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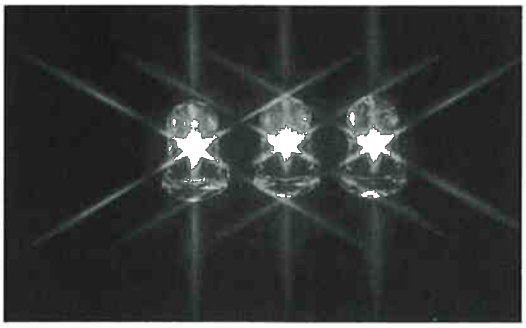
Blue LED shines with gas

High purity ammonia led to the development of the high-brightness blue LED

All three Novel Prizes in Physics are linked to industrial gas



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Blue LED shines with gas

Nobel Prize in Physics
Isamu Akasaki, Hiroshi Amano, and Shuji Nakamura
All 3 are closely linked to gas

The morning news of October 8 reported that 3 professors of Isamu Akasaki, Meijo University, and Hiroshi Amano, Nagoya University along with Shuji Nakamura of the University of California at Santa Barbara were jointly awarded the Nobel Prize in Physics. The Gas Review (*TGR*) has interviewed Dr. Nakamura several times, and was quite surprised that he had won the Nobel Prize.

Be that as it may, on the morning of October 9 we sent him an e-mail which ran, "Congratulations on winning the Nobel Prize in Physics. Would it be alright if we mentioned that high purity gas such as ammonia contributed to your winning the prize?" On October 11 a reply did come in, with the comment, "It is just as you pointed out. I can certainly think that I could go right along with that. Thank you very much."

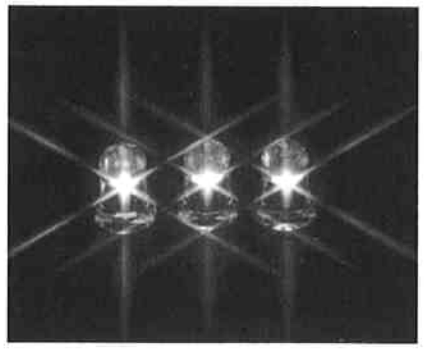
The first interview with Dr. Nakamura was held in July of 2003, when he was right in the midst of the whirlwind of the "blue LED lawsuit." It was during this that he became a man of the times. At that time, blue LEDs were being mass produced and the demand for high purity ammonia and trimethylgallium (TMG) or Ga(CH_3)3 was also growing sharply.

Dr. Nakamura is a very bright personality, very open and natural, very talkative and one who laughs a lot. He was tall and talked with a high pitch voice which came across very clearly. He spoke about technology in a way that was easy to understand.

Among the things he spoke about, one thing he mentioned was, "A major factor was the bringing about of high purity ammonia. This led to the development of the high-brightness blue LED." He pointed out the importance of gas and gas control technology, explaining that the involvement of other gases such as TMG and hydrogen, as well as nitrogen, led to the development of the amazing 2 flow MOCVD method. The close connection to gas he had when he was young was linked to his success.

High purity ammonia opened the way

Dr. Nakamura is the type of person who does not forget kindnesses. At an interview in 2003, when we asked about his initial encounter with industrial gas, looking back in time, he stated, "It was when I was in grad school, and I used liquid nitrogen for freezing. I became acquainted with Mr. Takatoshi Enozu of Tokushima Sanso (now Shikoku Taiyo Nippon Sanso). I greatly relied on



him for gas also when I was at Nichia." At that time, 20 years previous, he repeatedly said, "I really owed him a lot."

For 5 years after joining the firm, there was a duel with oxygen and hydrogen welding of quartz tubing. He was ordered to develop gallium phosphide (GaP) compound semiconductive material. High priced manufacturing devices could not be bought within a limited budget. He grew crystals in a reaction chamber but the reaction chamber had to be made, utilizing quartz tubings made based on oxygen and hydrogen welding on his own. "As quartz cannot be welded unless a temperature of 1,500℃ is reached it must be made intensely hot, and furthermore if cracks and fissures appear in the quartz, a great danger arises from that, leading to an explosion. In fact this has occurred frequently.

