ELECTRONIC AND OPTICAL PROPERTIES OF SEMICONDUCTORS

Optical Properties of AgGa$_x$In$_{1-x}$Se$_2$ Alloys

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Submitted April 4, 2007; accepted for publication June 6, 2007

Abstract—Coarse-grained crystals of AgGaSe$_2$ and AgInSe$_2$ ternary compounds and their alloys are grown by planar crystallization of the melts. For the crystals produced in this way, the transmittance spectra near the fundamental absorption edge are studied. From the experimental spectra, the band gap ($E_g$) and its variation with composition are determined. It is established that $E_g$ is a nonlinear function of the composition parameter $x$. The dependence $E_g(x)$ is calculated theoretically in the context of the Van Vechten–Bergstresser model and Hill–Richardson pseudopotential model.

PACS numbers: 78.20.Ci, 78.30.Er, 71.20.Nr, 81.05.Hd

DOI: 10.1134/S1063782608020061

1. INTRODUCTION

AgGaSe$_2$ and AgInSe$_2$ compounds belong to a large family of I–III–VI$_2$ ternary compounds that crystallize in a chalcopyrite structure (the $D_{2d}^{12}$ space group) and are the electronic and chemical analogues of II–VI binary compounds [1, 2]. AgGaSe$_2$ and AgInSe$_2$ compounds are characterized by a large absorption coefficient and direct interband transitions, which makes the materials promising for producing high-efficiency photovoltaic and injection lasers operating in a wide wavelength range [3–5]. The birefringence and isotropic point allow the use of these materials as narrowband filters [6, 7] and devices for frequency doubling and three-frequency mixing [8–10]. Although the properties of the AgGaSe$_2$ and AgInSe$_2$ compounds are understood rather well, their alloys are poorly known [7–9, 11].

The purpose of this study is to investigate the optical properties of AgGaSe$_2$ and AgInSe$_2$ compounds and AgGa$_x$In$_{1-x}$Se$_2$ alloys.

2. EXPERIMENTAL

Crystals of the AgGaSe$_2$ and AgInSe$_2$ compounds and AgGa$_x$In$_{1-x}$Se$_2$ alloys were grown by planar crystallization of the melt (horizontal modification of the Bridgman method) in accordance with the previously constructed constitution diagram of the AgGaSe$_2$–AgInSe$_2$ system [12]. The elementary components (99.999%–pure silver, gallium, indium, and selenium) served as the initial materials for the synthesis. The metal components were put into graphitized coneshaped quartz troughs placed at one end of a quartz ampoule. At the opposite end of the ampoule, there was a ground, we annealed the samples at 650 K for 3 h.

The equilibrium state and homogeneity of the alloys were verified by X-ray diffraction (XRD) measurements. The angle positions of the lines of the XRD patterns were recorded by an automatic computer-controlled DRON-3M X-ray diffractometer, with the use of CuKa radiation and a graphite monochromator. The samples to be studied were prepared by grinding the crystals and then pressing them into a special holder. In order to remove stresses produced in the samples when ground, we annealed the samples at 650 K for 3 h.

The composition of the grown crystals was determined from the unit cell parameters calculated by the

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least-squares method; in this case, we assumed that the Vegard relation is valid for the AgGaIn₁₋ₓSe₂ alloys [12].

The transmittance spectra near the fundamental absorption edge were recorded with the use of a Cary-500 spectrophotometer at 80 and 295 K in the wavelength range of 0.5 to 2.0 μm. To perform the measurements, single-crystal blocks were cut off from the ingots and then mechanically ground and polished at both sides to attain a thickness of ~20 μm. Just before the measurements, the samples were treated in Br₂ : C₂H₅OH = 1 : 3 etchant to remove the surface layer disrupted by the mechanical treatment of the crystals.

3. RESULTS AND DISCUSSION

The XRD data show that the AgGaSe₂ and AgInSe₂ ternary compounds and their alloys crystallize in the chalcopyrite structure. The equilibrium state and homogeneity of the alloys were judged from the resolution of the large-angle lines (2θ > 60°) in the XRD patterns.

From the experimentally recorded transmittance spectra, we calculated the absorption coefficient by the formula incorporating multiple internal reflection in a plane-parallel sample [13]:

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

Here, \( \alpha \) is the absorption coefficient, \( d \) is the sample thickness, \( T \) is the transmittance, and \( R \) is the reflectivity, equal to 0.25–0.27 for different \( x \).

It is known that I–III–VI₂ ternary compounds feature direct interband transitions and, therefore, their band gap \( E_g \) is determined by extrapolating the linear portion of the dependence of the quantity \((\alpha h\omega)^2\) on the photon energy \( h\omega \) to intersect the abscissa. The dependences of \((\alpha h\omega)^2\) on \( h\omega \) are shown in Fig. 1.

The resulting values of the band gap \( E_g \) are 1.244 eV (80 K) and 1.220 eV (295 K) for the AgInSe₂ compound and 1.788 eV (80 K) and 1.756 eV (295 K) for the AgGaSe₂ compound, in satisfactory agreement with the data reported in [2, 14–16]. The temperature coefficients of the band gap, \( \partial E_g / \partial T \), are \( 0.9 \times 10^{-4} \) and \( 1.9 \times 10^{-2} \) eV/K for the AgInSe₂ and AgGaSe₂ compounds, respectively. The dependences of the band gap of the AgGaIn₁₋ₓSe₂ alloys on the composition parameter \( x \) are shown in Fig. 2. It is evident that the variation in \( E_g \) with the parameter \( x \) at 80 and 295 K is nonlinear, as typical of the alloys formed by the I–III–VI₂ ternary compounds [10, 17–19].

For the AgGaIn₁₋ₓSe₂ alloys, the nonlinear dependence \( E_g(x) \) can be approximately described by the quadratic function

\[
E_g(x) = E_A + (E_B - E_A - c)x + cx^2.
\]

Here, \( E_A \) and \( E_B \) are the band gaps of the AgInSe₂ and AgGaSe₂ ternary compounds and \( c \) is the nonlinearity parameter that characterizes the degree of deviation of \( E_g \) from the linear dependence for the middle composition \( (x = 0.5) \); the parameter \( c \) is determined from the expression

\[
c = 4\Delta E_g(x = 0.5),
\]

where

\[
\Delta E_g = \frac{E_A + E_B}{2} - E_g(x = 0.5).
\]