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Growth and Characterization of Sulfur-doped GaSe Single Crystals

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Abstract: It is difficult to obtain high quality sulfur-doped GaSe single crystal due to the intensive convection and solution diffusion in the melt. High quality $GaSe_{0.89}S_{0.11}$ single crystal with dimensions of ϕ20 mm×60 mm was successfully grown by Bridgman method using modified furnace with crucible rotation technique. The crystal was characterized by using energy dispersive spectrometer, X-ray diffractometer, nanoindentation, and Fourier infrared spectrometer. The measured results indicate that the sulfur-doped GaSe crystal with sulfur level of 2.38wt% shows significantly improved mechanical properties. The infrared transmission tests indicate that it has slightly higher transmittance in the range of 0.62–12.5 μm than the pure GaSe crystal. The results demonstrate that the modified Bridgman method could be used to produce high quality sulfur-doped GaSe crystals.

Key words: $GaSe_{0.89}S_{0.11}$; doped; modified Bridgman furnace; crucible rotation

The ε-GaSe crystal is the best far-infrared nonlinear crystal due to its wide transparency range (0.62–18 μm) and large birefringence (0.35). Moreover, it has many other attractive features, such as large nonlinear coefficient (d_{22}=70–80 pm/V), high laser damage threshold, lower absorption coefficient, which determine its excellent performance for frequency conversion over a wide spectral region from near-IR to far-infrared and even to terahertz[1]. The main drawbacks of pure GaSe are the extreme softness and bad cleavage properties which complicate cutting and polishing of the optical faces. To overcome these drawbacks, many researches have considered the possibility of improving the GaSe mechanical properties by doping other elements, such as In[2-6], Te[6-8], S[4-7, 9-11]. These solid solution formations indeed strengthen the mechanical properties of the crystal and partly improve their optical parameters. Among these tested elements, sulfur seems to be the most promising. That is because both GaSe and GaS have the same laminar structure with each monolayer containing four covalently join atoms in the order X-Ga-Ga-X (X=S, Se) along *c*-axis. Ho, *et al*[9] investigated the influence of sulfur doping concentrations on its monolayer stacking phases and band gap. Several works were performed to study the transparency spectra of sulfur doped GaSe. Feng, *et al*[4] revealed that the transmittance of GaSe doped by sulfur at the level of 2wt% was obviously lower than that of pure sample. However, Das, *et al*[6] and Kang, *et al*[7] gave different results which revealed that sulfur doped GaSe with 2wt% had better optical qualities than the pure sample. Apparently, their experimental results disagreed with each other.

The above mentioned contradiction may appear from different crystal quality, which is strongly influenced by growth technology. The volatile component of Se, strong temperature oscillation near the growth interface[12], and the cracking of crystals as growing pure and doped GaSe crystal may spoil their qualities. The high-pressure vertical zone melting technique[13] and temperature difference method under controlled vapor pressure (TDM-CVP) technique[14] were used to produce pure GaSe single crystals. In our previous experiment, it was difficult to produce the large size sulfur-doped GaSe due to intensive convection and solution diffusion in the growth process, even if the growth parameters were similar to those of pure GaSe[15]. Therefore, it is very important to determine appropriate procedures and parameters for the growth of high quality sulfur doped GaSe crystal. In the present study, the modified Bridgman method was used to produce $GaSe_xS_{1-x}$ by ampoule rotation technique. The modified Bridgman furnace was designed according to the numerical simulation results obtained from Refs. [12] and [16]. The technical details are presented in section 1.

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1 Experimental procedure

The polycrystalline $GaSe_xS_{1-x}$ was prepared in two-zone horizontal furnace using high purity Ga (99.9999%) and Se (99.999%) with S (99.999%) doping concentrations of 3wt%. These high purity materials were made by EMEI Semiconductor Material Institute. Crystal growth was carried out by a modified Bridgman furnace using crucible rotation technique.

