tetragonal to monoclinic structure occurs at $x \approx 0.25$. The phase diagram of $TlGa_xIn_{1-x}Se_2$ system has been investigated previously and two eutectic phases have been found to exist at the limited regions from $x = 0$ to 0.25 and $x = 0.5$–1.[18,19] In the first and second regions, $TlGa_xIn_{1-x}Se_2$ crystallizes in the tetragonal and monoclinic structures, respectively. Mixed crystals having the composition $x \ge 0.5$ crystallize in a $TlGaSe_2$-type monoclinic lattice. Recently, the room temperature spectroscopic ellipsometry measurements have been carried out on the layer-plane (001) surfaces of $TlGa_{1-x}In_xSe_2$, $TlGa(S_{1-x}Se_x)_2$, $TlGa_{1-x}In_xS_2$, and $TlIn(Se_{1-x}S_x)_2$ mixed crystals.[20–23] The critical point energies in the above band gap region as a function of the composition in the studied mixed crystals were found from the analysis of the second-energy derivative spectra of the complex dielectric function.

The aim of the present paper was to study the effect of isomorphic atom substitution (gallium by indium and sulfur by selenium) on the band gap energies and refractive indices of $TlIn_{1-x}Ga_xSe_2$ $(0.5 \le x \le 1)$ and $TlGa_{1-x}In_xS_2$ $(0 \le x \le 1)$, $TlGa(S_{1-x}Se_x)_2$ $(0 \le x \le 1)$ and $TlIn(Se_{1-x}S_x)_2$ $(0.25 \le x \le 1)$ layered mixed crystals, respectively. These substitutions allow, at least in principle, the tailoring of several important physical properties.

II. EXPERIMENTAL DETAILS

Single crystals of $TlIn_{1-x}Ga_xSe_2$ $(0.5 \le x \le 1)$, $TlGa(S_{1-x}Se_x)_2$ $(0 \le x \le 1)$, $TlGa_{1-x}In_xS_2$ $(0 \le x \le 1)$ and $TlIn(Se_{1-x}S_x)_2$ $(0.25 \le x \le 1)$ were grown by the Bridgman method from a stoichiometric melt of starting materials sealed in the evacuated (10^{-5} Torr) and carbon coated silica tubes (15 mm in diameter and about 50 cm in length) with a tip at the bottom in our crystal growth laboratory. The ampoule was moved in a vertical furnace through a thermal gradient of 30 °C cm^{-1} at a rate of 1.0 mm h^{-1}. The resulting ingots appear from dark red to yellow in color. The chemical composition of the studied crystals was determined by the energy dispersive spectroscopic analysis using JSM-6400 electron microscope. The samples for the optical measurements were taken from the middle part of the ingots. The

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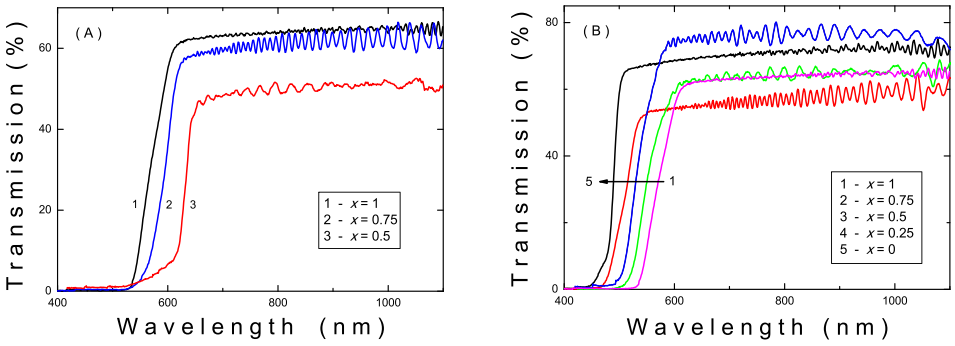

FIG. 1. The spectral dependencies of transmission of $TlIn_{1-x}Ga_xSe_2$ (A) and $TlGa(S_{1-x}Se_x)_2$ (B) mixed crystals.

freshly cleaved platelets (along the layer plane (001)) were mirror-like. That is why no further polishing and cleaning treatments of samples were required for optical measurements.

