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Defects in GaSe grown by Bridgman method

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Summary

Optical quality GaSe crystals have been grown by vertical Bridgman method. The structural properties and micromorphology of a cleaved GaSe(001) surface have been evaluated by RHEED, SEM and AFM. The cleaved GaSe(001) is atomically flat with as low roughness as ~0.06 nm excepting local hillock type defects. The hillock-type formations are round-shaped with a bottom diameter of ~200 nm and a height of ~20–35 nm. The drastic depletion of the hillock material by gallium has been indicated by EDX measurements.

Introduction

Gallium selenide, GaSe, is a well-known nonlinear optical crystal widely used for frequency conversion over visible, IR and THz spectral ranges (Fernelius, 1994; Singh *et al.*, 1998; Shi *et al.*, 2002; Feng *et al.*, 2008; Allakhverdiev *et al.*, 2009; Guo *et al.*, 2013a). During the last decade, the breakthrough application of GaSe for terahertz (THz) generation over an extremely wide spectral range under the pump by near-IR coherent sources was reported (Jiang & Ding, 2007; Chen *et al.*, 2009; Zhang *et al.*, 2011). Due to interesting semiconductor properties, GaSe is used in microelectronic and epitaxial technologies (Emery *et al.*, 1992; Rudolph *et al.*, 2005; Ho *et al.*, 2006; Huang *et al.*, 2010; Late *et al.*, 2012). The pronounced layered crystal structure of GaSe, space group $P\overline{6}m2$, where dense atomic layers are linked by relatively weak van der Waals forces, defines many specific physical and chemical properties of GaSe, such as high anisotropy of mechanical, thermal, linear and nonlinear optical parameters, higher doping and intercalation ability (Cenzual *et al.*, 1991; Fernelius, 1994; Singh *et al.*, 1998; Abdullaev *et al.*, 2002; Andreev *et al.*, 2006; Feng *et al.*, 2008; Abdinov *et al.*, 2010; Sarkisov *et al.*, 2010; Zhang *et al.*, 2011; Isik & Gasanly, 2012; Atuchin *et al.*, 2013a,b ; Kato *et al.*, 2013). The weak interlayer chemical bonds in the GaSe structure results in low mechanical properties and high GaSe crystal cleavage. This provides a possibility to prepare the large area (001) crystal surface by a simple cleavage technique, and the cleaved surface commonly possesses optical quality and atomic level flatness (Fernelius, 1994; Sarkisov *et al.*, 2010; Borisenko *et al.*, 2011; Isik & Gasanly, 2012; Atuchin *et al.*, 2013a,b; Guo *et al.*, 2013b; Ni *et al.*, 2013). It should be pointed that the cleaved GaSe(001) surface shows specifically high chemical inertness in the air under normal conditions similar to several other layered chalcogenides (Tambo & Tatsuyama, 1985; Atuchin *et al.*, 2011; Yashina *et al.*, 2013). Above this, the single or few atom tetralayer GaSe flakes can be prepared by the exfoliation in an appropriate solution under ultrasonical stimulation, and this method is actively used in nanotechnology because electronic structure of GaSe is strongly dependent on the tetralayer number (Allakhverdiev *et al.*, 1997; Gautam *et al.*, 2005; Rybkovskiy *et al.*, 2011; Hu *et al.*, 2012; Aksimentyeva *et al.*, 2013; Ma *et al.*, 2013). Recently, the formation of the 3D topological insulator state has been predicted for the GaSe surface (Zhu *et al.*, 2012). The defect existence, however, drastically limits the atomic level engineering of semiconductor materials and, in particular, restricts the area of exfoliated GaSe flakes. Thus, this study is aimed at the growth of a low-defect GaSe single crystal by the developed Bridgman technique and evaluation of defect structure of the crystals. The point defects will receive proper attention because doped GaSe commonly possesses increased hardness, and the creation of interlayer links by admixture atoms and defects may be supposed (Fernelius, 1994; Mosca *et al.*, 2002; Andreev *et al.*, 2006; Feng *et al.*,

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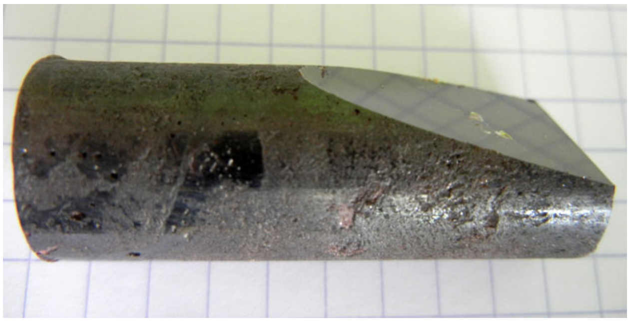

Fig. 1. GaSe ingot with a cleaved sector.

