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One step process for synthesis and growth of ZGP crystals using HGF technique

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Abstract

The growth of $ZnGeP_2$ (ZGP) crystals has been performed using 3-zone furnace by horizontal gradient freezing (HGF) technique. We found that the quality of ZGP crystals grown by using PBN coated boat is much better than the boron nitride and silicon nitride coated boats. In the present study we have successfully done the synthesis and growth together in single run of the experiment. We followed two-temperature method for the synthesis and afterwards the cold zone temperature was increased for the growth of ternary compound of ZGP. The growth was achieved by pulling the quartz tube with the rate of 1.8mm/hr in the temperature gradient of 2^0C/cm until the entire charge was solidified.

：

(HGF) $ZnGeP_2$(ZGP)   ，
PBN

ZGP   ，   ，
ZGP ，   ，   ZGP
，   1.8mm/hr 2^0C/cm   。

Introduction

Zinc-germanium-phosphide, $ZnGeP_2$ (ZGP), as other members of the $A^{II}B^{IV}C^{V}_2$ chalcopyrite series, is derived from III-V compounds, having a zinc blende-like type of structure. The atomic positions in the chalcopyrite compounds are shifted with respect to those of the zinc-blende structure, space group F**4**3m, leading to a tetragonal structure of space group I**4**2d [1], which is slightly distorted with respect to the zinc-blende structure.

The tetragonal distortion Δ in the chalcopyrite lattice defined as $\Delta=(2-c/a)$, where c and a are the lattice parameters, arises from the difference in atomic interactions between the Zn and Ge atoms towards the P atom [2].

$ZnGeP_2$ is a most interesting nonlinear optical material for infrared spectral range due to its unique set of optical properties [3] (wide potential transmission range of 0.7-13 µm, and high value of nonlinear susceptibility $D_{36}=75$ pm/V). Several different growth techniques have been used by researchers to obtain single crystals of $ZnGeP_2$. The problem of high-yield $ZnGeP_2$ synthesis is related to the presence of two volatile components (Zn and P) that can form thermally stable binary phases Zn_3P_2 (Tm= 1193°C) and ZnP_2 (Tm= 1040°C).

Solid $ZnGeP_2$ is less heat conductor than the liquid $ZnGeP_2$. This makes the crystallization heat removal through the crystal difficult. As a consequence, the temperature gradient near the interface must be lower in the liquid phase than in the solid one. For similar reasons high growth rates are thus unattainable. The most popular $ZnGeP_2$ growth methods are the Bridgman technique and the horizontal gradient freezing technique [4-7]. To the best of our knowledge no data is available regarding the synthesis and growth together in single step. Therefore, we have attempted to try the horizontal gradient freezing techniques (HGF) to synthesize and growth together in single run of the experiment to obtain the single crystals of ZGP.

Experimental

Powders of Zinc (Zn-99.999% purity), Germanium (Ge-99.9999% purity) and Phosphorous (P-99.9999% purity) were used. The constituent material was synthesized using 3-zone horizontal furnace. A mixture of predetermined amounts of the constituents Zinc (Zn), Germanium (Ge) and Phosphorous (P) were placed in a boat and cylindrical tube alternatively and then three times evacuated to $\sim 2x10^{-2}$ torr and purged with nitrogen and finally sealed at the pressure of $\sim 2x10^{-2}$ torr. The tube length of 50 cm and the wall thickness of 3mm was chosen to with stand the process pressure of $\sim$ 60 atoms or more. The boron nitride and silicon nitride coated quartz boat was used. The weighing and loading of the constituent materials into the tube was done in nitrogen atmosphere inside the glove box.

Synthesis of ZGP material

It is reported that the two-temperature method is not suitable for the growth of

ZGP due to the fact that if the cold zone temperature remains fixed throughout the run, the volatile binary phosphides would be condensed in the cold zone and no ternary compound would be produced. Therefore, cold zone temperature has to be increased. We have chosen a different arrangement of species for $ZnGeP_2$ as reported by Verozubova et al [3]. An equiatomic Zn-Ge mixture was placed in the hot zone and P in the cold zone. We considered that this arrangement is alright because the saturated Zn vapor pressure is lower than the P pressure. They have reported that the cold zone temperature 485°C, corresponded to a P pressure of 4.5 atm and the hot zone temperature 1030°C, the pure Zn vapor pressure being 4 atm. According to Raoult's law it is considered that the Zn pressure has to be decreased by a factor of about two because of its mixing with Ge. Under these conditions the Zn vapor was transported to the colder part of the reactor and ZnP_2 was formed on the reactor walls. The latter prevented the P transport toward the hot zone and free P remained in the reactor and an increase in the cold zone temperature may lead to an explosion.

