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学位論文題目	Development of novel techniques for the synthesis of nitride semiconductors by using solid nitrogen sources (固体窒素源を用いた窒化物半導体の新規合成法の開発)
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論文内容の要旨

GaN, InN and AlN are III-nitride semiconductors with direct band gap of 3.4 eV, 0.6 eV and 6.2 eV respectively. By controlling the composition of the solid solution, such as $\text{In}_x\text{Ga}_{1-x}\text{N}$ and $\text{In}_x\text{Al}_{1-x}\text{N}$, is possible controlling the band gap of the material which spans the range of 0.6-6.2 eV. Recently a lot of attentions have been attached due to their potential applications. Although film form of these nitride semiconductors has been widely studied in the application of optoelectronic devices, there are little researches about the particle form which is expected as potential photocatalyst. Especially, GaN powder has also been studied as fluorescent material by K. Hara et al. Up to now, III-nitride semiconductors have been successfully synthesized by various methods. For example, GaN can be synthesized by MOVPE, HVPE, MBE, ammonothermal method and flux method, InN can be synthesized by MOCVD and MBE for film form and gas-solid phase process for particulate, $\text{In}_x\text{Ga}_{1-x}\text{N}$ also can be synthesized by MOCVD and MBE for film form and no synthesis method of particulate was reported. In these studies, N_2 or NH_3 was used as nitrogen source in the synthesis process of either film or powder form. A. Mabuchi et al have been reported a novel synthesis method for GaN particles by using Li_3N as solid nitrogen source. Compared with the gaseous nitrogen source, the solid one has advantages of easy handling and the higher utilization efficiency. In this dissertation research, Li_3N or LiNH_2 was used as solid nitrogen source to synthesize GaN, InN and $\text{In}_x\text{Ga}_{1-x}\text{N}$ powder crystals. The mechanisms of these synthesis processes were investigated. Moreover, the photoelectrochemical properties of GaN particulate thin film electrode were also investigated.

In chapter 1, the background of this dissertation research was introduced.

In chapter 2, the crystal growth process of GaN by the reaction of Ga_2O_3 and Li_3N with metal Ga was investigated. As A. Mabuchi et al reported, GaN particles were synthesized by the reaction of Ga_2O_3 with Li_3N at N_2 atmosphere. Because the reaction was solid phase reaction, crystal size was limited by the size of starting materials and only several micrometers of GaN particles were obtained. By the reaction of Ga_2O_3 and Li_3N with metal Ga, the size of above 100 μm GaN crystal was obtained because Ga is liquid phase at the reaction temperature and was used as a flux to cause crystal growth. The synthesis of GaN was caused at more than 550°C. It was found that the amount of nitrogen source, Li_3N , has an important influence on crystal growth. With enough amount of Li_3N , the size of GaN increased with increasing reaction time. It was considered that GaN grows on the existing particles by continuous supplement of nitrogen source and caused the crystal growth. The mechanism of crystal growth was considered as a two-step reaction. At the initial step, GaN particles were formed by the reaction of Ga_2O_3 with Li_3N . At the second step, GaN grew on the existing GaN particles and crystal growth occurred.

In chapter 3, the crystal growth process of GaN by the reaction of Ga with LiNH_2 in NH_3 atmosphere was investigated. As discussed at chapter 2, in order to obtain bulk GaN crystal, enough amount of nitrogen source is necessary. Therefore, the atmosphere gas was changed from N_2 to NH_3 . NH_3 can be used as additional nitrogen source. GaN was successfully synthesized by the reaction of Ga with Li_3N in NH_3 atmosphere. It was found that Li_3N transformed to LiNH_2 by heating in NH_3 atmosphere. LiNH_2 was considered as more suitable nitrogen source than Li_3N because Li_3N easily reacts with water vapor in the atmosphere and causes the lack of nitrogen source. On the other hand, LiNH_2 is relatively stable in the atmosphere. It was also found that LiNH_2 can be reproduced in NH_3 atmosphere that make it as a suitable nitrogen source to supply enough amount of nitrogen. Therefore, LiNH_2 was expected as a useful nitrogen source to cause GaN crystal

growth. By the reaction of Ga with LiNH_2 in NH_3 atmosphere, above 100 μm of the size of GaN crystal was obtained. Compared the morphologies of GaN crystal which was obtained in the case of different reaction temperatures and different reaction times, the crystal size increased with increasing the reaction temperature and reaction time. From the finding of formation of Li_3GaN_2 by the reaction of Ga with LiNH_2 in N_2 atmosphere, it was deduced that the crystal growth in NH_3 atmosphere occurred by the reaction of Li_3GaN_2 with NH_3 . The mechanism was considered as two-step reaction. At the initial step, Ga reacted with LiNH_2 to form GaN particles. At the second step, GaN particles reacted with LiNH_2 to form Li_3GaN_2 . This ternary nitride compound reacted with NH_3 gas to decompose to GaN. GaN crystallized in Ga melt and grew on existing GaN particles to cause crystal growth.