The transmission and reflection measurements were carried out in the 400–1100 nm wavelength region with a "Shimadzu" UV-1201 model spectrophotometer, which consisted of a 20 W halogen lamp, a holographic grating, and a silicon photodiode. The transmission measurements were done under the normal incidence of light with the polarization direction along the (001) plane, which is perpendicular to the ***c***-axis of the crystal. For reflection experiments, the specular reflectance attachment with 5° incident angle was used.

III. RESULTS AND DISCUSSION

Figures 1 and 2 present the transmission (T) spectra of 14 compositions of $TlIn_{1-x}Ga_xSe_2$ (A), $TlGa(S_{1-x}Se_x)_2$ (B), $TlGa_{1-x}In_xS_2$ (C), and $TlIn(Se_{1-x}S_x)_2$ (D) mixed crystals registered in the wavelength range from 400 to 1100 nm.

The reflection measurements were carried out using the specimens with natural cleavage planes and the thickness such that $\alpha d \gg 1$. The sample thickness was then reduced until it was convenient for measuring the transmission spectra. The thickness of the thin samples were determined using transmission interference fringes at wavelength slightly longer than the intrinsic absorption edge, i.e., in a region with relatively high transmission (Figs. 1 and 2). We evaluated the thickness of the samples by measuring the wavelengths at which two adjacent transmission maxima occur[24]

$$d = \frac{\lambda_1 \lambda_2}{2n(\lambda_2 - \lambda_1)}. \tag{1}$$

The long-wavelength values of the refractive index were used to determine the thickness of the samples, which turned out to be about 10 μm for transmission measurements in most of the cases.

Figures 3 and 4 present the reflection (R) spectra of 14 compositions of $TlIn_{1-x}Ga_xSe_2$ (A), $TlGa(S_{1-x}Se_x)_2$ (B), $TlGa_{1-x}In_xS_2$ (C), and $TlIn(Se_{1-x}S_x)_2$ (D) mixed crystals registered in the wavelength range from 400 to 1100 nm.

The absorption coefficient α and the refractive index n were calculated using the following relations:[24]

$$\alpha = \frac{1}{d}\ln\left\{\frac{(1-R)^2}{2T} + \left[\frac{(1-R)^4}{4T^2} + R^2\right]^{1/2}\right\} \tag{2}$$

$$n = \frac{1+R}{1-R} + \left[\frac{4R}{(1-R)^2} - \left(\frac{\alpha\lambda}{4\pi}\right)^2\right]^{1/2}, \tag{3}$$

where d is the sample thickness.

Figure 5 demonstrates the absorption coefficient α as a function of photon energy $h\nu$ for the studied $TlIn_{1-x}Ga_xSe_2$, $TlGa(S_{1-x}Se_x)_2$, $TlGa_{1-x}In_xS_2$, and $TlIn(Se_{1-x}S_x)_2$ mixed crystals calculated by Eq. (2) using the experimental transmission and reflection spectra.

The analysis of the dependence of absorption coefficient on photon energy in the high absorption regions was carried out to obtain the detailed information about the energy band gaps. The absorption coefficient α and photon energy $h\nu$ can be related by[24]

$$\alpha(h\nu) = A\ (h\nu - E_g)^p. \tag{4}$$

In this equation, A is a constant that depends on the transition probability and p is an index that characterizes the optical absorption process, and it theoretically equals to 2 and 1/2

