Twin chamber sample assembly in DAC and HPHT studies on GaN nano-particles

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Abstract: In this paper, we have suggested a novel idea of twin chamber sample assembly for separating ruby from the sample to overcome certain problems during high pressure–high temperature experiments using diamond anvil cell. Two holes of diameter 70µm were drilled symmetrically about the centre of the preindented area (500 µm diameter) in a stainless steel gasket using EDM. Using ruby pressure calibration, good pressure correlation between these two holes was established up to about 15GPa. Also, high pressure - high temperature (HPHT) experiments on the III-V compound semiconductor GaN were performed up to ~ 3GPa and 2000K using the two chamber sample assembly and a laser heated diamond anvil cell facility. NaCl, both hydrous and anhydrous, were used as the pressure transmitting media in two separate experiments. Micro-Raman spectroscopy was used to characterise the HPHT treated samples. While GaN remained stable in its wurtzite phase when heated in anhydrous NaCl medium, it transformed to Ga$_2$O$_3$ with rocksalt structure in the hydrous NaCl medium.

1. Introduction

The diamond anvil cells (DACs) are well suited for in-situ high pressure study of various forms of samples ranging from solids and liquids to gases. Merely keeping the sample in between the diamonds in a DAC does not serve the purpose of achieving high pressure, because of various problems like the sample squeezing out at high pressures and anisotropic transmission of pressure, etc. This has been elegantly solved by using hard gaskets for containing the sample. Stainless steel or rhenium gasket is used as a container for the sample. The maximum static pressure attainable nowadays using the diamond anvil cell (DAC) technique has reached several mega bars (100 GPa=1 mbar) [1,2]. Simultaneously, high temperatures ~ 5000ºC can be generated by using the laser heated DAC (LHDAC) facility [3]. During laser heating experiments, the pressure calibrant is placed along with the sample. In certain experiments, this configuration is not desirable. For example, while working with porous silicon under high pressure, we can not measure the pressure using ruby in the same chamber, as their photoluminescence spectra overlap [4]. Also during synthesis of metal nitrides under HPHT condition, there should not be any oxygen source in the sample chamber. We know that ruby (Al$_2$O$_3$:Cr$^{3+}$) which decomposes above ~2000K becomes a source of oxygen and hence can not be used in the same chamber in the above experiment [5]. To overcome this situation, a two-hole sample assembly is desired, one for mounting the sample and the other for mounting Ruby pressure calibrant.

In DAC experiments, a gasket for holding the sample is prepared by pre-indenting it and drilling a central hole of desired size. For example, in a stainless steel gasket pre-indent to thickness of ~ 50 µm, 200-250µm diameter hole is drilled for carrying out experiments up to ~50-60GPa using 500µm culet diamond anvils. To attain higher pressure (~100GPa), smaller culet sizes (100-300µm) are used. The common method for drilling a hole larger than 100µm is by mechanical drilling using tungsten carbide drill bits. This process is very tedious and time consuming. Also, this process involves breaking of expensive drill bits and formation of burr while drilling. Drilling two holes in a single gasket by this method is difficult. To achieve this we have deployed a technique by modifying a low
cost electric discharge machine. A 50µm tungsten wire was used as one of the electrodes in the discharge machine and the gasket as the other electrode. A two hole sample assembly was made for studying the HPHT behaviour of GaN nanoparticles by loading GaN in one hole and the Ruby in the other. This twin chamber technique also can be used to study two samples, a reference sample and the actual sample under HPHT conditions.

2. Experiment

Drilling Holes by EDM: For drilling holes in SS gaskets, we have used a modified electric discharge machine (JOEMARS, Korea model no. TR 100) which supports voltages ranging from 100 to 240 V with max power consumption of 450 VA. The power was supplied through a variac transformer. The gasket was mounted on an x-y-z stage (Fig. 1) [6].

