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Mechanical properties of GaSe:Cr^{2+} crystals

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GaSe crystals doped with chromium selenide 0.005–0.065 wt.% (expressed for chromium) were grown by the Bridgman technique. The crystals are characterized by perfect cleavage. It was found that the chromium concentration increases along the boule (segregation coefficient >1). It was found that the introduction of chromium selenide increases the microhardness of GaSe-based crystals up to 0.122 GPa (0.065 wt.% Cr) and does not affect substantially optical properties of the crystals.
Keywords: gallium selenide, crystals, doping, chromium, microhardness.

Механічні властивості кристалів GaSe:Cr^{2+}. *О.К.Капустник, Н.О.Коваленко, І.С.Терзін, Д.С.Софронов, В.С.Задорожній*
Методом Бріджмена отримано кристали GaSe, леговані селенідом хрому з концентраціями 0,005–0,065 мас.% (у перерахунку на хром). Кристали характеризуються досконалою спайністю. Встановлено, що концентрація хрому вздовж зливка зростає (коефіцієнт сегрегації >1). Встановлено, що введення селеніду хрому дозволяє збільшити мікротвердість кристалів на основі GaSe до 0,122 ГПа (0,065 мас.% Cr) та істотно не впливає на оптичні властивості кристалів.

Методом Бриджмена выращены кристаллы GaSe, легированные селенидом хрома с 0,005–0,065 масс.% (в пересчете на хром). Кристаллы характеризуются совершенной спайностью. Установлено, концентрация хрома вдоль слитка возрастает (коэффициент сегрегации >1). Установлено, что введение селенида хрома позволяет увеличить микротвердость кристаллов на основе GaSe до 0,122 ГПа (0,065 масс.% Cr) и не оказывает существенного влияния на оптические свойства кристаллов.

1. Introduction

Gallium selenide (GaSe) crystal with the ε-polytype has been known since the 1930s for its ability to be optically converted and detectable over a wide wavelength range. It has a transparency window over 0.62–20 μm, which continues up to 50 μm for unpolarized light. Also, it has high birefringence ($B = 0.375$ at $\lambda = 10.6$ μm and 0.79 at terahertz (THz) range), a very high second-order nonlinear susceptibility ($d_{22} =$ 54 pm/V at 10 μm and 24.3 pm/V in the THz band) and low two-photon absorption coefficients at pumping 0.7–0.8 μm. GaSe has the second highest optical damage threshold among anisotropic nonlinear crystals [1].

Frequency conversion of laser radiation in the mid-infrared range in GaSe crystals was first carried out in 1972 [2]. Recently, GaSe crystals are considered to be promising materials for effective generation of ultrawideband radiation in the 0.8–5640 μm range and for electrooptic detection at unusually broad (120 THz) bandwidth.

However, despite these promising properties, GaSe crystals have not gained the same widespread acceptance as other nonlinear materials, such as $ZnGeP_2$ and ZnTe, in industrial applications. The lack of practical application is the result of difficulties in obtaining large single crystal boules of good optical quality; the reason is their extreme ability to cleave (perfect cleavage), which is due to the layered crystal structure with a weak interlayer van der Waals type bonding. Obtaining the required crystallographic orientation during sample processing is hampered because the GaSe hardness is measured to be close to 0 on the Mohs scale [3], which makes its mechanical processing impossible.

It is known that the GaSe crystal lattice is an excellent matrix for doping with elements that form isostructural binary compounds with gallium selenide (S, In, Te) [4–8], as well as non-isostructural compounds (Al, Er, Ag) [9–11]. Properties of GaSe crystals significantly change upon doping, and the dopant content is limited by the concentration at which the optical properties of the material deteriorate. For example, an increase of sulfur concentration up to 11 wt.% significantly raises the optical loss coefficient [4], while the introduction of In, Te, Er or Ag has a little influence on the optical loss coefficient [12]. It has been shown that the addition of In, Te, Er or Ag leads to a small (up to 20 %) increase in the hardness of the crystals, while the introduction of Al or S increases the hardness considerably [12]. However, it is noted that doping with more than 0.1 at.% Al significantly deteriorates the optical properties of the material. GaSe crystals doped with up to 11 wt.% S have good optic quality and the hardness large enough to cut the crystals in any direction and polish them.