He got in danger many times, but in 3 years he succeeded in commercializing gallium phosphide, and continuing along indeed he developed bulk crystal of gallium arsenic and commercialized them in 3 years as well. Even here, oxygen-hydrogen welding came into play. "I had to continue operations from morning to night without letting attention go. Even so, by searching for the reason for the explosions, I became familiar with the physical properties, and I had a lot of experience allowing me to become familiar with the process of crystal formation," he said.

Likewise he has a good memory. When on this occasion I asked him about how much gas he used, he came back with the reply quite quickly, "Put as a monthly average it was around 10 cylinders of hydrogen with a capacity of 47 liters. For oxygen it was about 2-3 cylinders."

Next there came the development of infrared-emitting diodes and red LEDs. He was freed from welding with the formation of thin film based on liquid phase epitaxial growth method. Hydrogen and nitrogen were used as the carrier gas. They too were commercialized in 4 years.

His linkage to specialty gas came after 10 years in the company. This was because at that time he appealed directly to the president of Nichia, Nobuo Ogawa, and became involved in the development of blue LEDs. "At that stage, I decided that there was only the MOCVD method for mass production of high quality crystal film." To acquire the MOCVD technology he studied at Florida University for the short time of 1 year.

He conducted an experiment in growing with gallium arsenide (GaAs). This was also his first experience using highly toxic gases such as arsine and phosphine as well as TMG. "Based on this experience I found that highly toxic gases were dangerous and difficult to handle. I came to the conclusion that these were problematical gases as safety measures such as an exhaust gas treatment system cost money."

Even during this time of studying in the US, he had to put together an MOCVD unit himself. Of what should have been 3 units, 2 of these were used by other professors. This was because remaining one was broken up into pieces. "It took 9 months to build the unit. This is an ironic tale as the piping and welding technology which I had cultivated for 10 years was of use here."

TGR asked him when he selected gallium nitride. "It was in March of 1989 just before I returned to Japan for a time after studying MOCVD technology in the US." The generally held knowledge worldwide of blue LEDs at that time concerned zinc selenide. This was because there was the most suitable substrate of gallium arsenide and a smooth, uniform crystal film could be formed. Gallium nitride was a completely minor material.

"I therefore certainly selected it. Medium and small size firms, which were behind in development, could not win out with the same method. Fortunately the zinc selenide high-brightness blue LED had not been made. Questioning what was commonly held and ignoring what had been written, I was ready for developing the blue LED based on gallium nitride for the crystal thin film, the MOCVD method as the manufacturing technology, sapphire as the substrate, and ammonia and TMG for the gases. With all of this my doubts vanished regarding the development of the blue LED."

Research and development began in April of 1989. However, although no problems arose with the crystal film in experiments initially, at some point the situation of crystal film deteriorated. "I did rework the facility several times as I thought there might be something wrong with the facility but I could not resolve the issue. While searching for the cause everywhere, I then came upon ammonia. Although no problems arise when new gas is used, when the residual gas in the cylinder reaches around under 1/3, there is a negative effect on the crystal film. In the end result, as ammonia is used, the moisture in the ammonia becomes concentrated, and as an impurity in the ammonia it is sent together into the reaction chamber. The discrepancy in the quality of the gas also stood out. I immediately complained to the gas supplier that this was not high purity ammonia and had him deal with this."

The problem then went away. "I made sure of everything with high purity ammonia being supplied and a purifier installed. This led to the development of the high-brightness blue LED."

Not just the ammonia, but

also nitrogen, hydrogen and TGM are required to be high purity but indeed it was the ammonia which was the problem.

"The environment in which the researchers and technicians are rewarded"

High purity ammonia and the 2 flow MOCVD method were important for the development of the high-brightness blue LED. "While repeatedly conducting experiments and making improvements of devices, I made a 2 flow MOCVD in October of 1990, which enabled an extremely high quality film to be formed. Then in November of 1993 this led to the development of a 1 candela high-brightness blue LED.