In chapter 4, photoelectrochemical properties of synthesized GaN were investigated. In order to investigate the photoelectrochemical properties, GaN particulate film electrode on Ti substrate was prepared. The weak connection between GaN particles blocked the transport of photogenerated electrons. Although sintering is a traditionally method to connect the particles, it was difficult to sinter the GaN particles. According to the crystal growth mechanism in chapter 3, LiNH_2 was added into GaN particulate film electrode and then thermally treated to improve the connection of particles. From current-voltage curves under illumination, anodic photocurrent was clearly observed which indicated that GaN synthesized in this study is an n-type semiconductor. Compared with the electrode without treatment, the electrode with LiNH_2 treatment exhibited higher anodic photocurrent because GaN formed between GaN particles to connect the particles. The improvement of electrical conductive connection facilitated the electron transport in the film and achieved higher photocurrent. Under UV light excitation yellow luminescence was observed at 560 nm. From the potential dependence of PL emission spectra, in the case of electrode without LiNH_2 treatment the PL intensities are constant independent on the bias voltage which means the insufficiency of electrical connection in the electrode. On the other hand the electrode with LiNH_2 treatment shows that increasing the anodic bias PL intensity decreased which means that the good electrical contact formed between the GaN particles.

In chapter 5, the synthesis of InN was investigated. Although GaN was successfully synthesized by the reaction of Ga_2O_3 with Li_3N and Ga with LiNH_2 as discussed in chapter 2 and 3, no InN was obtained by the similar reaction such as In_2O_3 with Li_3N and In with LiNH_2 . As the experimental result, it was confirmed that InN only can be synthesized by using InCl_3 as indium source and LiNH_2 as nitrogen source in N_2 atmosphere. The synthesis reaction occurred at the temperature range of 350-450°C. This temperature range was almost consistent with the decomposition temperature of LiNH_2 which was in the range of 340-440°C. Therefore, InN was synthesized by the reaction of InCl_3 with Li_2NH which was formed by the decomposition of LiNH_2 . When reaction temperature increased to 500°C, no InN was obtained. Because at this temperature almost Li_2NH decomposed to H_2 and N_2 , no nitrogen source reacted to synthesize InN. Compared the reaction yields in the case of different reaction times and different reaction temperatures, it was reached about 30% and it did not increased with increasing reaction time for each reaction temperature. This may be due to the decomposition of Li_2NH caused the lack of nitrogen source to suppress to reach higher reaction yield. And the formation of In-Li-O compound by the reaction of obtained InN with lithium compound such as Li_2O in products also caused the decreasing of reaction yield. The band gap of obtained InN was determined with the value of 0.83 eV, which was consistent with the reported result for InN.

In chapter 6, the synthesis of $\text{In}_x\text{Ga}_{1-x}\text{N}$ was investigated. Because only InCl_3 can be used as indium source as discussed at chapter 5, GaCl_3 and InCl_3 were used as III-group sources, LiNH_2 was used as nitrogen source to synthesize $\text{In}_x\text{Ga}_{1-x}\text{N}$. However, no $\text{In}_x\text{Ga}_{1-x}\text{N}$ but only the mixture of InN and GaN were obtained. It was considered that the particles of GaCl_3 and InCl_3 not contacted with each other and reacted with LiNH_2 individually to obtain GaN and InN. Therefore, the pre-treatment of starting materials was necessary to contact the particles of GaCl_3 and InCl_3 together. Acetonitrile was used as disperse medium to do the pre-treatment. The starting materials were dispersed in acetonitrile by ultrasonic wave and were evacuated to vacuum at 200°C for 1 hour to remove acetonitrile. Then the reaction system was heated at 400°C for 2 hours to synthesize $\text{In}_x\text{Ga}_{1-x}\text{N}$. From the results of XRD, EDX and XPS, it was considered that $\text{In}_x\text{Ga}_{1-x}\text{N}$ was obtained. When GaCl_3 and InCl_3 were used with a molar ratio of 1: 1, x of obtained $\text{In}_x\text{Ga}_{1-x}\text{N}$ has a value of 0.53 and the band gap is 1.85 eV.