It is also known that the introduction of chromium leads to hardening zinc selenide crystals [13]. However, the effects of chromium doping on the properties of GaSe crystals has not been researched.

Thus, the aim of this work was to study the influence of doping with chromium selenide on growth conditions, mechanical and optical properties of gallium selenide crystals.

2. Experimental

Elemental selenium, chromium powder, and metallic gallium were used as starting components. All starting materials were listed as especially pure.

2.1. Synthesis of gallium selenide and chromium selenide

Gallium selenide (GaSe) was obtained by the solid-state synthesis method in a quartz ampoule by direct interaction of gallium with selenium. 36.66 g of metallic gallium and 39.75 g of elemental selenium were charged into a quartz ampoule 20 mm in diameter and 300 mm in length. The ampoule was then sealed under vacuum. The sealed ampoule was placed in a heating furnace and slowly heated to 800°C for 48 h; after that it was kept at this temperature for 24 h. Then the temperature in the furnace was increased to 900°C at a rate of 2°C/h and the ampoule was kept at 900°C for 12 h. The synthesized gallium selenide was homogenized at 970°C for 6 h. Upon completion, the furnace was turned off and cooled to room temperature. The result of synthesis is a dark red boule of GaSe.

Chromium selenide (CrSe) was obtained by the solid-state synthesis method in a quartz ampoule by direct interaction of chromium with selenium. 3.47 g of chromium and 6.53 g of elemental selenium were charged into a quartz ampoule 10 mm in diameter and 300 mm in length. The ampoule was then sealed under vacuum. The sealed ampoule was placed in a heating furnace and was slowly heated to 800°C for 48 h, after that it was kept at this temperature for 24 h. Then the temperature in the furnace was increased to 900°C at a rate of 2°C/h and then it was kept at 900°C for 12 h. Upon completion, the furnace was turned off and cooled to room temperature. The result of synthesis is a boule of CrSe.

2.2. Crystal growth of GaSe:Cr^{2+}

The crystals were grown by the Bridgman method. Charges of gallium selenide (10 g each) and chromium selenide were placed into quartz tubes 10 mm in diameter and 200 mm in length. Concentration of chromium selenide varied between 0.05–2 wt.%. The charged ampoules were sealed under vacuum. The sealed ampoules were loaded into a container, which was placed in the heating unit of the growth furnace. The growth unit was evacuated to 0.1 atm, and then was filled with argon to a pressure of 10 atm. The crucible was heated to 970°C (at 10°C above melting point of pure gallium selenide) and the pressure in the growth unit was controlled in such a way that at 970°C its value was 23 atm. The melt was soaked for 12 h for its homogeni-

Fig. 1. The appearance of the grown GaSe crystals: a — GaSe (0.04 wt.% Cr); b — GaSe (5 wt.% Cr).

zation at a pressure of 23 atm, and then the crucible was pulled at a speed of 0.5 mm/h until the boule left the growth zone. Upon completion, a grown crystal was cooled at a rate of 30°C/h. As a result, optical quality crystals were obtained.

IR spectra of crystals were obtained on a Fourier transform IR spectrophotometer SPECTRUM ONE (PerkinElmer). Microhardness of the crystals was determined on a PMT-3 microhardness tester. The indentation load in the measurements was 0.05 N. The measurements were carried out on the (0001) planes of natural cleavages of the grown GaSe:Cr^{2+} and GaSe crystals that are characterized by a hexagonal crystal structure ($\bar{6}$ $2m$). 10 indentations with an indentation time of 10 s were carried out on each sample.

The concentration of chromium in the crystals was measured on an inductively coupled plasma atomic emission spectrometer TRACE SCAN Advantage from Thermo Jarrell Ash (USA).

3. Results and discussion

As a result, GaSe(Cr) crystal boules with a length of about 40 mm were obtained. The boules are characterized by perfect cleavage, which makes it possible to sufficiently obtain samples of various thicknesses. The

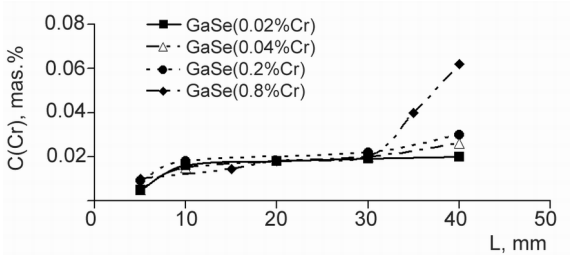

Fig. 2. Change in chromium concentration along the length (L) of grown crystals.