However, the common knowledge was that in the case of the conventional MOCVD, unless the gas was sent in one direction and turned into a laminar flow, the good film would not be formed. Dr. Nakamura then came up with a technology which sent the gas into both vertical and horizontal directions, which broke with the common knowledge. "Even if the gas is sent in from the side, the sapphire substrate in the reaction device generates a thermal convection at the high temperature of about 1,000 ℃, so that the gas jumps up and vapor deposition does not occur. Therefore, with ammonia, TMG, and hydrogen blew down hard as the main flow from the side, and nitrogen and hydrogen from above as the sub flow, a laminar flow is created, enabling gas to be supplied uniformly, and a high quality crystal film to be grown."

Put simply, the high-brightness blue LED was most certainly made by gas. Then in early 2000 mass production of the high-brightness blue LED was started by Nichia and Toyoda Gosei. They took the lead worldwide. However, his forecast, stating that, "The blue LED production will be pulled away by Taiwan," came true. He made this forecast when we interviewed him in July, 2007. Right now China and Taiwan are the largest supply centers for blue LEDs. They were mass-produced for such low cost applications as lighting and toys. Japan has only got stuck with the high quality products, and has been left in the dust.

The gas market has greatly changed. Looked at just from the point of view of Japan, in 1999 ammonia amounted to 119 tons, and TMG 300 kg, but in 2013 the figures had expanded to 2,919 tons and 2,000 kg. However, in the global market of ammonia Japan has fallen to fourth place, with 10,000 tons in China, 7,000 tons in Taiwan, and 6,000 tons in Korea. Nevertheless, Sumitomo Seika Chemicals and Showa Denko have moved into various East Asian nations such as Taiwan, Korea, and China and are supplying high purity ammonia products. They have been ringing up sales, with high quality giving them an edge.

Dr. Nakamura continued to speak in his very direct fashion. The following is his remark again made in 2007. "It is probably impossible for Japan to join the ranks of the US and Europe and compete with the US and Europe in terms of intellectual creation. It is because everyone around those engaged in intellectual creation as well as basic research and development tries to avoid them. In this sense the US and Europe are greatly different. In the US and Europe, intellectual creativity is highly prized, and researchers are respected. Japanese have a kind of belief whereby scientists must be pure of heart, poor, and beautiful. In the US, that first rate scientists create any number of venture capital businesses and reap profits is only natural. I feel that Japan, Korea, and Taiwan are similar in terms of basic characteristics. Mass production products are made based on technology developed in the US and Europe. In other words the difference is whether to copy is quick or slow. If it comes to this, the situation is greatly controlled by the speed of the management to make a decision. In this sense, Taiwan and China are on top."

Regarding the Japanese way of producing things, "It has been said that making things is important but researchers and technicians have not been rewarded at all. That investors and managers of pinball parlors do make money is unsound. However, I don't think that this will change," he noted bitterly. When he won the Nobel Prize too his tone was even sharper. That he is expressing anger but not going so far as despair might perhaps be due to Dr. Nakamura's sensitivity.

The MOCVD produced by Taiyo Nippon Sanso made the first gallium nitride blue LED

Under the leadership of Dr. Akasaki, Nagoya University, Nagoya Institute of Technology, and Meijo University form a global Mecca for research and development regarding gallium nitride compound semiconductors. Behind them is Toyota as well as the Toyota Group.

MOCVD units produced by Taiyo Nippon Sanso are installed in all 3 universities. At Nagoya University in1989 Dr. Akasaki as a professor with Dr. Amano as his assistant brought about the growth of high quality gallium nitride crystals, and for the first time caused a blue LED to shine its light on the world. Dr. Nakamura too worked in the method of combining gallium nitride and magnesium.

One of the major factors which led to the success of this was without a doubt the MOCVD produced by Taiyo Nippon Sanso. Also, that in Japan high purity ammonia as well as hydrogen, nitrogen, and TMG existed was one more factor. Universities do not have specific manufactures and suppliers since they employ the system of submitting bids but contribution of industrial gas companiies is indeed great. The Nobel Prize in Physics based on the blue LED awarded this year was based on the research and development of all the three, Dr. Akasaki, Amano, and Nakamura. Gas may also be said to have supported in the form of a triumvirate composed of gas, the MOCVD, and gas supply facilities. G

(The latest interview will be shown in the up-coming Gas Review Nippon No.64)