There are several tips about the modified Bridgman furnace. The schematic of furnace device is shown in Fig. 1. As shown, a sealed and unvacuum quartz tube is placed in the evacuated and sealed carbon-coated ampoule. When the temperature is gradually raised up to melting point, the quartz tube will expand and limit the space occupied by melt as small as possible. By limiting the free space above the melt, it could effectively restrain the S and Se evaporation from the sulfur-doped GaSe melt. Different materials of furnace-tubes were used in hot, adiabatic, and cold zones. In the hot and cold zone, the higher thermal conductivity carborundum furnace-tubes are used to obtain uniform temperature distribution, which could suppress melt convection and reduce the cracking of crystals. The adiabatic zone is composed by a mullite furnace-tube with lower thermal conductivity, which could provide a temperature gradient. As shown in Fig.1, some holes along furnace wall could be used to insert temperature-control thermocouples. By adjusting the temperature difference between hot and cold zone as well as the position of temperature-control thermocouples, one could obtain the desirable temperature distribution for the crystal growth.

Suppression of melt convection is a key to grow large size sulfur-doped GaSe. As we known, Wei, *et al*[12] provided an easy and effective method for suppressing melt convection by adjusting temperature boundary conditions in the process of growing semiconductors. Moreover, Lan[16] demonstrated the effects of ampoule rotation on the melt convection and dopant segregation in the process of vertical Bridgman crystal growth. However, the numerical simulations could just provide a general trend of temperature and flow distributions in the process of growing crystal. Therefore, after several doped GaSe growth experiments, we have obtained the optimized growth parameters of sulfur doped GaSe in this modified Bridgman furnace. The temperature difference of 140 K between hot and cold zone was distributed along the adiabatic zone ~15 cm in length. The maximum temperature gradients in adiabatic zone were about ~15 K/cm. The ampoule was rotated at a constant rate of 20 cycles per minute, and the growth speed was set to 2 cm/d. At the end of the process, the ampoule was cooled slowly to room temperature. Both sulfur doped GaSe (ϕ20 mm×60 mm) grown in this experiment and pure GaSe (ϕ24 mm×50 mm) grown in previous experiment are displayed in Fig. 2. The longer one is sulfur doped GaSe and the shorter one is pure GaSe.

Some samples cut from as-grown sulfur-doped GaSe single crystals were prepared for the measurements of its properties. The elemental compositions of as-prepared sample were analyzed by using an energy dispersive spectrometer (EDS) attached to a scanning electron microscope. The phase structure was characterized using X-ray diffraction (XRD) with the 2θ ranged from 10° to 70°. Transmittance spectra were measured by Fourier infrared spectrometer (FT-IR) at room temperature over the spectral range of 0.4–19 μm.

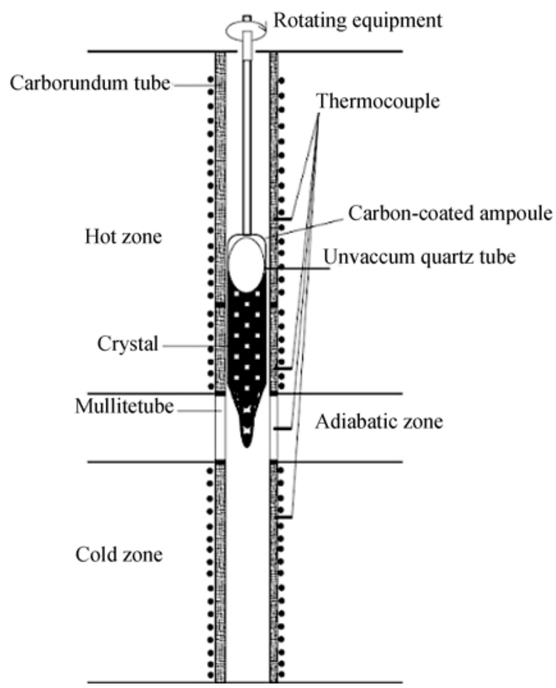

Fig. 1 The schematic of modified Bridgman furnace device

Fig. 2 The photograph of as-grown sulfur-doped GaSe and pure GaSe boule
The longer one is sulfur doped GaSe and the shorter one is pure GaSe