To analyze the problem, one can consider the diffusion equation for Zn vapor and can be written as [8]

$$j_{Zn} = -\frac{D}{RT}\Delta P_{Zn} + \frac{V}{RT}P_{Zn} \tag{1}$$

Here D is the diffusion coefficient, P_{zn} is the partial Zn pressure, R is the gas constant, T is the temperature, and V is the molar rate of flow for the mixture:

$$V = x_P V_P + x_{Zn} V_{Zn} \tag{2}$$

where x_{zn} and x_p are the mole fractions and V_{Zn} and V_p are the rates of the ordered motion for Zn and P. Assuming that the first term in Eq. (2) is larger than the second one, Then Eq. (1) can be written as:

$$j_{Zn} = -\frac{D}{RT}\frac{dP_{Zn}}{dx} - V\frac{p_{Zn}}{RT} \tag{3}$$

Since the first term in Eq. (3) is larger than zero the Zn diffusion will not occur if the second term associated with the mass transport of P is equal to, or larger, than the first term. If the P flow rate is sufficiently high, it will cause Zn vapor to flow back toward the hot reaction zone. Another factor hindering the Zn diffusion is a decrease in the diffusion coefficient as the total pressure is increased:

$$D \sim P^{-1}T^{3/2}, \hspace{4cm} (4)$$

Where P is the total pressure and T is the temperature. Thus, to prevent the Zn diffusion the cold zone temperature had to be increased, the total pressure and the P flow rate therewith being increased.

Results and discussion

The sealed ampoule was kept in the 3-zone resistance heating furnace for the experiment. After loading the material into the furnace the temperature was increased simultaneously of the cold and hot zone. The cold zone temperature was raised up to 520 ^{0}C and hot zone up to 1010 ^{0}C. After 1-2 hrs the P was completely reacted with the melt of Zn and Ge. When we found that there was no phosphorous left in the tube, the cold zone temperature was increased to 1010°C. Once ZnP_2 is formed, the temperature of cold zone and hot zone was further increased up to 1050 ^{0}C and 1060 ^{0}C respectively sufficiently above the melting of $ZnGeP_2$ ($\sim$1027^{0}C) to ensure the complete melting of constituent materials. The mixture was kept at 1050 ^{0}C for a period of 10-12 hours to promote the mixing of the constituent compounds and then it is allowed to cool just few degrees above the melting of the ZGP. The small temperature gradient in the tube causes some condensation of Zn and P at the end of the tube which helps to restrain the rate of pressure increase. The amount of the Zn and P which condenses at the end of tube is reproducible, so an extra amount of these constituents needs to be added with the initial mixture to compensate the condensation loss and thereafter to control the chemical composition of the end product. The growth was achieved by pulling the quartz tube with the rate of 1.8mm/hr in the temperature gradient of 2^{0}C/cm until the entire charge was solidified. Slow cooling after growth at the rate 5 ^{0}C/hr was used to prevent the cracking. Finally, after finishing the experiment, we have found that the grown crystal quality is not good. It was observed that the boron nitride coating of quartz boat is not good enough to prevent the sticking of ZGP with boat at a high temperature. In our first experiment the quartz boat was completely reacted with the material. In the next experiment we used thick coating of boron nitride and found that the result is better than the previous one. But still some bottom portion of the crystal got reacted with the quartz boat as can be seen in fig. 1(b). We had also tried with silicon nitride coated quartz boat but the result is still not

good. Finally, we tried with PBN coated graphite boat and found that the results are much better than the previous ones as shown in fig.1(c).

Conclusions

We have successfully done the trial experiment of the synthesis and growth of ZGP together in single run of the experiment using 3-zone horizontal furnace by HGF technique. This experience could be combined to grow the ZGP single crystal using transparent horizontal furnace. PBN coated boat has yielded much better quality crystal than the other coatings.

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Fig. 1: Photographs of ZGP crystals grown by three-zone HGF technique using different crucible and coating: (a) lesser thickness of boron nitride coated quartz crucible, (b) larger thickness of boron nitride coated quartz crucible, and (c) PBN coated graphite crucible

出席第五屆國際晶體生長膜模擬會議報告

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第五屆國際晶體生長模擬會議(IWMCG-5)於 2006 年九月十至十三日於德國的 Bamberg 市舉行。這個會議三年才舉辦一次,與會約一百五十人,來自二十三個國家。此會議雖小,但卻是晶體生長理論研究最重要的會議,本人在上一屆於福岡舉行時擔任過主席,而會議的重要論文也發表在 J. Crystal Growth 的專刊。此次會議共有 40 篇 oral paper,70 篇海報論文。本人有篇受邀演講,另外一篇口頭。

此次會議包括 Modeling on Nano-Scale,Modeling on Maso-Scale,ModelingofMelt Growth,Modeling of Convection Phenomena,Modeling of Defect Formation,以及 Global Modeling of Epitaxy and Vapor Growth 等子題。其中在微小尺度的模擬比重比以前高,顯示漸漸的大家對基礎的了解越來越覺得重要這些主題也反映了未來晶體生長的發展方向。

本人的報告有兩篇,受邀的一篇是對 faceting 動力學的三維模擬,另依篇是主要探討旋轉跟震動對垂直單向凝固晶體生長的偏析控制。尤其是可以提供簡便的外力控制來做軸向與徑向的摻雜控制,透過透明的晶體生長實驗觀察與電腦模擬研究,頗受與會者重視。者兩向外力控制技術,可容易的應用在工業的晶體生長上,頗有應用潛力。

此次會議國內只有三人與會,充分顯示國內在晶體生長模擬研究的萎縮。然而國內在半導體矽晶與光電應用的藍寶石單晶與 GaAs 單晶,無線通訊應用的 LT,都有很快速的進展。因此,國科會應多鼓勵並增加電子與光電產業上游原料(主要靠單晶生長)的研究與技術開發。此外,太陽能矽晶的進展這兩年也很快,晶體原料的品質也關係元件的性質,而晶體生長模擬對晶體生長的最佳化很有幫助,因此,希望國內有更多的學者進來個領域。