![Motorised tungsten electrode holder](image)

![Gasket mount](image)

![XYZ stage](image)

![EDM power supply](image)

**Figure 1.** Electric discharge machine (EDM) for drilling DAC gasket holes

Micro EDM involves a thermal process in which a spark is utilised to erode a conducting material [7,8]. As there is no contact between the tip of the tungsten wire and SS gasket, there is no force acting between them. An x-y-z stage is used for fixing the SS gasket and positioning of the tungsten wire at the desired point is done using a stereo zoom microscope. Both the wire and the SS gasket are submerged in dielectric fluid. De-ionized water is used as a dielectric. It acts as insulation in the gap, flushes out eroded particles, and also cools the electrodes. Depending upon the gap between the wire and gasket, a suitable voltage is applied to establish an electric field. The voltage applied must be enough to create an electric field higher than the dielectric rigidity of the fluid used in the process. The SS gasket stage is then slowly moved upwards toward the tungsten wire until the spark gap (the nearest distance between both electrodes) is small enough to ionize the dielectric. As the electric field is established between the wire and the gasket, the plasma channel is formed between them. The electrical resistance of such plasma channel would be very less. Thus all of a sudden, a large number of electrons flow from the wire to the gasket and ions from the gasket to the wire. This is called avalanche motion of electrons. Such movement of electrons and ions can be visually seen as a spark. Thus the electrical energy is dissipated as the thermal energy of the spark.

The high speed electrons then impinge on the gasket and ions on the wire, and create a localized heat flux. Such intense localized heat flux leads to instantaneous rise in temperature. Such localized extreme rise in temperature leads to material removal. Material removal occurs due to instant vaporization of the material as well as due to melting. If the potential difference is lowered below the threshold value, the plasma channel is no longer sustained. As the plasma channel collapses, it generates pressure or shock waves, which evacuates the molten material forming a crater of removed
material around the site of the spark. Due to the sudden decrease of internal pressure of the gas ball, the dielectric fluid breaks it making the ball to implode. As a consequence of this implosion, the molten metal gets ejected out. Since tungsten is a hard material, there is very little erosion of the tungsten wire. For high precision applications, the energy must be reduced and it will take longer time to make a hole. In our experiment, we used a 50µm diameter tungsten wire as electrodes for drilling two equidistant holes of diameter 70µm on a preindented SS gasket. We used a Mao-Bell DAC with 500 µm diamond culets.

**Synthesis of GaN Nanoparticles**

GaN nanoparticles were synthesized in the atmospheric pressure chemical vapour deposition (APCVD) technique using Ga (99.999%, Aldrich) as precursor and NH₃ as reacting gas for about 1.5 hrs. The growth temperature was kept at 900 °C. As a final product, powder like GaN matrix with light yellowish colour was formed around the source material within the alumina. Field emission scanning electron microscopy (FESEM, Zeiss Supra 40) image of GaN nanoparticles (Fig. 2), reveals an average particle size of ~ 100 nm with faceted morphology.

![SEM image of GaN nano-particles](image)

**Laser heating system:** HPHT studies of GaN nanoparticles by the two hole method was carried out using the LHDAC facility. A CO₂ laser was used for laser heating the sample. The diameter of laser spot on sample was ~40 µm.

**Micro-Raman Set up:** A high throughput Renishaw micro-Raman spectrometer (model Invia) was employed to record the spectra using the 514 nm laser excitations. The laser was focused to a spot size of about 2 µm with a 20× objective and the signal was detected by a CCD detector. Collection time for each spectrum was typically 100 seconds.

**3. Results and Discussion:**

**Pressure correlation in two chambers:**
Using the modified EDM, two holes of diameter ~ 70 µm equispaced from the centre of the culet impression of the diamond were made to separate sample and pressure calibrant. The schematic of the gasket is shown in Fig. 3a and the photo of the actual gasket containing two holes is shown in Fig 3b.
To the pressure correlation between the two holes, we put ruby particles in both the holes along with the sodium chloride as the pressure transmitting medium. Pressure was estimated using ruby fluorescence technique. It was seen that the pressure values in the two holes were almost same up to 15 GPa (Fig. 4), demonstrating that the two holes were equidistant from the centre of the preindented area. At higher pressures, there are chances for the sample chambers to be deformed disturbing the above correlation. Therefore, this process is well suited for the low pressure experiments.