2 Results and discussions

To control the elements distributions in the grown crystal, a sample cut from the crystal was tested by EDS at 9 independent points arranged as the 3×3 matrix in the 1 cm^2 area. Typical EDS spectrum is shown in Fig. 3. The characteristic peaks of Ga, Se, and S elements are clearly observed. The average atomic Ga: Se: S ratio is 49.94: 44.71: 5.33 ($GaSe_{0.89}S_{0.11}$) that corresponds to S 2.38wt%. The measured result of 2.38wt% is obviously lower than the starting charge value of 3wt%. This is reasonable to attribute the difference to sulfur loss during the polycrystalline $GaSe_xS_{1-x}$ synthesis due to higher S volatility. The sulfur content in as-grown $GaSe_{0.89}S_{0.11}$ crystal is higher than those in Refs. [4] and [6]. As the sulfur concentration increases, the doped crystal growth becomes considerably more difficult. Figure 4 displays the X-ray diffraction patterns measured from $GaSe_{0.89}S_{0.11}$ and pure GaSe grown in previous experiment. Both the samples show similar diffraction patterns close to the standard PDF card JCPDS 97-007-1082 (Space Group 187). The results demonstrate that GaSe: S single crystal growth at sulfur content of 2.38wt% does not change its phase composition.

Although the as-grown $GaSe_{0.89}S_{0.11}$ crystal could be cut easily using sharp blade, it is harder to cleavage along (0001) face compared with the pure GaSe. To observe the improvement of mechanical properties, the indentation modulus and the indentation hardness of $GaSe_{0.89}S_{0.11}$ and pure GaSe were measured by using a Nanoindenter G200. Ten points on the (0001) face were selected to be tested along c-axis, corresponding elastic modulus C_{13}. The mean indentation hardness is 0.87 GPa for pure GaSe, corresponding to the elastic modulus of C_{13}=12.5 GPa which is close to the known experimental value (12.6 GPa)[17]. The measured indentation hardness and elastic modulus are 1.25 GPa and 17.8 GPa respectively for $GaSe_{0.89}S_{0.11}$. The elastic modulus and the indentation hardness of $GaSe_{0.89}S_{0.11}$ are ~34% higher than those of pure GaSe.