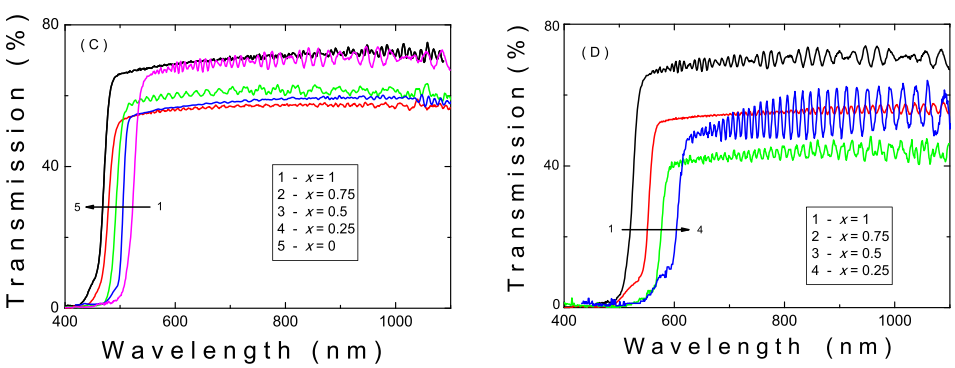

FIG. 2. The spectral dependencies of transmission of $TlGa_{1-x}In_xS_2$ (C) and $TlIn(Se_{1-x}S_x)_2$ (D) mixed crystals.

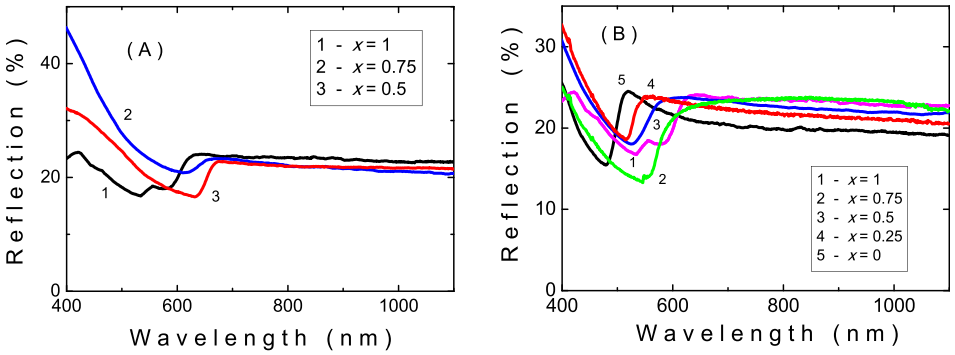

FIG. 3. The spectral dependencies of reflection of $TlIn_{1-x}Ga_xSe_2$ (A) and $TlGa(S_{1-x}Se_x)_2$ (B) mixed crystals.

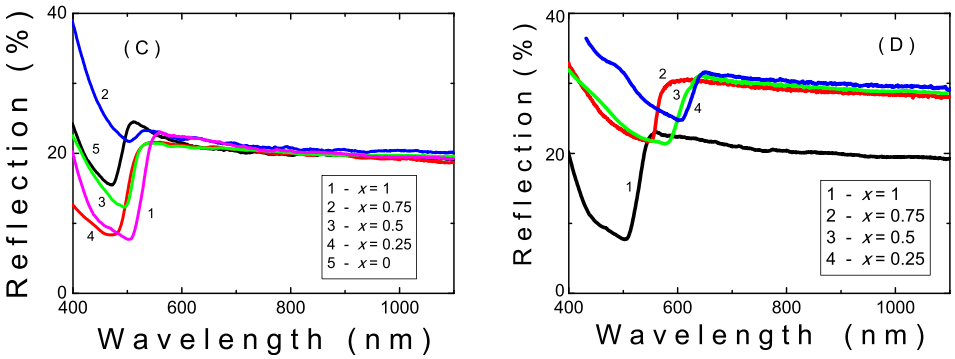

FIG. 4. The spectral dependencies of reflection of $TlGa_{1-x}In_xS_2$ (C) and $TlIn(Se_{1-x}S_x)_2$ (D) mixed crystals.