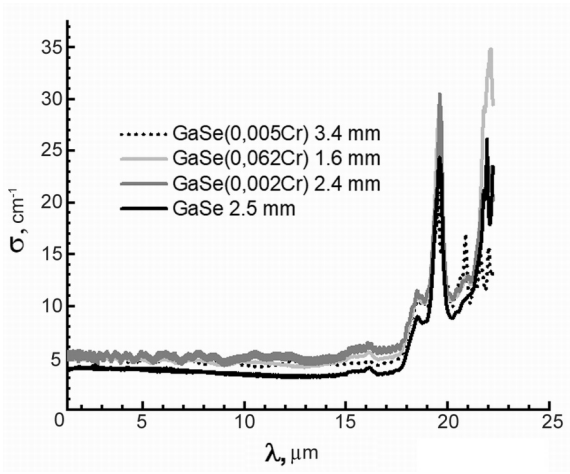

Fig. 3. Absorption spectra of GaSe(Cr) crystals.

cleavage indicates that the crystal structure of GaSe(Cr) remains layered. The CrSe content in the charge more than 5 % led to the formation of nontransparent non-cleaved crystalline boules, which did not allow further study of this material (Fig. 1b).

Fig. 2 presents the change in the chromium concentration along the length (L) of the crystal. Regardless of the initial concentration of chromium introduced into the mixture before growing, almost the same dynamics and changes in the chromium content along the length of the crystals are observed in the grown crystals. In the bottom part of the crystal (the beginning of the growth) the concentration of chromium is minimal (about 0.006–0.008 wt.%). As the crystal grows, the chromium content rapidly increases to 0.018–0.02 wt.% and remains almost unchanged (2/3 boule length). In the upper part of the crystal (the completion of the growth), an increase in the chromium content is observed. Moreover, the higher the concentration of chromium selenide in the loading mixture, the higher the chromium content in the upper part of the crystal.

Fig. 3 presents the absorption spectra of GaSe(Cr) crystals normalized with allow-

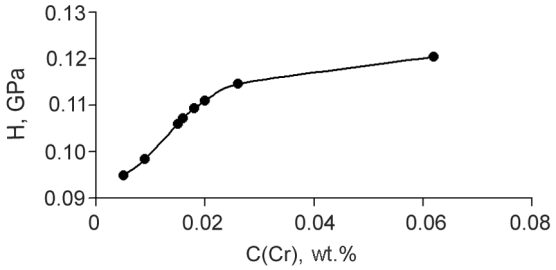

Fig. 4. Dependence of microhardness (*H*) of gallium selenide crystals on chromium concentration.

ance for the thickness of the samples. As follows from the obtained experimental data, the addition of chromium selenide to the crystal did not significantly affect the optical properties of the crystals. All the crystals were characterized by a rather low absorption level.

Fig. 4 shows the dependence of microhardness (*H*) of gallium selenide crystals on the of chromium concentration. The microhardness of the crystals increases with increasing chromium concentration. The dependence can be conditionally divided into two sections: the first one with 0.005–0.025 wt.% Cr is characterized by an intensive increase in microhardness with an increase in the content of the dopant; the second one with above 0.025 wt.% Cr shows a slight increase in microhardness with an increase of the concentration of the dopant. For comparison, the microhardness data of pure GaSe crystals given by various authors differ greatly: in [9] — 3 kgf/mm^2 (0.029 GPa), in [12] — 7.8 kgf/mm^2 (0.076 GPa).

4. Conclusions

Doped GaSe crystals with the chromium concentration of 0.005 to 0.065 wt.% were grown by the Bridgman method. The grown crystals retain the ideal cleavage determined by the layered crystal structure. Regardless of the initial concentration of chromium introduced into the mixture before growing, almost the same dynamics and changes in the chromium content along the length of the crystals are observed in the grown crystals. The chromium concentration in the upper part of the boule increases with an increase in chromium selenide content in the charge.

Doping of the GaSe crystals with chromium selenide allows us to increase the microhardness of crystals up to 0.122 GPa (0.065 wt.% Cr) and does not significantly affect the optical properties of the crystals.

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