In chapter 7, the summary of this dissertation was reported. In this dissertation, novel techniques for synthesis of

III-nitride semiconductors by using solid nitrogen source were reported. III-nitride semiconductors were successfully synthesized at low reaction temperature and low pressure. It is a simple and facile route to synthesize III-nitride semiconductor by using solid nitrogen source.

論文審査結果の要旨

近年 LED やレーザーなどに応用されている GaN は直接遷移型のワイドバンドギャップ半導体 ($E_g = 3.4 \text{ eV}$) である。耐酸性・耐アルカリ性などにも優れ、InN, AlN と固溶体を形成し 0.6~6.2 eV と広い範囲でのバンドギャップコントロールが可能である。これまで広く研究されてきた酸化物半導体と同様に光触媒や光電極などの光機能材料としても有望であると考えられている。

現在、発光素子として用いられる GaN は主として有機金属気相成長 (MOVPE) 法によりサファイア基板上にエピタキシャル成長により作製されているが、原料が高価である、高価な装置を必要とするなどの問題があり大量生産には不向きである。またアンモニア中、高圧下での反応によるアンモノサーマル法などによるバルク結晶の合成も試みられているがまだ研究段階である。

本論文は、窒化リチウムあるいはリチウムアミドといった固体窒素源を用いて窒化ガリウム、窒化インジウムなどの窒化物半導体の合成について検討したものである。これまでの研究の多くは窒素源に気体である窒素やアンモニアが用いられており、高温・高圧の条件や腐食性ガス中での反応が必要とされてきた。本研究では固体窒素源を用いることで常圧下、450~500°C というマイルドな条件で窒化物半導体の合成に成功している。なかでも光機能材料として重要な GaN については原料や反応雰囲気などの条件を変えることで結晶成長メカニズムを考察するとともにその光電気化学特性についても検討している。固体窒素源は取扱いが簡便であるとともに、原料の利用効率を高めることができ、排ガスの処理も最小限にとどめることができるなどの利点を持っている。

まず、当研究室の馬淵らによる酸化ガリウムと窒化リチウムの反応による GaN 合成法を進展させ、反応系に反応温度で液体となる金属 Ga を導入することによって数十から数百マイクロメートルの大きさの GaN 粉末の合成および結晶成長に成功している。また、その反応機構を考察し、結晶成長に必要な反応温度を決定している。

次に反応雰囲気を窒素からアンモニアに変化させ、ガリウム源を酸化ガリウムから金属ガリウムに変えることにより、さらに結晶成長した GaN が 90% 程度の高い収率で合成できることを見出している。またその反応機構の考察から反応中に窒化リチウムがリチウムアミドに変化して、このリチウムアミドが固体窒素源として適していることも見出している。

合成した GaN 粉末を用いてペースト電極を作製し、その光電気化学的評価を行っている。現在、半導体粉末や電極を使用した光触媒反応による環境浄化や水の光分解による水素製造が注目されているがその多くは酸化物半導体を用いたものであり、今後は窒化物についても応用が広がっていくことが期待される。作製した電極は n 型の半導体特性を示し、可視光領域にフォトルミネッセンスを示すことを報告している。

同様に、塩化インジウムとリチウムアミドを原料として窒素雰囲気中で InN の合成に成功している。350~450°C で合成した InN 粉末の吸収スペクトルからバンドギャップ 0.83 eV を決定している。

さらにこの方法を進展させ塩化ガリウム、塩化インジウム、リチウムアミドを原料として $\text{In}_x\text{Ga}_{1-x}\text{N}$ 固溶体の合成にも成功している。吸収スペクトル測定から、In:Ga=1:1 の条件で合成した粉末は 1.85 eV の可視光領域に相当するバンドギャップを持つことを報告している。

以上、本研究では窒素源に窒化リチウムあるいはリチウムアミドを用いて GaN, InN, $\text{In}_x\text{Ga}_{1-x}\text{N}$ 固溶体粉末の合成に成功した。固体窒素源を用いた窒化物粉末の合成例はまだ少なく、また従来法に比べて環境負荷の少ない合成法であり、今後の光機能材料応用への展開が期待される。

最終試験結果の要旨

2月6日に1時間半余りにわたって最終試験を実施した。約60分のプレゼンテーションとそれに続いて約30分の質疑を行った。研究目的に合致した発光材レベルの高品質化がまだ達成できていないこと、具体的にどのような応用が可能であるかなどやや不明確な部分があることなどが議論された。窒化ガリウム、窒化インジウム、固溶体粉末の簡便で環境負荷の少ない新規合成法に成功した点およびその特性評価は学位論文にふさわしい内容を含むと判断された。

以上のことから、最終試験に合格とした。