for indirect and direct allowed transitions, respectively. From the analysis of the experimental data, it was revealed that the absorption coefficient α is proportional to $(h\nu - E_g)^p$ with $p = 2$ or 1/2 in low- and high-energy regions of the spectra, respectively. Thus, the coexistence of the indirect and direct transitions were established from extrapolation of linear dependencies of the relations $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ versus $h\nu$, respectively. Figure 6 presents the variations of indirect (E_{gi}) and direct (E_{gd}) energy band gaps on composition of $TlIn_{1-x}Ga_xSe_2$ $(0.5 \le x \le 1)$, $TlGa(S_{1-x}Se_x)_2$ $(0 \le x \le 1)$, $TlGa_{1-x}In_xS_2$ $(0 \le x \le 1)$, and $TlIn(Se_{1-x}S_x)_2$ $(0.25 \le x \le 1)$ mixed crystals. Presently determined energy band gaps $E_{gi} = 2.45$ eV and $E_{gd} = 2.63$ eV ($TlGaS_2$), $E_{gi} = 1.97$ eV and $E_{gd} = 2.26$ eV ($TlGaSe_2$), and $E_{gi} = 2.27$ eV and $E_{gd} = 2.47$ eV ($TlInS_2$) agree well with the corresponding data of Refs. 25 and 26. As seen from Fig. 6, the energy band gaps $TlGa_{1-x}In_xSe_2$ and $TlGa_{1-x}In_xS_2$, and $TlGa(S_{1-x}Se_x)_2$ and $TlIn(Se_{1-x}S_x)_2$ mixed crystals decrease at the substitution of small gallium atoms by large indium and of small sulfur atoms by large selenium, respectively. It is worth noting here, that the covalent radii of the gallium, indium, sulfur and selenium atoms are equal to 0.126, 0.144, 0.104, and 0.114 nm, respectively. As was reported earlier, through the similar replacing of atoms (smaller atoms by larger ones) in the studied mixed crystals the lattice parameters and unit cell volumes showed the quite opposite behavior.[27]

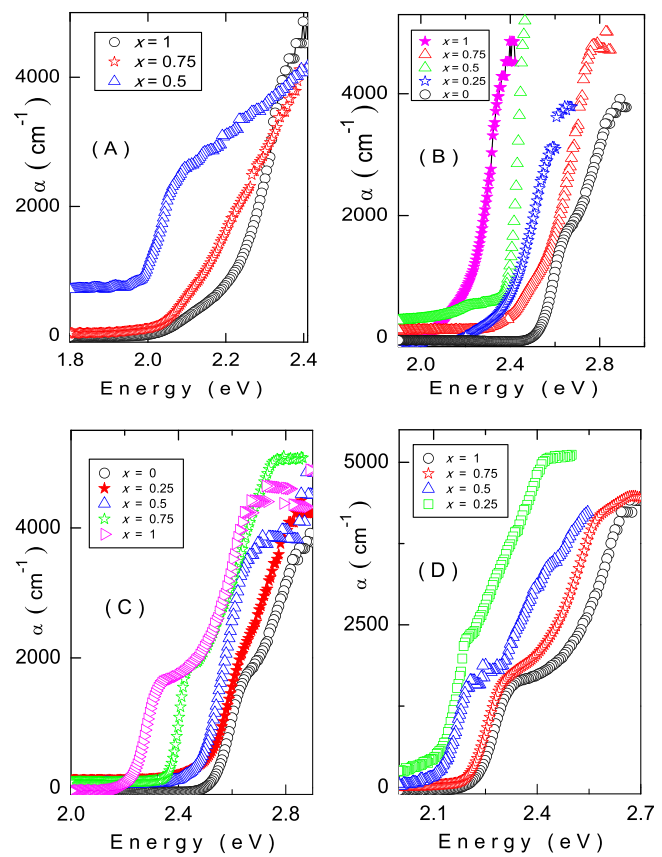

FIG. 5. The dependencies of absorption coefficient α on photon energy $h\nu$ of $TlIn_{1-x}Ga_xSe_2$ (A), $TlGa(S_{1-x}Se_x)_2$ (B), $TlGa_{1-x}In_xS_2$ (C), and $TlIn(Se_{1-x}S_x)_2$ (D) mixed crystals.