**Figure 3a.** Hole positions in the culet impression on SS gasket

**Figure 3b.** Two hole gasket mounted on piston cylinder of the DAC with the both chambers filled with ruby

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**Figure 4.** Pressure correlation in two holes of the gasket

**HPHT study of GaN nanoparticles using two chamber sample assembly:**

GaN is an III-V semiconductor with a band gap of 3.4eV and exists in wurtzite structure. To our knowledge, there are no reports on HPHT behaviour of GaN in the literature. Micro-Raman spectrum of GaN before heating certifies the existence of wurtzite structure at ambient pressure and temperature. The cell was pressurised to ~3GPa and laser heating was carried out for ~10 min and temperature was estimated to be ~2000K. Figure 5 shows the CO$_2$ laser heating of GaN inside DAC. Raman spectra of the laser heated sample do not show any change with respect to the spectrum of GaN obtained before heating. It is reported in literature that GaN converts to gallium oxide at ambient pressure at a temperature of ~900°C. The probable reason for not observing oxide formation may be due to the inert atmosphere present in the sample chamber. This is so because in the above sample assembly for laser heating, the NaCl was pre-heated before loading in DAC for up to 3 hours to remove the moisture.
For verifying the above conclusion, another experiment was carried out, wherein NaCl was used without pre-heating treatment for removal of moisture. Raman spectra before laser heating contains modes at 273 cm\(^{-1}\), 430 cm\(^{-1}\), 574 cm\(^{-1}\) and 737 cm\(^{-1}\) after laser heating it is observed that all the modes of GaN have disappeared along with appearance of new modes at 201 cm\(^{-1}\), 358 cm\(^{-1}\), 449 cm\(^{-1}\), 483 cm\(^{-1}\) and 780 cm\(^{-1}\). The Raman spectra before and after laser heating are shown in Fig 6. All the Raman modes observed after laser heating can be ascribed to Ga\(_2\)O\(_3\) confirming the conversion of GaN into Ga\(_2\)O\(_3\) under HPHT conditions in presence of moisture.

Figure 6. Raman modes of GaN before and after heating at various pressures. Complete transformation to Ga\(_2\)O\(_3\) is seen in the top most pattern. Bottom four graphs are before heating in anhydrous NaCl and top graph is after laser heating in hydrous NaCl.
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References:
1. Hemley R J and Ashcroft W 1998 *Phys. Today* **51** 26
2. Sahu P Ch, Chandra Shekar N V 2007 *Resonance* **12** 49; ibid 2007 *Resonance* **12** 10
3. Subramanian N, Chandra Shekar N V, Sanjay Kumar N R and Sahu P Ch 2006 *Curr. Sci.* **91** 176
4. Huang W Q, Zhang R T, Wang H X, Jin F, Xu Li, Qin S J, Wu K Y, Liu S R, Qin C J 2008 *Optical Communications* **281** 5229–5233
5. Horvath-Bordon E, Riedel R, Zerr A, McMillan P F, Auffermann G, Prots Y, Bronger W, Kniep R and Kroll P 2006 *Chem. Soc. Rev.* 35 987-1014.
6. Dayana Lonappan, Chandra Shekar N V, Sundaram L. M, Edwin T and Sahu P Ch, Solid State Physics: Proceedings of the55th DAE Solid State Physics Symposium 2010, Part A, Part B, edited by Garg A, Mittal R and Mukhopadhyay R, AIP Conf. Proc. No. 1349 (AIP, New York, 2011) p.461.
7. Driver C, Atkinson J, Helml H J, Li L 2004 *J. Mat. Proc. Tech.* **149** 296-303
8. Yap Ber-Chin and Fromm L 2003 *Electrical Overstress/Electrostatic Discharge Symposium EOS/ESD ‘03* pp.1-9.