2008; Rak *et al.*, 2010; Sarkisov *et al.*, 2010; Atuchin *et al.*, 2013a; Guo *et al.*, 2013a).

Experimental

The GaSe crystal growth was produced in the 18 mm diameter evacuated silica ampoules freshly washed in the HNO_3-HF mixture. Because of a high selenium pressure at the melting point of GaSe (1211K) the process was divided into two stages. Initially, the GaSe polycrystal was synthesized from high-purity (5N) elementary components taken at stoichiometric ratio 1:1. An elongated ampoule with the charge was sealed at 10^{-4} torr by the propane-oxygen flame. The components were gradually fused by sliding the ampoule into the single-zone furnace heated to 1250 K (Kokh *et al.*, 2011). After the synthesis during 10 h and cooling the synthesized material was transferred in a single-wall growth ampoule with a conical end and a pyrolitic carbon layer deposited onto the inner surface. The GaSe crystals were grown by the conventional Bridgman technique with 1240 and 1120 K in the upper and lower zones, respectively; and with a 20-cm long gradient interval between the zones. After homogenization at 1240 K during 24 h, the ampoule was pulled down to a lower zone with the speed of 10 mm/day. In the end of the experiment, the crystals were being cooled for 20 h with a switched-off furnace. As a typical layered compound, GaSe tends to grow laterally along the primary direction of the temperature gradient which, in turn, is aligned vertically in the Bridgman method. So, most of the crystals have the (001) cleavage plane to be sub-parallel with the ampoule axis, and the crystals with such primary orientation are able to grow without using a seed. The grown GaSe ingot is shown in Figure 1.

The GaSe(001) substrates were cleaved by a metal blade from the grown ingots parallel to (001) and were studied without any subsequent manipulations like washing, polishing, etc. The micromorphology of the cleaved GaSe(001) surface was observed by SEM using LEO 1430 and JEOL JSM 6700F devices and AFM with Solver P-47H device in the noncontact mode. The structural properties were evaluated by TEM and RHEED analysis using BS-513A and EFZ4 devices, respectively.

Results and discussion

The GaSe(001) substrates were characterized by a mirror-like cleaved surface. The selected area electron diffraction (SAED) patterns obtained for the flake exfoliated from the (001) surface show the crystal spot system with the hexagonal symmetry related to [001] GaSe (Kuhn *et al.*, 1975a,b). A typical SAED pattern is shown in Figure 2(A). The RHEED pattern measured from the (001) surface contains only Kikuchi lines, as shown in Figure 2(B), and this indicates high crystallinity of the cleaved GaSe surface. There are no reflexes or hallo related to a foreign crystal phase or amorphous component, respectively.

SEM observation of the cleaved (001) surface dominantly shows the flat homogeneous pattern with a uniform contrast. However, the presence of local defects was occasionally detected. The SEM pattern of the substrate edge is shown in Figure 3(A). At the image, the echelon of broken atomic layers is visible. The GaSe layer stocks are well packed and they are frequently bound by the angles of 120° that is a characteristic of hexagonal crystallographic axis [001] orthogonal to the cleaved surface. Generally, the basic cleaved surface GaSe(001) is very flat, as it can be seen at the left-lower part of the pattern. Besides, the spot like defects with a characteristic diameter of ~100–150 nm and smooth round boundary can be found at the surface. Occasionally, the defects can decorate some line structures on the surface with a chain formation as it is illustrated in Figure 3(B). Higher resolution SEM image of the defects is shown in Figure 3(C). Over this part of the GaSe(001) surface, the spots are scattered. Generally, the spots show a bright contrast at the SEM patterns, and a noticeable inrichment of the spot material by a heavy element, selenium in the case of GaSe, can be reasonably supposed (Goldstein & Yakowitz, 1975). It should be pointed that similar formations were earlier detected in several studies but without a detailed discussion (Abdullah *et al.*, 2010; Pashayev *et al.*, 2011; Zhirko *et al.*, 2012).

As it was shown by AFM observation, the cleaved GaSe(001) surface is almost entirely atomically flat with as low roughness as ~0.06 nm measured for the area of 5×5 μm^2. In several scans, hillock-type formations were detected with a bottom diameter of ~200 nm and ~20-35 nm high. The related topographical 10×10 μm^2 AFM image and surface profile are shown in Figure 4. Ga/Se ratio in the hillocks was estimated by EDX measurements. However, it should be kept in mind that the local volume analyzed by EDX is evidently larger than the hillock diameter and, supposedly, the depth. We may estimate the volume of solid phase subjected to electron beam as 350 nm in diameter and 500-700 nm in depth. For this reason, the Ga/Se ratio measured by EDX is overestimated and it relates to a combination of hillock material and GaSe bulk. Nevertheless, as low Ga/Se ratios as 0.55–0.84 were found from the EDX measurements of several hillocks and that indicates a drastic depletion of the hillock material by gallium. A detailed mechanism of the hillock defect formation in GaSe crystal is