The long-wavelength values of the refractive indices of $TlIn_{1-x}Ga_xSe_2$ $(0.5 \le x \le 1)$, $TlGa(S_{1-x}Se_x)_2$ $(0 \le x \le 1)$, $TlGa_{1-x}In_xS_2$ $(0 \le x \le 1)$, and $TlIn(Se_{1-x}S_x)_2$ $(0.25 \le x \le 1)$ mixed crystals were determined employing the Eq. (3). Figure 6 shows the variations of the refractive indices on composition of studied mixed crystals. It is evident from Fig. 6 that the refractive indices increase at the replacement of gallium atoms by indium and of sulfur atoms by selenium, respectively. The estimated values of the refractive indices $n = 2.51$ ($TlGaS_2$), $n = 2.80$ ($TlGaSe_2$), and $n = 2.55$ ($TlInS_2$) are well correlated with those reported earlier in Refs. 12 and 28–30. As a whole, the picture obtained is

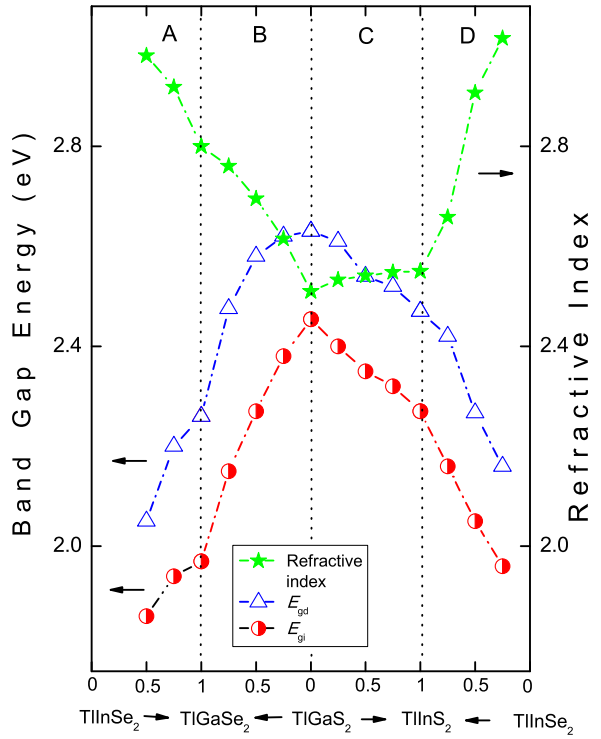

FIG. 6. Compositional variations of the indirect (E_{gi}) and direct (E_{gd}) energy band gaps and refractive indices for $TlIn_{1-x}Ga_xSe_2$ (A), $TlGa(S_{1-x}Se_x)_2$ (B), $TlGa_{1-x}In_xS_2$ (C), and $TlIn(Se_{1-x}S_x)_2$ (D) mixed crystals. The dashed-dotted lines are only guides for the eyes.

consistent with the well-known fact that the refractive index and the energy band gap are inversely related to each other.[24] Particularly, for the $TlGa_{0.5}In_{0.5}Se_2$ and $TlInS_{0.25}Se_{0.75}$ crystals, which have the smallest band gap energies among the studied materials ($E_{gi} = 1.86$ eV; $E_{gd} = 2.05$ eV) and ($E_{gi} = 1.96$ eV; $E_{gd} = 2.16$ eV), respectively, the refractive indices have the largest values $n = 2.98$ and 3.02, respectively.

IV. CONCLUSION

The optical properties of 14 compositions of $TlGa_{1-x}In_xSe_2$, $TlGa(S_{1-x}Se_x)_2$, $TlGa_{1-x}In_xS_2$, and $TlIn(Se_{1-x}S_x)_2$ layered mixed crystals were studied by means of transmission and reflection experiments in the wavelength range of 400–1100 nm. The analysis of absorption data revealed the presence of both optical indirect and direct transitions. It was established that the energy band gaps of studied mixed crystals decrease through replacing gallium atoms by indium ($TlGa_{1-x}In_xSe_2$ and $TlGa_{1-x}In_xS_2$) and of sulfur atoms by selenium ($TlGa(S_{1-x}Se_x)_2$ and $TlIn(Se_{1-x}S_x)_2$). Through the similar replacing of atoms (smaller atoms by larger ones) in the studied mixed crystals, the determined refractive index shows the quite opposite behavior.

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