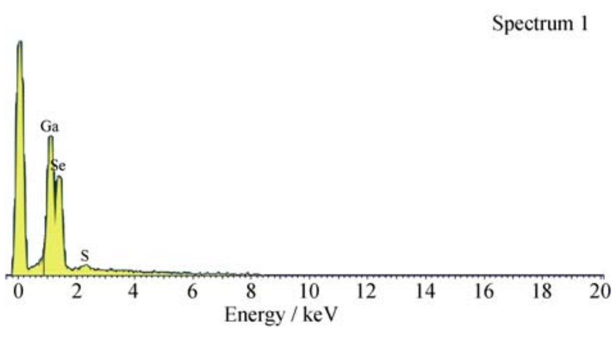

Fig. 3　EDS spectrum of the $GaSe_xS_{1-x}$ sample

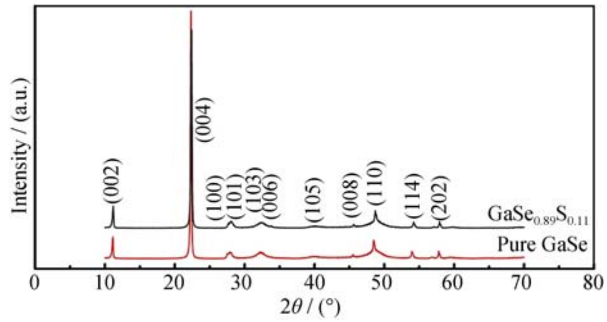

Fig. 4　XRD patterns of pure GaSe and $GaSe_{0.89}S_{0.11}$

The samples of pure GaSe and $GaSe_{0.89}S_{0.11}$ with thickness about 3.5 mm were prepared for the infrared transmission tests. The results are displayed in Fig. 5. As shown, both the samples show higher transmittance (about 65% in the range of 0.9–12.5 μm) than the samples with thickness of 1–3 mm (45%–60% in the range of 0.9–12.5 μm) reported in Refs. [4] and [7]. The absorption coefficient, calculated by the method proposed in Ref. [18], is about 0.1 cm^{-1} in the range of 0.9–12.5 μm. Similar to the $GaSe_xS_{1-x}$ samples as reported in Ref. [4] and Ref. [7], the $GaSe_{0.89}S_{0.11}$ crystal shows strong absorption beyond 15 μm. However, as shown in Ref. [4] and Ref. [6], there was no such tendency in the GaSe crystals doped by heavier atoms (In, Te). We infer that the strong infrared absorption beyond 15 μm derives from the phonon absorption of the substituting sulfur atoms, which produces higher phonon energy than selenium atoms in the sulfur-doped GaSe system. But the $GaSe_{0.89}S_{0.11}$ has slightly higher transmittance than the pure one in the range of 0.9–12.5 μm. The results indicate fine optical quality of the crystal grown by the modified method.

3 Conclusions

The high quality sulfur-doped GaSe crystal was successfully grown by Bridgman method using modified furnace with crucible rotation. The EDS measurements indicate that the sulfur content is ~2.38wt%, corresponding to

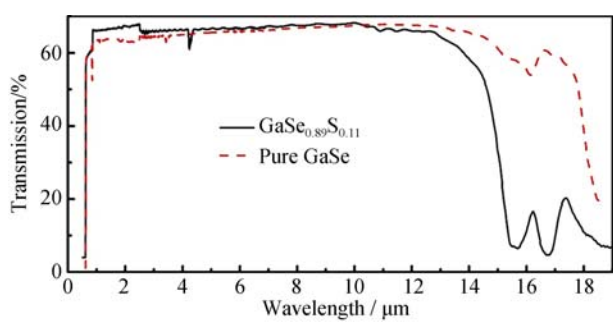

Fig. 5 Transmission spectra of pure GaSe and $GaSe_{0.89}S_{0.11}$ with about 3.5 mm thickness

the $GaSe_{0.89}S_{0.11}$ composition. The mechanical properties of $GaSe_{0.89}S_{0.11}$ are significantly improved compared to those of pure GaSe. Although it shows strong absorption beyond 15 μm, the infrared transmission tests demonstrate that it has slightly higher transmittance than those of pure GaSe in the range of 0.62–12.5 μm. The $GaSe_{0.89}S_{0.11}$ crystal is expected to be used for the fabrication of infrared nonlinear optical devices, especially for the tunable coherent infrared radiation output in the range of 8–14 μm.

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GaSe 晶体的掺 S 生长及性能研究

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摘 要: 当生长掺 S 的 GaSe 单晶时, 熔体的强烈对流和溶质扩散使得生长出大尺寸的晶体较为困难。本实验采用改进的 Bridgman 炉, 并结合坩埚旋转技术, 成功生长出了较大尺寸的 $GaSe_{0.89}S_{0.11}$ 单晶体(ϕ20×60 mm^3)。采用 X 射线粉末衍射仪、能谱仪、纳米压痕仪和傅里叶红外光谱仪测量其结构、成分、机械和光学性质。测试结果表明, 质量分数为 2.38%的 S 掺杂的 GaSe 晶体($GaSe_{0.89}S_{0.11}$)没有发生结构相变; 它的机械性能得到了明显的改善, 同时光学性能也得到了一定的提高。

关 键 词: $GaSe_{0.89}S_{0.11}$; 掺杂; 改进的 Bridgman 炉; 坩埚旋转

中图分类号: TQ174 **文献标识码:** A