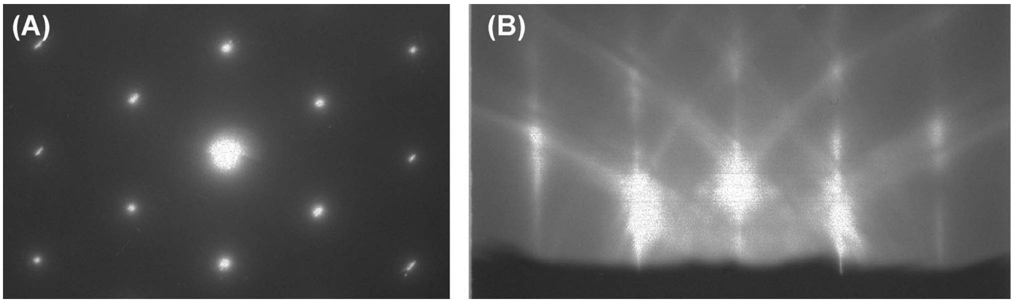

Fig. 2. SAED (A) and RHEED (B) pattern recorded from the GaSe(001) flake.

Fig. 3. SEM images recorded at (A,B) lower and (C) higher resolution.

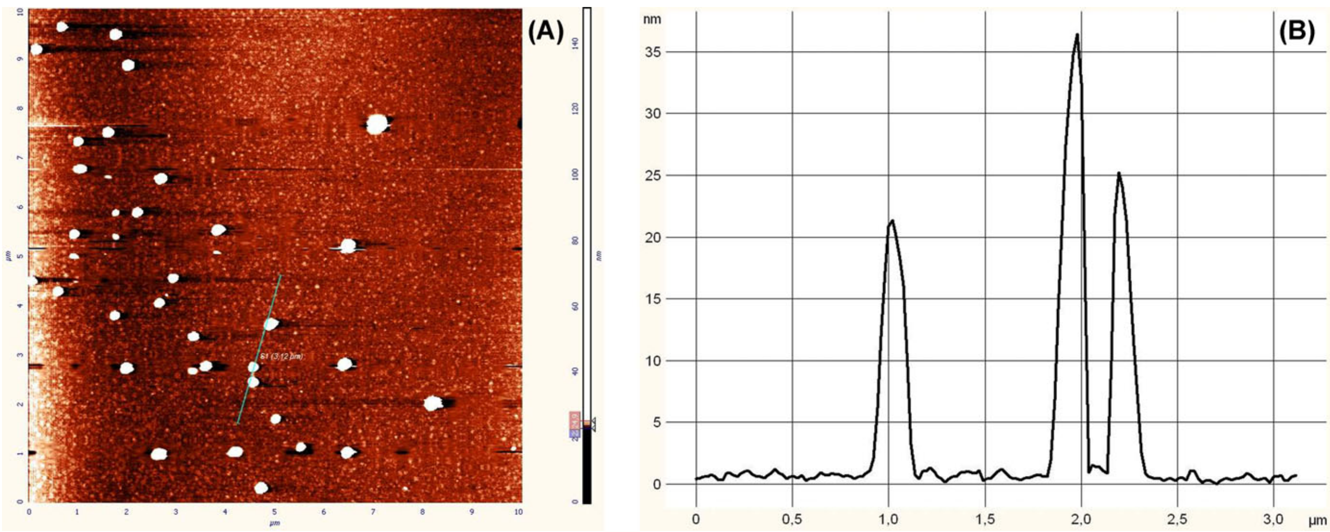

Fig. 4. AFM (A) panoramic image and (B) profile recorded from the GaSe(001) cleaved surface.

unclear now. Two possible variants may be considered. On the one hand, the selenium rich phase may precipitate on the cooling stage due to a decrease of Se solubility in GaSe. On the other hand, the precipitation may be a result of the presence of melt inhomogeneties on the crystallization front. In that case, the entrapment of Se-rich melt portion by the growing crystal may cause the origin of the inclusions.

Conclusions

Optical quality GaSe crystals are grown by the Bridgman technique, and a defect structure of cleaved GaSe(001) crystals surface is considered with the emphasis on the point defects. The hillock type defects are evaluated by SEM and AFM. The surface part containing the defects is local, but the hillock height is evidently above the thickness of several atomic layers in the GaSe structure. Respectively, the hillock defects can work as interlayer clips increasing the crystal rigidity. The hillock defects evidently decreases GaSe cleavage properties and the cleaved GaSe(001) surface quality. In the future, special crystal growth methods or subsequent treatments are topical to remove the hillocks.

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